DEVELOPMENT OF A HIGH-BRIGHTNESS ELECTRON BEAM SYSTEM
TOWARDS FEMTOSECOND MICRODIFFRACTION AND IMAGING AND ITS
APPLICATIONS

By

Kiseok Chang

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

Physics - Doctor of Philosophy

2014
ABSTRACT

DEVELOPMENT OF A HIGH-BRIGHTNESS ELECTRON BEAM SYSTEM TOWARDS FEMTOSECOND MICRODIFFRACTION AND IMAGING AND ITS APPLICATIONS

By

Kiseok Chang

To make a ‘molecular movie’, an ‘ultrafast camera’ with simultaneously very high spatial and temporal resolution to match the atomic dynamics is required. The ultrafast electron diffraction (UED) technique based on femtosecond laser technology can provide a basic framework for realizing such an ‘ultrafast camera’ although this technology has not achieved its full utility as a universal imaging and spectroscopy tool, due to limitations in generation and preservation of a high–brightness electron beam in the ultrafast regime.

With moderate electron pulse intensity ($10^3$-$10^4$ electrons per pulse), UED experiments have been successfully applied to investigate photo-induced non-thermal melting processes, structural phase transitions, and transient surface charge dynamics. Based on the previous development of ultrafast electron diffractive voltammetry (UEDV), we extend the UEDV with an aim to identify the different constituents of the measured transient surface voltage (TSV) and discuss their respective roles in Coulomb refraction. From applying this methodology on Si/SiO$_2$ interface and surfaces decorated with nano-structures, we are able to elucidate localized charge injection, dielectric relaxation, carrier diffusion, and enhancements on such processes through surface plasmon resonances, with direct resolution in the charge state and possibly correlated structural dynamics at these interfaces. These new results highlight the high sensitivity of the interfacial charge transfer to the nanoscale modification, environment, and surface plasmonics.
enhancement and demonstrate the diffraction-based ultrafast surface voltage probe as a unique method to resolve the nanometer scale charge carrier dynamics.

The future applications of the UED and UEDV techniques lie in the direct visualization and site-selected studies such as nano-structured interfaces, a single nanoparticle or domain, which can be enabled by the development of high-brightness ultrafast electron beam system for ultrafast electron diffraction. To realize the high-brightness beam, we have developed a high-brightness ultrafast electron beam column equipped with a 100 keV Pierce photoelectron gun and an RF compressor. We are able to generate up to $\sim 5 \times 10^6$ electron per pulse, and, more importantly with the capability of micro-focusing, we have achieved a high dose delivery to the sample by three orders of magnitude (up to $\sim 2000$ electron/$\mu$m$^2$) higher than those of conventional UED electron systems. In this high intensity pulsed electron beam system, the major challenge is overcoming strong Coulomb repulsion among electrons (space–charge effect) in the pulse, because the space–charge effect causes the electron pulse expansion in transverse and longitudinal direction. To correct the space–charge effect, we have implemented the magnetic lenses for transverse focusing of the electron pulse, and radio frequency (RF) cavity for longitudinal recompression of the pulse. Such a system will provide enough flexibility to manipulate electron pulse phase space, so various experiments that require high spatial and temporal coherence and/or high-density beam optimized for microdiffraction can be achieved.
To Soycon, Damian, and Gabriel ....
ACKNOWLEDGMENTS

First and foremost I would like to acknowledge my advisor Prof. Chong-Yu Ruan for his guidance and exceptional support, and our lab colleagues, Dr. Kihyun Kim, Tzong-Ru Terry Han, Zhensheng Tao, Nan Du, Faran Zhou and Didi Luo. All the works presented here would not have been possible to be achieved without their help. Especially, I can not imagine my PhD degree without the help of Tzong-Ru Terry Han and Zhensheng Tao both inside and outside of the lab.

I would also like to emphasize my deep appreciation to my previous advisor Prof. David Tomanek, my first graduate chair Prof. Bhanu Mahanti, theoretical colleagues Savas Berber and Teng Yang, my classmates and friends in Physics, Kyaw Zin Latt, Kritsada Kittimanpan and Tony Sunghun Ahn. I deeply appreciate all the MSU staffs, especially, Tom Palazzolo, Tom Hudson, Jim Muns and Rob Bennett in Machine Shop helping us to build our new ultrafast electron beam system and Reza Lolee to maintain and characterize our vacuum systems.

I would like to acknowledge specific contributions to the work presented here, Dr. Kihyun Kim and Tzong-Ru Terry Han for performing the surface plasmon project with Au nanoparticles; Zhensheng Tao, Austin Lo and Travis Salzillo for development of the new generation ultrafast high–brightness electron beam system; Zhensheng Tao and Nan Du for characterizing the high–brightness electron beam system; Ryan Murdick for initial development of the transient surface voltammetry technique; lastly, Prof. Chong-Yu Ruan for his energetic involvement in all the works mentioned above.

Finally, I deeply appreciate my wife Soyeon Kim, my sons Damian Hyunjun Chang and Gabriel Hyunsoo Chang, and my parents for their love and unconditional supports.
# TABLE OF CONTENTS

LIST OF TABLES ................................................................. ix

LIST OF FIGURES ............................................................... x

Chapter 1  Introduction .......................................................... 1
  1.1 Ultrafast Camera: Pump-Probe Technique ............................... 1
  1.2 Ultrafast X-ray Diffraction .............................................. 3
  1.3 Ultrafast Electron Diffraction ......................................... 4

Chapter 2  Current Status of Ultrashort Pulse Development: X-ray and Electron ......................................................... 8
  2.1 Ultrashort X-ray Pulse Generation ...................................... 8
    2.1.1 High Harmonics Generation (HHG) ................................. 9
    2.1.2 Laser Driven Plasma (LDP) ....................................... 10
    2.1.3 Free Electron Laser ............................................... 10
  2.2 Ultrashort Electron Pulse Generation ................................ 11
    2.2.1 Compact Electron Gun ........................................... 11
    2.2.2 Single-Electron Pulses ......................................... 12
    2.2.3 MeV Ultrafast Electron Microscope ............................ 13
    2.2.4 KeV Ultrafast Electron Microscope ............................ 14
  2.3 Radiation effects induced by X-rays and electrons .................. 14

Chapter 3  Beam Dynamics in High-Brightness Pulsed Electron Beam-line ...................................................... 17
  3.1 Electron Beam Phase Space Evolution ................................ 18
    3.1.1 Brightness and Emittance ...................................... 18
    3.1.2 Phase Space Evolution along Electron Optics Systems ....... 21
    3.1.3 Imaging and Aberrations ....................................... 25
  3.2 Phase Space Evolution in High-Brightness Electron Beam Line .... 29

Chapter 4  Design of High-Brightness UEM Electron Beam Line at Michigan State University ............................................. 35
  4.1 Electron Source: Pierce Geometry DC Photoelectron Gun .......... 39
  4.2 Magnetic Lenses ......................................................... 45
  4.3 Radio-frequency (RF) Cavity .......................................... 57
    4.3.1 RF Field in Pillbox Cavity .................................... 58
    4.3.2 RF Cavity in High-Brightness Electron Beam Line .......... 61
    4.3.3 RF Station for RF Field and Electron Pulse Synchronization . 63
  4.4 Charge-coupled Device (CCD) Camera ................................ 66
  4.5 Other Components for Optical and Electron Beam Delivery ........ 68
    4.5.1 266 nm Excitation Mirror Holder and Electron Beam Shield .... 69
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5.2</td>
<td>Electron Beam Deflector</td>
<td>70</td>
</tr>
<tr>
<td>4.5.3</td>
<td>Aperture Manipulator</td>
<td>71</td>
</tr>
<tr>
<td>4.6</td>
<td>The Ultra High Vacuum (UHV) Chamber</td>
<td>74</td>
</tr>
<tr>
<td>5.1</td>
<td>100 kV Pierce Geometry Electron Source</td>
<td>78</td>
</tr>
<tr>
<td>5.1.1</td>
<td>Measurement Procedure for Electron Beam Current</td>
<td>78</td>
</tr>
<tr>
<td>5.1.2</td>
<td>Electron Beam Current Measurement Results</td>
<td>85</td>
</tr>
<tr>
<td>5.1.3</td>
<td>Pepper Pot Technique for Emittance Measurement</td>
<td>88</td>
</tr>
<tr>
<td>5.1.4</td>
<td>Beam Emittance Measurement</td>
<td>92</td>
</tr>
<tr>
<td>5.2</td>
<td>Magnetic Lens Focusing Characterization</td>
<td>97</td>
</tr>
<tr>
<td>5.3</td>
<td>Phase Jitter of RF Compression</td>
<td>100</td>
</tr>
<tr>
<td>5.4</td>
<td>Performance Projection for UED Experiment</td>
<td>104</td>
</tr>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>108</td>
</tr>
<tr>
<td>6.2</td>
<td>Origins of Transient Photoinduced Surface Voltage</td>
<td>109</td>
</tr>
<tr>
<td>6.3</td>
<td>Surface Diffraction and Rocking Map Characterization</td>
<td>111</td>
</tr>
<tr>
<td>6.4</td>
<td>The General Formalism of Electron Diffractive Voltammetry</td>
<td>115</td>
</tr>
<tr>
<td>6.5</td>
<td>Ultrafast Electron Diffractive Voltammetry Experiment: Photoemission Contribution</td>
<td>119</td>
</tr>
<tr>
<td>6.6</td>
<td>Near Surface Field Induced by Photoemission</td>
<td>124</td>
</tr>
<tr>
<td>6.7</td>
<td>Modeling of The Surface Photovoltammetry</td>
<td>127</td>
</tr>
<tr>
<td>6.8</td>
<td>Surface Photovoltage</td>
<td>130</td>
</tr>
<tr>
<td>6.9</td>
<td>Summary</td>
<td>135</td>
</tr>
<tr>
<td>7.1</td>
<td>Surface Charging of Pure SiO₂/Si Interface</td>
<td>137</td>
</tr>
<tr>
<td>7.2</td>
<td>Surface Charging of Au Nanoparticle Decorated Si/SiO₂ Surface</td>
<td>139</td>
</tr>
<tr>
<td>7.3</td>
<td>Photo-induced Field Enhancement with Localized Surface Plasmon of Nanostructures</td>
<td>144</td>
</tr>
<tr>
<td>7.3.1</td>
<td>Localized Surface Plasmon of Gold Nanoparticles</td>
<td>149</td>
</tr>
<tr>
<td>7.3.2</td>
<td>Localized Surface Plasmon of Hollow Gold Nano-shell</td>
<td>150</td>
</tr>
<tr>
<td>7.3.3</td>
<td>Surface Plasmon Mediated Charge Dynamics of Au Nanoparticle Decorated SiO₂/Si Interface</td>
<td>154</td>
</tr>
<tr>
<td>7.3.4</td>
<td>Plasmon Mediated Spectral Hole Burning of Hollow Gold Nano-shell on Si/SiO₂ Surface</td>
<td>156</td>
</tr>
<tr>
<td>7.4</td>
<td>Summary</td>
<td>159</td>
</tr>
<tr>
<td>7.4</td>
<td>Summary</td>
<td>166</td>
</tr>
<tr>
<td>8.1</td>
<td>Shadow Imaging and Beam Alignment</td>
<td>167</td>
</tr>
<tr>
<td>8.1</td>
<td>Shadow Imaging and Beam Alignment</td>
<td>167</td>
</tr>
</tbody>
</table>
8.2 Convergent Beam .................................................. 169
8.3 RF Compression of High-Brightness Electron Beam: VO$_2$ ............... 172

Chapter 9 Summary and Outlook ...................................... 182

APPENDICES ................................................................. 184
Appendix A Diffraction Theory for Ultrafast Electron Diffraction ............ 185
Appendix B Experiment Setup of Ultrafast Electron Diffraction ............. 197
Appendix C Formalism of diffracted voltammetry under small angle condition ............................................................ 209
Appendix D Magnetic Annealing Procedure .................................. 213
Appendix E Optimization of Pierce Geometry Electron Gun ................. 214
Appendix F List of Initials and Acronyms .................................. 217

BIBLIOGRAPHY ............................................................... 219
LIST OF TABLES

Table 2.1 Comparison among X-ray sources [23, 24]
† High average power mode with 10 W driving lasers, e.g., 2 mJ, 5 kHz
‡ Linac Coherent Light Source at Stanford Linear Accelerator Center 9

Table 2.2 Energy deposited in biological specimens [27] 15

Table 4.1 The location of the optical components in the high-brightness UED column 57

Table 4.2 Aperture Position 74

Table 5.1 Electron dose $D = N_e/A$ with CML1=1.0 A and Obj.ML=1.3 A 104

Table 5.2 Comparison of the electron dose among different high-flux UED source
a Michigan State University
b University of Toronto/University of Hamburg Group
c McGill University
d Brookhaven National Laboratory
e Michigan State University (preliminary results) 106

Table 8.1 The electron beam properties with different conditions
$N$ is the number of electrons per pulse.

$D = \frac{N}{A}$ is the electron dose, $A = \pi (HWHM)^2$.

$\Delta \theta$ is a half divergence angle.

$\sigma$ is the $\sigma$-width of the electron spot on the sample, not FWHM.

$\varepsilon_{x,n}$ is the normalized transverse emittance.

$L_t$ is the coherence length.

$B_{4D} = \frac{N}{\varepsilon_{x,n}^2}$ is the 4D brightness. 170
LIST OF FIGURES

Figure 1.1  Schematic diagram of the pump-probe experiment setup. The relative time delay between pump(red) and probe(blue) pulses is controlled by the translational delay stage. ........................................ 2

Figure 1.2  (a) Time-dependent diffracted intensity for (220) reflections. Red curves are Gaussian fits to the data, corresponding to 10 to 90% fall times of 280 fs [17] (b) X-ray diffraction efficiency of the (222) Bragg peak as a function of time delay between the optical pump pulse (fluence 6 mJ/cm$^2$) and the X-ray probe pulse. The solid line is fitted to the experimental data. The decrease of the mean value of the X-ray signal (dotted line) is explained by the Debye-Waller effect, and reflects the increasing random component of the atomic motion [18]. .................................................. 3

Figure 1.3  Angular shift of (111) gold Bragg peak as a function of delay time from the same nanocrystal. (a) and (b) are from different individual nanocrystals. The blue dots are the experimental data and the solid red line is the modeled peak shift [19]. ........................................ 5

Figure 1.4  The melting dynamics of 2 nm Au nanoparticles. (Left) mRDF map constructed by stacking mRDFs of UEC patterns at a sequence of delays between 5 and 2300 ps at irradiation fluence F=31 mJ/cm$^2$. Surface melting (enclosed by the dashed white line) is visible. (Right) mRDF map for F=75 mJ/cm$^2$. Full scale melting is observed. The liquid state (enclosed by dashed white line) is characterized by the drop of second nearest density (at 5 Å) to (1 - 1/e) of the static value (at negative time) [29]. ........................................ 6

Figure 3.1  Schematic illustration of a transfer matrix in a trace space: Left side is an initial trace space ($x_i, x'_i$) and right side is a final trace space ($x_f, x'_f$). Transfer matrix $R$ maps an object in the initial trace space into the final trace space: a line → a line, a point → a point, ellipse → ellipse, a curve → a curve. .................................................. 22
Figure 3.2  Schematic illustration of electron beam dynamics in drift / magnetic lens / drift system: (a) the beam line structure illustration in real space, (b) the emittance of the electron pulse at Z₀, (c) the emittance of the electron pulse at Z₁ (drift region). Dashed line is the emittance at Z₀, and the blue arrow indicates the electron motion in the trace space, (d) the emittance of the electron pulse at Z₂ (after magnetic lens focusing). Dashed line is the emittance at Z₁, and the blue arrow indicates the electron motion in the trace space, (e), (f) the emittance of the electron pulse at Z₃, Z₄ respectively.

Figure 3.3  Schematic illustration of an image system with one lens.

Figure 3.4  The 6D emittance $\varepsilon_x\varepsilon_y\varepsilon_z$ vs. the number of emitted electrons $N^{emit}$ for the extended electron sources with sizes $\sigma_T$ (100 µm, 1 mm), thermionic guns [69], Schottky, cold field-emission guns (CFEG), and heated field emission guns (HFEG).[63]

Figure 4.1  RF-enabled high-brightness ultrafast electron beam system at Michigan State University.

Figure 4.2  (a) Photoelectron pulse trajectory along an ultrafast electron beam column equipped with RF compression. The shaded regions represent the locations of the electron optical elements. (b) A scale-up view of the pulse profiles near the sample plane for nano-area diffractive imaging containing $10^5$ electrons/pulse. An aperture with a radius of 15 µm is employed to thin out the peripheral electrons to achieve a divergence angle $\alpha \leq 1.7$ mrad. The minimum transverse radius $\sigma_T$ is 0.64 µm, and the minimum longitudinal pulse length $\sigma_L$ is 0.80 µm. (c) A scale-up view of the pulse profiles near the sample plane for an ultrafast single-shot UED containing $10^8$ electrons/pulse. The minimum transverse radius $\sigma_T$ is 51 µm, and the minimum longitudinal pulse length $\sigma_L$ is 0.88 µm [68].

Figure 4.3  Cathode and anode of Pierce geometry photoelectron gun: (a) electric field calculation using Field Precision [74]. (b) Pierce geometry photoelectron gun design in the high-brightness UED electron gun chamber. Cathode and anode are electrically isolated through four 10 inch MACOR insulation rods. Right below the anode, there is first condenser magnetic lens to focus the electron beam after the anode. (c),(d) are the electric potential and field profile along the electron pulse propagation direction. The profiles at different radial locations are almost identical. This indicates that the field distribution is uniform along the beam propagation direction.
Figure 4.4  Pierce geometry photoelectron gun head assembly: (a) Fully assembled Pierce gun head, (b) The assembly procedure and the design of all parts. .......................................................... 41

Figure 4.5  Pierce geometry photoelectron gun: (a) the whole Pierce photoelectron gun housed in a UHV chamber, (b) the zoom-in view of the cathode and high voltage isolation using a ceramic disk as the base, (c) triple point shielding geometry design at the junction of MACOR rods and anode. ......................................................... 43

Figure 4.6  Current stability monitor (a) after the electron gun conditioning, (b) before the conditioning .......................................................... 46

Figure 4.7  Schematic illustration of non-uniform magnetic field (red lines) at the center of the magnetic lens pole-piece. The hole through the pole-piece is called bore and the disconnected region inside of the bore is called a gap. .......................................................... 47

Figure 4.8  Condenser magnetic lens No. 1: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the condenser lens No. 1: The black arrow indicates the electron pulse propagation direction and the the plot has the cylindrical symmetry along the beam propagation direction. (c) Magnetic field strength profile along the different radial coordinates, R = 0.0, 0.5, 1.0, 1.5, 2.0 (mm). .......................................................... 48

Figure 4.9  Condenser magnetic lens No. 2: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the condenser lens No. 2: the black arrow indicates the electron pulse propagation direction and the the plot has the cylindrical symmetry along the beam propagation direction. (c) Magnetic field strength profile along the different radial coordinates, R = 0.0, 0.5, 1.0, 1.5, 2.0 (mm). .......................................................... 49
Figure 4.10  Objective magnetic lens: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the objective magnetic lens: the black arrow indicates the electron pulse propagation direction and the the plot has the cylindrical symmetry along the beam propagation direction.  (c) Magnetic field strength profile along the different radial coordinates, $R= 0.0, 0.5, 1.0, 1.5, 2.0$ (mm). The kinks at $R=1.5, 2.0$ mm profiles are artifact because the objective lens exit hole radius is 1.5 mm.

Figure 4.11 (a) Magnetic lens current calibration simulation: Solid lines are AGM simulation without space-charge effect, and the dashed lines are Field Precision [74] simulation of non-interacting single electrons, calculated with the relative permeability shown in (b). The initial transverse size of the Gaussian electron pulse in AGM simulation is $100 \mu m$ and $50 \mu m$ with angular spread $0.1$ mrad. In Field Precision simulation, the initial position of single electrons is at $R=100$ $\mu m$ and $50$ $\mu m$, and each line represents different initial ray angles, $\pm 0.1, \ 0$ mrad.

Figure 4.12  Field Precision simulation of an electron trajectory with non-interacting particles (Red line) scheme and with space-charge effect induced by the self-generated electric field of a continuous high current electron beam (blue line). Red and blue solid lines are calculated with the same focusing condition with $CML1=550$ A, $CML2=450$ A, and $Obj.ML=750$ A, and the dashed line is calculated with with $CML1=0$ A, $CML2=450$ A, and $Obj.ML=750$ A. The black dashed vertical lines indicates electron optics components: (1) the photocathode surface, (2) $CML1$, (3) $CML2$, (4) RF cavity, (5) $Obj.ML$, (6) the sample, and (7) CCD screen. The shaded region shows where the electron beam is focused by the Pierce geometry gun.

Figure 4.13  Pillbox cavity with radius $R$ and length $d$: (a) illustration of the pillbox geometry, (b) top view and side view of transverse magnetic mode electromagnetic field in pillbox cavity, (c) top view and side view of the transverse electric mode electromagnetic field in pillbox cavity.

Figure 4.14  RF cavity: (a) The actual design of geometry optimized RF cavity and the $\text{TM}_{010}$ mode RF field in the RF cavity (The red ring is a magnetic field and the black line is an electric field), (b) Phase space volume evolution with RF compression.
Figure 4.15  Block diagram of the Phase lock loop. ........................................ 64

Figure 4.16  Structure of charge coupled device (CCD) camera mount. (a) Schematic illustration of image acquisition optics in front of CCD camera main body: Al film and phosphor screen are coated on the optical face-plate surface, and an optical taper focuses a signal with 2:1 ratio onto an intensifier input window. The Al film screens the background photon from room light and pump laser, and the phosphor film converts the electron signal to photons which is amplified by the intensity. The red box indicated the intensifier. (b) a schematic diagram of the micro-channel plate (MCP) in the intensifier. The MCP is composed of more than $10^6$ micro-channels which are individual miniature electron multipliers. (c) design of the fully assembled CCD camera. All the components are made of glass, so, using the optical grease, we make smooth contacts between parts to minimize the signal loss. ................................................................. 67

Figure 4.17  266 nm excitation mirror holder and electron beam shield. ........ 69

Figure 4.18  Electron beam deflector. (a) The design of the electron beam deflector: the electron pulse propagates from the bottom to the top (blue arrow), and two pairs of stainless steel rods generate two orthogonal directions electric fields which are perpendicular to the electron pulse propagating direction. Eight MACOR insulation cylinders electrically isolate the high voltage applied rods from the stainless steel deflector body. The MACOR cylinders are secured with 2-56 set-screws. (b) The electron beam deflection angle as a function of applied voltage between the stainless steel rods in two orthogonal directions. ................................................................. 72

Figure 4.19  Aperture manipulator. (a) Stereoscan 360 scanning electron microscope aperture manipulator. The red circle in (a) shows where four apertures are mounted at the same time. We can manipulate the position of each aperture with two micrometers shown at the end of the aperture manipulator, x, y axis. (b) Actual design of the SEM aperture manipulator assembly with the second electron beam deflector. The gap between two O-ring seals (white dot) is pumped down with a dry pump to make the gap region pressure down to $10^{-3}$ torr. Then, two O-ring seals can hold the UHV pressure difference. ... 73

Figure 4.20  Schematic diagram of the high-brightness UED chambers: (1) the 100 kV electron gun chamber, (2) 266 nm laser mirror chamber, (3) RF cavity, (4) main specimen chamber. .................................................. 75
Figure 5.1  Schematic illustration of Faraday cup: To prevent the escape of an elastic scattered electron, there is an aperture at the entrance hole. Picoammeter directly measures the current produced by the charged particles in a vacuum. Typical size of the aperture is a few hundreds micrometer. .......................... 79

Figure 5.2  Single electron count events of attenuated electron beam on CCD camera. The yellow square boxes indicates the regions of interest (ROI) 5 × 5 in pixels. .......................... 81

Figure 5.3  (a) The probability profile of the integrated intensity of single–electron events. The square is the experimental measurement and a blue line is the fitting with Poisson distribution function. The ADU is 4500 with image intensifier gain 9 V. (b) ADU under different image intensifier gain voltage, after considering the factor 2.1 following the calibration of electron counts through a Woods horn beam trap. 83

Figure 5.4  (a) The design of the beam trap. The copper tubing outer diameter is 2.0 mm and the inner diameter is 1.6 mm. The copper tube is held by a MACOR insulation cylinder, and the end of the copper tube is connected to a UHV compatible electrical wire which is Kepton–insulated silver–plated copper wire. (b) Schematic illustration of the copper tube cross-sectional view. Copper tube can trap the electrons that enter the copper tube, and the curvature reduces the probability for the elastically scattered electrons to escape from the tube. .......................... 84

Figure 5.5  The number of emitted electrons per pulse. (a) Simulation results of the number of emitted electrons per pulse $N_e^{emit}$ plot as a function of the number of generated electrons $N_e^0$, which is proportional to the input power of 266 nm pulse laser, at various surface extraction field $F_a$. This plot shows evidence of virtual cathode (VC) formation [63]. (b) Experimental measurement of the number of emitted electrons $N_e^{emit}$ as a function of input power of 266 nm pulse laser. The experimental measurement shows consistent linear dependence on input power below the VC limit, and 1/3 power dependence above the VC limit. .......................... 87

Figure 5.6  Illustration of the emittance measurement scheme .......................... 90
Figure 5.7  Electron beam image and profile on the CCD camera. (a) is a image of the full electron beam of $10^6$ electron per pulse, and (b) is one beamlet image after going through the 50 $\mu$m aperture. (c) and (d) are the beam profiles along the horizontal direction. With the acquired intensity and divergence angle of each pixel, we can construct the phase space distribution and the emittance at the aperture location. ................................. 93

Figure 5.8  Electron beam trace space plot $(x,x')$ of 10 electron per pulse and $10^6$ electron per pulse. Each data point represents the position and the transverse momentum of each beamlet, and error bar is the momentum spread of the each beamlet. ................................. 94

Figure 5.9  Dependence of the transverse emittance $\varepsilon_x$ on the number of emitted electrons ($N_{\text{emit}}$) and the extraction field $F_a$. The inset shows the temporal evolutions of $\varepsilon_x$ at $F_a = 0.32$ and 1.0 MV/m (all with $10^7$ electrons), where generally $\varepsilon_x$ reaches a steady state after 40 ps. The red dot indicates our transverse emittance measurement $\varepsilon_x = 0.167 \mu$m at a location right after the RF cavity [63]. ................................. 95

Figure 5.10  (a) Schematic illustration for the beam propagation along the electron column with CML1 and CML2 focusing. The distance shown in the figure is the actual distance of our electron beam line (see Fig. 4.1), (b) Focal length of three magnetic lenses as a function of the applied current. Each focal length measurement is with non-focused electron beam directly from the electron gun, except the objective lens. The focal length measurement of the objective lens is with CML1 and CML2 focusing. ................................. 98

Figure 5.11  Comparison between Field Precision trajectory simulation and experiment. (a) The non-interacting single-electron trajectories from Field Precision simulation. Green, blue, red, black vertical lines indicate the optical components along the high-brightness UED column: photocathode, CML1, CML2, CCD camera. Each horizontal line is a single-electron trajectory generated at different initial locations $R$. Initial condition of the electron is a completely zero energy particle and it is accelerated only by 100 kV acceleration voltage. The numbers right next to CCD position are the initial emitting location $R$ on the photocathode. (b) Ray angle vs. location $R$ on the CCD screen. The red squares are the experimental measurement of the ray angles with 10 electron per pulse shown in Fig. 5.8, and black squares are the simulation. ................................. 99
Figure 5.12  Schematic illustration of the phase jitter. (a) Perfect phase match between RF field and the electron pulse arrival time: the COM velocity of the electron pulse has no change. The relative phase mismatch causes (b) decelerating the COM velocity of the electron pulse, and (c) accelerating the COM velocity.  

Figure 5.13  Beam size and energy variation of electron pulse with different relative phase between electron pulse and RF field. (a) Beam size variation with the relative phase: the shaded areas are the compression regions and the unshaded ones are stretch regions where the faster electrons are accelerated and the slower electrons are decelerated. The top red sine curve illustrates the corresponding RF field oscillation at $\sim$1 GHz. Time zero is set at the exact timing for the perfect pulse compression. The beam size oscillates with the pulse compression: strong compression induces the transverse expansion and strong stretch suppresses the transverse expansion. At $t=0.75$ ps, the beam size is consistent with the beam size without RF compression. (b) Electron energy variation with different relative phase at 420 W RF power. $t=0$ ps is the perfect in-phase, 100 keV. Inset plot is the electron pulse arrival time on the sample as a function of the relative phase (-0.2~0.2 ps range). (c),(d) the electron pulse images on CCD at completely out of phase (stretch (c)), and the perfect in-phase (compression (d)).  

Figure 6.1  Transient photoinduced charge redistribution near surface. (a) The three mechanisms of photoexcitation that cause redistribution of charges at the surface, bulk, and vacuum levels near Si/SiO$_2$ surface. (b) Transient surface potential diagram caused by various photoinduced charge redistribution. (c) The refraction of the electron beam in each field region can be modeled by an index of refraction with $n = \sqrt{(\Delta V + V_0)/V_0}$, where $eV_0$ is the electron beam energy.
Figure 6.2 Surface electron diffraction pattern in different conditions. (a) Ewald sphere construction in the grazing incidence angle geometry. By tilting (rocking) the angle of incidence between the electron beam and the sample, the Ewald sphere intercepts the reciprocal lattice rods (rlrods) at different heights. The in-phase condition is satisfied when the intercept is at the reciprocal lattice node. The inset shows the reciprocal node structure, which is effectively determined from a Fourier Transform (FT) of the crystalline region in the sample defined by its persistence lengths. (b) Expected rocking map of a smooth, pristine surface in RHEED. (c) Experimental rocking map taken from a smooth Si/SiO₂ surface. The dashed line shows where the diffraction pattern in the inset is taken. (d) Expected rocking map of a nanostructured surface. (e) Experimental rocking map pattern taken from a highly oriented pyrolytic graphite (HOPG) surface. (f) Experimental rocking map taken from a Si/SiO₂ surface sample along a Kikuchi-enhanced diffraction peak. (g) Diffraction pattern of the Si/SiO₂ surface, showing visible Kikuchi pattern.

Figure 6.3 The idealized slab model for considering the transient surface voltage. The top trajectory is the electron scattering from the crystal planes with the presence of a surface field. The electron beam, incident at $\theta_i$, is Bragg scattered at $\theta_B$, exiting the surface at $\theta_o$. Introducing an attractive surface potential $V_s$ will cause the electron beam to be 'refracted' deeper into the crystal($\theta'_i$) and the same for the Bragg diffracted beam that would ultimately exit the crystal at $\theta_o$ with a net shift $\Delta_B$ relative to $\theta_o$.

Figure 6.4 The refraction-induced shift($\Delta_B$) for diffraction peak located at $\theta_o$ at $V_s$=1 volt calculated for difference surface diffraction condition characterized by $a = 0, 1, 2$ (see Fig. 6.2). The solid lines are exact solution from voltammetry formalism. The dashed lines are calculated employing small angle approximation (see text). The incidence angle ($\theta_i$) is set at 2.01°.
Figure 6.5 Shadow imaging experiment to characterize the properties of photoemission. (a) Schematic experiment setup of the experiment, in which the incident electron beam is displaced by $x_0$ from the photoinduced region by 800nm pump laser. The surface scattered electrons form a shadow image of the electron cloud on the CCD screen as they are scattered away from the collective field associated with photoelectrons. In parallel, the surface diffracted beam experiences the electric field associated with photoemitted electron cloud, and deflects according to its location relative to the cloud. (b) The diffraction pattern from Si/SiO$_2$ surface is shown with the striped regions selected for extracting the shadow image evolution (yellow) and the diffracted beam reflection (cyan). (c) & (d) show the snap-shot shadow images of the photoemitted electron cloud at different time delays. (e) The respective Gaussian fitting of the shadow images. (f) Results extracted from fitting the shadow image of the photoemitted electron cloud, showing the evolution of the CoM position and the cloud width.

Figure 6.6 N-particle shadow projection imaging simulation at two different time delays.

Figure 6.7 Experiments to characterize photoelectron dynamics and surface photovoltage performed at $F=65 \text{ mJ/cm}^2$. (a) Data (symbols, colored in red) show the deflection of a selected diffracted beam by the electric field associated with photoelectrons and the image charges on the surface acquired in the shadow imaging experiment setup. N-particle simulations with surface dielectric relaxation times ($\tau_r$) ranging from 0, 16, 21 ps, and $\infty$ are used to fit the data. (b) The voltammetry results (symbols, colored in red) obtained from the same diffracted beam, but at the overlapped voltammetry geometry. An N-particle simulation to estimate the refraction contribution associated with photoemission is shown (solid line, colored in blue) for comparison.

Figure 6.8 (a) An effective circuit model depicting the transient surface voltage $V_S(t)$ measurement via the refraction shift across SiO$_2$/Si interface with 20 nm Au nanoparticle decoration. The electromotive potential $\varepsilon(t)$ comes from the hot carriers generated at the Si substrate. (b) Example showing the photovoltage $V_S(t)$ measured at the interface as a function of $\varepsilon(t)$. The relationship can be seen as a convolution with kernel function $h(t)$ characteristic of the RC circuit.
Figure 6.9  Theoretical modeling of transient surface voltage $V_s(t)$. Using RC time of 30.8 ps, the corresponding electromotive force $emf$ is deduced, showing a spontaneous rise and a long decay. .......................................................... 131

Figure 6.10  Transient surface voltage caused purely by $\Delta DP$. $\Delta PE$ contribution is subtracted from total TSV, and the surface voltage is calculated by Eq. (6.16). The surface voltage is fitted by an RC charging and discharging model with $\tau_c=30.84$ (ps), and $\tau_d=296.47$ (ps). Inset: Charging/discharging dynamics in a log time scale. ........................................ 133

Figure 7.1  Charge redistribution at nanomaterials interfaces subject to photoexcitation. (a) Dielectric realignment; (b) carrier diffusion; (c) interfacial charge transfer .......................................................... 138

Figure 7.2  Trasient voltammetry from three diffracted beams from Si/SiO$_2$ interface. (a) The angular shift of (0,3,24), (0,1,21), and (0,1,24) beams excited at F=65mJ/cm$^2$. (b) The rocking map characterization of (0,3)-relrod, showing a surface diffraction condition $a=1$. (c) The photo voltage deduced from (0,3,24), (0,1,21), and (0,1,24) beams based on Eq. (6.10) using $a=1$. .......................................................... 142

Figure 7.3  (a) A sample of Au nanoparticles (NPs) immobilized on a functionalized Si substrate. (b) The chemical form of the AEAPTMS linker molecule. (c) Schematic of an electron beam scattering from the ordered self-assembled monolayer chain and the corresponding diffraction pattern [25] .......................................................... 146

Figure 7.4  (a) An effective circuit model depicting the transient surface voltage $V_s(t)$ measurement via the refraction shift of the diffracted beams through SAM. The $R_S$, $C_S$, $R_M$, $C_M$ are the effective resistance and capacitance of the substrate (S) and the SAM (M). The electromotive potential that can drive the photocurrent through the SiO$_2$ layer ($i_S$) and further through SAM ($i_M$) is mainly from the hot carriers generated from the Si ($\varepsilon_1(t)$); whereas the short-lived photoexcited hot carriers generated within the Au nanoparticle (NP) can also drive the charge transfer in the opposite direction ($\varepsilon_2(t)$). (b) The overall refraction shift determined by SAM diffracted beam (labeled $V_s$), the background (labeled $V_B$) obtained from SiO$_2$/Si interface, and the molecular charge transport contribution, obtained by subtracting $V_B$ from $V_s$ .......................................................... 147
Figure 7.5  Schematic illustration of localized surface plasmon oscillation induced by an oscillating electric field in a metal nanoparticle. The displacement of conduction electron cloud relative to the nuclei is shown. The frequency of the localized surface plasmon resonance is denoted $\omega_p$.  

Figure 7.6  Hollow gold nanoshell (HGN) surface plasmon resonance. (a) Schematic illustration of localized surface plasmon oscillation induced by an oscillating electric field in a hollow gold nanoshell (HGN). The displacement of conduction electron cloud relative to the nuclei is shown. The frequency of the localized surface plasmon resonance is denoted $\omega_p$. (b) A UV-visible absorption spectra of nine HGN samples varying diameter and wall thickness.  

Figure 7.7  An energy diagram of plasmon hybridization in a HGN describes the interaction between the metal sphere plasmon and cavity plasmon in bulk metal. Two HGN plasmon modes are an antisymmetrically coupled (antibonding) $\omega_+$ plasmon and a symmetrically coupled (bonding) $\omega_-$ plasmon.  

Figure 7.8  Ultrafast transport at gold nanoparticle (NP)/SAM/silicon interface near surface plasmon resonance (SPR) excitation. (a) The maximum transient photovoltage response near SPR excitation, as compared to the absorption of the similar nanoparticles in water, bulk gold, and silicon substrate. It is evident that while both show characteristic SPR peak at $\sim$525 nm the nanoparticles $V_s$ spectrum at surface (colored in green) lacks the background seen in the optical absorption spectrum of similar nanoparticles in water (colored in red). (b) The enhancement of hot carrier generation at Si surface (channel II) can be achieved via SPR evanescent field within the Si surface or charge carrier injection from highly excited Au nanoparticle (channel I).  

Figure 7.9  (a) The statistics of HGNs diameter before fs laser irradiation and after irradiation (the number of HGN sampling is $\sim$700 individual HGNs in each case), (b) SEM image of the morphology of HGNs distribution on the SiO$_2$/Si substrate and the scale bar corresponds to 1$\mu$m, (c) and (d) are the SEM image of HGNs before and after irradiation, respectively, and the scale bar corresponds to 100 nm.
Figure 7.10  (a) Debye-Waller factor (DWF) analysis of the diffraction intensity drop. This indicates the lattice temperature as a function of the irradiation fluence. (b) DWF profiles of different wavelength pump laser are fitted with power function, $y = ax^b$. (c) Transient surface voltage ($V_s$) generation as a function of different laser wavelength.  . 164

Figure 8.1  CeTe$_3$ sample image on 1000 mesh TEM grid: (a) optical microscope image, (b) Projection Shadow image of a full grid with high-brightness UED, (c) Projection shadow image with 50 $\mu$m aperture selected area, a white square shown in (b).  . 168

Figure 8.2  Convergent beam test to maximize the electron dose $N_e/A$. With the constant current of CML1=1.0 A and CML2=2.7 A and 170 $\mu$m aperture, the electron beam is focused on the sample position with adjusting Obj. ML current shown in the each image. Minimum beam size is smaller than 7 $\mu$m which is the limitation of our measurement resolution. This gives us $D > 2000$ electron/$\mu$m$^2$. (The whole image is the same size region, 505×620 pixels.)  . 171

Figure 8.3  (a) Convergent beam diffraction of TaS$_2$ with 50 $\mu$m aperture (exposure time 500 ms). Hexagon indicates the charge density wave (CDW) diffraction peak. (b) Parallel beam diffraction of TaS$_2$ with 170 $\mu$m aperture (exposure time 2 s). Upper right panel is zoom-in image of the lower left red square showing CDW diffraction peak. (c) Convergent beam diffraction of CeTe$_3$ with 50 $\mu$m aperture (exposure time 4 s) after the implementation with the beam trap extension and Teflon spacer to minimize the sample column vibration.  . 173

Figure 8.4  (a) Crystal structure of VO$_2$ in metallic rutile phase: the gray ball is the V atoms and red ball is O atoms. The arrows are the dimerization direction of V atoms in V chain along c axis.  (b) and (c) are the schematic illustration of VO$_2$ density of state of VO$_2$ in metallic and insulator phase, respectively.  . 174
Figure 8.5  (a) Optical microscope image of VO$_2$ film sample which is grown on the 5 nm thickness amorphous silicon membrane. The eight square windows are the VO$_2$ film with 5 nm thickness Si membrane and a long black rectangle is a broken window. Each square window size is 100 $\mu$m x 100 $\mu$m, and the displacement between windows is 200 $\mu$m, (b) Diffraction pattern of poly-crystalline VO$_2$ film, (c) Integrate diffraction intensity profile along the wave vector corresponding to the radial direction in real space image. The arrows indicate the V-V dimerization symmetry peaks in a monoclinic insulation phase (302, 313).

Figure 8.6  The photo-induced phase transition measurement with VO$_2$ with different RF power compression of $\sim 7 \times 10^4$ electrons per pulse: the measurements are relative diffraction peak intensity change as a function of the time.

Figure 8.7  Pulse duration measurement from VO$_2$ phase transition: VO$_2$ phase transition experiment is performed with $\sim 7 \times 10^4$ electrons per pulse.

Figure 8.8  (a) Electron pulse arriving time fluctuation during the experiment. Zero fluctuation means the electron energy is exactly 100 keV, and due to the phase mismatch, the COM velocity of electron pulse is fluctuated. (b) RF phase stability monitor. The red line shows the phase fluctuation before temperature instability correction and blue line shows the phase fluctuation after the correction.

Figure A.1  Different kinds of electrons scattering from the specimen

Figure A.2  Derivation of Bragg equation $2d \sin \theta = n \lambda$

Figure A.3  The phase angle difference of incident beam is $\mathbf{k} \cdot \mathbf{r} = 2\pi \sin \varphi / \lambda$ and the path difference at $O$ and $\mathbf{r}$ is $r \sin \varphi$. For diffracted beam, the phase angle difference is $-\mathbf{k}' \cdot \mathbf{r}$. The total phase angle difference is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$, and the beam scattered from $dV$ at $\mathbf{r}$ has the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ relative to the beam scattered from a volume element at the origin $O$.  

xxiii
Figure A.4  Ewald sphere construction: The points are reciprocal lattice points of the crystal. The vector $\mathbf{k}$ is drawn in the direction of the incident beam, and the origin is chosen such that $\mathbf{k}$ terminates at any reciprocal lattice points. We draw a Ewald sphere of radius $k = 2\pi/\lambda$ about the origin of $\mathbf{k}$. A diffracted beam will be formed if Ewald sphere intersects any other reciprocal lattice points. The Ewald sphere as drawn intercepts a point connected with the end of $\mathbf{k}$ by a reciprocal lattice vector $\mathbf{G}$. The diffracted beam is in the direction $\mathbf{k}' = \mathbf{k} + \mathbf{G}$. The angle $\theta$ is the Bragg angle of Fig. A.2.

Figure B.1  Ultrafast electron diffraction experiment geometry with ultrafast electron microscope system. (a) A schematic diagram of the UEC optics setup. Both 400 and 800 nm beam lines are shown entering the delay line, but one of them is blocked based on the choice of excitation. The time delay between pump laser pulse and electron probe is controlled by delay stage adjusting traveling path length. Also, pulse shaper is shown in the diagram, but it has not been tested yet. (b) In UHV specimen chamber, the 100 kV UEM column beam goes from top down, and 40 kV UED electron beam goes horizontally. The pump laser lands on the sample with $45^\circ$ tilting.

Figure B.2  Schematic picture of the femtosecond laser source: (1) femtosecond seed pulse (Mai-Tai), (2) amplifier for femtosecond pulse (Spitfire), (3) continuous wave pump laser for amplification (Empower).

Figure B.3  Universal electron gun design. (a) Zoom-in of the electron gun head part, (b) actual image of the fully assembled universal electron gun before installation into the chamber, (c) overall layout of the electron gun including the gun chamber with 6” conflat flange.

Figure B.4  Performance characterization of the 40 kV universal electron gun. (a) Analog-to-digital unit (ADU) measurement: CCD camera response of a single electron event is about 175 intensity of one pixel. (b) the number of electron per pulse with the measured ADU as a function of a different magnetic lens focusing strength. The reason for the increase in the number of electron with stronger focusing is more electrons able to pass through the 100 $\mu$m aperture because of stronger focusing. (c) the beam size at the sample location and the CCD camera as a function of a different magnetic lens focusing. (d) divergence angle of the electron beam with different focusing strength. The divergence angle is calculated by the beam sizes at the sample and CCD camera with the camera distance between the sample and CCD camera.
Figure B.5 Structure of charge coupled device (CCD) camera design. (a) Schematic illustration of CCD camera structure: in front of CCD camera, we have the optical taper to focus a signal in large area into small CCD camera input window (2:1 ratio). On the optical taper face, we have an optical face-plate, and the 60 nm aluminum film and phosphor film are coated on the face-plate surface. The Al film screens the background photon from room light and pump laser. The phosphor film converts the electron signal to photon to amplify the intensity. Red box indicates the intensifier. (b) the schematic diagram of the MCP in intensifier. MCP is composed of more than $10^6$ micro-channels which are individual miniature electron multipliers. (c) design of the fully assembled CCD camera.

Figure E.1 (a) Schematic illustration of a non-interacting photoemission electron generation on a cathode: R is the initial location where the electron is generated and $\theta$ is the divergence angle caused by the focusing field of Pierce gun geometry. (b) Field Precision simulation result of the electron divergence angle at different initial position (R) at various gap distances between the cathode and anode: a gap distance of the current design is 20 mm and the surface extraction field is 2.2 MV/m field, and 20% smaller gap distance, 16 mm, generates 45% higher extraction field, 3.2 MV/m.
Chapter 1

Introduction

1.1 Ultrafast Camera: Pump-Probe Technique

Making a ‘molecular movie’ to unravel the atomic processes in complex materials is one of the greatest dreams in condensed matter physics and material science. To make this dream come true, an ‘ultrafast camera’ with simultaneously very high spatial and temporal resolution on the scales matching the atomic dynamics is required. The ultrafast pump-probe scheme based on femtosecond laser technology can provide the basic framework for realizing such an ‘ultrafast camera’ thanks to significant advancements in photonics and electronics, and more recently with accelerator technologies [1]. In a pump-probe experiment station as illustrated in Fig. 1.1, two pulses are employed: one acting as a pump and the other as a probe. The pump pulse initiates an ultrafast process in a target by providing an impulsive excitation, whereas a second probe pulse, which can be an optical, electron, X-ray pulse or other ultrafast detection scheme, is employed to characterize the ensuing ultrafast dynamics. A well defined time delay ($\Delta t$) is required to provide the time stamps of individual events. A series of responses at various $\Delta t$ can be used to construct a full temporal evolution of a process induced within the optically excited target.

The diversity in pump-probe schemes arises from the varied nature of the probe. For example, using optical detection (transmission and reflectance), the optical constant changes
Figure 1.1 Schematic diagram of the pump-probe experiment setup. The relative time delay between pump (red) and probe (blue) pulses is controlled by the translational delay stage.

over different spectroscopic regimes which manifest the photoexcited electronic properties [2, 3, 4, 5, 6, 7, 8, 9] and even their coupling to the lattice dynamics [10, 11, 12, 13] can be deduced. The latest development of ultrafast angular resolved photoemission technique zooms in on the momentum space of the electron dynamics and offers specific information on the perturbation and reconstruction of Fermi surface, which is particularly important to understand the electronic phase transitions [14] and surface electron dynamics [15, 16].

To directly visualize the structural dynamics, the probe also requires the atomic scale resolution and only hard X-ray and high energy (∼keV) electron probes with sub-angstrom de Broglie wavelength fulfill this requirement through either diffraction or imaging. In the following sections, some of the recent ultrafast X-ray/electron diffraction experiments will be discussed.
1.2 Ultrafast X-ray Diffraction

Diffraction of X-rays from crystalline materials is a standard tool for determining equilibrium atomic structures. Using modern development of ultrashort X-ray pulse (see Chapter 2), the time evolution of photoinduced structural changes can be studied in a direct way by using ultrafast X-ray diffraction techniques.

Earlier ultrafast X-ray studies focused on the optically induced phase transitions and the selected modes that are crucial for the events. After photoexcitation with high intensity of ultrashort laser pulse, a substantial fraction of electrons is excited from bonding valence band to anti-bonding conduction band orbitals. This causes the solid to melt and lose the long-range order. If the melting occurs before the electronic and lattice temperatures are in thermal equilibrium, then this process is called non-thermal. A. M. Lindenberg and
his colleagues have observed non-thermal melting in a semiconductor InSb with ultrashort X-ray probe [17]. Femtosecond pump laser changes the interatomic potential energy surfaces and thus induces atomic displacements, eventually leading to the transition from a crystalline solid to a disordered liquid (Fig. 1.2(a)). Sokolowski-Tinten and colleague have succeeded in directly measuring the coherent atomic displacement of the lattice atoms close to a phase transition in photoexcited bismuth [18]. Excitation of large-amplitude coherent optical phonons gives rise to a periodic modulation of the X-ray diffraction efficiency (Fig. 1.2(b)). Stronger excitation corresponding to atomic displacements exceeding 10% of the nearest-neighbor distance leads to a subsequent loss of long-range order, which is most probably due to melting of the material. Recently, Clark and his colleagues have achieved the characterization of lattice displacements in individual nanoparticles over 10-100 ps scales with atomic sensitivity [19]. Fig. 1.3 shows the Bragg peak position changes of two different individual nanocrystals (∼400 nm) with 800 nm femtosecond laser excitation, and measure the subsequent ps evolution of acoustic phonons in single gold nanocrystals using ultrafast X-ray pulses generated by the Linac Coherent Light Source (X-ray Free Electron Laser).

1.3 Ultrafast Electron Diffraction

Ultrafast electron diffraction (UED) has a lot in common with ultrafast X-ray diffraction in the applications, and the achieved spatiotemporal resolution of the two techniques in current development are quite comparable [20, 21, 22, 23, 24, 25, 26]. However, electrons have significantly higher scattering cross-section (10^5-10^6 times) than that of X-rays [27], and ultrafast electron sources with sufficient signal-to-noise ratio for UED experiments are
Figure 1.3 Angular shift of (111) gold Bragg peak as a function of delay time from the same nanocrystal. (a) and (b) are from different individual nanocrystals. The blue dots are the experimental data and the solid red line is the modeled peak shift [19].

available in a table-top setup. In comparison, similar studies using X-rays usually are facility-based. Pros and cons in various electron and X-ray developments will be discussed in section 2.3.

UED experiment has been successfully applied to investigate photoinduced non-thermal melting processes [28, 29, 30, 31, 32, 33], structural phase transitions [34, 35, 36, 37, 38], and transient surface charge dynamics [39, 40, 41], as summarized in a recent monograph on this subject [42]. Photoinduced crystalline-liquid (or amorphous) phase transformation of gold nanoparticles has been directly studied [29]. In this nanoparticle study conducted at MSU’s ultrafast electron crystallography laboratory, the real space atomic bond distribution is extracted using a modified radial distribution functions (mRDF) method [29]. Fig. 1.4 shows the photoinduced melting process of 2 nm gold nanoparticles with two different fluences, 31 mJ/cm² and 75 mJ/cm². During the process, the depletion of the major bond density at ∼5, 8 Å is coupled to the enhancement of slightly longer bond density around the neighboring region, and this indicates that photoinduced nanoparticle melting process
Figure 1.4 The melting dynamics of 2 nm Au nanoparticles. (Left) mRDF map constructed by stacking mRDFs of UEC patterns at a sequence of delays between 5 and 2300 ps at irradiation fluence $F=31 \text{ mJ/cm}^2$. Surface melting (enclosed by the dashed white line) is visible. (Right) mRDF map for $F=75 \text{ mJ/cm}^2$. Full scale melting is observed. The liquid state (enclosed by dashed white line) is characterized by the drop of second nearest density (at $5 \text{ Å}$) to $(1 - 1/e)$ of the static value (at negative time) [29].

resembles a conformation change between selected minimum energy structures on the free energy landscape, rather than random dissociation in thermal melting. However, to pin down the exact pathway for size-dependent melting, ultrafast diffraction investigation on the single-particle level is required and this investigation is not possible with the current UED setups.

Using UED, phase transitions in solid crystals of strongly correlated materials [43, 37, 44, 35, 45, 46] and nano-materials [47, 34, 48, 49, 50] have also been investigated with sub-ps resolution. Moreover, exploiting the charge sensitivity of the electron probe, ultrafast electron diffraction voltammetry (UEDV) has been developed to directly measure the transient surface charge dynamics [40, 51, 41].
As shown in this chapter, UED has been successfully demonstrated with the capability to resolve ultrafast dynamics with atomic and sub-picosecond spatiotemporal resolution while, in various developments of UED, the electron pulses with $10^3$-$10^5$ electrons per pulse are also available. Nonetheless, for studying molecular processes on the nanometer scale such as a single nanoparticle and a single domain of crystals, a figure of merit is the electron dose, which is still limited to $\sim 1$ electron/$\mu$m$^2$, per pulse. Therefore, the high-brightness ultrafast electron source development which is one of the major topics in this thesis, is required to overcome this limitation for pushing ultrafast electron diffraction and imaging into nanoscale domains. The main contributions to the development described in this thesis are the design and construction of the electron gun, and the complete electron beam line, including the various electron optical components, the diffraction chamber, and the detector systems, and the work on RF cavity and characterization of the electron beam system performance are results of collaboration with Zhensheng Tao and Nan Du. The rest of the thesis is organized as the following. In Chapter 2, the current status of developing ultrashort electron and ultrashort X-ray source will be introduced. In Chapter 3, relevant beam dynamics associated with a high-brightness electron beam system will be discussed. In Chapter 4 and Chapter 5, the design and the characterization of a Radio-Frequency (RF) enabled high-brightness electron beam system at MSU will be covered. Work in further development of UEDV for studying ultrafast charge dynamics in nanostructure interfaces will be also presented in Chapter 6 and 7. In Chapter 8, the preliminary experiments with the high-brightness ultrafast electron beam system under development will be shown.
Chapter 2

Current Status of Ultrashort Pulse Development: X-ray and Electron

Both ultrafast X-ray and electron beams can achieve high combined spatial-temporal resolution, but both have faced some fundamental limits, such as the limitation in the source strength and parasitic effects including radiation damage, loss of coherence, etc. In this chapter, the current state of development of ultrashort X-ray and electron sources will be introduced, which will serve as a baseline in evaluating the development of a high-brightness ultrafast electron diffraction and imaging system at MSU.

2.1 Ultrashort X-ray Pulse Generation

X-ray sources are one of the strongest candidates to probe ultrafast atomic scale processes. Different types of X-ray sources have been developed for several decades: (1) table-top tunable extreme ultraviolet (EUV, 10 - 120 eV) source with high harmonic generation (HHG), (2) table-top soft X-ray (0.1 - 5 keV) source with laser driven plasma (LDP), (3) high intensity tunable X-ray source with free electron laser (FEL), from EUV to hard X-ray (1 - 10 keV). A comparison among the X-ray sources is summarized in Table 2.1.
2.1.1 High Harmonics Generation (HHG)

Employing gas phase targets, intense femtosecond lasers can generate photons in table-top scale tunable EUV source with high spatial and temporal coherence through HHG. The strong electromagnetic field of a femtosecond-laser enables the electrons in atoms to tunnel through the potential barrier of ions. The liberated electrons are subsequently accelerated by the strong laser field up to $\sim 10$ eV, and the kinetic energy gained can be released in the form of coherent radiation at the harmonics of the driving femtosecond-laser as the electrons decelerate and recombine with the ions. The photons emerge in such a cooperative interacting region as a burst of broadband coherent radiation with a duration in the femtosecond-to-attosecond regime. The major advantage of this HHG technique is low cost and table-top scale compared to accelerator-based X-ray sources.
2.1.2 Laser Driven Plasma (LDP)

LDP X-ray source is also a table-top system generating a large number of photons per pulse and high average power in the soft X-ray regime. When a high intensity ultrashort laser pulse impinges a solid target, such as a metal surface, photo-induced ionization turns the surface into a high density plasma. In the dense plasma, energetic hot electrons are accelerated by the incident laser field, and the X-rays are generated by impingement of the accelerated electrons into the target material [23]. The compact and bright plasma-based soft X-ray source can operate in the 10-50 nm wavelength region [52].

2.1.3 Free Electron Laser

X-ray free electron laser (X-FEL) is distinguished by their extremely high intensity (higher than $10^{10}$ photons/pulse), high coherence, and short pulse duration ($\sim 100$ fs), typically with a repetition rate of $\sim 100$ Hz. The X-FEL radiation is achieved by the self-amplification of spontaneous emission of high-energy, high-peak current, and ultrashort pulsed electron bunches [23]. For hard X-ray generation, X-FEL uses an undulator, which is a periodic arrangement of magnets with alternating poles generating a magnetic field across the beam path. As a relativistic electron beam passes through the undulator, the transverse acceleration of the electron beam by the undulator results in synchrotron radiation which is monochromatic, but incoherent. However, when the synchrotron radiation becomes sufficiently strong, the transverse electric field of the radiation interacts with the transverse electron beam. This interaction causes some electrons to gain and others to lose energy to the optical field via the ponderomotive force. This energy modulation evolves into electron density modulations with a period of one optical wavelength. The modulated electrons are
called microbunches, separated by one optical wavelength along the axis. Whereas conventional undulators would cause the electrons to radiate independently, the radiation emitted by the bunched electrons are in phase, and the emitted field adds together coherently. Therefore, the X-ray free electron laser can generate up to a 10 fs X-ray pulse containing up to $10^{13}$ photons per pulse in a narrow spectral bandwidth [53].

2.2 Ultrashort Electron Pulse Generation

In the electron source development, the generation of a high density electron pulse is relatively straightforward, but preserving the time resolution of the electron pulse after generation is challenging due to the space-charge effect. The space-charge–led transverse expansion effecting the focusing power may be compensated by various types of electron optics, but space-charge–led longitudinal expansion, which degrades the time resolution, is quite difficult to handle. To overcome such the space-charge effect, four different approaches have been developed: (1) minimization of the propagation distance with a compact electron beam system, (2) elimination of the space-charge effect with single-electron pulses, (3) minimization of the space-charge effect with relativistic electrons, (4) reversal of the electron pulse expansion with radio-frequency (RF) pulse compression.

2.2.1 Compact Electron Gun

One of the simplest ways to minimize the space-charge broadening is reducing the source-to-sample distance. Such compact electron beam systems have been successfully demonstrated by several groups [54, 55, 20, 25]. Most recently, the Baumert group at University of Kassel has developed a compact UED system with a 8.5 mm cathode-to-sample distance.
(cathode-to-anode distance $\sim$3.5 mm and anode-to-sample distance $\sim$5.0 mm [54]). To reduce the cathode-to-sample distance, a magnetic lens is mounted after a sample. While this arrangement does not allow focusing the electron pulse, it may be operated in a lensless imaging mode, such as projection imaging. This system has achieved a $\sim$200 fs time resolution with 5000 electrons per pulse. The Dwayne Miller group has also developed a compact electron diffraction system having a $\leq$ 3 cm cathode-to-sample distance [55]. This system structure is similar to the UED system at MSU, but, to reduce the cathode-to-sample distance, a cathode and an anode are inside of the magnetic lens, and the anode is located directly front of the magnetic lens pole. This system has achieved $\sim$300 fs time resolution with $\sim$10$^4$ electrons per pulse [20]. These compact electron guns have achieved good temporal resolution, however, they typically lack sufficient flexibility to meet different applications in pulse characteristics. For example, the compact setup does not allow for front illumination of the photocathode, whereas the back illumination has a low threshold for the onset of virtual cathode effects, which limits the emitted electron density. It is also difficult to reach sub-$\mu$m scale focusing for microdiffraction applications.

2.2.2 Single-Electron Pulses

Using single-electron pulses, the space-charge effects can be significantly reduced, but increasing the repetition rate by $\sim$100 MHz is required to maintain a sufficient signal-to-noise ratio. The Zewail group at Caltech has built the first ultrafast electron microscope (UEM) with single-electron pulses [56]. The major advantage of this scheme is that a conventional transmission electron microscope (TEM) can be modified without introducing major components to handle the associated space-charge effects in the intense short-pulsed beam.
The time resolution of such a UEM is fundamentally limited by the timing jitter associated with photoelectron generation, and a temporal resolution of $\sim$70 fs has been achieved by optimizing the excitation photon energy [56]. However, the applications to material studies are limited because the MHz repetition rate requires a robust reversible process to occur.

### 2.2.3 MeV Ultrafast Electron Microscope

It is known that the space–charge effect can be significantly reduced when charged particles are accelerated to the relativistic energy regime [57]. For example, when the electron pulse propagates in free space, the acceleration in the longitudinal pulse broadening, $\frac{d^2 l}{dt^2}$, caused by Coulomb repulsion, is inversely proportional to $\gamma^3$ ($\gamma$: Lorentz factor) with a negligible transverse motion [57]. Therefore, the space–charge–led broadening of an intense electron pulse can be overcome by accelerating the electron pulse to $\sim$MeV energies. Using a radio-frequency (RF) photogun, a 1-3 MeV electron pulse is easily achievable with up to $\sim10^7$ electrons per pulse. The incorporation of an RF photogun for UED experiment has been demonstrated by several groups [58, 59], achieving $\sim$100 fs pulse generation. MeV ultrafast electron beam systems, however, face other challenges. One challenge is knock-on damage [27]. The energy deposited in materials by elastic and inelastic scattering of $\sim$MeV electrons can be $\sim$100 eV, whereas the displacement energy associated with light atoms, such as, C, N, O, is typically $\sim$25 eV. This means that atoms in such samples can be knocked out by the MeV electron probe. The second limitation is that the relatively lower elastic scattering cross-section at higher energy reduces the effective scattering signal strength. The last challenge is that MeV electron beams require non-standard electron optics and detectors: especially the corresponding angle for a given momentum transfer is significantly reduced.
at high energies leading to the requirement of long baseline and increased construction cost.

### 2.2.4 KeV Ultrafast Electron Microscope

With electron energies on the order of 100 keV (80 - 500 keV; 0.017 - 0.043 Å), the energy deposited by an electron pulse is moderate (< 20 eV), and the ~keV energy electron beam can be controlled by standard electron optics. However, in this energy range, the space–charge–led pulse broadening is severe. The broadening can be understood from the accelerated development of a momentum-space correlation in the longitudinal phase space led by the Coulomb repulsion between electrons. The high-energy electrons at the front of the pulse are propelled to gain further momentum, whereas the lower-energy electrons at the tail are further pushed back and decelerated by the Coulomb repulsion [60]. With a well synchronized RF field, one can flip such a correlation by decelerating the electrons at the front and accelerating electrons at the tail, leading to a recompressing of the electron pulse downstream (see section 4.4.3). This RF compression scheme has been widely employed in accelerator design and has recently been demonstrated in a sub-relativistic beam (~95 keV) by the Luiten group at Eindhoven University of Technology [60, 21]. Near 100 fs electron pulses with ~10^6 electrons per pulse have been generated. A high-brightness electron beamline feeding a UEM system at MSU is also equipped with an RF compression scheme, which will be detailed in Chapter 4 and Chapter 5.

### 2.3 Radiation effects induced by X-rays and electrons

High intensity X-ray and electron pulse irradiation can liberate electrons from atoms in a material, thereby ionizing the material. The ionization leads to formation of highly
reactive sites, which disrupt crystal lattices and, eventually, cause structural deformation. This process is called radiation damage.

<table>
<thead>
<tr>
<th>Ratio (inelastic/elastic) scattering events</th>
<th>Electrons 0.02 Å</th>
<th>X-ray 1.5 Å</th>
<th>X-ray 30 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanism of radiation damage</td>
<td>Secondary e⁻ emission</td>
<td>Photoelectric e⁻ emission</td>
<td>Photoelectric e⁻ emission</td>
</tr>
<tr>
<td>Energy deposited per inelastic event</td>
<td>20 eV</td>
<td>8 keV</td>
<td>400 eV</td>
</tr>
<tr>
<td>Energy deposited per elastic event</td>
<td>60 eV</td>
<td>80 keV</td>
<td>400 keV</td>
</tr>
<tr>
<td>Energy deposited relative to electrons:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inelastic</td>
<td>1</td>
<td>400</td>
<td>20</td>
</tr>
<tr>
<td>elastic</td>
<td>1</td>
<td>~1000</td>
<td>~10000</td>
</tr>
<tr>
<td>Elastic mean free path relative to electrons</td>
<td>1</td>
<td>$10^5 - 10^6$</td>
<td>$10^2 - 10^3$</td>
</tr>
</tbody>
</table>

Table 2.2 Energy deposited in biological specimens [27]

Minimizing the unexpected radiation damage from incident probing X-rays and electrons is a key issue for implementing ultrafast diffraction experiments. The radiation damage is generally caused by two different types of interaction between the probe and a sample: elastic scattering and inelastic scattering. To compare the radiation damage, we define the amount of the energy deposited by inelastic scattering per elastic scattering [27]. Fundamentally, when a photon interacts with objects (atoms or molecules), the electromagnetic field of the photon oscillates valence electrons of the objects and the induced oscillating dipole of the objects radiates (1) the identical energy photon (Reyleigh scattering, elastic
scattering), and the lower energy photon (Compton scattering, inelastic scattering). Similarly, the incident electrons in the objects experience a static electric field generated by the ion and electron cloud, and the propagation direction is bent (1) without energy loss (Rutherford scattering, elastic scattering), and with energy loss (inelastic scattering). Two distinct ways of the interactions lead to different energy deposition on the sample, summarized in Table 2.2 [27]. According to the ratio of inelastic to elastic events for electron and X-ray shown in Table 2.2 [61], the amount of the energy deposited per elastic event by 0.02 Å electrons is much less than than the deposited energies of 1.5 Å and 30 Å X-ray, by 1000 times and 10000 times, respectively.

The different radiation effects and the scattering cross-section associated with the X-ray and electron beams give us two complementary perspectives to enable atomic level probing ultrafast dynamics. For example, the extremely high scattering cross-section of electrons (10⁵-10⁶ higher than X-ray) makes electron sources best for studying nanoscale or mesoscale systems, surfaces, and gas phase dynamics, whereas the smaller scattering cross-section and greater penetration depth make X-ray sources best for the study of solution phase, biological, and macro-systems. From a technical perspective, the penetration depth of a keV electron beam naturally matches that of the optical excitation (typically 10-100 nm), whereas an X-ray beam has a longer penetration depth (10-100 µm) and must be implemented using a grazing angle or using very thin samples compared to static X-ray experiments. High-brightness electron sources are also easier and less expensive to implement than the equivalent X-ray source.
Chapter 3

Beam Dynamics in High-Brightness

Pulsed Electron Beam-line

In the development of high-brightness electron beamlines for ultrafast electron diffraction (UED) and imaging (UEM) experiment, one of the most critical components is the electron source. The definition of the brightness in the acceleration community is \( \frac{N}{\varepsilon_x\varepsilon_y\varepsilon_z} \) (see Eq. 3.5), where \( N \) is the number of electrons per pulse and \( \varepsilon_x\varepsilon_y\varepsilon_z \) is the phase space volume [62]. The phase space evolution along the beam propagation is directly related to the electron beam quality such as spatial and temporal resolution: coherence length \( L_t = \frac{\hbar \sigma_x}{2 m_e \varepsilon_x} \), and \( \varepsilon_z = \frac{\Delta t \Delta E}{m_e c \gamma} \) (see Eq. 3.35, Eq. 3.37) [63]. In the accelerator community, the technique and theory for high-brightness electron beam generation and evolution have been studied for several decades. To understand and develop a new generation of UED and UEM with high-brightness electron sources, the fundamental theory of beam physics and the concept of phase space are introduced in the following section, followed by a discussion of the phase space evolution of the electron beam along the high-brightness UED system.
3.1 Electron Beam Phase Space Evolution

The basic physical principles of electron beam dynamics can be represented by the Cartesian coordinate system \((x, y, z)\), where \(x\) and \(y\) refer to the transverse coordinate while \(z\) is the longitudinal coordinate along the beam propagation direction. Each electron in the full beam pulse is represented by position and momentum \((x, p_x; y, p_y; z, p_z)\) in a six-dimensional phase space. A detailed understanding of the motion of the charged particle requires the study of the center of mass motion (COM) of the electron beam as well as the motion of the relative coordinates with respect to the COM. The assumption about the relative motion is that all the charged particles in a pulse are confined within a finite region, hence the motion is bounded within a finite volume of the phase space. Study of this relative motion is key to understanding the beam dynamics.

3.1.1 Brightness and Emittance

By definition, a beam such as our electron pulse, is an ensemble of particles that are defined by 6-dimensional (6D) phase space coordinates, \(P(x, p_x; y, p_y; z, p_z)\). During the electron pulse propagation, we can define two distinct locations: the initial position \(P_i(x_i, p^i_x; y_i, p^i_y; z_i, p^i_z)\) and the final position \(P_f(x_f, p^f_x; y_f, p^f_y; z_f, p^f_z)\), and construct a relation between the two locations with a transfer matrix \(R_p\):

\[
P_f = R_p P_i, \tag{3.1}\]

where \(R_p\) is a \(6 \times 6\) matrix that maps the 6D coordinates of an electron within the electron
pulse from $P_i$ to $P_f$ under the condition $\det(R_p)=1$ in a beam system governed by Liouville’s theorem. This transfer matrix $R_p$ can be established for the various regions/optical components between the two locations, such as the drift regions, the magnetic lenses, and the RF cavity.

In a high energy beam, the longitudinal $z$-component of the momentum $p_z$ is generally much larger than the other two components $p_x$ and $p_y$ ($p_z \gg p_x, p_y$), and it is often possible to decouple the four dimensional transverse phase space $(x, p_x; y, p_y)$ from the longitudinal phase space $(z, p_z)$. For reasons that will become obvious later, the transverse phase space is often reconstructed as the trace space with the unitless momentum component corresponding to the divergence angle: $(x', y')$, where $x' \equiv \frac{p_x}{p_z}$, $y' \equiv \frac{p_y}{p_z}$. The longitudinal phase space is reconstructed as $(z, \delta)$, where $\delta \equiv \frac{p_z-<p_z>}{<p_z>}$. Therefore, a particle coordinate in the 6D trace space can be represented as

$$X^T = (x, x', y, y', z, \delta), \quad (3.2)$$

where $X^T$ is the transpose vector of $X$.

Because the variables in the 6D trace space may be correlated, we define the beam matrix $\Sigma$ using a covariance matrix:
The elements of the beam matrix are the centered second-order moments associated to the beam trace space distribution with the mean vector \( \langle X^T \rangle = 0 \). The beam matrix of the propagating electron pulse \( \Sigma_f \) can be calculated with the initial beam matrix \( \Sigma_i \) and the transfer matrix \( R \) (\( cf. R_p \) is in phase space, and \( R \) is in trace space.), which represents the optical components in high-brightness UED:

\[
\Sigma_f = R \Sigma_i R^T \tag{3.4}
\]

Statistically, a 6D Gaussian beam \( \rho(X) \) in trace space can be represented with a beam matrix:

\[
\rho(X) = \frac{1}{(2\pi)^3 \varepsilon_x \varepsilon_y \varepsilon_z} N \exp\left( -\frac{1}{2} X^T \Sigma^{-1} X \right), \tag{3.5}
\]

where \( N \) is the number of electrons per pulse and \( \varepsilon_x \varepsilon_y \varepsilon_z \) is the volume in trace space. The 6D beam brightness \( B_{6D} \equiv \frac{N}{\varepsilon_x \varepsilon_y \varepsilon_z} \) corresponds to the electron density in trace space. The emittance, \( \varepsilon_x, \varepsilon_y, \varepsilon_z \), in trace space are defined as
\[ \varepsilon_q \equiv \sqrt{<q^2> - <qq'>^2}, \quad (3.6) \]

where \( q \) represents \( x, y, z \) spatial coordinates. The emittance is statistically a quantity of the covariance between \( x \) and \( x' \), and, geometrically, an area in trace space \( (x, x') \): the emittance is an occupied area where the electrons of one pulse are distributed in the trace space.

The emittance \( \varepsilon_x, \varepsilon_y, \varepsilon_z \) defined in trace space. \( (x, x', y, y', z, \delta) \) is not conserved during acceleration because the variables \( (x, x') \) in trace space are not canonical conjugates. Instead, one defines the normalized emittance \( \varepsilon_{xn} \):

\[ \varepsilon_{xn} = \beta \gamma \varepsilon_x, \quad (3.7) \]

where \( \beta = v/c, \gamma = 1/\sqrt{1 - \beta^2} \) are relativistic factors. This normalized emittance \( \varepsilon_{xn} \) refers to the area in the canonical phase space, and is conserved during acceleration.

In the following section, the transfer matrix representing various electron optic components, such as a drift region, magnetic lens, and radio-frequency cavity, will be introduced.

### 3.1.2 Phase Space Evolution along Electron Optics Systems

When the electron pulse travels through a beam column, the evolution in phase space can be represented by the action of a transfer matrix. The transfer matrix in the linear phase space motion has the following properties, as illustrated in Fig. 3.1:
Figure 3.1 Schematic illustration of a transfer matrix in a trace space: Left side is an initial trace space \((x_i, x'_i)\) and right side is a final trace space \((x_f, x'_f)\). Transfer matrix \(R\) maps an object in the initial trace space into the final trace space: a line \(\rightarrow\) a line, a point \(\rightarrow\) a point, ellipse \(\rightarrow\) ellipse, a curve \(\rightarrow\) a curve.

1. Transfer matrix \(R\) preserves area. (*Liouville's Theorem*)

2. Different initial points have different final points.

3. Continuous curves stay as continuous curves.

4. Closed curves stay as closed curves.

5. A point inside of a closed curve stays inside of a closed curve.

Also, if the transfer matrix is linear, then we also have:

1. Straight lines stay as straight lines.

2. Ellipses stay as ellipses.

In our high-brightness electron beam column (as to be introduced in Fig. ??), the major optical components are the magnetic lenses and the radio-frequency (RF) cavity.
Figure 3.2 Schematic illustration of electron beam dynamics in drift / magnetic lens / drift system: (a) the beam line structure illustration in real space, (b) the emittance of the electron pulse at \( Z_0 \), (c) the emittance of the electron pulse at \( Z_1 \) (drift region). Dashed line is the emittance at \( Z_0 \), and the blue arrow indicates the electron motion in the trace space, (d) the emittance of the electron pulse at \( Z_2 \) (after magnetic lens focusing). Dashed line is the emittance at \( Z_1 \), and the blue arrow indicates the electron motion in the trace space, (e), (f) the emittance of the electron pulse at \( Z_3, Z_4 \) respectively.

\[
x_1 = x_0 + l \cdot x_0'
\]
\[
x_1' = x_0'
\]
\[
x_2 = x_1
\]
\[
x_2' = -\frac{1}{f} x_1 + x_1'
\]
The propagating electron pulse is focused by the magnetic lenses in the transverse direction and focused by the RF cavity in the longitudinal direction. We can treat our column as two types of sections, one as the drift region, where the pulse propagates without any external force, and the other as the focusing region, where the momentum of the electron pulse is controlled along the transverse or the longitudinal direction. In the drift region without the space-charge effects, the electrons in the pulse travel with the conserved \((x, y, z)\) momenta, and, in the focusing region, the momenta of the electrons are changed by electron optics. Fig. 3.2 shows a schematic illustration of the pulse envelope evolution in trace space when the electron pulse propagates along the drift and the focusing regions.

When the electron pulse travels in the drift region, from \(z_0 \sim z_1\), we can define the transverse coordinates \(x_0, x_0', x_1, x_1'\) with the following relations:

\[
x_1 = x_0 + l \cdot x_0' \tag{3.8}
\]

\[
x_1' = x_0' \tag{3.9}
\]

where \(l\) is the flight time of the electron pulse from \(z_0\) to \(z_1\). Therefore we can construct the transfer matrix as

\[
R_{Drift} = \begin{pmatrix} 1 & l \\ 0 & 1 \end{pmatrix}. \tag{3.10}
\]

This transfer matrix of the drift region has \(x'\) constant, shown in Eq. 3.8 and Eq. 3.9, and moves \(x\) by an amount proportional to \(x'\). Therefore, the trace space envelope is horizontally sheared, as shown in the Fig. 3.2(c).
As the electron pulse passes an ideal, infinitesimally thin magnetic lens (the magnetic lens shown in Fig. 3.2), its trace space envelopes \((x_1, x'_1)\) right before the magnetic lens and \((x_2, x'_2)\) right after the magnetic lens are related by the relations:

\[
x_2 = x_1 \tag{3.11}
\]

\[
x'_2 = -\frac{1}{f} x_1 + x'_1, \tag{3.12}
\]

and we can construct the transfer matrix as following:

\[
R_{ML} = \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix}, \tag{3.13}
\]

where \(f\) is the focal length of the magnetic lens. This transfer matrix flips the trace space of the electron pulse with respect to the \(x\) axis. After this magnetic lens, the pulse travels in the drift region again and the trace space envelope starts a horizontal shearing motion. When the electron pulse reaches the focal point (beam waist), the trace space envelope is aligned along the \(x'\) axis as shown in Fig. 3.2(e).

### 3.1.3 Imaging and Aberrations

The transfer matrix of each optical component shown in Fig. 3.2 can be combined as one transfer matrix \(R_{tot}\). Fig. 3.3 shows the simplest example of an imaging system consisting of drift\((l_1)\)-lens-drift\((l_2)\). The transfer matrix of this system can be constructed:
Figure 3.3 Schematic illustration of an image system with one lens.

\[ \mathbf{X}_f = R_{Drift} R_{ML} R_{Drift} \mathbf{X}_i \]
\[ = R_{tot} \mathbf{X}_i, \]

where \( R_{tot} \) is

\[ R_{tot} = \begin{pmatrix} 1 & l_2 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -\frac{1}{f} & 1 \end{pmatrix} \begin{pmatrix} 1 & l_1 \\ 0 & 1 \end{pmatrix} \]
\[ = \begin{pmatrix} 1 - \frac{l_2}{f} & l_1 + l_2 - \frac{l_1 l_2}{f} \\ -\frac{1}{f} & 1 - \frac{l_1}{f} \end{pmatrix}. \]

To form an image as shown in Fig. 3.3, the various rays from the initial positions have to be reunited at the final position on the imaging plane. In other words, the final position of a ray is independent of its initial angle and only depends on the initial position. Therefore,
we can construct a boundary condition of the transfer matrix:

\[
\begin{pmatrix}
x_f \\
x'_f 
\end{pmatrix}
= R_{tot}
\begin{pmatrix}
x_i \\
x'_i 
\end{pmatrix}
= \begin{pmatrix}
(x|x) & (x|x') \\
(x'|x) & (x'|x') 
\end{pmatrix}
\begin{pmatrix}
x_i \\
x'_i 
\end{pmatrix},
\]  
(3.17)

where \((x|x')=0\) and \((x|x)\) represents the magnification. Using these conditions, Eq. 3.16 can be rewritten into the conventional form of imaging equations based on focal length \(f\) and the magnification of a lens:

\[
l_1 + l_2 - \frac{l_1 l_2}{f} = 0 \rightarrow \frac{1}{l_1} + \frac{1}{l_2} = \frac{1}{f},
\]  
(3.18)

and the magnification can be deduced:

\[
1 - \frac{l_2}{f} = -\frac{l_2}{l_1}.
\]  
(3.19)

In full 6D trace space, we can represent the transfer matrix with initial and final vector coordinates:
This linear mapping with the transfer matrix between the initial and the final vector coordinates describes the major part of the beam motion, but to study the effects of the motion more precisely, it is necessary to consider higher order effects and the higher order terms can be expressed with the following equations [64]:

\[
\begin{pmatrix}
x_f \\
x'_f \\
y_f \\
y'_f \\
z_f \\
z'_f 
\end{pmatrix} = \begin{pmatrix}
(x|x) & (x|x') & (x|y) & (x|y') & (x|z) & (x|z') \\
(x'|x) & (x'|x') & (x'|y) & (x'|y') & (x'|z) & (x'|z') \\
(y|x) & (y|x') & (y|y) & (y|y') & (y|z) & (y|z') \\
(y'|x) & (y'|x') & (y'|y) & (y'|y') & (y'|z) & (y'|z') \\
(z|x) & (z|x') & (z|y) & (z|y') & (z|z) & (z|z') \\
(z'|x) & (z'|x') & (z'|y) & (z'|y') & (z'|z) & (z'|z')
\end{pmatrix} \begin{pmatrix}
x_i \\
x'_i \\
y_i \\
y'_i \\
z_i \\
z'_i 
\end{pmatrix}. \quad (3.20)
\]

\[
x_f = \sum(x|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'} \quad (3.21)
\]

\[
x'_f = \sum(x'|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'} \quad (3.22)
\]

\[
y_f = \sum(y|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'} \quad (3.23)
\]

\[
y'_f = \sum(y'|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'} \quad (3.24)
\]

\[
z_f = \sum(z|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'} \quad (3.25)
\]

\[
z'_f = \sum(z'|x)x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}x^{i}x^{i'}y^{i}y^{i'}z^{i}z^{i'}, \quad (3.26)
\]
where the sums go over all six-tuples \((i_x,i_x',i_y,i_y',i_z,i_z')\). The coefficients 
\((k|x^ix'y^iy'z^i z'z')\), where \(k = x, x', y, y', z, z'\), of second or higher order terms are called \textit{aberrations}. In an imaging system, \((x|x)\), \((y|y)\) are the magnifications as shown in Eq. 3.19, and the ideal image, namely without any distortion present, has no higher order matrix elements:

\[(x|xx) = 0, (y|yy) = 0, (x|xy) = 0, (x|xxx) = 0, \ldots \] (3.27)

In a real imaging system such as an electron microscope or a camera, the higher order effects are often not negligible, and the image will be distorted. For example, when rectangular images are distorted into the shape of pincushions or barrels, it is caused by non-vanishing of \((x|xyy)\) and \((y|yxx)\) terms. Also, ideally, there should be no effects of initial angles on positions in higher order terms, \(i.e.\ (x|x'i' i'y'y') = (y|x'i' i'y'y') = 0\), but if any of these terms prevails, then they will cause spherical aberration. Similarly, the positions should not depend on the longitudinal energy of the beam, \(i.e.\ (x|z') = 0\) and \((y|z') = 0\), but, if these terms are not negligible, then chromatic aberration will be caused.

### 3.2 Phase Space Evolution in High-Brightness Pulsed Electron Beam System

To develop a high brightness pulsed electron source, the biggest challenge is overcoming the space-charge effects caused by Coulomb interactions among electrons within the high-density electron pulse. The focused high density beam results in degrading beam quality, in terms of spatial, temporal, and spectroscopic resolutions, in particular, the stochastic space-
charge effects, such as Boersch effect [65, 66, 63], which manifests as stochastic processes causing uncorrectable defocusing of the beam. The stochastic space-charge effect leads to (1) in the transverse direction, an increased beam divergence angle causing image blurring that differs from the blurring induced by the linear portion of space-charge effect, and (2) in the longitudinal direction, an increase in energy spread that also affects the time resolution [66]. To achieve combined atomic and sub-ps spatiotemporal resoultion, careful understanding of the coherence and phase space evolution of the high-density electron pulse is required and we can start from the uncertainty principle to understand the intrinsic limit of the resolution in a high-density electron pulse.

The photons in the femtosecond laser pulse can occupy the same state in the phase space of a confined coherent pulse because of the bosonic property of photons. However, the phase space volume of electrons in the pulse is limited by the Pauli exclusion principle. As discussed in the previous section, the phase space volume is defined as the emittance. The emittance can be divided into the minimum unit cell as determined by the uncertainty principle:

$$[\Delta x \Delta y \Delta z] \cdot [\Delta p_x \Delta p_y \Delta p_z]_{cell} \sim h^3. \quad (3.28)$$

The energy state of one electron in the unit volume is quantized, and if the probability is closed to one in the unit volume, then we have to consider the statistics with the states of electron population and the correlation of electrons. To consider this, the degeneracy parameter $\eta$ is introduced [67]. The degeneracy parameter $\eta$ is very small if the number of electrons per pulse is small, which is the case for Caltech’s UEM systems with a single-electron per pulse being deployed, while in our high-brightness system $\eta$ is significantly
larger because the targeted number of electrons per pulse is $\geq 10^6$. Generally, the degeneracy $\eta$ is defined by the number of electrons per unit cell in the phase space, and we can define the number of electrons per pulse, $N$, as:

$$N = \eta \cdot \zeta,$$

(3.29)

where the number of the occupied unit cells $\zeta$ can be defined as

$$\zeta = \frac{\varepsilon_x \varepsilon_y \varepsilon_z}{h^3}.$$

(3.30)

The highest achievable $\eta$ is two, because of the Pauli’s exclusion principle, considering up and down spins. At the emittance–limited (to be contrasted to the aberration–limited) beam waist, the emittance in Eq. 3.6 can be simplified as

$$\varepsilon_{x,n} = \frac{1}{m_e c} \sqrt{\langle x^2 \rangle \langle p_x^2 \rangle},$$

(3.31)

$$\varepsilon_{y,n} = \frac{1}{m_e c} \sqrt{\langle y^2 \rangle \langle p_y^2 \rangle},$$

(3.32)

$$\varepsilon_{z,n} = \frac{1}{m_e c} \sqrt{\langle z^2 \rangle \langle p_z^2 \rangle},$$

(3.33)

where $m_e$ is the mass of an electron, and $c$ is the speed of light. Then we can represent the transverse beam coherence length $L_t$ with the transverse emittance. For the coherent diffraction perspective, the transverse beam coherence length is defined as [68]

$$L_t \equiv \frac{\lambda}{2\alpha},$$

(3.34)

where $\lambda$ is the wavelength of the electron pulse and $\alpha$ is the half divergence angle. We
can rewrite $L_t$ with transverse emittance under two conditions: (1) symmetric transverse emittance $\varepsilon_x = \varepsilon_y$ and (2) the beam emittance at the beam waist $\varepsilon_{x,n} = \frac{\sigma_x \sigma_{px}}{m_e c}$ (from Eq. 3.31), where $\sigma_x = \sqrt{\langle x^2 \rangle}$ is the pulse width and $\sigma_{px} = \sqrt{\langle p_x^2 \rangle}$ is the rms transverse momentum spread:

$$L_t = \frac{\hbar \sigma_x}{2m_e c \varepsilon_{x,n}}. \quad (3.35)$$

Also, the longitudinal emittance can be represented by the energy spread $\Delta E$ and temporal uncertainty $\Delta t$. In Eq. 3.28, we can decompose

$$\varepsilon_{z,n} = \frac{1}{m_e c} \sigma_z \sigma_{pz}, \quad (3.36)$$

under similar considerations mentioned above, and, using the relation $\sigma_{pz} = \frac{\Delta E}{\gamma v_z}$ ($E = \frac{p_z^2}{2m_e}$), we can rewrite Eq. 3.36 as

$$\varepsilon_{z,n} = \frac{1}{m_e c} \frac{\Delta t \Delta E}{\gamma}, \quad (3.37)$$

where $\gamma$ is the relativistic Lorentz factor and $\Delta t = \sigma_z / v_z$. If we generalize Eq. 3.37 beyond the two conditions, then the longitudinal emittance $\varepsilon_{z,n}$ must be smaller than $\frac{1}{m_e c} \frac{\Delta t \Delta E}{\gamma}$ because the general definition of $\varepsilon_z$ shown in Eq. 3.6 is $\varepsilon_{z,n} = \frac{1}{m_e c} \sqrt{<z^2> <p_z^2> - <zp_z>^2}$ [63].

To characterize the density of an electron beam in 6D phase space, we can use the brightness $B_{6D} = \frac{N}{\varepsilon_{x,n} \varepsilon_{y,n} \varepsilon_{z,n}}$ or the degeneracy $\eta = \frac{N h^3}{\varepsilon_{x,n} \varepsilon_{y,n} \varepsilon_{z,n}} = B_{6D} h^3$. Fig. 3.4 shows the degeneracy $\eta$ for different operational regimes of conventional transmission electron microscope (TEM) electron guns and the simulation of a flat metallic photocathode
Figure 3.4 The 6D emittance $\varepsilon_x\varepsilon_y\varepsilon_z$ vs. the number of emitted electrons $N_{\text{emit}}$ for the extended electron sources with sizes $\sigma_T$ (100 $\mu$m, 1 mm), thermionic guns [69], Schottky, cold field-emission guns (CFEG), and heated field emission guns (HFEG).[63]
gun [63]. In conventional TEM, the lowest emittance is established with a cold field emission gun (FEG) having a 6D emittance volume of \(10^{-11} \text{ \(\mu\)m}^3\) or \(\eta \sim 10^{-5}\) \([\varepsilon_x \sim 1 \text{ nm and } \varepsilon_z \sim 10 \text{ pm (statistical)}]\) [69]. In contrast, a flat metallic photocathode widely used in ultrafast electron diffraction has a degraded \(\varepsilon_x \sim 20 - 200 \text{ nm}\) [63]. In Fig. 3.4, however, the extended sources of flat metallic photocathode have the emittance volume \(\varepsilon_{x,n}\varepsilon_{y,n}\varepsilon_{z,n}\) scale favorably, leading to a gain in \(\eta\) for electron bunches up to \(N_{\text{emit}} = 10^6\) for a typical laser pulse size (100 \(\mu\)m \(\sim\) 1 mm). The highest acceleration fields, e.g. \(F_a = 10 \text{ MV/m}\) in DC guns or \(F_a = 100 \text{ MV/m}\) in RF guns, do not improve \(\eta\) significantly. In the high charge limits (\(10^5 \sim 10^6\) electrons per pulse), the degeneracy figures are comparable to FEGs, implying that similar performance (with proper phase space manipulation) could be reached using a portion of the transverse emittance volume, for example by using apertures, whereas in the single-shot limit, the emittance volume is expected to be equivalent to those of thermionic guns.
Chapter 4

Design of High-Brightness UEM Electron Beam Line at Michigan State University

Ultrafast electron diffraction (UED) with $10^3$-$10^4$ electrons per pulse has achieved sub-picosecond temporal resolution and atomic resolution, but the current development of UED has not achieved direct imaging or coherent diffractive imaging due to insufficient beam density within the sampled volume in the specimen. High-brightness ultrafast electron sources and optical systems maintaining highly compact beam delivery to the sample will ultimately allow us to realize sub-micron scale coherent diffractive imaging and direct space ultrafast electron microscope (UEM), which will be a revolutionary technique to visualize atomic and sub-picosecond processes in nanoscale materials. At Michigan State University, we have developed a new UED system with an RF-enable high-brightness ultrafast electron source and delivery system (Fig. 4.1). Such a system is already an ultrafast electron microdiffraction system targeting atomic and sub-picosecond processes within micron or submicron scale materials. The ultimate target with the continuing development of projection imaging optics is the direct imaging of photo-induced ultrafast atomic dynamics, energy, and charge transfer.
Figure 4.1 RF-enabled high-brightness ultrafast electron beam system at Michigan State University
A crucial factor to characterize the high-brightness ultrafast microdiffraction or imaging systems is a six-dimensional normalized beam brightness $B_{6D}$, which is defined by the number of electrons per pulse $N$ with normalized transverse emittance $\varepsilon_{x,n}$ (under assumption, $\varepsilon_{x,n} = \varepsilon_{y,n}$) and normalized longitudinal emittance $\varepsilon_{z,n}$:

$$B_{6D} = \frac{N}{\varepsilon_{x,n}^2 \varepsilon_{z,n}}. \quad (4.1)$$

The first requirement for the number of electrons per pulse $N$ can be established by the Rose criterion [70]: for adequate gray scaling, an average detector signal for a pixel requires $\sim 100$ electrons for imaging. Therefore, a $1k \times 1k$ CCD camera requires $\sim 10^8$ electrons for one image with a single pulse, and, with a single electron detectable CCD, one diffraction pattern requires $\sim 10^6$ electrons per pulse. The second requirement for the transverse emittance $\varepsilon_{x,n}$ can be established with a coherence length $L_t$. To obtain a sufficient signal, the coherence length $L_t$ needs to be long enough to cover a couple of unit cells of a crystal lattice: $L_t \geq 1$ nm. Then, using the coherence length $L_t = \frac{\hbar}{2mec \varepsilon_{x,n}}$ at the beam waist, the transverse emittance $\varepsilon_{x,n}$ has to be smaller than $\sim 0.12$ $\mu$m if the electron beam size $\sigma_x$ at the sample is $\sim 100$ $\mu$m.

Considering the requirements, we carefully designed the high-brightness UED system consisting of a 100 kV Pierce geometry photoelectron gun, a series of magnetic lenses, and an RF cavity to deliver the high intensity electron pulse to a specimen. Using an idealized analytical Gaussian model (AGM) [71, 71, 72], we evaluated the best configuration of our column arrangement to achieve the atomic and sub-picosecond spatiotemporal resolution (shown in Fig. 4.2) [68]. In this chapter, we present actual designs of components of our high-
Figure 4.2 (a) Photoelectron pulse trajectory along an ultrafast electron beam column equipped with RF compression. The shaded regions represent the locations of the electron optical elements. (b) A scale-up view of the pulse profiles near the sample plane for nano-area diffractive imaging containing $10^5$ electrons/pulse. An aperture with a radius of 15 $\mu$m is employed to thin out the peripheral electrons to achieve a divergence angle $\alpha \leq 1.7$ mrad. The minimum transverse radius $\sigma_T$ is 0.64 $\mu$m, and the minimum longitudinal pulse length $\sigma_L$ is 0.80 $\mu$m. (c) A scale-up view of the pulse profiles near the sample plane for an ultrafast single-shot UED containing $10^8$ electrons/pulse. The minimum transverse radius $\sigma_T$ is 51 $\mu$m, and the minimum longitudinal pulse length $\sigma_L$ is 0.88 $\mu$m [68].
brightness ultrafast electron beam system: our home-built Pierce geometry photoelectron gun, magnetic lenses, RF cavity, charge-coupled device (CCD) camera, deflectors, and chambers.

4.1 Electron Source: Pierce Geometry DC Photoelectron Gun

As discussed in Chapter 2, we adopt the 100 keV energy electron source for the high-brightness ultrafast electron microdiffraction with the following features: (1) cost-efficient table-top high intensity source, (2) the low knock-on energy caused by the probe, (3) better matched inelastic scattering length to the optical penetration depth of the pump laser.

The development of the electron beam source has a long history and a variety of electron sources have been designed and utilized in diverse beam applications. The Pierce gun was originally suggested by J. R. Pierce in 1940 [73] and has been widely used to generate a high intensity electron beam for various applications. We implement this Pierce geometry in our photoelectron gun design with a cone-shaped anode with a flat cathode to achieve weakly self-focusing and to accommodate a relatively large operable beam emitting area up to 1 mm in diameter at ~100 keV range for high intensity beam generation.

In the Pierce geometry photoelectron gun (shown in Fig. 4.3), the photoemission electron pulse is generated on a silver photocathode surface by 266 nm pulse laser irradiation, and the photoelectron pulse is accelerated by 100 kV DC bias between anode and cathode. The Pierce geometry provides a weakly converging electric equipotential to counter the beam divergence caused by the space-charge effects. Using Field Precision code [74], we optimized the cathode and anode geometry to achieve three aspects:

1. A sufficiently large diameter hole on the anode for 266 nm excitation laser to be able
Figure 4.3 Cathode and anode of Pierce geometry photoelectron gun: (a) electric field calculation using Field Precision [74]. (b) Pierce geometry photoelectron gun design in the high-brightness UED electron gun chamber. Cathode and anode are electrically isolated through four 10 inch MACOR insulation rods. Right below the anode, there is first condenser magnetic lens to focus the electron beam after the anode. (c),(d) are the electric potential and field profile along the electron pulse propagation direction. The profiles at different radial locations are almost identical. This indicates that the field distribution is uniform along the beam propagation direction.
2. High extraction field to suppress the virtual cathode effect causing beam current saturation.

3. Low non-linearity of the field to reduce turbulent flow causing irreversible beam emittance growth.

As shown in Fig. 4.3(b), the anode design allows the front-illuminating 266 nm laser to access the photocathode at up to $\sim 1^\circ$ tilt angle. The simulated electric potential and field profiles shown in Fig. 4.3(c) and Fig. 4.3(d) are highly homogeneous, despite the opening hole, so that emission from a relatively large radial position ($\sim 1$ mm) experiences a similar accelerating field along the propagation direction as does emission from the center of the cathode. The extraction field strength on the surface is about $2.5 \text{ MeV/m}$, which is sufficient to generate more than $10^6$ electrons per pulse according to a theoretical study on the short-pulse virtual cathode effect [63]. The maximum field strength is more than $5 \text{ MV/m}$ along the optical axis.

We consider a flexible photocathode design to accommodate various technical circum-
stances. The first consideration is for accommodating two different illumination schemes: front-illumination and back-illumination. The front-illumination has to be implemented to generate a sufficient number of electrons per pulse ($>10^6$ electrons), and the back-illumination is required for beam and column alignment in an initial setup of the system. The second consideration is for different types of photocathode: bulk and thin film. A bulk type photocathode is easier to prepare and can afford higher quantum efficiency materials than the thin film type, but the bulk type does not allow us to implement a back-illumination scheme. This flexibility also allows us to experiment with different types of materials for photoemission experiments. For example, to minimize the initial transverse emittance, the work function of the photocathode material has to match the 266 nm laser pulse energy (4.66 eV) because excess photon energy can cause larger initial transverse momentum spread of the photoemitted electrons [68]. In our first experiment, we adopt 40 nm thick silver film (the work function is 4.26-4.74 eV [75, 76, 77]) as the photocathode operable both with the back- and front-illumination schemes for our high-brightness electron beam system.

The switchable photocathode is shown in Fig. 4.4. The cathode head assembly can be dismounted easily from the cathode body (see Fig. 4.3(b)), and we can take the part out through a 6” port of the cathode chamber. The full cathode assembly consists of the stainless steel cathode head, the stainless steel photcathode holder, and the sapphire window. To prepare the photocathode, the sapphire window is first secured on the photocathode holder with UHV comparable silver-paste. The photocathode holder is then mounted at the center of the stainless steel cathode head through the 3/4-20 thread. After assembling all the parts, we deposit the 40 nm thickness silver film on the sapphire window surface using a thermal evaporator. If we need to change the photocathode material or the type,
then we can simply replace the silver coated sapphire window with a differently prepared one.

One of the most critical issues in 100 kV electron gun design (shown in Fig. 4.5) is the stability of the high voltage, because, if the local electric field strength at the surface is too high, then a vacuum breakdown may occur due to the ionization of the residual gas between the cathode (-100 kV) and ground (0 V). Furthermore, the gas discharge may also lead to surface breakdown of the insulating materials between the cathode and the anode, creating a conducting path. These breakdowns lead to electrical arcs inside of a chamber that might cause damage to other parts or electronics. Although a generic microscopic mechanism for triggering the vacuum breakdown is not yet established in practical implementation.
of a high voltage device, the rule of thumb is to avoid creating sharp edges or rough surfaces. Generally, the ionized charged particles around the cathode can be accelerated to high energy, and subsequent collisions of the accelerated particles with residual gas lead to further ionization, and ultimately an avalanche. According to Paschen’s law [78], this dielectric breakdown voltage depends on the product $p \cdot d$, where $p$ is pressure and $d$ is the distance between cathode and anode. While the breakdown voltage at $\sim 10^{-5}$ torr may be as high as 25 MV/m between two flat electrodes [79], the practical breakdown limit is around 8 MV/m at $10^{-8}$ torr. Our acceleration field strength is below this practical vacuum breakdown limit. A lower breakdown threshold may be due to local curvature of the surface. The sharp edge of the surface causes an order of magnitude higher local field, and this field enhancement might initiate the vacuum breakdown. Therefore, all the parts near the high voltage are electro-polished to smooth the microscale sharp edges. As shown in Fig. 4.5(b), the high voltage feedthrough pin has the sharp edge directly buried in the cathode body without any additional connectors. Thus, we completely eliminate the sharp edges around the high voltage region.

A conducting path can also be established along the surface of an insulator, and this dielectric breakdown is called a dielectric flash-over or surface tracking. Especially when the field lines are parallel to the surface of the insulator, the released electrons that gain energy hop toward the anode through the insulator surface and establish a conducting path on the surface. To minimize the energetic electron hopping rate, we designed two insulation stages with two orthogonal surface directions (shown in Fig. 4.5): (1) the high voltage cathode is mounted at the center of the ceramic disk, and the field direction is along the radial direction of the chamber, (2) four MACOR rods connect the ceramic disk and
the anode, and the field direction is along the electron pulse propagation direction. Also, triple points, which are junctions of three different media, have to be avoided or shielded properly because the electric field strength at the triple points can be enhanced, and the enhanced field causes the dielectric breakdown through the locally charged insulator [80]. Triple points arise naturally at the location where a conductor connects to an insulator in a vacuum chamber. To minimize the local field enhancement, the rods are mounted on the counter sink of an anode surface, shown in Fig. 4.5(c).

Given these precautionary measures, it is still extremely hard to completely eliminate dielectric breakdown, due to microscale whiskers and fragments on the surfaces of the chamber or various parts. Microscale whiskers and fragments can be removed by conditioning the high voltage photoelectron gun. The conditioning can be simply done by gradually increasing the high voltage until breakdown occurs and then quickly lowering the high voltage. With this iterative conditioning procedure, the spontaneous but short-lived breakdowns will clean up the microscale whiskers and fragments gradually. Through constantly monitoring the high voltage current, we can decide how much the photoelectron gun surface is cleaned up with the current fluctuation. If the current fluctuation level is within $\sim 10$ nA, then it is stable enough to operate the system (see Fig. 4.6).

4.2 Magnetic Lenses

In designing the magnetic lens, we need to consider two key aspects: (1) the gap geometry inside of the bore of a pole-piece and (2) wound coils to apply the current. The pole-piece is a cylindrically symmetric structure made by a soft magnetic material such as soft-iron (our magnetic lens material is described in Appendix D.) with a hole drilled through it, called
Figure 4.6 Current stability monitor (a) after the electron gun conditioning, (b) before the conditioning
Figure 4.7 Schematic illustration of non-uniform magnetic field (red lines) at the center of the magnetic lens pole-piece. The hole through the pole-piece is called bore and the disconnected region inside of the bore is called a gap.
Figure 4.8 Condenser magnetic lens No. 1: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the condenser lens No. 1. The black arrow indicates the electron pulse propagation direction and the plot has the cylindrical symmetry along the beam propagation direction. (c) Magnetic field strength profile along the different radial coordinates, R= 0.0, 0.5, 1.0, 1.5, 2.0 (mm).
Figure 4.9 Condenser magnetic lens No. 2: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the condenser lens No. 2: the black arrow indicates the electron pulse propagation direction and the the plot has the cylindrical symmetry along the beam propagation direction. (c) Magnetic field strength profile along the different radial coordinates, R= 0.0, 0.5, 1.0, 1.5, 2.0 (mm).
Figure 4.10 Objective magnetic lens: (a) The geometry of the lens. The yellow box region is filled with coils. (b) The magnetic field map near the pole-piece (region highlighted by the red box in (a)) of the objective magnetic lens: the black arrow indicates the electron pulse propagation direction and the the plot has the cylindrical symmetry along the beam propagation direction. (c) Magnetic field strength profile along the different radial coordinates, R= 0.0, 0.5, 1.0, 1.5, 2.0 (mm). The kinks at R=1.5, 2.0 mm profiles are artifact because the objective lens exit hole radius is 1.5 mm.
the bore of the pole-piece. Inside the bore of the pole-piece, there is a gap in the middle of the bore (shown in Fig. 4.7), and this gap geometry determines the magnetic focusing strength. Using a finite element numerical method (Field Precision (Commercial Software) [74]), we optimize the gap geometry and the bore diameter of three magnetic lenses: (1) condenser magnetic lens No.1 (CML1) right after the Pierce geometry photoelectron gun, (2) condenser magnetic lens No.2 (CML2) before the RF cavity, and (3) objective magnetic lens (Obj.ML) right before the sample. The location of the three magnetic lenses are shown in (a) of Fig. 4.8 (CML1), Fig. 4.9 (CML2) and Fig. 4.10 (objective magnetic lens). The panel (b) in Fig. 4.8, Fig. 4.9 and Fig. 4.10 shows the magnetic field calculation near the bore gap, where the vector fields have cylindrical symmetry along the black arrow indicating the electron pulse propagation direction. The panel (c) shows the magnetic field profiles along the propagation direction at different radial coordinates. The non-uniform field with cylindrical symmetry along the optical axis transversely focuses the propagating electron pulse.

The second issue of the magnetic lens design concerns how much current is required to focus the electron beam at the desired locations, because the applied current on magnetic lens determines the focal length. Based on a previous theoretical study with the analytical Gaussian model (AGM) [68], we establish the lower limit of the required current for each magnetic lens design. In AGM, the evolution of an electron pulse described by Gaussian distribution in the phase space is governed by following differential equations [72]:

\[
\frac{d\sigma_i}{dt} = \frac{2}{m_e} \gamma_i; \quad (4.2)
\]
\[
\frac{d\gamma_i}{dt} = \frac{1}{m_e} \left( \eta_i + \frac{\gamma_i^2}{\sigma_i} \right) + \frac{1}{4\pi\epsilon_0} \frac{Ne_i^2}{6\sqrt{\sigma_i^3}} L_i + M_i \sigma_i, \quad (4.3)
\]
\[
\frac{d\eta_i}{dt} = -\frac{2\gamma_i \eta_i}{m_e \sigma_i}, \quad (4.4)
\]

where \(\sigma_i\) is the spatial beam variance, \(\eta_i\) is the local momentum variance, \(\gamma_i\) is the momentum chirp and \(L_i\) is the parametrized function to quantify the ellipticity (more details are in Ref. [72]) in the transverse and longitudinal directions, that is \(i = \{T, z\}\), respectively. \(N\) is the number of electrons in the Gaussian pulse, and \(\epsilon_0, e,\) and \(m_e\) are the vacuum permittivity, and the charge and rest mass of the electron, respectively. The last \(M_i, (i = T, z)\) is the parameter specifying the strength of a magnetic lens for transverse focusing and RF cavity for longitudinal focusing, respectively. (Note: the emittance, \(\sqrt{\sigma_i \eta_i}\), is conserved in the dynamic equation.) The \(M_T\) parameter that determines the magnetic focusing strength corresponds to the magnetic lens focusing with a certain applied current.

To calibrate the required lens current with the parameter \(M_T\), we compare the AGM simulation [68] with ray tracing calculation using Field Precision. Fig. 4.11 shows the results of AGM simulation and Field Precision simulation. The blue solid line is the AGM simulation without space-charge effect (\(N=0\)). The initial transverse width is 100 \(\mu\)m and 50 \(\mu\)m, and the initial transverse momentum spread is \(2 \times 10^4\) (m/s) corresponding to 0.1 mrad divergence angle of a 100 keV electron beam entering the lens. The dashed lines are the non-interacting electron trajectories calculated by Field Precision. To match the prescribed magnetic lens focusing by AGM, we adjust the current of the lens, so the resulted focal distance is the same as the AGM. Fig. 4.11 shows that the 100 keV electrons at \(R=100\) \(\mu\)m and 50 \(\mu\)m with ray angle, \(+0.1\) and 0 mrad, travel through the magnetic
Figure 4.11 (a) Magnetic lens current calibration simulation: Solid lines are AGM simulation without space–charge effect, and the dashed lines are Field Precision [74] simulation of non-interacting single electrons, calculated with the relative permeability shown in (b). The initial transverse size of the Gaussian electron pulse in AGM simulation is 100 µm and 50 µm with angular spread 0.1 mrad. In Field Precision simulation, the initial position of single electrons is at $R=100$ µm and 50 µm, and each line represents different initial ray angles, ±0.1, 0 mrad.

Based on this lens focusing simulation, CML1, CML2 and Obj.ML require 550 A, 450 A and 750 A total currents, respectively. In the magnetic lens fabrication, we have to be concerned about the the relative permeability used in magnetic field calculation because the actual permeability of the materials strongly depends on the post-processing such as annealing process (Appendix D). Re-machining after annealing process may also change the permeability. In the design stage, we used the generic relative permeability of the soft iron
shown in Fig. 4.11(b), but we need to calibrate the relative permeability by comparing the performance of the fabricated lenses with the predictions (to be discussed in Chapter 5). Due to the uncertainty of the relative permeability, we set the projected lens currents as the lower limit for the magnetic lenses and allocate the space for coils to achieve ~5 time higher desired currents than the projected values. We use the UHV comparable electrical wires (22 AWG Kepton insulated wire with 5.5 A current rating from Accu-Glass Products, Inc. (Part number: 112615)) for the CML1 and the Obj.ML coils because the CML1 and the objective lens are installed inside the UHV chamber (see Fig. 4.1), while a normal magnetic coil (18 AWG, 10 A current rating) is used for the CML2, which is mounted externally under the atmosphere. To generate the required currents considering the current rating of electrical wires and the applied current for the lenses, CML1, CML2, and Obj.ML have 550 (1 A applied current), 150 (3 A applied current), 750 (1 A applied current) coil windings, respectively.

To characterize the beam path along the whole electron beam column, we simulate electron beam trajectories under the exact column geometry using two different simulation methods implemented in Field Precision. The first simulation is ray tracing calculation based on non-interacting electrons, without space–charge effects. The second simulation is with space–charge effects induced by the self-generated electric field of a continuous electron beam, shown in Fig. 4.12. The non-interacting ray tracing calculates the single–electron trajectories only considering the external field generated by the optical components, while the simulation with space–charge effects considers both the external field and the self-generated electric field to calculate the trajectory where the space–charge contribution is adjusted at each time step. The vertical lines in Fig. 4.12 indicate the optical component
Figure 4.12 Field Precision simulation of an electron trajectory with non-interacting particles (Red line) scheme and with space–charge effect induced by the self-generated electric field of a continuous high current electron beam (blue line). Red and blue solid lines are calculated with the same focusing condition with $CML1=550$ A, $CML2=450$ A, and $Obj.ML=750$ A, and the dashed line is calculated with with $CML1=0$ A, $CML2=450$ A, and $Obj.ML=750$ A. The black dashed vertical lines indicates electron optics components: (1) the photocathode surface, (2) $CML1$, (3) $CML2$, (4) RF cavity, (5) $Obj.ML$, (6) the sample, and (7) CCD screen. The shaded region shows where the electron beam is focused by the Pierce geometry gun.
locations, summarized in table 4.1: (1) the photocathode surface, (2) CML1, (3) CML2, (4) RF cavity, (5) Obj.ML, (6) the sample, and (7) CCD screen. The trajectories are calculated under the same focusing condition with CML1=550 A, CML2=450 A, and Obj.ML=750 A. In the non-interacting electron simulation, the electron initial energy is zero and accelerated by the 100 kV acceleration field, and, in the simulation considering space–charge effects, the initial beam current is defined as 8 mA, which corresponds to $5 \times 10^6$ electrons per 100 ps, a density relevant to our elongated pulsed electron beam. The solid red line is the convoluted trajectory of non-interacting electrons emitted from five different initial positions: $R=10, 20, 30, 40, 50$ $\mu$m, and the solid blue line is the electron trajectory under the influence of the space–charge effects at the continuous high-current beam limit. Fig. 4.12 shows that the electron beam without space–charge effects is strongly focused by the Pierce gun, and, due to this tight focusing occurring at CML1, CML1 does not further focus the beam significantly, shown in the comparison between the solid red line and the dashed red line. The latter is the result with CML1=0 A, CML2=450 A, and Obj.ML=750 A. With space-charge effects, the Pierce geometry provides a central focusing role to reduce the initial divergence of the electron beam (divergence angle changes from 40 mrad to 10 mrad), shown in the shaded region (Fig. 4.12), to bring the beam to convergence at 1 mrad. The CML2 can further focus the electron beam to travel through RF cavity, and the Obj.ML can control the electron beam focusing for a nearly parallel beam focused at CCD screen or a convergent beam focused at the sample. In the microdiffraction mode, which requires focusing the electron beam on the sample as shown in Fig. 4.12, the coherence length at the sample (the beam waist) can be calculated by $L_t = \frac{\lambda_e}{2\Delta \theta}$, where $\lambda_e$ is the 100 keV electron wavelength, and $\Delta \theta$ is the divergence angle. From the Field Precision simulation
considering the space–charge effect, \( L_t \) is \( \geq 1 \) nm with the 100 keV electron wavelength \( \lambda_e=0.0037 \) nm, and the divergence angle \( \Delta \theta=1.6 \) mrad. Therefore, in the design stage, the optical components fulfill the appropriate functionality to deliver a high density electron pulse to the sample with the expected requirement of the coherence length. In Chapter 5, the actual high-brightness electron pulse characterization will be discussed.

<table>
<thead>
<tr>
<th>Optical Components</th>
<th>Position (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photocathode surface</td>
<td>0.000</td>
</tr>
<tr>
<td>CML1</td>
<td>0.070</td>
</tr>
<tr>
<td>CML2</td>
<td>0.360</td>
</tr>
<tr>
<td>RF cavity</td>
<td>0.640</td>
</tr>
<tr>
<td>Obj. ML</td>
<td>1.090</td>
</tr>
<tr>
<td>Sample plane</td>
<td>1.110</td>
</tr>
<tr>
<td>CCD screen</td>
<td>1.441</td>
</tr>
</tbody>
</table>

Table 4.1 The location of the optical components in the high-brightness UED column

4.3 Radio-frequency (RF) Cavity

With a high-intensity electron pulse \((\geq 10^6 \) electron/pulse), pulse compression is required to overcome the collective space–charge effects, causing pulse broadening. We implemented the RF cavity to compress the longitudinally broadened electron pulse. In the following sub-sections, for conceptual understanding the performance of RF cavity, the simplest RF
4.3.1 RF Field in Pillbox Cavity

The pillbox cavity, a simple cylinder with radius $R$ and length $d$ as shown in Fig. 4.13(a), is the simplest geometry for generating an resonant RF field. To derive the RF resonance of pillbox cavity, we can start from the general wave equation for the radiation field $\Psi$:

$$\frac{\partial^2 \Psi}{\partial R^2} - \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2} = 0.$$  \hspace{1cm} (4.5)
Using cylindrical coordinates, we can rewrite Eq. 4.5 as

\[
\left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right\} \Psi = 0. \tag{4.6}
\]

If we define the \( \Psi(r, \varphi, z, t) = \Psi_r(r)\Psi_\varphi(\varphi)\Psi_z(z)\Psi_t(t) \) with \( \Psi_z(z) = \cos(k_z z) \) and \( \Psi_t(t) = \cos(\omega t) \), then Eq. 4.6 can be derived as

\[
\left\{ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2}{\partial \varphi^2} - k_z^2 + \frac{1}{c^2} \omega^2 \right\} \Psi = 0. \tag{4.7}
\]

Now, we can derive the RF field of the pillbox cavity from the following solution of the general wave equation:

\[
\Psi(r, \varphi, z, t) = \Psi_0 J_m(kr) \cos(m\varphi) \cos(k_z z) \cos(\omega t), \tag{4.8}
\]

where \( J_m \) is the \( m - th \) Bessel function of the first kind and \( k_z^2 = \omega^2/c^2 + k_z^2 \) with angular frequency \( \omega = 2\pi f \). If the pillbox wall is perfectly conducting and contains a lossless medium characterized by a permittivity \( \epsilon \) and a permeability \( \mu \), then we can construct two boundary conditions:

\[
\Psi(R, \varphi, z, t) = 0, \tag{4.9}
\]

\[
\Psi(r, \varphi, 0, t) = \Psi(r, \varphi, d, t) = 0. \tag{4.10}
\]

The solution of the general wave equation, Eq. 4.8, imposes two different kinds of resonance modes, transverse electric (TE) modes and a transverse magnetic (TM) modes, shown in Fig. 4.13 (b), (c). The longitudinal (\( \hat{z} \)) component of the electric field of TM modes \( E_z \) is the pulse compression component. With the boundary conditions, Eq. 4.9 and
Eq. 4.10, we can derive the longitudinal component of TM modes as

\[ E_z(r, \varphi, z, t) = E_0 J_m(kr) \cos(m\varphi) \cos(k_z z) \cos(\omega t), \] (4.11)

\[ k = \zeta_{mn}/R, \] (4.12)

\[ k_z = \pi l/d, \] (4.13)

where \( \zeta_{mn} \) is the \( n \)-th root of \( J_m(kr) = 0 \) \((m, n, l \in \mathbb{N})\). The resonance frequency of TM\(_{mnl}\) in the pillbox cavity is given by

\[ \omega_{mnl} = \frac{1}{\sqrt{\varepsilon \mu}} \sqrt{\frac{\zeta_{2mn}^2}{R^2} + \frac{\pi^2 l^2}{d^2}}. \] (4.14)

The mode numbers \( m, n, l \) are the number of nodes in the \( \hat{r}, \hat{\varphi}, \) and \( \hat{z} \) direction respectively.

With \( E_z(r, \varphi, z, t) \), we can evaluate the electromagnetic field of the simplest TM mode, TM\(_{010}\) which dominantly affects the pulse compression:

\[ E_z(r, z, t) = E_0 J_0\left(\frac{\zeta_{01}}{R} r\right) \cos(\omega_{010} t), \] (4.15)

\[ B_\varphi(r, \varphi, t) = \sqrt{\varepsilon \mu} E_0 J_1\left(\frac{\zeta_{01}}{R} r\right) \sin(\omega_{010} t). \] (4.16)

Other components of TM\(_{010}\) mode are zero, and the resonance frequency is \( \omega_{010} = \omega_0 = \frac{\zeta_{01}}{R \sqrt{\varepsilon \mu}} \). If the cavity wall conductivity is not perfect, then it causes energy loss, \( P_{\text{loss}} \). The ratio between the time-averaged energy gain \( U_{\text{gain}} \) and the energy loss, \( P_{\text{loss}} \).
per cycle is defined as the quality factor (Q-factor) $Q$:

$$ Q = \omega_0 \frac{U_{gain}}{P_{loss}}. $$

(4.17)

This Q-factor represents the quality of the RF cavity power conversion efficiency. The gap $d$ of the actual RF cavity is 22.5 mm, and the resonance frequency is $\sim$1 GHz. For Eq. 4.14 with $\omega_{010}$, the required radius $R$ of pillbox cavity is $\sim$12.8 mm, and the Q-factor is $\sim 4.6 \times 10^3$.

### 4.3.2 RF Cavity in High-Brightness Electron Beam Line

The RF cavity implemented in our high-brightness electron beam line is more efficient than the pillbox cavity because the cavity geometry is optimized to improve the Q-factor of $\text{TM}_{010}$ mode at $\sim$1 GHz resonance frequency. The Q-factor of the RF cavity is $\sim 2.2 \times 10^4$, and the peak electric field on the optical axis is 1~3 MV/m. The actual RF cavity design is shown in Fig. 4.14 (a). The optimized geometry RF cavity has a torus shape, and the magnetic field of the $\text{TM}_{010}$ mode in Eq. 4.16 has cylindrical symmetry and the electric field is along the optical axis where the electron pulse propagates (shown in Fig. 4.14 (a)).

When the electron pulse passes through the RF cavity, the faster electrons at the front of the electron pulse are decelerated by the negative direction of the RF field and the slower electrons at the tail are accelerated. In the phase space shown in Fig. 4.14 (b), the faster electrons are distributed in the upper-right area and the slower electrons are in the lower-left area before RF compression. After passing through the RF field region, the momenta of upper-right area electrons are flipped down to negative due to the deceleration, and the momenta of the slower electrons are flipped up. During the electron pulse drifting in free
Figure 4.14 RF cavity: (a) The actual design of geometry optimized RF cavity and the \( \text{TM}_{010} \) mode RF field in the RF cavity (The red ring is a magnetic field and the black line is an electric field), (b) Phase space volume evolution with RF compression.
space, the positive momentum leads electrons to move in the positive direction, and the negative momentum leads the electrons to move in the negative direction. At the focal point, the phase space volume is aligned along the momentum axis. The focal length $f_L$ is determined by [81]

$$\frac{1}{f_L} \approx \frac{eE_0\omega_0 d}{m_e\gamma^3 v_C^3} \sin \phi_0,$$  \hspace{1cm} (4.18)

where $E_0$ is electric field amplitude, $\omega_0$ is RF cavity resonance frequency, $d$ is gap distance in RF cavity, $m_e$ is electron mass, $\gamma$ is the Lorentz factor of the center of mass velocity of the electron pulse, and $\phi_0$ is the relative phase between electron pulse and the RF field. Therefore, we can control the RF compression focal length with control of the RF power.

4.3.3 RF Station for RF Field and Electron Pulse Synchronization

As mentioned before, the basic concept of the pulse compression is that the faster electrons at the front of the pulse are decelerated while the slower electrons at the tail of the pulse are accelerated with a fast oscillating electric field generated by the RF cavity. Then, during the subsequent drift region, the pulse starts to be compressed and reaches the minimum longitudinal length at the sample location. The oscillating electric field in the $TM_{010}$ mode of the RF cavity resonates at $\sim 1$ GHz, and the polarity switching time of the oscillating electric field has to be precisely synchronized with the arriving time of the electron pulse at the RF cavity. The synchronization between the RF electric field and the electron pulse is achieved by synchronization between the femto-second laser pulse train of the laser source and the RF field because the electron pulse in our high-brightness UED is originally generated by the femto-second laser. This RF synchronization station has been developed by my colleague Zhensheng Tao, and the more technical details can be found in
his thesis [82]. In this section, the basic concepts and the key factors of RF compression synchronization will be briefly introduced.

The synchronization means tightly lock the RF electrical signal inside the RF cavity with the fs laser pulse train, and, in order to achieve the synchronization, we developed a phase-locked Loop (PLL) [82] with our high-brightness UED independently. Basically, a PLL is an electrical circuit to lock the phase of output onto the input, and a PLL can be considered an oscillator whose phase is locked onto the phase of the reference (fs laser pulse train) input signal. Fig. 7.10 shows a block diagram of a general PLL. The phase detector compares the phase of feedback and the reference signals, and it develops the output voltage ($V_1$) proportional to the phase difference ($\Delta \varphi$) between the two signals with the following relation:

$$v_1 = K_p \Delta \varphi + V_{po},$$  \hspace{2cm} (4.19)

where $K_p$ is the phase detector gain, and $V_{po}$ is the inherent free running offset voltage.
When the loop is locked, the two input frequencies, reference and feedback signals ($\omega_i = \omega_o$) are the same, and the signals are represented by the following wave equations:

$$\Psi_{\text{Ref}} = A \cos(\omega_i t + \varphi_i), \quad (4.20)$$

$$\Psi_{\text{Feedback}} = B \cos(\omega_i t + \varphi_o), \quad (4.21)$$

and, if we apply the mixer as a phase detector, the output, $V_1$, of the phase detector is proportional to two frequencies:

$$v_1 \propto \Psi_{\text{Ref}} \cdot \Psi_{\text{Feedback}} = \frac{AB}{2} [\cos(2\omega_i t + \varphi_i + \varphi_o) + \cos(\Delta \varphi)]. \quad (4.22)$$

The low-pass filter removes the high frequency component $2\omega_i$, and this filtering range is determined by the loop filter gain $K_F(\omega)$. The output voltage $V_2$ of the low-pass filter is applied to a voltage-controlled oscillator (VCO) as a control voltage in order to adjust the output signal phase with the following relation:

$$\Delta \omega = K_c(V_2 - V_{co}), \quad (4.23)$$

where the $K_c$ is VCO gain, and $V_{co}$ is the control voltage when PLL is locked ($\omega_o = \omega_i$).
4.4 Charge-coupled Device (CCD) Camera

The first requirement for the image acquisition system of high-brightness UED is the high sensitivity to detect a single electron event. To achieve single electron sensitivity, we implement PIXIS-XF charge-coupled device (CCD) camera from Princeton Instruments with a HAMAMATSU image intensifier (V7670U-04) for signal amplification. To suppress the background noise level, we operate the CCD camera at a -35°C set temperature.

Fig. 4.16 shows the design of the image acquisition system consisting of a CCD camera main body and image acquisition optics (Optical face-plate, Optical taper, and intensifier). A 60 nm thick aluminum film is coated on the optical face-plate of the image acquisition optics to block the background photon signals which come from the pump laser or room light. The penetration depth of visible wavelength photon in Al is $\sim$15 nm, while that of 100 keV electron beam is $\sim \mu$m range. Therefore, most of the ambient background photons are blocked by this Al film. The electrons passing through the Al film strike a phosphor screen and generate a burst of photons in the visible range. These photons are focused by a 2:1 ratio optical taper on the image intensifier input window. When the photon enters the intensifier, the photons are converted back into electrons at the front of the image intensifier by a photocathode. The generated photo-electrons are accelerated and enter the micro channel plate (MCP). The MCP is composed of more than $10^6$ micro-channels that are 6 $\mu$m diameter individual miniature electron multipliers. Each MCP can provide an amplification of up to 1000 times with the accurate spatial resolution, and the image intensifier consists of 3 MCPs, thus allowing a gain of up to $10^9$. The amplified electrons strike another phosphor screen to convert the electrons to much a larger number of photons
Figure 4.16 Structure of charge coupled device (CCD) camera mount. (a) Schematic illustration of image acquisition optics in front of CCD camera main body: Al film and phosphor screen are coated on the optical face-plate surface, and an optical taper focuses a signal with 2:1 ratio onto an intensifier input window. The Al film screens the background photon from room light and pump laser, and the phosphor film converts the electron signal to photons which is amplified by the intensity. The red box indicated the intensifier. (b) a schematic diagram of the micro-channel plate (MCP) in the intensifier. The MCP is composed of more than $10^6$ micro-channels which are individual miniature electron multipliers. (c) design of the fully assembled CCD camera. All the components are made of glass, so, using the optical grease, we make smooth contacts between parts to minimize the signal loss.
(see Fig. 4.16(a)). This amplified signal in the form of photons is incident on the CCD camera.

The major issue in the CCD camera mount design is the UHV components and non-UHV components: the phosphor screen on the optical face-plate has to be in the UHV chamber and the image intensifier is a UHV non-compatible part. Using an O-ring, which can hold the high vacuum level only, we mount the optical face-plate as shown in Fig. 4.16(c) (O-ring black circle). To achieve chamber pressure down to the UHV level, we implement the differential pumping scheme. As shown in Fig. 4.16(c), a gap in the image acquisition optics is sealed by three O-rings: the 1st and 2nd O-ring are at the boundary between UHV and the gap region and the 3rd O-ring is at the boundary between the gap and the atmosphere. Pumping down this gap region using a dry pump, the UHV chamber pressure can be held by a series of O-ring seals because the pressure difference at each O-ring seal is not at UHV level, but at a high vacuum level. Another technical concern for the design is that all of the parts in CCD mount assembly are made of glass, so we cannot easily compress them, but we have to compress them sufficiently to avoid a leak between components. To achieve this, we have to have perfect dimensions for the stainless steel housing, but practically we cannot avoid machining error. For this issue, we design another O-ring that can compensate for the machining tolerance at the adjustable disk (blue color in Fig. 4.16), which is easy to modify.

4.5 Other Components for Optical and Electron Beam Delivery

In the previous sections, we introduced the major parts of the high-brightness beam system, the Pierce geometry photoelectron gun, the magnetic lenses, the RF cavity, and the CCD
camera. As shown in Fig. 4.1, there are additional parts that also have critical functions to operate the UED experiments in an optimum condition. In this section, function and design of the other key components are briefly introduced.

4.5.1 266 nm Excitation Mirror Holder and Electron Beam Shield

To generate the electron pulse in the Pierce geometry DC photoelectron gun, access is required for the 266 nm laser pulse. For back-illumination, the photocathode back-side has a pin hole for the 266 nm laser to be able to access the photocathode directly, but, for front-illumination, a 266 nm UV grade mirror is required because it is not possible for
the laser to access the photocathode directly from the front-side. The first design issue is with the 266 nm UV mirror mount. The 266 nm mirror has to be mounted very close to the center of the chamber where the electron beam propagates because of the extremely limited space of the bore of CML1 and the anode hole. Fig. 4.17 shows the mirror mount structure with an electron beam shield. To make the space large enough for an electron pulse to go through, the mirror mount holder is mounted $\sim17$ cm away from the CML1. Another issue is charge accumulation on the mirror substrate (quartz) because the 266 nm mirror edge is only $\sim3$ mm away from the electron pulse beam axis. The static field caused by the accumulated charges can disturb electron pulse propagation. To minimize charge accumulation, we designed the electron beam shield on top of the mirror as shown in Fig. 4.17.

4.5.2 Electron Beam Deflector

In principle, if all of the parts in the high-brightness UED system are perfectly fabricated without any errors and the electron pulse travels through the exact center of the high-brightness UED column, then an electron beam deflector is not required. However, it is not possible to fabricate the exact dimension and perfectly symmetric components. All of the machined parts have a tolerance of $\sim0.001^\prime\prime$, and the accumulated machining tolerance in each part might not be negligible in a whole assembly. To compensate for this inherent systematic error, a beam control mechanism is required. In the high–brightness UED system, we implement two electron beam deflectors that control the electron beam direction with a static electric field, as shown in Fig. 4.1. The detailed design of the first deflector is shown in Fig. 4.18(a). It consists of two pairs of stainless steel rods which generate an
electric potential difference and the MACOR cylinder which electrically isolates the rods from the stainless steel deflector body. Electron pulse propagation is from the bottom to the top in the figure (blue arrow). Each pair of rods generates an electric field in two orthogonal directions, which are perpendicular to the electron pulse propagation. Using this electron beam deflector, we can control the beam direction to align it to travel through the center of the major components such as the magnetic lens and RF cavity.

4.5.3 Aperture Manipulator

To align the electron beam along the high-brightness UED column and reduce the beam emittance, we need several different sizes of apertures, but it is technically too expansive to fabricate them from scratch because a customized aperture manipulator has to be designed and a UHV compatible precise motion manipulator is extremly expansive. Therefore, we use the aperture manipulator that was used for our old scanning electron microscope (Steroscan 360, Cambridge Instrument), shown in Fig. 4.19 (a). We designed the adapter to mount the SEM aperture manipulator (shown in Fig. 4.19 (b)). The manipulator is able to mount four different sizes of apertures, 30 µm, 50 µm, 170 µm, and 3 mm. However, this manipulator was used for the SEM high vacuum chamber, not for UHV. We applied the differential pump scheme with two O-ring seals in order to use the SEM aperture holder in the UHV chamber of our high-brightness UED system (shown Fig. 4.19). Fig. 4.19 also shows the second electron beam deflector which is right below the aperture.
Figure 4.18 Electron beam deflector. (a) The design of the electron beam deflector: the electron pulse propagates from the bottom to the top (blue arrow), and two pairs of stainless steel rods generate two orthogonal directions electric fields which are perpendicular to the electron pulse propagating direction. Eight MACOR insulation cylinders electrically isolate the high voltage applied rods from the stainless steel deflector body. The MACOR cylinders are secured with 2-56 set-screws. (b) The electron beam deflection angle as a function of applied voltage between the stainless steel rods in two orthogonal directions.
Figure 4.19 Aperture manipulator. (a) Stereoscan 360 scanning electron microscope aperture manipulator. The red circle in (a) shows where four apertures are mounted at the same time. We can manipulate the position of each aperture with two micrometers shown at the end of the aperture manipulator, x, y axis. (b) Actual design of the SEM aperture manipulator assembly with the second electron beam deflector. The gap between two O-ring seals (white dot) is pumped down with a dry pump to make the gap region pressure down to $10^{-3}$ torr. Then, two O-ring seals can hold the UHV pressure difference.
<table>
<thead>
<tr>
<th>Aperture Diameter (µm)</th>
<th>x (mm)</th>
<th>y (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000</td>
<td>4.11</td>
<td>2.75</td>
</tr>
<tr>
<td>170</td>
<td>4.30</td>
<td>9.85</td>
</tr>
<tr>
<td>50</td>
<td>4.30</td>
<td>17.85</td>
</tr>
<tr>
<td>30</td>
<td>4.30</td>
<td>25.65</td>
</tr>
</tbody>
</table>

Table 4.2 Aperture Position

4.6 The Ultra High Vacuum(UHV) Chamber

The UHV chambers of our high-brightness electron beam system consists of an electron gun chamber, a 266 nm laser mirror chamber, an electron beam column, and a main specimen chamber. Although all the chambers are connected to each other, in order to achieve and maintain low enough pressure for the specific function of each chamber, the connection scheme among the chambers has to be carefully considered because each chamber’s base pressure requirement is different due to the vacuum components in the chambers.

The lowest pressure chamber is the electron gun chamber because of the 100 kV high voltage. The electron gun chamber pressure can reach down to $\sim 10^{-10}$ torr with careful baking of the chamber, but the usual operational pressure is $\sim 2.0 \times 10^{-8}$ torr because the main specimen chamber can reach down to $\sim 10^{-8}$ torr and RF cavity pressure is higher than $10^{-8}$ torr. Fig. 4.20 shows the schematic diagram of the UED chamber. When we designed the chambers, we expected that the main chamber base pressure would not actually be UHV level because of the O-ring seal door which we intentionally implemented to switch.
Figure 4.20 Schematic diagram of the high-brightness UED chambers: (1) the 100 kV electron gun chamber, (2) 266 nm laser mirror chamber, (3) RF cavity, (4) main specimen chamber.
the sample conveniently, nor would the RF cavity pressure be at the UHV level due to outgassing. Therefore, we had to carefully consider the high pressure of the adjacent chambers to design the low-pressure electron gun chamber. The electron gun chamber is primarily pumped down by an ion pump (Ion SEM 45, Agilent Technologies), of which the pumping speed is 45 l/s for nitrogen, and it is connected to the 266 nm laser mirror chamber through a 50 mm length, 6 mm ID hole, but completely isolated from the main chamber by closing a 6” CF gate valve (6” GV). Through 50 mm ID bypass, the 266 nm laser mirror chamber is directly pumped down by a 8” CF turbo pump (Hipace700, Pfeiffer Vacuum: Pumping speed 700 l/s) mounted at the main specimen chamber because the RF cavity, which has the highest pressure, is located between the 266 nm laser mirror chamber and the main specimen chamber. To minimize the direct contamination of the electron gun chamber from the RF cavity, we implement 190 mm length and 10 mm ID copper tube which is enclosed by the CML2. To pump down the RF cavity efficiently, we add another 35 mm ID pump path between the main chamber and RF cavity.
Chapter 5

Characterization of The Electron Beam System

Achieving atomic and sub-picosecond spatiotemporal resolution is a challenging problem due to the space–charge effects [83, 84, 68]. Generally, there are two types of space–charge–led phase–space degradation. The first type is caused by the collective space–charge effect manifested in the electron pulse elongation and expansion from the development of the phase space correlation (chirping). This space–charge effect is significantly accelerated by the internal Coulomb fields of the electron pulse [83], but it can be corrected by the RF compression and electron optics, which are able to reverse the momentum distribution of electrons in the phase space, as explained in Chapter 3. The second type is caused by the stochastic space–charge effect [63], which is correlated with an irreversible growth in phase space volume (the beam emittance), due to fluctuating components of nonlinear electron dynamics. Moreover, in the high–density femtosecond electron beam generation, the stochastic space–charge effect is often coupled to formation of the virtual cathode (VC) [63]. In this chapter, we will discuss the systematic measurement of the high–brightness electron beam intensity and the emittance and show beam characteristics of the high–brightness electron beam system based on the comparison with previous theoretical study of the stochastic space–charge effect and the virtual cathode limit [63].
5.1 100 kV Pierce Geometry Electron Source

As we discussed in Chapter 4, $10^6$ electrons per pulse are required to get a sufficient contrast ratio in the diffraction pattern with a single electron pulse [70], and the coherence length $L_t$ needs to be longer than 1 nm to cover a sufficient number of unit cells in a crystal lattice. This coherence length $L_t$ requirement constrains the normalized transverse emittance $\varepsilon_x, n \leq 0.12 \, \mu m$ with $\sigma_x \sim 100 \, \mu m$, which is a typical sample size. Under these conditions, the collective and stochastic space–charge effects are severe in the phase space evolution of the electron pulse [63]: the electron pulse is not only expanding dramatically (collective space–charge effect), but the emittance also increases (stochastic space–charge effect), which reduces the coherence length $L_t$. The projected lengthening of the pulse envelop caused by the collective space–charge effects is reversible using magnetic lens focusing and RF compression [60]. We investigate the feasibility of the focusing and compression methods for the high–intensity electron pulse and quantify the performance of our high-brightness electron beam system: electron beam intensity (the number of electrons per cross-sectional area), the transverse emittance and the electron pulse length. In the following sections, we introduce the measurement techniques and characterization results.

5.1.1 Measurement Procedure for Electron Beam Current

To count the number of electrons per pulse, there are two independent methods. The simplest one uses a Faraday cup and a picoammeter, shown in Fig. 5.1. The Faraday cup is a metal cup designed to catch charged particles in a vacuum, as shown in Fig. 7.1. When an electron pulse hits the interior of a Faraday cup, the Faraday cup gains a net charge
Figure 5.1 Schematic illustration of Faraday cup: To prevent the escape of an elastic scattered electron, there is an aperture at the entrance hole. Picoammeter directly measures the current produced by the charged particles in a vacuum. Typical size of the aperture is a few hundreds micrometer.

due to the electron absorption. The metal cup produces a current that is equivalent to the number of impinging electrons \( N = \frac{I}{e} \Delta t \). Basically, the Faraday cup is a collector for electrons in a vacuum. The Faraday cup is not as sensitive as an electron multiplier detector, but it is highly regarded for accuracy because of the direct relation between the measured current and the number of electrons. This is the reason why a picoammeter is required. The advantage of this method is that the Faraday cup is a universal charge detector, independent of energy, mass, chemistry, etc. of the charged particles, and is limited primarily by the ability to measure a very small beam current.

The second method that we applied is counting the number of electrons using our charge-coupled device (CCD) camera coupled with an image intensifier, which is capable of detecting single–electron events. Basically, the CCD consists of a two-dimensional array
of pixels. In our set up, when a photon burst generated by the phosphor screen under an electron impinging event, is received by the image intensifier (see Fig. 4.16), the intensifier amplifies the signals by adjusting a biasing voltage. The amplification follows power-law growth with respect to the biasing field, which is directly proportional to the gain voltage, a control parameter in our experiment. The amplified optical signals then are recorded by the CCD below. The CCD stores such information as the charges in each pixel, which accumulate over a finite acquisition time. Afterwards, the charges are read out from pixels by means of a clocked transfer of the charges along the rows of the CCD. The CCD controller converts the analog signal (electric charge) into a digital signal (bits), and stores the image. The acquisition time must be controlled properly to prevent the potential wells associated with the pixels from overflowing (saturation). Our CCD has 2048 × 2048 pixels, each of which is 13.5 µm × 13.5 µm in size.

As we discussed in Chapter 4, the amplification through the image intensifier is up to $10^9$, which allows us to detect single–electron events. We can quantify the number of electrons per pulse by measuring the Analog-to-Digital conversion unit (ADU), which corresponds to the single–electron signals recorded by the CCD. In general, $2^{16}$ (=65536, maximum value of a 16-bit integer) counts correspond to the saturation level of the potential well of the CCD pixels. One of the most powerful properties of the CCD detector is its linearity. If the saturation is ~65K counts, then the linearity is generally assured for the counts from the background level (typically 800) to ~50K. When the counts are close to saturation, the detector sensitivity diminishes.

To determine the ADU, single–electron events are established by reducing the intensity of the main electron beam, so the random arrival of single electrons is recorded on the
Figure 5.2 Single electron count events of attenuated electron beam on CCD camera. The yellow square boxes indicate the regions of interest (ROI) $5 \times 5$ in pixels.
CCD camera, as shown in Fig. 5.2. Each single–electron event shown as a dot in Fig. 5.2 is counted with its integrated intensity over the nearby pixels and the statistics of such an integrated intensity for the single–electron events is constructed. The procedure is as follows:

1. Select the single–electron event with a certain size of the region of interest (ROI).
2. Count the integrated intensity of the selected ROI after background subtraction.
3. Construct the probability distribution that represents the number of single–electron events as a function of integrated intensity of ROI.

This procedure is repeated for a sufficient number of single–electron events, which is usually ~ 600 events in total. Fig. 5.3 (a) shows the probability profile of single–electron events with the Poisson distribution fitting (blue line). To determine the ADU, we have to use the maximum gain (9V) for the image intensifier in order to have a sufficient signal of the single–electron events, while we need to use a low gain (4V) to measure the electron beam current because the number of electrons per pulse is too high to measure at the high gain. Fig. 5.3 (b) shows the ADU as a function of the image intensifier gain, indicating that the image intensifier amplification is $\times 4.6$ on 1 V gain control voltage increment. It is important to note here that at low gain the detector doesn’t have enough sensitivity to count single–electron events, so there is a calibration factor to correlate the partially counted electron events to the total electron events. In the data presented in Fig. 5.3(b), we calibrate the ADU by the number of electrons per pulse determined by the direct measurement of the electron beam current using a Woods horn beam trap to serve as the Faraday cup (shown in Fig. 5.4) to measure electron current. The advantage of the Woods horn beam trap is
Figure 5.3 (a) The probability profile of the integrated intensity of single-electron events. The square is the experimental measurement and a blue line is the fitting with Poisson distribution function. The ADU is 4500 with image intensifier gain 9 V. (b) ADU under different image intensifier gain voltage, after considering the factor 2.1 following the calibration of electron counts through a Woods horn beam trap.
Figure 5.4 (a) The design of the beam trap. The copper tubing outer diameter is 2.0 mm and the inner diameter is 1.6 mm. The copper tube is held by a MACOR insulation cylinder, and the end of the copper tube is connected to a UHV compatible electrical wire which is Kepton–insulated silver–plated copper wire. (b) Schematic illustration of the copper tube cross-sectional view. Copper tube can trap the electrons that enter the copper tube, and the curvature reduces the probability for the elastically scattered electrons to escape from the tube.
the compactness and ease of implementation. The implemented Woods horn beam trap is designed as an arc shaped copper tube (shown in Fig. 5.4). The copper tube geometry can trap the electrons when they enter the tube, and an arc curvature reduces the possibility for the elastically scattered electrons to escape from the tube.

If we assume the ADU events recorded at gain of 9V represent all of the single-electron events, we determine that the electron current recorded by the picoammeter is a factor of 2.1 higher than the counting experiment. Correspondingly, the ADU factor shown in Fig. 5.3(b) has considered this factor.

5.1.2 Electron Beam Current Measurement Results

To characterize the space–charge effect in the electron pulse dynamics along the high-brightness electron beam column, we measure the number of electrons per pulse using the ADU counting method. According to a photoemission beam dynamics study [63], the stochastic space–charge effect is strongly coupled to virtual cathode (VC) formation at the limit of intense ultrashort photoelectron pulse generation. The analytical model [85] of the VC effect in the short pulse limit showed that a higher current density may be generated than anticipated by the Child-Langmuir current limit [63, 86]. The onset of the VC suppresses the photocurrent from its linear growth with increasing incident photon-flux. A fast multiple method (FMM) simulation considering stochastic scattering and imaging charge effects shows that the exponent of the photocurrent growth is reduced to 1/3 after the onset of a VC using a Gaussian pulse profile [63].

Fig. 5.5 shows the comparison between FMM theoretical calculation [63] and the experimental measurement of the actual number of electrons per pulse which travel from the
electron gun down to the CCD camera. In our experimental measurement, we directly measure the number of emitted electrons $N_{\text{emit}}^e$ at the CCD camera, based on the calibrated ADU value presented in Fig. 5.3(b). We may compare our measurements directly with the simulation results presented in Fig. 5.5(a), where the initially photoexcited electrons $N_e^0$, are proportional to the incident laser power $P$: $N_e^0 = PA/(h\nu)/f$, where the illuminated area $A = \pi R^2$, $R$ is the laser beam radius, and $f$ is the laser repetition rate. The experimental value of $N_{\text{emit}}^e$ is a factor of $\sim 4$ lower than the simulation data, whereas the incident area is also different (simulation $R = 100$ $\mu$m and experiment $R \sim 50$ $\mu$m). Furthermore, the threshold value $N_{\text{emit}}^e$, defined as the $N_{\text{emit}}^e$ observed at the onset of VC, has a linear dependence on bias voltage (inset in Fig. 5.5 (b)) in agreement with the simulation. As observed experimentally, low incident laser flux prior to VC onset (orange line) shown in Fig. 5.5 (b) are consistent with simulation data. We note that the suppression of this linear growth after the onset of the VC in our experiments also shows initially (at 70 kV bias) to 1/3 power exponent, as indicated from the simulation. A decrease of this exponent at a higher bias $V$ seems to appear, which awaits further studies. For a quantitative comparison, we conduct the extraction field ($F_a$) calculation for our Pierce gun geometry using Field Precision code [74]. We obtain the conversion factor $k = F_a/V$ to be $22$ $m^{-1}$. Given this, we can directly compare the $N_{\text{crit}}^e$ at the onset of VC. From the experiment, $N_{\text{crit}}^e$ at 100 keV (corresponding to $F_a=2.2$ MV/m) is $6 \times 10^6$, whereas from interpolating the simulated data, it is $\sim 1 \times 10^7$.

This comparison provides us with a handle to evaluate the feasibility for conducting UED and UEM experiments. The observed $N_{\text{crit}}^e$ of $6 \times 10^6$ per pulse at 100 keV is still slightly low compared to the $10^7$-$10^8$ estimate for single-shot UEM imaging, but is sufficient
Figure 5.5 The number of emitted electrons per pulse. (a) Simulation results of the number of emitted electrons per pulse $N_e^{emit}$ plot as a function of the number of generated electrons $N_e^0$, which is proportional to the input power of 266 nm pulse laser, at various surface extraction field $F_a$. This plot shows evidence of virtual cathode (VC) formation [63]. (b) Experimental measurement of the number of emitted electrons $N_e^{emit}$ as a function of input power of 266 nm pulse laser. The experimental measurement shows consistent linear dependence on input power below the VC limit, and 1/3 power dependence above the VC limit.
for single-shot UED, which requires $10^5 - 10^6$ electrons per pulse (depending on sample scattering strength). However, perhaps the most challenging issue for imaging is the stochastic blurring effect at high density limit. In principle, we can increase the surface field strength by reducing the gap distance between the cathode and the anode, but, in a Pierce geometry photoelectron gun, the highest field (established around the edge of the cathode and the anode as shown in Fig. 4.4) has already reached $\sim 10$ MV/m which is close to the practical breakdown limit. We may easily develop a gun with slightly different geometry to ameliorate this high edge field strength so the $N_{\text{crit}}^c$ can be improved (see Appendix E). Another solution is to push the VC limit up by using longer pulses by shaping the 266 nm laser pulse. Since the VC effect is largely controlled by the instantaneous electron density at the cathode surface, longer pulses reduce the instantaneous current. Nonetheless, this is at the expense of temporal resolution, which may not be recoverable using RF compression if the initial pulse is too long.

5.1.3 Pepper Pot Technique for Emittance Measurement

In the accelerator community, there are three general techniques to measure the emittance: (1) quadrupole magnet scan method, (2) lens drift scan method, and (3) Pepper Pot method. The quadrupole magnet scan and the lens drift scan require sufficient drift space to perform the measurements, so these two methods are practically very hard to implement in our system. However, the Pepper Pot method can be easily applied in our system, as the relevant aperture and imaging systems are readily available. Moreover, while the quadrupole magnet scan and the lens drift scan are good for high energy beams ($\sim$ MeV), the Pepper Pot method is more suitable for high space-charge densities and beams with
high energy spread beam in the keV energy range [87]. For a space–charge–dominated high–intensity beam, the small aperture collimation of the beam into beamlets reduces the space–charge effects sufficiently to allow the beamlets to expand under the influence of emittance, instead of space charges.

The emittance of the electron beam is obtained by measuring the electron beam’s spatial and angular distribution sampled along the cross-sectional area of the incident beam. While this is typically done with a mask with small aperture arrays (hence the name Pepper Pot), we can achieve the same result by adjusting an aperture to various locations within the full beam envelope, as shown in Fig. 5.6, given that the beam is stable and reproducible in our set up. Each beamlet reveals the local transverse momentum spread, which is recorded at the CCD with single–electron sensitivity, allowing us to fully reconstruct the electron pulse phase space, $x, p_x$. The adjustable apertures (30 µm, 50µm) and the CCD camera are depicted in Fig. 4.1 along the electron beam line. The electron beam is sampled by the aperture, producing a beamlet that is allowed to drift freely before striking the CCD pixels. While drifting, the beamlet disperses according to its transverse velocity distribution. Therefore, the spatial profile of the beamlet at the CCD plane is a direct measurement of the angular divergence of the beamlet. By scanning the aperture across the full beam, the spatial and angular distribution of the beam in the trace space ($x, x'$) can be constructed.

The emittance data are stored as an array of beam intensity $I(x_i, x'_{i,j})$ measured at different aperture positions $x_i$ and the different divergence angle $x'_{i,j}$ of the j-th CCD pixel. With the drift length $L$ between the aperture and CCD plane, the measured trace space distribution is constructed by a series $x_i$ (i-th beamlet) of distinct angular distribution, $x'_{i,j}$. 
Figure 5.6 Illustration of the emittance measurement scheme.
(j-th pixel within i-th beamlet) defined as

\[ x_{i,j} = \frac{x_{ij} - x_{ij,c}}{L}, \quad (5.1) \]

where \( x_{ij} \) is a coordinate of the j-th pixel of i-th beamlet, and \( x_{ij,c} \) is the center location of CCD image of the i-th beamlet.

As with the rms emittance definition shown in Eq. 3.6, we can define the transverse emittance as

\[ \varepsilon_x \equiv \sqrt{< x^2 > < x'^2 > - < xx' >^2}, \quad (5.2) \]

and we can measure the \( < x^2 >, < x'^2 >, \) and \( < xx' > \) with the following equations:

\[ < x^2 > = \frac{\sum_i \sum_{j=1}^{\text{range}} (x_i - x_c)^2 I(x_i, x'_{i,j})}{I_{\text{tot}}}, \quad (5.3) \]

\[ < x'^2 > = \frac{\sum_i \sum_{j=1}^{\text{range}} (x'_{i,j} - x'_c)^2 I(x_i, x'_{i,j})}{I_{\text{tot}}}, \quad (5.4) \]

\[ < xx' > = \frac{\sum_i \sum_{j=1}^{\text{range}} (x_i - x_c)(x'_{i,j} - x'_c) I(x_i, x'_{i,j})}{I_{\text{tot}}}, \quad (5.5) \]

\[ < x_c > = \frac{\sum_i \sum_{j=1}^{\text{range}} x_i I(x_i, x'_{i,j})}{I_{\text{tot}}}, \quad (5.6) \]
\[ <x'_c> = \frac{\sum_i \sum_{j=1}^{\text{range}} x'_j I(x_i, x'_i, x'_j)}{I_{\text{tot}}}, \quad (5.7) \]

\[ I_{\text{tot}} = \sum_i \sum_{j=1}^{\text{range}} I(x_i, x'_i, x'_j). \quad (5.8) \]

The normalized emittance is defined by

\[ \varepsilon_{n,x} = \beta \gamma \varepsilon_x, \quad (5.9) \]

where \( \beta = v_z/c \) and \( \gamma = 1/\sqrt{1-\beta^2} \). Using this formula, we will show the transverse emittance measurement of our electron pulse in the following sub-section.

5.1.4 Beam Emittance Measurement

To construct the phase space of an electron pulse, sufficient precision of the spatial resolution of the CCD camera is required. As introduced in Chapter 4, our CCD camera window size is 2048×2048 pixels, and each pixel is able to detect single-electron events in a 27×27 (\( \mu \text{m}^2 \)) area. Each pixel has a well defined location and the high spatial resolution of the CCD camera allows us to measure the divergence angle with sufficient precision. Fig. 5.7(a) shows direct images of the full beam consisting of the \( \sim 10^6 \) electron pulse. From the beam profile recorded on the CCD as shown in Fig. 5.7(c), the FWHM of the beam is determined to be 59 pixels, which corresponds to \( \sim 1.6 \) mm. Fig. 5.7(b) and Fig. 5.7(d) show the image and the beam profile of the beamlet after going through the 50 \( \mu \text{m} \) aperture. With a series of such images after aperture scanning across the full beam, we can clearly define the center
of each beamlet and calculate the divergence angle for each individual beamlet.

According to the FMM theoretical study [63], above the VC limit, the strong image–charge field and the stochastic space–charge effects lead to an irreversible emittance growth. To avoid this irreversible emittance growth, we keep the laser power right below the VC limit, which is shown in Fig. 5.5. Fig. 5.8 shows the measurements of the transverse phase space distribution for low electron density (∼10 electron/pulse), and high electron density (∼5×10^6 electron/pulse), both below the VC limit. As expected, the phase space distribution has a linear distribution in both cases. This indicates that the electron pulse has no
Figure 5.8 Electron beam trace space plot \((x,x')\) of 10 electron per pulse and \(10^6\) electron per pulse. Each data point represents the position and the transverse momentum of each beamlet, and error bar is the momentum spread of the each beamlet.

severe non-linear dynamics during the propagation. With this phase space reconstruction and the intensity profiles of each beamlet shown in Fig. 5.7, we can calculate the transverse emittance with the equations shown in the previous sub-section.

Fig. 5.9 shows a theoretical study of normalized transverse emittance \(N_{\text{emit}}^e\) as a function of the extraction field and the number of electrons emitted based on the fast multiple method [63]. This theoretical study considers two different scenarios with image–charge dynamics: (1) the image–charges are pinned on the surface, (2) the image–charges are fully responsive to the motion of the emitted electron pulse. In Fig. 5.9, we can clearly see a strong increase of transverse emittance \(\varepsilon_x\) around the VC limit. When the image charges are pinned, such as on a rough surface where the image charge dynamics are restricted, the
Figure 5.9 Dependence of the transverse emittance $\varepsilon_x$ on the number of emitted electrons ($N_e^{\text{emit}}$) and the extraction field $F_a$. The inset shows the temporal evolutions of $\varepsilon_x$ at $F_a=0.32$ and 1.0 MV/m (all with $10^7$ electrons), where generally $\varepsilon_x$ reaches a steady state after 40 ps. The red dot indicates our transverse emittance measurement $\varepsilon_x=0.167 \, \mu\text{m}$ at a location right after the RF cavity [63].
increase of the transverse emittance with $N_e$ is nearly double that in the absence of the pinning, while the VC limit is the same for both cases. The inset of Fig. 5.9 shows that the transverse emittance generally reaches a steady state after 40 ps. In the simulation [63] with the experiment condition, 2.2 MV/m extraction field, the transverse emittances of $10^6$ and $10^7$ electrons per pulse with initial $R=100$ µm are calculated as 0.0745 µm and 0.208 µm (Note: these data are not shown in Fig. 5.9.), respectively, which agree well with the measured value of 0.167 µm at $5\times10^6$ electrons per pulse. In comparison, at 10 electrons per pulse, the transverse emittance is 0.053 µm, which is nearly a factor of 2 larger than the simulation. However, we note that the minimum measurable emittance based on our approach is limited by the signal-to-noise ratio of a beamlet of the low–density electron pulse because the emittance measurement from the relatively low signal of the 10 electrons per pulse is highly affected by how we subtract the background level. On the theoretical side, at 10 electrons per pulse, the emittance is predominantly in the space–charge–free limit given by the three–step model [88], which is subject to the accuracy of the work function.

In the current setup of the high-brightness electron beam system, the direct measurement of the longitudinal emittance is not straightforward, but we can establish an upper-bound of the longitudinal emittance in the following way. As defined in Eq. 3.37, the longitudinal emittance $\varepsilon_z$ is directly proportional to $\Delta t \Delta E$ for an optimally compressed beam, where $\Delta t$ is the electron–pulse duration, and $\Delta E$ is the energy spread of the pulse. We might be able to determine $\Delta E$ and $\Delta t$ simultaneously by monitoring how the Bragg angle variation $\Delta \theta$ corresponding to the diffraction peak width is affected by $\Delta E$ (see Eq. 8.1, and Eq. 8.2):
\[ \Delta E = 2 \frac{\Delta \theta}{\theta} E, \]  

(5.10)

and the pulse duration of the electron pulse from the temporal response in an UED experiment.

It is important to note that the diffraction peak width is determined not only by \( \Delta E \), but also by the variations in the structure such as those due to thermal vibration. We can determine \( \Delta E \) by deconvoluting from the space–charge–led angular broadening based on

\[ \delta \theta_{sc} = \sqrt{\delta \theta^2_N - \delta \theta^2_{N=0}}. \]

We can extract the energy spread-induced angular broadening by comparing the Bragg angle variation of a high-density electron pulse to that of a low-density electron pulse. So far, we have not yet consistently implemented such experiments.

## 5.2 Magnetic Lens Focusing Characterization

To characterize the performance of each magnetic lens, we measure the focal length of the magnetic lens under different applied current shown in Fig. 5.10(b). As targeted, the CML1 focuses the high density electron pulse to avoid beam divergence induced by strong space–charge effect, and, with 1.0 A applied loop current (corresponding to 550 A total current in the simulation because of 550 times coil winding), CML1 focuses the diverging beam at the CML2 level. CML2 can focus the pulse at the RF cavity or the sample position with different applied loop currents, \( \sim 3.0 \) A \([3.0 \times 150(\text{coil winding})=450 \text{ A}]\) and \( \sim 1.8 \) A \([1.8 \times 150(\text{coil winding})=270 \text{ A}]\), respectively. (Note: the number of coil winding in each magnetic lens is shown in Chapter 4.) With CML1= 1 A and CML2=2.7 A to establish the
Figure 5.10 (a) Schematic illustration for the beam propagation along the electron column with CML1 and CML2 focusing. The distance shown in the figure is the actual distance of our electron beam line (see Fig. 4.1), (b) Focal length of three magnetic lenses as a function of the applied current. Each focal length measurement is with non-focused electron beam directly from the electron gun, except the objective lens. The focal length measurement of the objective lens is with CML1 and CML2 focusing.

As discussed in Chapter 4, the actual magnetic lens current to generate a certain field in an experiment can be different from the current set by the simulation because of the difference in permeability in the actual magnetic materials used. To calibrate the permeability, we search for those conditions in the non-interacting single–electron simulation that can reproduce the experimental measurements. Under the assumption that the dynamics of 10 electrons per pulse is close enough to the dynamics of a non-interacting electron, we directly compare the simulated trajectories to the emittance measurement conducted at 10 electrons per pulse (shown in Fig. 5.8). Fig. 5.11(b) shows the comparison of the ray–angle between
Figure 5.11 Comparison between Field Precision trajectory simulation and experiment. (a) The non-interacting single–electron trajectories from Field Precision simulation. Green, blue, red, black vertical lines indicate the optical components along the high-brightness UED column: photocathode, CML1, CML2, CCD camera. Each horizontal line is a single–electron trajectory generated at different initial locations $R$. Initial condition of the electron is a completely zero energy particle and it is accelerated only by 100 kV acceleration voltage. The numbers right next to CCD position are the initial emitting location $R$ on the photocathode. (b) Ray angle vs. location $R$ on the CCD screen. The red squares are the experimental measurement of the ray angles with 10 electron per pulse shown in Fig. 5.8, and black squares are the simulation.
the experiment (red square) and the simulation (black square) as a function of the position on the CCD screen. The agreement in the ray–angle comparison indicates that the field distributions in the experiment and the simulation are consistent, while the applied current of CML2 (275 A) in the simulation is inconsistent with the actual applied current (405 A) in the experiment. This inconsistency of CML2 is corrected by the calibration factor for the permeability, 1.47, and we applied this calibration factor to all further simulations. (Note: the calibration factor of CML2 is 1.47 while the factor of the CML1 and the objective lens are 1 because CML2 has been re-machined after the annealing process, and it might cause a change in permeability.)

5.3 Phase Jitter of RF Compression

In the RF synchronization, the most important issue is the precision of the relative phase stability between the fs laser pulse train and the RF field, especially the phase jitter caused by environmental fluctuations, such as temperature and humidity, impacting the performance of the electronics (VCO, photodiode, etc.). These fluctuations are a major challenge to optimization of the pulse compression. As shown in Fig. 5.12, when the electron pulse arrival time and the node of RF field do not match at the center of the cavity, the center of mass (COM) velocity of the electron pulse can be accelerated or decelerated. Then the zero of time (ZoT), defined as the time when an electron pulse and a pump laser pulse arrive at the sample plane at the same time, fluctuates, and the fluctuation limits the time resolution of the high-brightness UED. (Note: This limit on the temporal resolution is independent of the pulse duration.) If we define (1) \( t_0 \) to be the electron pulse arrival time at the sample, namely zero energy change (perfect synchronization between the RF field and the electron
Figure 5.12 Schematic illustration of the phase jitter. (a) Perfect phase match between RF field and the electron pulse arrival time: the COM velocity of the electron pulse has no change. The relative phase mismatch causes (b) decelerating the COM velocity of the electron pulse, and (c) accelerating the COM velocity.
pulse phase, $\phi_e = (t - t_0) \cdot \omega = 0$, shown in Fig. 5.12(a)), and (2) $t_d$ and $t_a$ to be the decelerated or accelerated electron pulse arrival times (caused by phase mismatch, $\phi_e \neq 0$, shown in Fig. 5.12(b), (c)), then the dispersion-limited time resolution of the high-brightness UED experiment is limited by $|t_d - t_a|$. As described below, this phase-jitter-led dispersion could easily become the limiting factor of the time resolution.

Fig. 5.13 is an experimental measurement of the electron pulse transverse size and energy variation for controlled phase differences between the electron pulse and the RF field. In this experiment, the applied RF power is 420 W and, while maintaining the RF power and the phase, we adjusted the electron pulse arrival time by changing the 266 nm laser path length using a delay stage. In Fig. 5.13, at $t = 0$ (perfect phase match for pulse compression), the electron pulse energy is 100 keV and we observe that the electron beam transverse size is at a maximum (Fig. 5.13(d)), while at $t = 500$ ps (completely out of phase; pulse stretched) the electron beam size is at a minimum (Fig. 5.13(c)). This indicates that the pulse compression induces additional transverse expansion and pulse stretching suppresses the preexisting expansion. Fig. 5.13(b) shows the energy of the electron pulse as a function of electron arrival time. Note here, that the electron energy is determined based on the electron crystallographic pattern changes by mounting a VO$_2$ sample at the sample plane. The energy shifts of the impinging electrons at the sample cause a shift in the Bragg angle (see section 8.2). We can clearly see that the electron energy is well correlated with $\phi_e$ as described above. Since the electron pulse is short compared to the RF period, we can assume that during cavity gap crossing the electron pulse sees a constant accelerating field. Given that we can extract the RF field: $E_{RF} = \frac{|U - U_0|}{d}$, where $U_0 = 100$ kV, $U$ is the electron pulse energy, and $d$ is the RF cavity gap distance $d = 22.5$ mm. We determine
Figure 5.13 Beam size and energy variation of electron pulse with different relative phase between electron pulse and RF field. (a) Beam size variation with the relative phase: the shaded areas are the compression regions and the unshaded ones are stretch regions where the faster electrons are accelerated and the slower electrons are decelerated. The top red sine curve illustrates the corresponding RF field oscillation at $\sim 1$ GHz. Time zero is set at the exact timing for the perfect pulse compression. The beam size oscillates with the pulse compression: strong compression induces the transverse expansion and strong stretch suppresses the transverse expansion. At $t = 0.75$ ps, the beam size is consistent with the beam size without RF compression. (b) Electron energy variation with different relative phase at 420 W RF power. $t = 0$ ps is the perfect in-phase, 100 keV. Inset plot is the electron pulse arrival time on the sample as a function of the relative phase (-0.2~0.2 ps range). (c),(d) the electron pulse images on CCD at completely out of phase (stretch (c)), and the perfect in-phase (compression (d)).
that at 420 W, the RF field amplitude is 2.4 MV/m.

From the energy gain, we can extract the arrival time of the electron at the sample plane: \( t = l/[c\sqrt{1 - \frac{1}{(U/(m_ec^2)+1)^2}}] \), where \( c \) is the speed of light, \( m_e \) is electron mass and \( l \) is the distance from the RF cavity to the sample. Then we can compare the arrival time to the phase jitter, here controlled via \( \phi_e \) and expressed in terms of \( t_{jitter} \). The inset of Fig. 5.13(b) shows this result: 1 ps arrival time variation (-0.5 ps - 0.5 ps) corresponds to \( \sim 300 \) fs (-0.15 ps - 0.15 ps) variation of the relative phase, \( \phi_e = (t - t_0) \cdot f \). This can be quantified from the slope \( \alpha = \frac{dt}{dt_{jitter}} \) of the inset, which shows the electron pulse arrival time vs. the relative phase. At 420 W RF power, 343 fs \((\alpha = 343)\) at the level of RF field phase jitter is minimally required to achieve 1 ps time resolution. With higher RF power generating higher RF field, the energy variation is also higher, as shown in Fig. 5.13(b), and hence the requirements on the phase jitter needed to achieve sub-picosecond temporal resolution become more stringent.

5.4 Performance Projection for UED Experiment

<table>
<thead>
<tr>
<th>CML2 (A)</th>
<th>2.51</th>
<th>2.61</th>
<th>2.71</th>
<th>2.81</th>
<th>2.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D(e/\mu m^2) )</td>
<td>4.87</td>
<td>5.13</td>
<td>5.33</td>
<td>3.90</td>
<td>3.97</td>
</tr>
</tbody>
</table>

Table 5.1 Electron dose \( D = N_e/A \) with CML1=1.0 A and Obj.ML=1.3 A

We have demonstrated the performance of our high-brightness ultrafast electron beam line to be within a factor of 2 of the theoretical source emittance and the capability of generating in excess of \( 10^6 \) electrons per pulse. Here, we will further evaluate its feasibility.
for ultrafast electron diffraction implementation by quantifying electron dose and coherence length. First, on the electron dose, based on the transverse emittance of 0.167 μm at $N_e = 5 \times 10^6$ electrons per pulse, to achieve 1 nm coherence length ($L_t$ in Eq. 3.35), the electron beam diameter needs to be 150 μm in $\sigma$–width, according to Eq. 3.35. Another figure of merit for studying nanomaterials is the electron dose $D = N_e/A$ ($A$: area of the beam spot on the sample). $D$ is closely related to the 4D brightness of the beam $B_{4D} = D_{xy}$ (factors related to transverse emittance). By using a selected–area aperture, we can reduce the beam diameter, and hence $N_e$, but not necessarily the dose. Table 5.1 shows the characterizations of $D$ based on the shadow imaging under the following conditions: CML1=1.0 A and Obj.ML=1.3 A, and for different CML2 currents with a 170 μm beam slicing aperture ($N_e$ of the full beam is $\sim 2 \times 10^6$). Table 5.2 shows the comparison among the $D$s achieved from different UED systems worldwide.

For parallel beam generation (CML1=1.0 A, CML2= 2.7 A, Obj.ML=1.3 A), we obtain an envelope beam divergence angle of 2 mrad, for a sliced beam with 170 μm aperture and $N_e \approx 10^5$, based on beam size at the sample and at the CCD camera. This value sets a lower limit of the coherence length $L_t$ with $\varepsilon_{x,n} = \frac{\sigma_x \sigma_p}{m_ec}$ (from Eq. 3.31):

$$\varepsilon_{n,x} = \frac{P_z}{m_ec} \sigma_x \Delta \theta,$$

(5.11)

where $P_z$ is the momentum along the propagation, $\sigma_x$ is the $\sigma$–width of the beam spot on the sample, and $\Delta \theta = \frac{\sigma_p}{P_z}$ is the divergence angle. Then the lower limit of coherence length $L_t$ is $\sim 1.2$ nm. We show that reducing the beam size with an aperture, while also reducing $N_e$, can improve the $L_t$ while maintaining $D$ up to $5$ e/$\mu m^2$ per pulse. Using a
V<sub>e</sub> (kV) 30 60 80 2.8 MV 100

D(e/µm<sup>2</sup>) 0.5 0.5 1.0 1.0 5.3

N<sub>e</sub> 500 10<sup>4</sup> 10<sup>5</sup> 10<sup>5</sup> 10<sup>5</sup>

FWHM (µm) 30 150 300 300 130

∆t (fs) 300 250 300 300 –

Table 5.2 Comparison of the electron dose among different high-flux UED source

<table>
<thead>
<tr>
<th>Source</th>
<th>Microbeam UED&lt;sup&gt;a&lt;/sup&gt;</th>
<th>High-flux UED&lt;sup&gt;b&lt;/sup&gt; [20]</th>
<th>RF MeV UED&lt;sup&gt;c&lt;/sup&gt;[81]</th>
<th>MeV RF UED&lt;sup&gt;d&lt;/sup&gt;[45]</th>
<th>High-Brightness UED&lt;sup&gt;e&lt;/sup&gt;</th>
</tr>
</thead>
</table>

Our results indicate that at 420 W RF power, the achievable RF field strength is 2.4 MV/m. Using Eq. 4.18, the focal length with 420 W RF compression is \( \sim 680 \) mm using our experimental parameters, \( \omega_0 = 1 \) GHz, \( d = 22.5 \) mm. To achieve the sub-picosecond time resolution, \( \sim 520 \) W RF compression power is required to focus the pulse on the sample (the sample distance is \( \sim 440 \) mm), and the phase jitter stability within the 200 fs level must be accomplished. Such a phase jitter stability (< 100 fs) has been achieved in our RF system over a short period (\( \sim 2 \) hours) [82]. Long term operation is subject to the temperature stability of the laboratory. The specified power from our RF station is 3 kW, but currently
the thermal dissipation of the RF connector seems to be limited by the temperature stability at a lower power level when running in continuous mode. Pulse mode operation could easily match the required RF power for full compression at the sample plane.
Chapter 6

Further Development of Ultrafast Electron Diffractive Voltammetry

6.1 Introduction

The ultrafast electron diffraction technique is shown to be able to investigate the charge transfer dynamics at an interfaces due to the sensitivity of the probing electrons to the transient electric field distribution [89, 90, 91], causing a modification of the surface diffraction pattern [40, 39], which is loosely characterized as the ‘refraction effect’. The methodology of measuring the interfacial photovoltage via monitoring changes in the Bragg diffracted electron beams can be characterized as a ultrafast electron diffractive voltammetry (UEDV) [40, 51]. In this chapter, we extend the prior work on UEDV, by Ryan Murdick [40, 51] with the aim to identify the different constituents of the measured transient surface voltage (TSV) and discuss their respective roles in Coulomb refraction. We also develop a general formalism that can quantitatively describe these phenomena based on surface diffraction features.
6.2 Origins of Transient Photoinduced Surface Voltage

The photoinduced transient surface charge redistribution can appear in the sub-surface level (carrier separation, electronic excitation), at interfaces (charge transfer), and above the surface (photoemission), as exemplified in Fig. 6.1. The magnitude of the surface voltage \( V_s \) can be described generally from the sum of these components [40, 51]:

\[
V_s = \int_{z_0}^{z_1} E_Z(z)dz, \tag{6.1}
\]

where \( z_1 \) is the position at which the probing electron beam enters the field region and \( z_0 \) is the position of the diffractively probed region. The effects of the these charge redistribution channels are categorized into respective photovoltages. Firstly, on the bulk level, the inner potential change \( \Delta \text{IP} \) resulting from the adjustment of valence electronic distribution
can cause an abrupt refraction shift at the interface, whereas the adjustment/creation of a space charge region defines a transient voltage $\Delta SC$ within the dielectric screening length. Secondly, on the surface level, the photoinduced interfacial charge transfer over a thin insulating barrier can create a dipole field region, which defines a voltage component $\Delta DP$ on a nm length scale. Thirdly, photoemission can occur into the vacuum region, particularly for high intensity excitations. Subsequently subsurface charge dynamics are induced to screen the field associated with photoelectron from penetrating into the bulk materials. Together, they create a near surface field imparting a potential difference $\Delta PE$ on a time-dependent length-scale defined by the recovery of the photoelectrons to the surface. These four different mechanisms of surface voltage generation have characteristic time and length scales, their influences on the probing electron beam ultimately vary with incidence and exit angles and the interfacial structure. Generally, these photovoltages are linearly superposable, which allows them to be treated independently, and the overall surface voltage can be expressed as:

$$V_s = \Delta IP + \Delta SC + \Delta DP + \Delta PE.$$  \hspace{1cm} (6.2)

As a prototype example, photoinduced charge redistribution at a Si/SiO$_2$ interface (Fig. 6.1) is examined here, in which the voltammetry is contributed significantly from $\Delta DP$ as the probing electron beam fully penetrate the top SiO$_2$ layer, whereas the electron beam has only a short penetration depth ($\approx 1$ nm) into the Si underlayer. Since the screening length in a semiconductor is relatively large($\approx 1$ $\mu$m), the short penetration of the probing electron beam picks up only a small fraction of the voltage drop along the top SC region, whereas the surface dipole voltage across the SiO$_2$ layer is fully sampled. Thus, for a scenario where interfacial charge transfer occurs, $\Delta DP$ can dominate over $\Delta SC$. Meanwhile,
\( \Delta \text{IP} \) is generally small if a phase transition is not involved. The contribution of \( \Delta \text{PE} \) is more difficult to assess. In the case of Si, the hot carriers are created with a high transient temperature, which can induce thermionic emission, and under an strong photofield from an intense laser irradiation the multiphoton photoemission is also possible [92], leading to a non-negligible photoelectron contribution to the overall photovoltage. Nonetheless, due to the very different length scales involved in interfacial charge transfer and photoemission, we expect the dynamics to be rather different, which will be investigated with controlled experiments.

6.3 Surface Diffraction and Rocking Map Characterization

Since diffractive voltammetry employs diffracted beams, it is necessary to link the photo-induced distortion of diffraction pattern with the surface voltage generation. First, we examine the formalism of electron diffraction from different types of surfaces, which has been a source of confusion to properly understand the ultrafast surface electron diffraction process and a central topic to elucidate for deducing \( V_s \). Fig. 6.2(a) describes the production of the diffraction pattern from a grazing incident electron beam. The Ewald sphere is constructed to predict the diffraction pattern based on the intercept regions between the Ewald sphere and the reciprocal lattice network. This methodology is founded on a kinematic (Fourier) theory and can be extended to understand nanoscale diffraction, in which the size of the reciprocal lattice nodes, as depicted in the inset of Fig. 6.2(a), is determined by the persistent length of the lattice probed by the electrons. For a long-range-ordered smooth surface, the in-plane persistent length is very large (\( L_a \) in the inset of Fig. 6.2(a)) as compared to the penetration depth of the electron (\( L_c \)), producing very thin reciprocal rods.
Figure 6.2 Surface electron diffraction pattern in different conditions. (a) Ewald sphere construction in the grazing incidence angle geometry. By tilting (rocking) the angle of incidence between the electron beam and the sample, the Ewald sphere intercepts the reciprocal lattice rods (relrods) at different heights. The in-phase condition is satisfied when the intercept is at the reciprocal lattice node. The inset shows the reciprocal node structure, which is effectively determined from a Fourier Transform (FT) of the crystalline region in the sample defined by its persistence lengths. (b) Expected rocking map of a smooth, pristine surface in RHEED. (c) Experimental rocking map taken from a smooth Si/SiO$_2$ surface. The dashed line shows where the diffraction pattern in the inset is taken. (d) Expected rocking map of a nanostructured surface. (e) Experimental rocking map pattern taken from a highly oriented pyrolytic graphite (HOPG) surface. (f) Experimental rocking map taken from a Si/SiO$_2$ surface sample along a Kikuchi-enhanced diffraction peak. (g) Diffraction pattern of the Si/SiO$_2$ surface, showing visible Kikuchi pattern.
(relrods). In the limit of \( L_c = 0 \) (single layer), the reciprocal lattice becomes two-dimensional (2D) array of relrods, and the diffracted beam is defined by the intercept between the Ewald sphere and the relrod network, rendering circular diffraction patterns, generally described as the Laue zones in reflective high-energy electron diffraction (RHEED). For nanostructured surfaces, \( L_c \approx L_a \), the relrods widen significantly, and the diffraction pattern can deviate significantly from circular Laue patterns. Therefore, observing more than one diffraction peaks along a single relrod is possible.

To examine the relrod structure, we use rocking map characterization, which is conducted by rocking the sample plane against electron incidence, so Ewald sphere intercept rolls along the relrod. The rocking map is constructed by slicing a reflection stripe showing a relrod normal to the shadow edge in the diffraction image and stitching these stripes together as a function of incidence angle (\( \theta_i \)). A diagonal line with slope (a) equal to 2 in the rocking map exposes the relrod structure in terms of \( \theta_{tot} \) vs. \( \theta_i \), as depicted in Fig. 6.2(b). The reciprocal node, which is a Fourier transform of a probed crystalline region defined by the persistence lengths of the samples as depicted in the inset of Fig. 6.2(a), can be examined from the out-of-phase to in-phase conditions in the rocking map. Near \( \theta_i = 0 \), the relrod structure is continuous. As \( \theta_i \) increases the relrod becomes spotty, due to the increase of persistent length (\( L_c \)) with the increasing electron penetration depth as a function of \( \theta_i \). This trend is evidenced in an experimental rocking map produced from a relatively flat Si surface, as shown in Fig. 6.2(c). For the sake of clarity in discussion, we will refer to RHEED pattern only when dealing with a smooth surface that produces sharp circular Laue patterns, which is especially useful for monitoring the layer-by-layer growth in molecular beam epitaxy [93]. In so speaking, RHEED experiment is not well suited
for studying structural dynamics study as neither does the position of the RHEED peak indicate the respective position of the reciprocal lattice node, nor does RHEED intensity directly inform lattice fluctuations, such as Debye Waller factor. Only through the inspection of the rocking map can the reciprocal lattice be exposed for structural investigation, nonetheless, such experiments are tedious to perform for dynamics study [94].

Fortunately, more informative results can be obtained for nanostructured surfaces and interfaces where the diffraction mechanism differs from ‘RHEED’. In fact, typical ultrafast electron crystallography (UEC) studies [95, 36, 37, 47, 34], rely on transmitted surface diffraction features produced with the grazing incidence electrons to determine structural dynamics. When the transverse persistent length ($L_a$ in the inset of Fig. 6.2(a)) is short, such as steps and nanostructure-decorated surfaces, the widened relrods can extend several periods of the interferences (Bragg reflections), taking advantage of the high energy electron having a large Ewald sphere radius ($\approx 90 \text{Å}^{-1}$ at 30 keV) for extensive overlap with reciprocal lattice. As a result, the slope of the in-phase diffraction in the rocking map changes from 2 to 0, as it is now possible to penetrate the samples and produce transmission patterns. A simulated rocking map (Fig. 6.2(d)) shows this trend, which is verified by a study of highly oriented pyrolytic graphite (HOPG) [34], shown in Fig. 6.2(e). This type of features differ from ‘RHEED’ in that the transmitted diffraction spots carry the symmetry of the lattice and can be used for structural determination. With UEC operated in such circumstances, the intensity of transmitted Bragg peaks have been used to monitor the integrity of the lattice structure, including laser-induced thermal fluctuations and phase transition [34], and have been exploited to investigate the surface-supported nanoparticles [29, 96]. What’s essential here for formulating the surface diffractive voltammetry is that
the diffraction condition under \( a = 0 \) has: 
\[
\theta_i + \theta_o = \theta_{tot} = n\lambda/c,
\]
where \( \lambda \) is the electron wavelength, \( n \) is the diffraction order, and \( c \) is the lattice constant, can be used to formulate the diffracted beam trajectory under the presence of transient surface field, as described in Fig. 6.3. Details of the general formalism of UEDV for \( a=0 \) or \( 2 \) under different surface diffraction conditions will be described in detail in section 6.4. We also like to point out it is generally difficult to know the circumstances of surface diffraction without examining rocking map. For example, when employing resonance diffraction peaks appearing along a Kikuchi line [97] for UEDV, the surface diffraction must be characterized according to \( a = 1 \), as shown in Fig. 6.2(f)(map) and (g) (Kikuchi pattern). For this reason, it is critical to identify the surface diffraction circumstance from the rocking map characterization before a proper interpretation of the data can be established.

6.4 The General Formalism of Electron Diffractive Voltammetry

We derive the general formalism for describing the TSV-induced distortion of the diffraction pattern under different surface diffraction circumstances. We firstly generalize the problem in a simplified infinite long slab geometry, as depicted in Fig. 6.3, where a field region exists near the surface, caused by a photoinduced redistribution of charges. We consider the ‘refraction’ effect separately for the incident and outgoing beams. As the electron beam enters the slab, the incidence angle is changed from \( \theta_i \) into \( \theta'_i \) due to the refraction effect imposed by the surface field region. A similar refraction effect occurs as the diffracted beams cross the same region to reach the detector screen, which changes the exit angle from \( \theta'_o \) in the diffraction region to \( \theta_o' \) as the diffracted beam leaves the field region. The degree of change depends on the strength of field integrated along the incident and exit
Figure 6.3 The idealized slab model for considering the transient surface voltage. The top trajectory is the electron scattering from the crystal planes with the presence of a surface field. The electron beam, incident at $\theta_i$, is Bragg scattered at $\theta_B$, exiting the surface at $\theta_o$. Introducing an attractive surface potential $V_s$ will cause the electron beam to be ‘refracted’ deeper into the crystal($\theta'_i$) and the same for the Bragg diffracted beam that would ultimately exit the crystal at $\theta_o''$ with a net shift $\Delta_B$ relative to $\theta_o$.

paths. Due to the grazing incidence geometry the change in $\theta$ is dominated by the field normal to the surface, we can relate the change in $\theta$ to $V_s$ based on momentum–energy relationship along z direction for the incoming beam:

$$p^i_{z1} - p^i_{z0} = 2meV_s,$$

(6.3)

where $p^i_{z1}$ and $p^i_{z0}$ are the momenta of the incident beam projected along z at $z_0$ and $z_1$.

Expressed in terms of angle $\theta$, Eq. (6.3) can be rewritten as:

$$\tan^2 \theta'_i = \tan^2 \theta_i + \frac{\chi}{\cos^2 \theta_i},$$

(6.4)

where $\chi = V_s/V_0$, by utilizing $\tan \theta'_i = p^i_{z1}/p_x$, $\tan \theta_i = p^i_{z0}/p_x$, and $eV_0$ is the beam energy prior entering the field region. Similarly for the outgoing beams, we have:
\[
\tan^2 \theta'_o = \tan^2 \theta''_o + \frac{\chi}{\cos^2 \theta''_o}.
\] (6.5)

Since the electric field integration is linear, different components of the surface potential can be superposed on each other, thus the details of \(V_s\) composition are not important here. The voltammetry is established when \(V_s\) can be deduced as a function of the observable \(\Delta B\), which is defined as the angular shift of the diffracted beam (\(\Delta B \equiv \theta_o'' - \theta_o\)). The derivation of \(\chi(\Delta B)\) requires the knowledge of surface diffraction. To make the voltammetry generally applicable to different type of interfaces, we consider all scenarios discussed in Fig. 6.2 by relating \(\theta_o\) and \(\theta_i\) with

\[
\Delta \theta_o = (a - 1) \Delta \theta_i,
\] (6.6)

where \(a\) is the slope along the in-phase diffracted beams in the rocking map. For example, \(a = 2\) belongs to the case of RHEED (Fig. 6.2(b)), \(a = 0\) is associated with the transmitted Bragg diffraction (Fig. 6.2(d)), and \(a = 1\) can be attributed to Kikuchi diffraction (Fig. 6.2(f)). Following the notation in Fig. 6.3, at the diffracted region:

\[
\theta'_o = (a - 1)(\theta'_i - \theta_i) + \theta_o,
\] (6.7)

which allows us to rewrite \(\tan \theta'_o\) in Eq. (6.5), which we define as \(D\), in terms of \(\theta_i\) and \(\theta_o\):

\[
\tan \theta'_o = \frac{\tan[\theta_o + (1 - a)\theta_i] - \tan[(1 - a)\theta'_i]}{1 + \tan[\theta_o + (1 - a)\theta_i] \tan[(1 - a)\theta'_i]} \equiv D; \quad (6.8)
\]

where \(\theta'_i = \tan^{-1}\left(\sqrt{\frac{\sin^2 \theta_i + \chi}{1 - \sin^2 \theta_i}}\right)\) according to Eq. (6.4). From Eq. (6.5) at given \(V_s\), \(\theta_i\) and \(\theta_o\):
Figure 6.4 The refraction-induced shift($\Delta_B$) for diffraction peak located at $\theta_o$ at $V_s=1$ volt calculated for difference surface diffraction condition characterized by $a = 0, 1, 2$ (see Fig. 6.2). The solid lines are exact solution from voltammetry formalism. The dashed lines are calculated employing small angle approximation (see text). The incidence angle ($\theta_i$) is set at 2.01°.

\[
\theta''_o = \sin^{-1} \sqrt{\frac{D^2 - \chi}{1 + D^2}}. \tag{6.9}
\]

To get $V_s$-induced angular shift in the diffraction pattern:

\[
\Delta_B = \sin^{-1} \sqrt{\frac{D^2 - \chi}{1 + D^2} - \theta_o}. \tag{6.10}
\]

Since $D$ is a function of $\chi$, it is difficult to deduce $\chi(\Delta_B, \theta_i, \theta_o)$ directly from Eq. (6.10). Small angle approximation allows inverting Eq. (6.10) to obtain $\chi(\Delta_B)$ for different $a$, which is presented in the Appendix C. One salient feature of the refraction-induced shift is that the magnitude of $\Delta_B$ increases as $\theta_o$ decreases. This is easily seen in Fig. 6.4,
where $\Delta B$ is calculated for $a = 0, 1, 2$ at $V_s = 1V$, following the exact solution based on Eq. (6.10). We note that the corresponding change in $\Delta B$ at $a = 0$ is nearly twice the value at $a = 1$, whereas at $a = 2$, $\Delta B$ remains to be 0 for all $\theta_0$. We also calculate $\Delta B$ using small-angle solutions (Eqs. (C.7) & (C.10)) in the Appendix C. The difference between the two is barely noticeable. These results show that voltammetry is best performed using nanostructured materials where transmitted Bragg diffraction is possible (i.e. $a = 0$), whereas UEDV would be impossible under strictly RHEED condition. Nonetheless, in real circumstances, even for a relatively flat surface, $a$ is usually not exactly equal to 2, as shown in Fig. 6.2(c). Deviation from $a = 2$ results in a small, but non-negligible sensitivity to $V_s$. Generally, the angular dependence of $V_s$-induced shift is opposite to the structure-related one, as the Fourier relationship: $d\theta/\theta \sim -dr/r$ demands that if only the structural change is present $\Delta B$ would increase as $\theta_0$ increases. In contrast, the refraction-induced shift responds to $V_s$ oppositely, resulting in non-uniform cancellation of structure-induced shift. This nonreciprocal feature is the basis of a Fourier phasing method [25], used to correct the $V_s$-induced distortion in the diffraction pattern in order to accurately assess the structural dynamics.

6.5 Ultrafast Electron Diffractive Voltammetry Experiment: Photoemission Contribution

As discussed in section 6.2, the photoemission contribution in UEDV measurement is hard to assess, but we expect the dynamics to be different because the length scales involved in interfacial charge transfer and photoemission are very different. To isolate the photoemis-
sion contribution in the vacuum region, *i.e.* $\Delta PE$, we conduct a controlled study in which the photoelectron dynamics and the surface photovoltage are characterized simultaneously. This is achieved by using ultrafast electron shadow projection imaging, which has been reported previously for studying photoemission from an HOPG surface [98]. The advantage of electron projection imaging is that it can be implemented *in situ* with the voltammetry experiment by simply displacing the electron beam from the pump-probe overlap position by a distance $(x_0)$ (Fig. 6.5(a)), thereby investigating the photoelectron dynamics under the same excitation condition as the voltammetry experiment. In addition, the diffracted beams, which are also visible in the shadow images, are affected only by photoemitted electrons above the surface generated by the pump laser, but not affected by the subsurface fields probed in the voltammetry geometry, thus establishing a clean way to evaluate the effect of $\Delta PE$ in voltammetry.

In principle all the relevant information pertaining to photoemission for creating the transient near-surface field can be obtained from the projection imaging study. Fig. 6.5(c), (d) show two selected snap-shots of the shadow images of the photoemitted electron cloud obtained at $t=42$ ps and 62 ps under a laser fluence of 65 mJ/cm$^2$. The initial lateral dimension of the electron cloud is determined by our pump laser incident at $45^\circ$ to the surface normal. As a result, the laser footprint is elliptical with $\sigma_x = 330\mu m$ and $\sigma_y = 233\mu m$, which are determined by the cross-correlation response by scanning the probe beam across the laser-illuminated region [25]. The projection distance (source-to-camera) employed in this study is 16.5 cm and the offset distance $x_0 = 2.23 mm$, giving a magnification factor $\sim 74$. The linescan of the shadow images (integrated vertically along the yellow stripe depicted in Fig. 6.5(b)) contains the respective temporal evolution of Gaussian-like elec-
electron cloud together with a near-surface build-up (lines colored in red in Fig. 6.5(c), (d), and from fitting the linescans [98] (Fig. 6.5(e)) at different times the temporal evolution of cloud width ($\sigma_z$) and center-of-mass position ($z_{CoM}$) can be determined, as depicted in Fig. 6.5(f) for $t = 0 \sim 100 \text{ ps}$. From these temporal profile changes, we observe a linear increase of position and width, and extract an electron cloud expansion velocity $v_{\sigma_z} = 0.336 \mu m/\text{ps}$ and an initial CoM velocity $v_{CoM} = 1.02 \mu m/\text{ps}$.

The creation of shadow images can be understood based on scattering of the probing electrons from the collective field established by the photoelectrons:

$$E_{PE} = \frac{1}{4\pi\varepsilon_0} \sum_{i=1}^{N} \frac{e}{(r - r_i)^2}.$$  \hspace{1cm} (6.11)

The deflection from the collective field reduces the numbers of originally forward-going electrons reaching the CCD camera, thus effectively creating a shadow of the electron cloud. This process can be directly simulated by an N-particle simulation employing Monte Carlo sampling of a 3D Gaussian electron distribution, which is parameterized based on $\sigma$'s obtained from fitting the shadow images. We then send rays of electrons representing the probing electron beam across the 3D electron cloud whose collective field is calculated first by summing the pair-wise fields from individual electrons within the cloud. To speed up the calculation, we establish a mean-field model to match the results calculated from the multi-particle calculation based on the impact parameter to the electron cloud. We note that the deflection caused by the collective field is linear with respect to the electron density in the regime of interest here, which warrants the usefulness of the mean-field approach. To simulate the shadow formation, $10^7$ electron rays are used along the line of sight to establish the shadow line scans and the electron counts on the CCD screen are
Figure 6.5 Shadow imaging experiment to characterize the properties of photoemission. (a) Schematic experiment setup of the experiment, in which the incident electron beam is displaced by $x_0$ from the photoinduced region by 800nm pump laser. The surface scattered electrons form a shadow image of the electron cloud on the CCD screen as they are scattered away from the collective field associated with photoelectrons. In parallel, the surface diffracted beam experiences the electric field associated with photoemitted electron cloud, and deflects according to its location relative to the cloud. (b) The diffraction pattern from Si/SiO$_2$ surface is shown with the striped regions selected for extracting the shadow image evolution (yellow) and the diffracted beam reflection (cyan). (c) & (d) show the snap-shot shadow images of the photoemitted electron cloud at different time delays. (e) The respective Gaussian fitting of the shadow images. (f) Results extracted from fitting the shadow image of the photoemitted electron cloud, showing the evolution of the CoM position and the cloud width.
Figure 6.6 N-particle shadow projection imaging simulation at two different time delays. Calculated with and without intervening by the 3D electron cloud. The shadow profiles are constructed by dividing the electron counts along the line scans with the rays being intersected by the 3D cloud in the path and the line scans without intersection and compared with the experimental results. Fig. 6.6 shows the comparison at two different delay times at $t=42$ and 62 ps (solid lines are N-particle simulation results and dashed lines are the fitted Gaussian profiles obtained from experimental shadow images). The agreement between the N-particle simulations and the shadow imaging results are excellent. Since the depth of the shadow is proportional to the photoemitted electron density, the agreement between the experiment and simulation not only indicates the robustness of the shadow imaging technique in profiling the photoemission, but also offers a measurement of the photoelectron density created by the photo-illumination.

An independent approach to deduce the photo-electron density is through a single-beam deflection experiment across the photo-emitted electron cloud [99]. Importantly, the 3D cloud geometry established by the shadow imaging technique can be confirmed by the deflection of a diffracted beam from Si(111) surface diffraction, as it traverse through the collective field associated with photoelectrons. Single-beam deflection experiment has the advantage of being highly sensitive to the field and so is applicable even at very long times.
(ns) when the electron cloud becomes too diffusive to monitor by the shadow imaging approach. To extend the field characterization to longer time, we analyze the Si-111 beam deflection data contained in the diffraction images obtained from shadow imaging experiment. The analysis is of a Kikuchi diffraction enhanced peak (with $\theta_i=2.01^\circ$ & $\theta_o=5.76^\circ$) along the central stripe region circled by the dashed line in cyan in Fig. 6.5(b)). Fig. 6.7(a) shows the temporal evolution of the angular shift. The up and down swings of the beam can be associated with the beam crossing from above and under the 3D electron cloud [99]. Importantly, the electron density required to correctly simulate the shadow profile can now be directly confirmed by simulating the specific electron trajectory using an N-particle calculation as described earlier. Furthermore, the absolute downward shift of the diffracted beam is also affected by the counter image force associated with the image charges that are created on the surface responding to the photoemission, which is also modeled numerically as described below.

6.6 Near Surface Field Induced by Photoemission

To fully simulate the diffracted beam trajectory, which extends to 2 ns, we need to know the projectile motion of the 3D electron cloud and the corresponding image charge dynamics that provide additional field component. To comply with the rate and the magnitude of beam deflection, a metal-like dielectric response with a very large $\epsilon$ at early times due to the excessive amount of charges initially built up on surface is considered. $\epsilon$ decays exponentially to the equilibrium value of 3.9 for SiO$_2$ [100], and can be described by $\epsilon_{SiO_2}=3.9 + A e^{-t/\tau_r}$. The field model for image charges is included with the dielectric relaxation process and is described by [101]:

124
Figure 6.7 Experiments to characterize photoelectron dynamics and surface photovoltage performed at F=65 mJ/cm². (a) Data (symbols, colored in red) show the deflection of a selected diffracted beam by the electric field associated with photoelectrons and the image charges on the surface acquired in the shadow imaging experiment setup. N-particle simulations with surface dielectric relaxation times ($\tau_r$) ranging from 0, 16, 21 ps, and $\infty$ are used to fit the data. (b) The voltammetry results (symbols, colored in red) obtained from the same diffracted beam, but at the overlapped voltammetry geometry. An N-particle simulation to estimate the refraction contribution associated with photoemission is shown (solid line, colored in blue) for comparison.
\begin{equation}
E_{Img} = -\frac{1}{4\pi\varepsilon_0} \frac{\varepsilon SiO_2 - 1}{\varepsilon SiO_2 + 1} \sum_{i=1}^{N} \frac{e}{(r - r_i)^2}.
\end{equation}

The time-dependent angular shift of the diffracted beam is calculated using:

\begin{equation}
\Delta \theta = \frac{\int Edl}{2V_0 \cos^2 \theta'},
\end{equation}

where \( V_0 = 30 \text{kV} \) and \( E \) in the path integral contains contributions from photoelectrons (Eq. (6.11)) and image charges (Eq. (6.12)). The integration takes place over \( 3 \times \text{FWHM} \) across the Gaussian cloud. Previously, an analytical model [99] and N-particle simulation [39] of the transient field associated with photoelectron cloud and image charges has been implemented to account for deflection of a probing electron beam. The dielectric response of the surface has not been explicitly included. The necessity of incorporating the surface dielectric relaxation to account for the change in \( \varepsilon \) is evident from comparing the models with different dielectric relaxation times and the experimental data, which are shown in Fig. 6.7(a). We find \( A = 10^4 \) and \( \tau_r = 16 \text{ ps} \) provide a reasonable agreement to the experimental data. To comply with the deflection data at long times, the knowledge of the photoelectron cloud beyond the initial linear trajectory is needed. The return rate of the photoelectrons to the surface is determined by the strength of the image force, which is gradually weakened as the expansion of the photoelectron cloud into the surface will lead to cancellation of the image charges even before the CoM trajectory reaches the turning point and weakens the image force. We apply an additional 3rd order term to account for this effect. The deflection of the diffracted beam can be calculated self-consistently by varying the coefficients of the 2nd and 3rd order polynomials to fit the deflection data. We note that the fitting is based on a fixed initial condition (electron density and CoM and
expansion velocity) determined by shadow imaging, but the results from fitting deflection data extend our knowledge of the surface field development beyond the timescale (0-150 ps) obtainable from the shadow imaging, and serve as the basis for estimating the long time behavior for the voltammetry measurement.

6.7 Modeling of The Surface Photovoltammetry

The transient electron diffractive approach can be used to investigate electron transport in molecular contacts [102, 103, 104, 105, 106]. In a nanoparticle decorated interface, Au NP/SiO$_2$/Si, a transient charging of the nanoparticle is caused by photoinduced charge transfer between the substrate and the nanoparticle through insulating buffer layers (SiO$_2$). The transient charging establishes a voltage determined by the charging energy of the nanoparticles with respect to the driving surface potential and the resistance of the buffer layers, which can be conceptualized as an effective RC circuit as depicted in Fig. 6.8(a). The diffracted beams are employed to investigate the charge transfer dynamics between the nanoparticles and the substrate. The capacitance $C$ can be calculated directly from the geometry of the interface using a finite element method. When $C$ is known, the resistance of the buffer layer can be directly deduced by the RC time in the charging and discharging of the nanoparticle decorated interface.

To simulate the photovoltammetry dynamics driven by the $emf$ of the photoexcited carriers, we can construct equivalent circuit models. As an example, we examine the interfacial charge transfer from semiconductor photoreceptor (Si) across the insulating tunnel junction (SiO$_2$) layer to the surface with metallic (Au) nanoparticles or with just the surface states. The schematic layout of such a nanocircuit is depicted in Fig. 6.8. The photoexcitation of
Figure 6.8 (a) An effective circuit model depicting the transient surface voltage $V_s(t)$ measurement via the refraction shift across $\text{SiO}_2$/Si interface with 20 nm Au nanoparticle decoration. The electromotive potential $\varepsilon(t)$ comes from the hot carriers generated at the Si substrate. (b) Example showing the photovoltage $V_s(t)$ measured at the interface as a function of $\varepsilon(t)$. The relationship can be seen as a convolution with kernel function $h(t)$ characteristic of the RC circuit.
the semiconductor substrate generates electron/hole pairs that elevate the electrochemical potential at semiconductor surface, which can be a source of emf driving carriers across the insulating junction. The injection of hot carriers into the metal surface results in charge separation, which forms a photovoltage $V_s$ between the semiconductor and metal surface. Such a photovoltage generation is fundamentally limited by the charging time, $\tau = R_J C_J$, of the junction, where $R_J$ and $C_J$ are the junction resistance and capacitance. The photovoltage $V_s(t)$ determined here can be used to derive the emf if the response time $\tau$ is known, based on the linear response of the nanocircuit model:

$$V_s(t) = \int_{-\infty}^{\infty} \varepsilon(\tau) \cdot h(t - \tau) d\tau,$$

where $h(t) = 1/RC e^{-(t-t_0)/RC} u(t)$, $u(t)$ is the heaviside step function, and $t_0$ is the zero-of-time. In this formulation, the transient surface voltage $V_s(t)$ is the convoluted response of the electromotive potential $\varepsilon(t)$ by the kernel function $h(t)$. $h(t)$ is inherent to the circuit setup and can be obtained by the inverse Laplace transformation of the effective reactance ratio $\gamma$, which, in the case of the RC circuit describe in Fig 6.8 (a), is $Z_C/(Z_R + Z_C)$, where $Z_C = 1/Cs$ is the reactance of capacitor, and $Z_R = R$ is the reactance of the resistor in the complex frequency ($s$) domain. Applying Laplace transformation on both sides of Eq. (6.14), we establish the relationship between $V_s$ and $\varepsilon$ in the s-domain:

$$\tilde{V}_s(t) = \tilde{\varepsilon}(s) \frac{1/RC}{s + 1/RC},$$

from which we can derive $\tilde{\varepsilon}(s)$, based on $\tilde{V}_s(s)$, and use it to deduce $\varepsilon(t)$ through inverse
Laplace transform. Fig. 6.8 (b) depicts three examples of $V_s(t)$ driven by different $\varepsilon(t)$. For an impulse $\varepsilon(t)$, the $V_s(t)$ is simply the kernel function $h(t)$, an exponential decay with $\tau = RJC_J$. For a square pulse, the $V_s(t)$ rises exponentially with $\tau = RJC_J$. In practice, the carriers electromotive potential will likely have a form of nonexponential rise and decay, as depicted in the bottom panel of Fig. 6.8 (b). Given a typical nanodevice dimension, such as 10nm nanoparticle next to a gold electrode with a $\approx$ 2nm tunneling gap, the effective RC time is on the order of 10 ps. This timescale is fundamentally much shorter than the contemporary integrated device with a typical switching time $\geq$ 50ps. On the other hand, the RC time is on the upper end of the interfacial charge transfer timescale reported by optical and photoemission techniques, which is at the limit of state-to-state population dynamics, and fundamentally different from the tunneling time [107]. Using Eq. (6.15), we can deduce the effective emf dynamics based on photovoltammetry data, which shows rise and decay times of $\tau_C = 30.84ps$, and $\tau_d = 296.47ps$, respectively, for surface charging and discharging. Using $\tau$ of 30.8ps, we can deduce the $\varepsilon(t)$ as depicted in Fig. 6.9, where a spontaneous rise and long decay is seen which is consistent with the carrier density dynamics calculated using the Boltzmann transport coupled TTM [51].

6.8 Surface Photovoltage

Having obtained the near surface field associated with the photoelectrons from the shadow imaging and diffracted beam deflection measurements in the offset geometry, we can now evaluate the contribution associated with photoemission in the voltammetry experiment conducted by shifting the beam from the offset geometry to the overlap geometry, as reported in Fig. 6.7(b) (line and symbols, colored in red). The diffracted beam used in the
Figure 6.9 Theoretical modeling of transient surface voltage $V_s(t)$. Using RC time of 30.8 ps, the corresponding electromotive force $emf$ is deduced, showing a spontaneous rise and a long decay.
voltammetry experiment appears at the intercept of a Kikuchi line and a 2D reciprocal lattice rod (Fig. 6.2(g)). We characterize the diffraction being a two-step process, where the incident beam is first scattered randomly to form an isotropic source, and then scattered into surface Laue Zones. This is consistent with $a = 1$ observed in the $\theta_{tot}$ vs $\theta_i$ relationship obtained from the rocking map analysis presented in Fig. 6.2(f), implying that only the refraction along the exit path contributes to $\Delta B$, and so we can simplify the generalized TSV formula accordingly, and deduce the photovoltage based on: $\chi = -\Delta B(\Delta B + 2\theta_o)$ (see Appendix C, Eq. (C.11)).

We evaluate the contribution $\Delta PE$ in the overall photovoltage measurement by building on the knowledge of near surface fields induced by photo-emission characterized by the shadow imaging and deflection experiments. The $\Delta B$ associated with $\Delta PE$ can be calculated by an N particle simulation of $\Delta B$ along the exit beam path at $\theta_o$, similar to that in evaluating the deflection experiment, but under an overlap geometry used in the voltammetry experiment. The simulated $\Delta B$ is depicted in Fig. 6.7(b) (solid line, colored in blue) to represent the $\Delta PE$ contribution, and compared to the overall $\Delta B$ measured experimentally. Remarkably, the photoemission-associated $\Delta B$ matches very well with the long-time tail of the voltammetry measurement, but contributes maximally about 25-30% of the total angular shift at the early times. This indicates that the slow dynamics of TSV at the long time are controlled by the return of the photoemitted electrons to the surface, whereas interfacial charge transfer across the SiO$_2$ layer is more relevant at the short times. By excluding the $\Delta PE$ contribution from the overall $\Delta B$, we deduce a $V_S(t)$ relevant to the surface charging dynamics, as depicted in Fig. 6.10.
Figure 6.10 Transient surface voltage caused purely by $\Delta DP$. $\Delta PE$ contribution is subtracted from total TSV, and the surface voltage is calculated by Eq. (6.16). The surface voltage is fitted by an RC charging and discharging model with $\tau_C$=30.84 (ps), and $\tau_d$=296.47 (ps). Inset: Charging/discharging dynamics in a log time scale.
By fitting the $\Delta$PE subtracted $V_s(t)$ with an effective RC-charging/discharging model:

$$V_s = V_{fit}(1 - e^{-t/\tau_c})e^{-t/\tau_d},$$

we determined the RC time constants: $\tau_c=30.84$ ps, and $\tau_d=296.47$ ps respectively for surface charging and discharging. We attribute the difference between the two to the change of hot electron photoconductivity across the SiO$_2$ interface. The photo-generated hot electrons facilitate the surface charging through access to the excited states, leading to a much shorter RC time than the discharging, which involves a cooler interface with a reduced photoconductivity, leaving the SiO$_2$ surface to stay charged for a longer period of time.

We compare the TSV results reported here for a smooth Si/SiO$_2$ interface with one reported previously for a step Si/SiO$_2$ interface [40]. We find that the timescales in charging and discharging the interface in the two studies are similar, whereas the TSV induced in the smooth interface (maximum 1.7V at 65 mJ/cm$^2$) is smaller than the stepped interface (maximum 3V at 72 mJ/cm$^2$). By applying the shadow imaging technique under the same conditions (electron incidence/exit angles and laser fluences) as the voltammetry experiment, we are able to quantitatively identify the contribution of photoemission on the overall voltammetry result, where photoemission is mainly responsible for the slow decay, but does not contribute significantly to the short time dynamics, which clarifies the origin of the diffracted beam movement [99]. For cases where photoexcitation can cause significant structural changes, a correction on the refraction-induced shift in diffraction pattern is needed. We point to the first ultrafast electron crystallography investigation of
Si(111) surface, which was performed using 266 nm laser pulse [94]. Because of the much shorter laser penetration depth (4nm), the absorbed optical density is concentrated near the surface, propelling not only hot electron dynamics, but also surface structural changes. From examining the reported time-dependent rocking curve (Fig.4(a) in the paper [94]), the movement of the ‘in-phase’ Bragg peak at small angle (\(\sim 3.1^\circ\)) is slightly larger than that of a peak at higher angle (\(\sim 3.9^\circ\)), which is consistent with a surface refraction phenomenon being present. But the surface charging is not the full story, as the ‘surface’ structural dynamics was also examined in the ‘out-of-phase’ condition (Fig.4(b) in the paper [94]), where the presence of multiple interference peaks is a signature of transmitted diffraction from surface nanostructure. Such a pattern was modeled using a slab model that identified the changes are from the top surface layer and the sub-surface (111) layers, contributing the contrasting movements of the two different peaks separated in \(\approx 30\) ps. The surface dynamics could be mediated by the impulsive strain induced by ultrafast laser pulse heating and/or surface charges. Further controlled study is needed to clarify the nature of the surface dynamics on surface charging, photo-emission and the corresponding structural dynamics, which can be achieved using the methodologies provided here.

6.9 Summary

We have established a general formalism for the UEDV concept, which is applied to investigate the photoinduced charge migration from the substrate to nanostructured interfaces. We show that the surface diffraction and boundary conditions need to be accounted to correctly formulate the ultrafast voltammetry based on Coulomb refraction-induced diffracted beam dynamics. We identify that the voltammetry appears on the surface, subsurface,
and vacuum levels, associated with interfacial charge transfer, carrier diffusion, and photoemission respectively, under intense laser irradiation. From quantitative shadow imaging techniques performed at the same condition as voltammetry and N-particle simulations, we are able to assess the voltammetry contribution associated with photoemission, and quantitatively deduce the surface charging dynamics from the overall voltammetry. We find that the photoemission impacts the voltammetry most in the long time, whereas the interfacial charge dynamics dominates the voltammetry at the ultrafast (0-100 ps) timescale. The surface photovoltage, the capacitance of the nanointerface, and the resistance of the buffer layers can be conceptualized as an effective RC circuit and, using the RC time of the effective RC circuit, we can deduce a corresponding electromotive force. A spontaneous rise and long decay of the electromotive force is consistent with the carrier density dynamics of the Boltzmann transport coupled two-temperature model calculation [51].
Chapter 7

Photo-Induced Charge Carrier Dynamics at Nanostructured Interfaces

In previous chapter, we presented an ultrafast electron diffractive voltammetry technique to investigate the surface charge carrier dynamics at the nanometer scale. This diffraction-based method utilizes the feature-gated nanomaterial diffraction pattern to identify the scattering sites and to deduce the associated charge dynamics from the nanocrystallographic refraction-shift observed in the ultrafast electron diffraction patterns. By applying this methodology on Si/SiO$_2$ interface and surfaces decorated with nanostructures, we are able to elucidate the localized charge injection, dielectric relaxation, and carrier diffusion, with direct resolution of the charge state and possibly correlated structural dynamics at these interfaces, which are central to nanoelectronics [108], photovoltaics, and photocatalysis [109, 110] development.

Through the sensitivity of the diffracted electron beams to the local electric fields, three prominent charge redistribution processes induced by photoexcitation can be observed as described in Fig. 7.1: (1) Dielectric realignment: The alignment of the dipolar elements within the dielectrics changes, resulting in displacement fields even though there is no ac-
Figure 7.1 Charge redistribution at nanomaterials interfaces subject to photoexcitation. (a) Dielectric realignment; (b) carrier diffusion; (c) interfacial charge transfer.

Tual carrier current in the materials. (2) Carriers diffusion: The photocarriers in the excited region diffuse to the unexcited region, inducing internal photocurrent. (3) Interfacial charge transfer: The photoexcitation changes the balance of chemical potential at the interface, resulting in charge transfer to counteract the shift in free energy. Decay of these photovoltages might involve drift and dipolar relaxation, in addition to carrier recombination, diffusion, and radiative decays.

To demonstrate the proof of principle, systematic investigations were conducted at interfaces with progressively grown complexities. First, a planar Si/SiO$_2$ surface was investigated with infrared laser pulse to drive the hot carriers through the SiO$_2$ layer. In the sub-10 nm dielectric SiO$_2$ layer, ultrafast surface charge dynamics is shown to strongly couple to the sub-surface carrier dynamics, exhibiting drift-diffusion relaxation behavior. Second, gold nanoparticles decoration was incorporated with molecular linkers connecting the nanoparticles to the surface. The large curvature of the nanoparticle surface facilitates the field focusing effect, which can enhance the carrier dynamics across the interface through the field-assisted tunneling. Third, surface plasmon enhancement effects were investigated. Strong dielectric-induced spectral shift in the response function highlights the mode-selective optical antenna effects between the nanostructures and their surroundings.
These studies elucidate the key features of light-driven charge transfer dynamics around these interfaces, which help to understand the fundamental processes relevant to nanoelectronics, photovoltaics, and photocatalysis.

7.1 Surface Charging of Pure SiO$_2$/Si Interface

The SiO$_2$/Si interface is the fundamental building block of CMOS devices. The nature of charge transfer, trapping, and detrapping at the SiO$_2$/Si interface has gained notable interest as the dielectric oxide layer necessarily becomes thinner as the elemental feature size continues to shrink. Moreover, this interface has also been tapped as the electronic grade interface to grow molecular electronic devices, with increasing effort exploring different avenues of fabricating interfaces using self-assembled monolayers (SAMs) [104] and nanoparticles [102, 104, 111, 105, 106]. For validating the diffractive photovoltammetry methodology, the SiO$_2$/Si interface provides a simplest test ground. Under ultrafast laser irradiation, a fraction of the valence band (VB) electrons in Si are promoted to the conduction band (CB), followed by charge rearrangement at the interface, depending on the nature of the excitation (laser intensity, energy, etc.). The very large band gap of SiO$_2$ (8.9 eV) ensures that the SiO$_2$ layer is transparent to the incident visible light. The field arises from charge separation at the interface as carriers are transported from the bulk to the surface. In ultrathin SiO$_2$ layers (1−10 nm), the charge transport across the SiO$_2$ layer is predominantly via tunneling, which makes both surface charging and discharging relatively efficient processes. However, the details of the dynamics remain nontrivial for photocarriers as both direct or field-induced (Fowler-Nordheim) tunneling [112, 113, 114] are driven by the increase of the quasi-Fermi level of hot electrons (holes) above the conduction (va-
lence) band offset. The possibility of dielectric enhancement of the interface dipole, as well as thermionic and multiphoton-mediated photoemission, can also add to this near-surface field [99, 98, 39].

Several techniques have been employed to examine charge transfer mechanisms associated with this interface, most notably, EFISH (electric field-induced second harmonic generation), which has been applied to characterize leakage currents through oxide layers, long-lived trap states, and band offsets [115, 116]. Photoelectron spectroscopic methods have been effective in elucidating the interfacial electronic structures [117, 118], as well as monitoring the surface state populations directly [119, 120, 121]. Bulk carrier dynamics in Si have been studied extensively at the pico- to femtosecond time scales with a variety of time-resolved techniques [120, 49, 122, 123, 124, 38]. Many of the surface-sensitive experiments were performed with high repetition rate lasers, on the order of 80 MHz, implying that the system is pumped every ≈ 13 ns, which is before trapped charges can relax, such that the residual charge level is continuously pumped. The amount of the residual charge depends on the integrity of the interface, or, more directly, the density of interface states.

Using standard RCA cleaning protocols, a thin (2−5 nm) insulating SiO₂ layer can be reliably grown on single crystalline Si substrate. Because the penetration depth (l) of the infrared pump laser (800 nm) for Si is significantly longer (1 μm) [125] than that of the electron beam (≈ 5 nm, incident angle 6.8°), characteristic carrier lifetime (τ_i) probed at the surface (≈ 700 ps), which can be estimated based on τ_i = l²/D, where D ≈15 cm²/s [126] is the diffusivity of the electrons, is significantly longer than the electron-phonon coupling time (≈ 5 ps), thus allowing the stored photon energy to be maintained within the photoexcited region. Meanwhile, due to the large disparity in the electronic and lattice heat capacities,
even at a relatively high fluence of 65 mJ/cm$^2$, the lattice temperature rise is very small ($\approx 40$ K) [40]. This is in sharp contrast to the more than three orders of magnitude increase of the carrier density in the surface excited region from the intrinsic level [126] by photoexcitation, thereby creating a favorable condition for studying hot electron-driven interfacial charge transfer across the SiO$_2$ layer without worrying too much of lattice effect.

Using the formalism from Sect. 6.4, the changes in diffraction angle are converted to surface voltage, which is presented in Fig. 7.2. The objective here is to analyze the Bragg peak dynamics from multiple peaks. This was to see if the agreement is robust as incidence angle and diffraction order are varied. In principle, the transient surface voltage $V_s$ should remain the same as different relrods are examined. We choose to investigate (0,3,24), (0,1,21), (0,1,24) on the (0,3) and (0,1) relrods with $N = 7$ and 8 (crystallographic notation for diffraction order is multiplied by a factor of 3 due to the ABC layering of the Si(111) surface), corresponding to $\theta_i$ of 6.24°, 4.15°, and 4.70°, and $\theta_o$ of 3.50°, 4.02°, and 4.63°, respectively. The excitation fluence is fixed at 65 mJ/cm$^2$. Under photoillumination, the transient movement of the three diffracted beams, depicted in Fig. 7.2(a), indeed exhibits nonreciprocal signatures as described previously, i.e. the higher order Bragg peak shifts less than the lower order one, which is characteristic of the surface voltage-induced effect [40]. Closer examination of the shifts shows that nonreciprocity applies only to $\theta_o$, but not to $\theta_i$, as the maximally shifted beam is (0,3,24), which has a $\theta_i = 6.24°$ larger than the rest, whereas its corresponding $\theta_o$ is 3.50°, which is smaller than the rest. This angular dependence is confirmed by the rocking map analysis for the relrods exhibiting $a = 1$ near the in-phase diffraction, as shown in Fig. 7.2(b) for (0,3) relrod. By applying $a = 1$ in Eq. (6.10), we deduce $V_s$ for the three diffracted beams and successfully reproduce $V_s$ largely
Figure 7.2 Transient voltammetry from three diffracted beams from Si/SiO₂ interface. (a) The angular shift of (0,3,24), (0,1,21), and (0,1,24) beams excited at F=65mJ/cm². (b) The rocking map characterization of (0,3)-relrod, showing a surface diffraction condition $a = 1$. (c) The photo voltage deduced from (0,3,24), (0,1,21), and (0,1,24) beams based on Eq. (6.10) using $a = 1$. 
independent of $\theta_i$, indicating the slab model description is a good model for describing the essential photovoltage response observed by diffraction.

Our diffractive voltammetry results contain sufficient information to understand the origin of the photovoltage, which might include fields along the surface dielectric SiO$_2$ layer, the subsurface bulk space charge region, and even the near-surface vacuum region. In the case of the band photovoltage induced in the bulk space charge region, the limit is the flat-band value of approximately 300 mV [127, 128]. As our $V_s$ exceeds such a limit, we rule out that the band bending induced by the space-charge layer is responsible for the $V_s$ observed here. This is further evidenced by the fact that the space-charge layer in Si is rather thick ($\approx 1 \mu$m) as compared to the penetration depth of the electron probe ($\leq 10$ nm). We turn our attention to the surface charging across SiO$_2$ dielectric layer, where the surface field is fully probed by the electron beam. The subsurface carrier dynamics is strongly coupled to the net surface charges, which, through the elevated carrier screening, defines a dynamical space charge region. In the previous investigation of surface charging processes by EFISH [129, 115, 130, 131, 132, 133], the sub-surface electric field is deduced based on modeling the field-enhancement of optical second harmonic generation signal as well as photoemission [119]. We find that the field strength $E \sim 1V/nm$ obtained in our study is very similar to what was found in EFISH studies under similar excitation conditions [129, 115], but because of a lower laser repetition rate applied here (1 kHz, compared to $\sim 80$ MHz in EFISH) cyclic residual charge accumulation from deep trap states [11, 134, 135, 136] is avoided, allowing ps interfacial charging dynamics to be resolved directly.
7.2 Surface Charging of Au Nanoparticle Decorated Si/SiO$_2$ Surface

The scope of nanoparticle research spans many disciplines with vast possibilities of incorporation into practical use, including nanoelectronics [137, 138], photovoltaics [109, 139, 140, 141, 142] and even quantum-dot-based lasers [143, 144]. On the biological/life sciences side, it has recently been shown that gold and silver nanoparticles, when delivered to site-selective cancerous cells, can destroy them upon exposure to a pulsed-laser source, without damaging surrounding tissue [145, 146]. Noble metal nanoparticle also serves as electron trap that enhances charge separation in the near junction region. Of recent interest is the concept of using a nanoparticle as an optical antenna by exploiting the plasmon-based near-field enhancement, which is capable of surpassing the diffraction limit for spatial resolution [147]. It has been observed that the same near-field optical-enhancement effect improves the carrier generation in the nearby semiconductor substrate and boosts the efficiency of the solar cell [148] or photocatalyst. At a fundamental level, the photoinduced carrier dynamics and possible plasmonic enhancement effects at the contact region can be investigated via diffractive voltammetry by monitoring the photovoltage between the nanoparticles and the substrate, which in this case is directly related to the charge state of the nanoparticle: $V_s = Q/C$, where $Q$ is the surface charge of the nanoparticle and $C$ is the capacitance of the nanoparticle/SAM/Si interface. Because of the large curvature of nanoparticle surface, the surface charges on SiO$_2$/Si surface can strongly interact with the injected charges in the nanoparticle through field focusing at the contact region, leading to enhanced carrier transport and charge separation. Two different mechanisms should be
considered, namely: (I) The hot electron-driven process, where the strong light sensitization at metallic nanoparticles generates high-temperature carriers with higher efficiency to tunnel through the SAM energy barrier, creating a photoelectron current from nanoparticle to the substrate; and (II) The photovoltage-driven dynamics initiated by electrons at Si CB edge, created by photoexcitation. While the net effect of enhancing the hot carriers concentration at metal-semiconductor interface is the same, the net photo-current flow in the two cases is opposite, which can be measured directly with diffractive photovoltammetry. When channel (I) is dominant, it leads to a positive charging of the nanoparticle, thereby causing the diffracted beam to shift upward. If channel (II) is dominant, the nanoparticle will be negatively charged, and consequently the diffraction peaks will move downward in addition to the movement induced by the surface charging of the SiO₂.

Monodisperse metallic nanoparticles (Fig. 7.3) can be deposited on Si substrates by way of SAM of aminosilanes AEAPTMS [25, 149]. The aminosilane chains, which are anchored to the Si substrate, immobilize the nanoparticles through the formation of strong van der Waals bonds. When an ensemble of nanoparticles is sampled by the electron beam, a powder diffraction pattern results [25], which is constituted from the many different crystal faces that the beam samples in its footprint on the surface. In addition, the linker molecules that take part in the anchoring of nanoparticles tend to orient themselves in a manner that is sufficiently ordered, such that very clear diffraction spots from the linker molecules are present in the patterns (Fig. 7.3(c)). Here, the charging dynamics will be examined for an interfacial structure consisting of the interconnected nanoparticle/SAM/semiconductor geometry discussed here, shown in Fig. 7.4(a). The fortuitous discovery of SAM diffraction peaks in conjunction with the extension of diffractive voltammetry to arbitrary geome-
Figure 7.3 (a) A sample of Au nanoparticles (NPs) immobilized on a functionalized Si substrate. (b) The chemical form of the AEAPTMS linker molecule. (c) Schematic of an electron beam scattering from the ordered self-assembled monolayer chain and the corresponding diffraction pattern [25]
Figure 7.4 (a) An effective circuit model depicting the transient surface voltage $V_S(t)$ measurement via the refraction shift of the diffracted beams through SAM. The $R_S$, $C_S$, $R_M$, $C_M$ are the effective resistance and capacitance of the substrate (S) and the SAM (M). The electromotive potential that can drive the photocurrent through the SiO$_2$ layer ($i_S$) and further through SAM ($i_M$) is mainly from the hot carriers generated from the Si ($\varepsilon_1(t)$); whereas the short-lived photoexcited hot carriers generated within the Au nanoparticle (NP) can also drive the charge transfer in the opposite direction ($\varepsilon_2(t)$). (b) The overall refraction shift determined by SAM diffracted beam (labeled $V_S$), the background (labeled $V_B$) obtained from SiO$_2$/Si interface, and the molecular charge transport contribution, obtained by subtracting $V_B$ from $V_S$.

tries, fuels an ongoing effort toward using the SAM dynamics for uncovering the charge transport (forward or backward) across the interface from semiconductor to nanoparticle, or vice versa. Following photoexcitation, hot electrons are generated in the substrate and nanoparticles, from which a charge transfer process will ensue depending on the relative offset between the transient electrochemical potentials of the two systems. Quantifying this process would provide an additional technique for the investigation of molecular transport, an area of notable interest [103, 150].

In our first experiment studying the molecular transport, 20 nm gold nanoparticles were used, and the interface is illuminated with 800 nm near-infrared laser pulse [25]. This ar-
rangement avoids the surface plasmon excitation of the nanoparticles (≈ 500 nm), and we expect the interfacial charge dynamics between the nanoparticle and the SiO$_2$/Si is determined by two competing processes as described in Fig. 7.4(a). Specifically, the transient voltage induced by charge transfer between the substrate and the nanoparticle can be monitored by analyzing the SAM diffraction peaks corresponding to momentum transfers, $s = 2.75, 5.27, 7.98\text{Å}^{-1}$ (orders N = 13), as depicted in Fig. 7.3(c). The total transient shift $\Delta B$ includes two serial voltage drops: one across the SiO$_2$/Si surface ($V_B$), and the other across the SAM ($V_M$), as depicted by the effective RC-circuit in Fig. 7.4(a). To isolate the voltage across the linker molecule, the contribution from $V_B$ must be subtracted out. Typically, the $\Delta B$ associated with a bare SiO$_2$/Si surface has an exponential down turn followed by a $\approx$200 ps recovery. The presence of an additional upward swing followed by a downward swing to recovery can be discerned with careful analysis, which is shown in Fig. 7.4(b). These additional components sampled by diffraction through SAM suggest a new channel of photo-current emerges between the silicon substrate and the nanoparticles, which creates a more positive potential at the interface to account for the initial upswing of the diffracted beams [25].

These results strongly indicate that both processes (I) and (II) are at play. Process (I) is a key player at 1-40 ps due to the hot electrons generated within the strongly sensitized gold nanoparticle. However, because of the lifetime of the hot electrons in gold nanoparticle is limited by the electronphonon coupling on the few ps timescale, the $emf\ \varepsilon_2(t)$ is short-lived. Meanwhile the photoexcited CB carriers at silicon surface is very long-lived, limited mainly by the drift-diffusion carrier recombination at $\geq 200$ ps timescale [40]. The $\varepsilon(t)$ is persistent and ultimately dominant at long times driving the photocurrent across the
Examining the data in Fig. 7.4(b) shows a charging and discharging time of $8 \pm 1\text{ps}$. Based on the effective RC model, we obtain a resistance $R_M = 2.74 M\Omega$ using $C = 2.92 \times 10^{-18}$ Farad, deduced from finite element modeling of the interface. It is rather interesting to compare this molecular resistance with the steady-state value of $12.5 M\Omega$ obtained by applying a bias voltage across the molecular interface [149] using $10 \text{nm}$ (thus a covered area by the functional molecules is $\sim 4$ times smaller than that of $20 \text{nm}$ Au NP) Au nanoparticle. The $R_M$ obtained using ultrafast voltammetry is four times smaller than the steady-state measurement for $10 \text{nm}$ particle, which shows the molecular resistivity obtained from two different methods are nearly identical.

### 7.3 Photo-induced Field Enhancement with Localized Surface Plasmon of Nanostructures

The photo-induced surface charge transfer shown in bare SiO$_2$/Si interface and gold nanoparticle decorated SiO$_2$/Si interface has is excited by $800 \text{nm}$ pump laser which is out of the resonance of a gold nanoparticle surface plasmon frequency. In novel metal, the conduction electrons can be excited into collective oscillatory motion about the heavy ionic core. This occurs when the frequency of light photons matches the natural frequency of surface electrons oscillating against the restoring force of positive nuclei. The surface plasmon resonance in nanometer-sized structures is called localized surface plasmon resonance (LSPR) shown in Fig. 7.5. LSPR exhibits enhanced near-field amplitude at the resonance frequency. This field is highly localized at the nanostructures and enhances surface charge transfer at the
Figure 7.5 Schematic illustration of localized surface plasmon oscillation induced by an oscillating electric field in a metal nanoparticle. The displacement of conduction electron cloud relative to the nuclei is shown. The frequency of the localized surface plasmon resonance is denoted $\omega_p$.

interface between a nanostructure and a surface. In this section, we present photo-induced charge transfer enhancement due to LSPR.

7.3.1 Localized Surface Plasmon of Gold Nanoparticles

The conduction band electrons in a metal nanoparticle can collectively oscillate with the incident external field of which the wavelength is much larger than the nanoparticle size, and this collective motion can be described by the dipole approximation of Mie theory.[151, 152] In this approximation the wavelength-dependent extinction cross-section of a single particle, $C_{ext}(\omega)$, which defines the energy losses in the direction of propagation of the incident light due to both scattering and absorption by the particle, is described in terms of the dielectric function of the metal, $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, and the dielectric constant of the medium, $\varepsilon_m$, as shown below:
\[ C_{\text{ext}}(\omega) = \frac{12\pi R^3 \varepsilon_m^{3/2}}{c} \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2}, \] (7.1)

where \( \omega \) is incident light frequency, and \( R \) is the nanoparticle radius.

As can be seen from Eq. (7.1), the extinction cross-section of a particle depends on the dielectric function of the metal of which the particle is composed. This gives rise to very different absorption and scattering characteristics for different metal nanoparticles. The maximum of \( C_{\text{ext}}(\omega) \), the resonance condition, will take place when the denominator of the right-hand side of the equation becomes minimal. This is fulfilled approximately at the frequency, \( \omega_p \) for which \( \varepsilon_1(\omega_p) = -2\varepsilon_m \), if the imaginary part of the metal dielectric function, \( \varepsilon_2(\omega_p) \) is small. The frequency of the surface plasmon resonance, \( \omega_p \), is depicted in Fig. 7.5 in terms of the period of the oscillation of the electric field and the conduction electrons within a metal nanoparticle.

The large absorption cross-section values of the surface plasmon resonance band imply that a NP is able to efficiently acquire a vast amount of energy when irradiated with light at the appropriate wavelength. Thus, it is interesting to ask questions about the excited state deactivation pathways and their corresponding dynamics in gold nanoparticles. In other words, how efficient is the deactivation of a photoexcited gold nanoparticle? It is useful to clarify what is meant by excited state deactivation in the context of the surface plasmon resonance in metal nanoparticles. Because the surface plasmon resonance is a manifestation of a coherent oscillation of the conduction band electrons, the loss of coherence is a form of deactivation of the excited state and it may have observable effects. However, this loss of coherence does not involve any energy redistribution, but merely the change of the plane
in which each electron oscillates (i.e. the change of the plasmon wave vector), thus leading to the loss in coherence. This process is very fast, on the order of a few femtoseconds. We are instead interested in the deactivation of the NP excited state via energy dissipation through a charge transfer and the discussion in this section focuses on this process only.

The charge transfer for the equilibration of the photoexcited electrons in the Au NP after photoexcitation is electron-electron relaxation. The high energy electrons after the photoexcitation can undergo collisions with other electrons present in the volume of the nanoparticle, leading to the partition of the energy between the electrons. This process leads to a change in the energetic distribution of electrons from the highly non-thermal distribution present immediately after the photoexcitation to a statistical Fermi-Dirac distribution with a high temperature Fermi level. These hot electrons further lose their kinetic energy due to collisions with the ionic crystal lattice of the NP. This process, usually referred to as electron-phonon relaxation, leads to the lowering of the Fermi level and thermalization of the crystal lattice of the nanoparticle.[153] Hodak et al. showed that the electron-phonon-relaxation time constant in gold NPs did not depend on the size of nanoparticles for samples within the 2.5 nm to 120 nm size range,[8] and that its value (0.7 ps) was very similar to that measured for bulk gold films.[154] Since higher laser power causes a higher temperature jump of the electrons after electron-electron relaxation, the electron-phonon-relaxation time constant depends on the power of the excitation beam, as shown experimentally by various researchers.[153, 8, 155] A spectacular phenomenon related to the heating of the crystal lattice of gold NPs due to the electron-phonon relaxation has been demonstrated by Hodak et al.[156] The researchers observed coherent oscillations in the signal of the surface plasmon resonance band bleach in a femtosecond transient absorption experiment.
The induced collective electron oscillations associated with the surface plasmon resonance give rise to induced local electric fields near the nanoparticle surface. The induced electric field originating from the charge separation in the nanoparticle during the plasmon resonance oscillations is very large at very small distances from the surface. For silver nanoparticles the values of the induced field can be tens of times larger than the incident electric field values. Hao and Schatz performed calculations for a silver sphere with a 20 nm diameter and found that due to the surface plasmon resonance the incident electric field is enhanced by 13 times at the immediate particle surface. This enhancement factor quickly drops to smaller values as the distance from the surface increases. These enhanced local fields are responsible for increased rates of field-dependent processes at surfaces of nanostructured metals.

While phenomena in which the local field effect plays a crucial role include surface-enhanced photochemistry and second-harmonic generation perhaps the most celebrated analytical technique based on the local electric-field enhancement by metal surfaces is Surface-Enhanced Raman Spectroscopy. Jeanmaire and Van Duyne found in the late 1970s that pyridine molecules physisorbed onto a rough silver electrode exhibit an unusually strong Raman signal. It is agreed today that the enhanced intensity of the Raman scattering signal of molecules adsorbed on rough metal surfaces is largely due to the enhanced local field effects in the close proximity of the nanostructured metal surface. These signal enhancements can be as large as $10^{14}$, of which a factor of $10^7 - 10^8$ is attributed to the local field effects. The large improvement in the detectability afforded by the signal enhancement resulted in a number of analytical techniques, including methods allowing one to probe single molecules.
7.3.2 Localized Surface Plasmon of Hollow Gold Nano-shell

The surface plasmon resonance absorption of the nonspherical nanostructures strongly depends on the shape or the size of the nanomaterial [161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171], and the surface plasmon resonance of various metal nanostructures has been successfully demonstrated: nanorods, nanowires, nanocages, nanospheres, nanoprisms, and nanoplates or sheets [172, 173, 174, 175, 176]. A hollow gold nano-shells (HGNs) is another example having a unique capability for the surface plasmon applications because HGNs have a broadly tunable surface plasmon resonance in the entire visible to near infrared depending on both their core diameter as well as the shell thickness. Fig. 7.6 illustrates the resonance mode of electrons in HGNs and the UV-visible adsorption spectra of nine HGN samples with varying diameters and shell thickness.[177] The diverse surface plasmon resonance absorption of HGNs is the result of multiple resonances in the structure, and the mechanism of the diverse surface plasmon resonance generation can be understood by a plasmon hybridization model [178, 179, 180, 181].

The highly geometry-dependent plasmon response of HGNs can be seen as an interaction between the essentially fixed-frequency plasmon response of a nanosphere and that of a nano-cavity (Fig. 7.7). The sphere and cavity plasmons are electromagnetic excitations that induce surface charges at the inner and outer interfaces of the metal shell. Because of the finite thickness of the shell layer, the sphere and cavity plasmons interact with each other. The strength of the interaction between the sphere and cavity plasmons is controlled by the thickness of the metal shell layer. This interaction results in the splitting of the plasmon resonances into two new resonances: the lower energy symmetric or bonding plasmon and the higher energy antisymmetric or antibonding plasmon (Fig. 7.7). The different com-
Figure 7.6 Hollow gold nanoshell (HGN) surface plasmon resonance. (a) Schematic illustration of localized surface plasmon oscillation induced by an oscillating electric field in a hollow gold nanoshell (HGN). The displacement of conduction electron cloud relative to the nuclei is shown. The frequency of the localized surface plasmon resonance is denoted $\omega_p$. (b) A UV-visible absorption spectra of nine HGN samples varying diameter and wall thickness.[177]
binations of the nanosphere and the nano-cavity geometries generate the diverse plasmon responses at different energies.

7.3.3 Surface Plasmon Mediated Charge Dynamics of Au Nanoparticle Decorated SiO$_2$/Si Interface

From section 7.3, it is shown that there are two non-mutually exclusive channels of charge transfer between the nanoparticle/semiconductor interface. In this section, we investigate how these channels will be enhanced by the SPR excitation. To evaluate the SPR enhancement effect, we monitor the correlation between the SPR intensity and the transient surface voltage ($V_s$) on nearby silicon substrate using UEDV technique.

The wavelength $\lambda$ of the incident laser pulses is varied from 400 to 800 nm using an optical parametric amplifier (OPA), while keeping the fluence $F$ at a constant value of 4 mJ/cm$^2$. The spectrum of maximum $V_s$ obtained at different $\lambda$ exhibits a Gaussian-like function centered at 525 nm, as depicted in Fig. 7.8(a) (green curve). This excitation spectroscopy of $V_s$ has a peak similar in position and bandwidth to that of the light absorption spectrum measured in water (red curve in Fig. 7.6(a)) [155]. The strong resonance at $\lambda \sim 525$ nm is identified as the dipolar resonance mode - a dominant extinction mode for particle smaller than 50 nm.

On the other hand, the photovoltage spectrum does not contain the background seen in the optical measurement. The lack of non-SPR background in photovoltage measurement is a strong indication that surface charge dynamics is driven by dipolar resonance structure highly localized at the interface between Si and the nanoparticle. In contrast, the far-field absorption response obtained in optical spectroscopy has components not necessarily
Figure 7.7 An energy diagram of plasmon hybridization in a HGN describes the interaction between the metal sphere plasmon and cavity plasmon in bulk metal. Two HGN plasmon modes are an antisymmetrically coupled (antibonding) $\omega_+$ plasmon and a symmetrically coupled (bonding) $\omega_-$ plasmon.
Figure 7.8 Ultrafast transport at gold nanoparticle (NP)/SAM/silicon interface near surface plasmon resonance (SPR) excitation. (a) The maximum transient photovoltage response near SPR excitation, as compared to the absorption of the similar nanoparticles in water, bulk gold, and silicon substrate. It is evident that while both show characteristic SPR peak at $\sim 525$ nm the nanoparticles $V_\text{s}$ spectrum at surface (colored in green) lacks the background seen in the optical absorption spectrum of similar nanoparticles in water (colored in red). (b) The enhancement of hot carrier generation at Si surface (channel II) can be achieved via SPR evanescent field within the Si surface or charge carrier injection from highly excited Au nanoparticle (channel I).
localized at the interface. The photovoltage measurements at 400 and 800 nm, both of which are far off from the dipolar resonance spectral range, are nearly an order of magnitude smaller than that at dipolar resonance (at 525 nm). Therefore, the near-field enhancement factor of photocarrier generation at Si surface by dipolar resonance excitation is at least a factor of 10.

7.3.4 Plasmon Mediated Spectral Hole Burning of Hollow Gold Nano-shell on Si/SiO₂ Surface

Potential application of HGNs is a drug delivery agent. HGNs encapsulate a drug inside of the shell or HGNs carry a drug attached on the outer surface. In 2010, Lu et al. successfully bioconjugated HGNs with siRNA on the outer surface and triggered a photothermally induced siRNA release via pulsed laser irradiation [182]. If drug molecules are encapsulated inside the HGNs, then the triggering mechanism to release the drug molecules on the target location is required. One possible triggering method is laser-induced fragmentation of the HGNs. In the research reported by Lu et al. [182], the pulsed laser irradiation can lead to fragmentation of the HGNs. There were indications of solid AuNP formation due to HGN fragmentation, but the detailed fragmentation mechanism is still not well understood.

Using ultrafast electron diffraction (UED) and scanning electron microscope (SEM), we investigate the photo-induced structural changes of HGNs. The HGNs samples were prepared by Damon Wheeler in Jin Zhang’s group at University of California–Santa Cruz: using size controlled cobalt nanoparticle templates, the gold nanoshell is grew on the surface of the cobalt nanoparticle template, and the core cobalt template can be removed with the a chemical reaction [183, 184]. The HGN diameter is controlled by the size of the cobalt
Figure 7.9 (a) The statistics of HGNs diameter before fs laser irradiation and after irradiation (the number of HGN sampling is \( \sim 700 \) individual HGNs in each case), (b) SEM image of the morphology of HGNs distribution on the SiO\(_2\)/Si substrate and the scale bar corresponds to 1\( \mu m \), (c) and (d) are the SEM image of HGNs before and after irradiation, respectively, and the scale bar corresponds to 100 nm.
nanoparticle templates and the shell thickness is controlled by the gold solution concentration. In UED experiment, which is a collaboration between myself and Dr. Kihyun Kim and Terry Han in our group, HGNs are deposited on the functionalized silicon substrate, and the deposited HGNs are secured by the van der Waals force between the HGN and the substrate (the sample preparation procedure will be presented in the next paragraph.). This secured HGN structure on the substrate allows us define the irradiated and non-irradiated area for UED experiments. Using SEM, we directly image and compare the irradiated and non-irradiated samples after UED experiment. Also, using UED experiment, we quantify the nonlinear response of lattice temperature and surface charge dynamics with different wavelength fs-laser pump irradiation (600 - 800 nm).

The sample preparation procedure has been adapted from wet chemistry methods [185] that are now commonly employed in fabricating ordered 2D assembly of nanoparticles on substrates [186, 149, 187, 188, 189]. The process can be broken down into 3 steps as described below.

1. **Surface pre-treatment:**
   Silicon wafers are cleaned by ultrasonic agitation in acetone and then in methanol to remove macroscopic contaminants. Thereafter, they are carried through a modified RCA-like process [190, 191] to thoroughly clean the surface of all organic and inorganic residues. This involves immersion in the following solutions for 10 min each:

   1. H$_2$SO$_4$/H$_2$O$_2$ (7:3), at 90$^\circ$C to remove organic residues.

   2. 40% NH$_4$F solution in deionized (DI) water at room temperature, to remove the native oxide layer on silicon.

   3. NH$_4$OH/H$_2$O$_2$/H$_2$O (1:1:6) at 90$^\circ$C to remove metallic contaminants and establish a fresh, thin (1-2 nm) oxide layer with hydroxyl (-OH) coating.
4. HCl/H$_2$O$_2$/H$_2$O (1:1:5) at 90$^\circ$C to remove final trace metal & ionic contaminants introduced in the steps above.

The substrate is throughly rinsed in copious amounts of DI water in between each of the above mentioned steps, which finally results in a clean, hydroxyl (-OH) terminated silicon substrate.

2. **Surface functionalization**: The organic molecule used in this study for surface functionalization (creation of the SAM layer) is (3-Aminopropyl) trimethoxysilane [H$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$] abbreviated as APTMS. Other organosilane molecules with differing alkane chain lengths may also be employed. The clean substrate is immersed for 60 min in a dilute solution (≈ 9mM) of APTMS in DI water, with some acetic acid to enhance functionalization. (APTMS:Acetic Acid:DI water = 1:5:480). This is followed by a thorough rinse in DI water and drying under dry-nitrogen gas. It is then heated to 120$^\circ$C to strengthen the siloxane (Si-O) bond between the terminal silane group of the SAM and the Silicon substrate [186].

3. **HGN deposition**: Finally, the surface functionalized substrate is immersed in a citrate stabilized colloidal HGN solution for a period of 1-2 hours to allow the HGNs to anchor onto the SAM surface. Immersion of the substrate in the solution protonates the terminal amine (NH$_2$) groups of the SAM molecules to form positively charged NH$_3^+$ end groups [188]. The HGNs, on the other hand, are covered by negatively charged citrate ligands that stabilize them against agglomeration via mutual repulsion. These negatively charged ligands bind electrostatically to the protonated NH$_3^+$ groups of the SAM, thus immobilizing the HGNs on the surface [189]. There would of course be a large number of SAM molecules underneath a single HGN to help anchor the nanocrystal firmly onto the substrate. Any
loosely bound nanocrystals are removed by a final rinse and dry cycle. Figure 7.9 shows the sample morphology obtained by this procedure.

The SPR frequency of the HGNs used in our experiment is 654 nm which is red-shifted into NIR from the ∼520 nm resonance of typical solid Au NPs. The statistics of irradiated and non-irradiated HGNs from SEM images (∼700 HGNs sampling in each case) in Fig. 7.9(a) clearly shows that ∼35 nm outer diameter of non-irradiated HGNs on the silicon substrate are transformed into ∼25 nm diameter HGNs after irradiation. The SEM images in Fig. 7.9(c) and Fig. 7.9(d) also show that the HGNs’ outer diameter is reduced and appearance of larger clusters may be formed through melting of aggregated HGNs. Due to the structure transformation of HGNs under irradiation, the UED results indicate the new state achieved after the systems undergoing transformation. Using UED, we could quantify a non-linear response as a result of these changes, via lattice temperature change and the transient surface voltage change as a function of applied excitation wavelengths and fluences.

The lattice temperature microscopically corresponds to the random atomic vibration, and the random vibration diminishes the intensity of the diffraction spectra by a Debye-Waller factor (DWF), $e^{-2M}$, where $M = \frac{s^2 \bar{u}^2}{4}$, $\bar{u}^2$ is the mean-square atomic displacement perpendicular to the reflecting planes, and $s = \frac{4\pi}{\lambda_e} \sin(\theta/2)$ is the momentum transfer associated with the maxima located at the scattering angle. Thus, the change in the mean-square atomic displacement, $\Delta \bar{u}^2$, measured relative to the unperturbed state at negative times, determines the rise in lattice temperature and can be calculated from the diffraction intensities as $ln[I(t)/I_0] = -s^2 \Delta \bar{u}^2/4$.

With HGNs structure dynamics induced by off-resonance pump, 800nm, we observe
Figure 7.10 (a) Debye-Waller factor (DWF) analysis of the diffraction intensity drop. This indicates the lattice temperature as a function of the irradiation fluence. (b) DWF profiles of different wavelength pump laser are fitted with power function, \( y = ax^b \). (c) Transient surface voltage (\( V_s \)) generation as a function of different laser wavelength.
that \(\sim15\) ps after irradiation, photoexcited HGNs have the maximum change in lattice temperature and transient surface voltage. We fix the 15 ps time delay from the irradiation moment, and observe the lattice temperature and transient surface voltage with different pump laser wavelength and the fluence, shown in Fig. 7.10. In Fig. 7.10(a) and (b), we can see that lattice temperature with on-resonance pump, 654 nm, is not linear response (2.7\pm0.8 power dependence) in the fluence scan whereas, with off-resonance, it is linear response. This non-linearity indicates that the lattice heating and restructuring of HGN are mediated by surface plasmon resonance. In Fig. 7.10(a), the lattice temperature change with off-resonance pump laser irradiation at low fluence is higher than that of on-resonance pump laser irradiation, and this measurement shows the similarity to the spectral hole burning. Moreover, the transient surface voltage (Fig. 7.10(c)) induced by different pump wavelength also shows the spectral hole burning feature. The drastic decrease in transient surface voltage at 654 nm indicates disappearance of HGNs absorbing at the surface plasmon resonance frequency.

The persistent spectral hole burning characteristics of HGNs induced by fs laser pulse has been proposed to account for melting of HGNs [183]. Although we could not observe the structure dynamics directly, based on ultrafast electron diffraction responses and scanning electron microscope data, we have shown that HGNs structure is modified by fs laser, and the shrinking of the size caused thickening in shell wall and the blue shift of surface plasmon resonance frequency.
7.4 Summary

We successfully extend the UEDV methodology to investigate ultrafast charge transfer process induced by fs-laser at various nanostructures/molecule/Silicon interfaces. We have identified two non-mutually exclusive channels of charge transfer at the interfaces, and the measured molecular resistivity is consistent with the steady-state measurement at the moderate laser irradiation. A factor of 10 SPR enhancement of the surface charge transfer is directly measured and the low non-SPR background in the surface photovoltage measurement indicates that the surface charge dynamics is driven by dipolar resonance structure highly localized at the interface between Si and the nanoparticle. While the current applications of UEDV are concentrated in cases where the charge transfers are driven in an ensemble of nanostructures, the mechanisms associated with different microscopic processes can still be discerned through examining the fine voltammetry features, such as the ultrafast charging dynamics in an individual nanoparticle interface. The future application of this methodology lies in a more definitive, site-selected voltammetry study on a single nanostructured interface, which can be enabled by the development of nanometer scale high-brightness ultrafast electron beam system for ultrafast electron microscope [56, 192, 68].
Chapter 8

Preliminary Experiment with High-Brightness Electron Beam System

In this chapter, we discuss the latest progress in implementing experiment protocols for achieving high spatial and temporal focusing for ultrafast electron microdiffraction experiments.

8.1 Shadow Imaging and Beam Alignment

An important target of our high-brightness electron beam system is to achieve microscale high-dose beam delivery to investigate structural dynamics at selected particles or domain sites. First, we have established an experimental protocol for identifying such particles or domains using the flexible electron optical arrangement, in order to optimize our beam for conducting ultrafast measurements of the precise sites. The shadow imaging of microscale samples can be readily implemented by adjusting the focal plane of the beam relative to the sample plane. Fig. 8.1 shows that, by using an objective lens, we can directly monitor the sample in situ by projection shadow imaging. Fig. 8.1(a) and Fig. 8.1(b) show the
Figure 8.1 CeTe$_3$ sample image on 1000 mesh TEM grid: (a) optical microscope image, (b) Projection Shadow image of a full grid with high-brightness UED, (c) Projection shadow image with 50 µm aperture selected area, a white square shown in (b).

optical image and the corresponding shadow image of the sample on a 1000 mesh full TEM grid using the projection imaging with a full beam crossing between the sample and CCD camera. Fig. 8.1(c) shows the shadow image with a 50 µm aperture to select a single sample for diffraction investigation: the location of the sample is marked as the white square inside the full image of Fig. 8.1(b). The TEM grid bar thickness is 6 µm, and the square opening is 19 µm, which provides a measurement of the actual sample size. From the contrast, a calibration can also be established to provide a thickness map of the sample. The shadow image capability thus provides a convenient way to identify the sample for a pump-probe overlap and to characterize the beam properties at the sample plane.

Shadow imaging can also serve to diagnose the beam properties. We note that, from
Fig. 8.1(b), we can observe image distortion of the TEM grid at four edges: the TEM grid shadow image is shown as an arc, not a straight line (pincushion). This image distortion is from the field distortion caused by the first deflector rods— an artifact to be corrected in the future. However, the distortion occurs only at the edges of the full scale view, whereas in practice only a small region is inspected. How much the image distortion can affect our experiment is still under investigation. In the design of the deflector, there is a 2.5 mm diameter beam alignment pinhole centered around the two pairs of deflector rods, separated by 2.0 mm each. The rods are mounted 30 mm below the aperture. Although the beam size at the deflector level is $\sim 300 \mu m$, it is possible for the electron pulse to travel close to the deflector rod, breaking the symmetry ($1^\circ$ tilt causes $\sim 450 \mu m$ shift at the deflector location). Therefore, it might be necessary to increase the deflector rod gap and/or reduce the distance between the aperture and the deflector rods.

8.2 Convergent Beam

To evaluate the feasibility for ultrafast electron microdiffraction, the electron pulse is tightly focused on the sample level with different applied currents of Obj. ML. Fig. 8.2 shows the direct beam images with the 1000 mesh TEM grid on the CCD screen. With the 170 $\mu m$ aperture, the electron beam can be focused down to $\sim 7 \mu m$ (FWHM, Obj.ML=3.4 A) on the sample, and the electron dose $D$ is 2042 electrons/$\mu m^2$ which is 3 order higher than other ultrafast electron diffraction systems (see Table 5.2) with the compromise for 50% reduction of $L_t$, 0.474 nm, as shown in Table 8.1. Furthermore, we can fully manipulate the beam properties with different Obj.ML currents and different aperture sizes. As shown in Table 8.1, using an Obj.ML=2.9 A, we can focus the electron beam down to $\sim 15 \mu m$.
on the sample. With this condition, the electron dose $D$ is still 449 electron/µm$^2$ and the coherence length $L_t$ is 0.568 nm with the divergence angle $\Delta \theta = 4.0$ mrad, calculated by $L_t = \frac{h}{2P_\sigma \Delta \theta}$ derived from Eq. 3.31 and Eq. 5.11. Also, with different size of the aperture, 50 µm aperture offers us the longer coherence length 0.689 nm with maintaining the electron does 260 electron/µm$^2$ as shown in Table 8.1. With the adjustment of Obj.ML focusing (divergence angle), the diffracted electron beam signal can be enhanced by a factor of $\sim 50$ while maintaining the coherence length $\sim 1$ nm. This is enough flexibility to manipulate electron pulse phase space, which enables us to investigate various materials using different experiments requiring high spatial and temporal coherence and/or high-density beam optimized for microdiffraction.

<table>
<thead>
<tr>
<th>Aperture (µm)</th>
<th>Obj.ML (A)</th>
<th>$N$ (e/µm$^2$)</th>
<th>$D$ (e/µm$^2$)</th>
<th>$\Delta \theta$ (mrad)</th>
<th>$\sigma$ (µm)</th>
<th>$\varepsilon_{x,n}$ (nm)</th>
<th>$L_t$ (nm)</th>
<th>$B_{4D}$ (e/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.9</td>
<td>5000</td>
<td>260</td>
<td>3.3</td>
<td>2.1</td>
<td>3.673</td>
<td>0.689</td>
<td>370.640</td>
</tr>
<tr>
<td>170</td>
<td>2.9</td>
<td>80000</td>
<td>449</td>
<td>4.0</td>
<td>6.4</td>
<td>13.568</td>
<td>0.568</td>
<td>434.569</td>
</tr>
<tr>
<td>170</td>
<td>3.4</td>
<td>80000</td>
<td>2042</td>
<td>4.8</td>
<td>3.0</td>
<td>7.632</td>
<td>0.474</td>
<td>1373.451</td>
</tr>
</tbody>
</table>

Table 8.1 The electron beam properties with different conditions
$N$ is the number of electrons per pulse.
$D = \frac{N}{A}$ is the electron dose, $A = \pi (\text{HWHM})^2$.
$\Delta \theta$ is a half divergence angle.
$\sigma$ is the $\sigma$-width of the electron spot on the sample, not FWHM.
$\varepsilon_{x,n}$ is the normalized transverse emittance.
$L_t$ is the coherence length.
$B_{4D} = \frac{N}{\varepsilon_{x,n}^2}$ is the 4D brightness.

Fig. 8.3 shows the convergent beam diffraction of TaS$_2$ and CeTe$_3$ samples with 50 µm aperture. The convergent beam diffraction pattern shown in Fig. 8.3(a) is not clear
Figure 8.2 Convergent beam test to maximize the electron dose $N_e/A$. With the constant current of CML1 = 1.0 A and CML2 = 2.7 A and 170 µm aperture, the electron beam is focused on the sample position with adjusting Obj. ML current shown in each image. Minimum beam size is smaller than 7 µm which is the limitation of our measurement resolution. This gives us $D > 2000$ electron/µm$^2$. (The whole image is the same size region, 505×620 pixels.)
enough due to insufficient exposure time (500 ms) which is limited by the strong main beam intensity and a sample stage instability (random vibration). In this first setup, the main beam cannot be fully blocked by the beam trap because of the limitation of the beam trap motion range. Also, because the beam size of the focused electron beam has reached $\sim 1$ $\mu$m scale, the sample holder and electron beam stability become central for the diffraction pattern quality. To achieve convergent beam diffraction, we temporarily implement a beam trap extension to block the beam and a Teflon spacer underneath the sample transfer arm to minimize the vibration. With the implementation, the convergent beam diffraction pattern of CeTe$_3$ shown in Fig. 8.3(c) is significantly improved. Currently, we have not fully achieved the convergent beam diffraction dynamics yet, but we have seen the feasibility of the high-brightness electron beam system for convergent beam microdiffraction to study micron or sub-micron scale materials. To ultimately resolve these problems for the ultrafast microdiffraction experiments, we may consider implementing the following setup: (1) a new beam trap considering with the convergent main beam position, (2) a more stable Obj. ML with a fine feedback to provide stable lens focusing at high magnification (or focusing), (3) a retractable fork to stabilize the stage.

8.3 RF Compression of High-Brightness Electron Beam: VO$_2$

We have implemented our first characterization of RF compression of a high-brightness electron beam based on measuring the temporal response of a well-defined ultrafast structural phase transition. While indirect, this measurements allow us to understand the limit of electron beam performance in a diffraction experiment. Our ultimate diagnosis is based on the shadow imaging technique [98] employing a diagnostic imaging electron gun at the
perpendicular direction of the high-brightness electron beamline direction (see Appendix B.2). The shadow imaging technique will allow direct characterization of beam transverse and longitudinal profiles under RF compression. In the following, we report the results of temporal characteristics based on UED experiments on optical response of a VO$_2$, of which the phase transition time is within hundreds of femtoseconds [193, 194]. According to the reported phase transition time of the VO$_2$ sample, we can deconvolute the time resolution of the high-brightness electron pulse with a different level of RF compression.

Vanadium dioxide VO$_2$ is one of the prototypical systems which has the metal-insulator transition (MIT), from a metallic rutile structure into an insulator monoclinic structure at a critical temperature ($T_c \approx 340K$). There has been extensive debate over whether the origin of the VO$_2$ MIT is Pierls [195, 196] or Mott-Hubbard [197] physics. However, the MIT in VO$_2$ is clearly a structural transition from the rutile structure (>$340K$) to a monoclinic structure (<$340K$), in which two V atoms in each V chain are dimerized along the $c$-axis with a twisting of V-V pairs due to an anti-ferroelectric shift toward the oxygens.
Figure 8.4 (a) Crystal structure of VO$_2$ in metallic rutile phase: the gray ball is the V atoms and red ball is O atoms. The arrows are the dimerization direction of V atoms in V chain along c axis. (b) and (c) are the schematic illustration of VO$_2$ density of state of state of VO$_2$ in metallic and insulator phase, respectively.
lying along an axis perpendicular to the $c$-axis, as shown in Fig. 8.4(a). The answer to the argument about the MIT microscopic pathway is how we discriminate between two types of orbitals and corresponding bands: (1) lower energy $\pi^*(d_{xy})$ orbitals in $t_{2g}$ orbitals with direct overlap between the neighboring V in V chain, and (2) $d_{||}(d_{xz}, d_{yz})$ orbitals in $t_{2g}$ orbitals. In the rutile phase, the $d_{||}$ band overlaps with the $\pi^*$ band, resulting in an isotropic metallic state shown in Fig. 8.4(b). The twisting in the monoclinic phase increases the V-O hybridization and moves the $\pi^*$ band up above the Fermi level. Therefore, only the $d_{||}$ band is partially occupied, and the band is split by the dimerization, leading to insulating state, shown in Fig 8.4(c). The V-V dimerization can be directly monitored by the diffraction peak after photoexcitation, and this phase transition time is short enough to measure the time resolution of the current setup of high-brightness UED.

Fig. 8.5 shows the optical image of VO$_2$ film sample and a diffraction pattern of the ground state of the VO$_2$. The 50 nm thickness VO$_2$ film is grown on the 5 nm thickness amorphous silicon membrane using pulsed laser deposition, and the VO$_2$ film on the silicon membrane is poly-crystaline, so the diffraction pattern corresponds to a powder diffraction image as shown in Fig. 8.5(b). We integrated the diffraction ring as a function of the wave vector, which corresponds to the ring radius in the real space image of Fig. 8.5(b), to produce the profile shown in Fig. 8.5(c). The two small peaks at $\sim$3.35 Å$^{-1}$ and $\sim$4.11 Å$^{-1}$ correspond to the V-V dimerization symmetries, $\bar{3}0\bar{2}$, 313, respectively. After photoexcitation, the dimerization in monoclinic insulator phase is instantaneously dissociated completely due to perturbation in electron-electron and electron-phonon coupling initiated by photon energy. Then we can directly monitor the phase transition dynamics with the variation of diffraction peak intensity.
Figure 8.5 (a) Optical microscope image of VO$_2$ film sample which is grown on the 5 nm thickness amorphous silicon membrane. The eight square windows are the VO$_2$ film with 5 nm thickness Si membrane and a long black rectangle is a broken window. Each square window size is 100 $\mu$m $\times$ 100 $\mu$m, and the displacement between windows is 200 $\mu$m, (b) Diffraction pattern of poly-crystalline VO$_2$ film, (c) Integrate diffraction intensity profile along the wave vector corresponding to the radial direction in real space image. The arrows indicate the V-V dimerization symmetry peaks in a monoclinic insulation phase (302, 313).
To run the experiment with RF compression, the first requirement is the synchronization of the electron pulse and RF field as discussed in Chapter 4 and 5. The phase mismatch between electron pulse arriving time and RF field causes the COM mass velocity change of the electron pulse, and this COM velocity can be accurately measured with the diffraction peak position in real space image because the COM velocity determines the kinetic energy of an electron pulse and the kinetic energy determines the scattering angle:

\[ \lambda = \frac{h}{\sqrt{2m_eE}}, \]  
\[ \sin \theta_B = \frac{1}{2}|K|\lambda, \]

where \( m_e, E \) are electron mass and the kinetic energy of electron pulse, respectively, \( K \) is the change of the wave vector due to diffraction from the certain symmetry lattice plane, and \( \theta_B \) is Bragg angle. In other words, if the electron kinetic energy is changed, then the diffraction ring radius in Fig. 8.5(b) is changed. In order to synchronize the phase between an electron pulse and RF field, we adjust the 266 nm laser path length to perfectly match the diffraction patterns with RF compression and without RF compression. With the optimized phase condition of the RF compression, a longitudinal length of the electron pulse has to be focused on the sample position, and the focal length \( f_L \) of RF compression [81] shown in Eq. 4.18 can be controlled by the RF field \( E_0 \).

Fig. 8.6 shows the phase transition dynamics of VO\(_2\) induced by 800 nm, 45 fs laser pulses and measured with electron pulses compressed by different RF power. To avoid damaging the sample, which is only a few tens of nanometer thick, we maintained a pump laser fluence of 3 mJ/cm\(^2\) (the damage threshold \( \sim 5 \) mJ/cm\(^2\)). The phase transition
Figure 8.6 The photo-induced phase transition measurement with VO$_2$ with different RF power compression of $\sim 7 \times 10^4$ electrons per pulse: the measurements are relative diffraction peak intensity change as a function of the time.
response is determined by a fit using an Error function:

$$f(x) = \frac{2A}{\pi} \int_0^{\frac{x-x_0}{\sqrt{2\sigma}}} e^{-t^2} \, dt,$$  

(8.3)

where $A$, $x_0$, $\sigma$ are fitting parameters. Time resolution of the high-brightness electron pulse is extracted based on the response time $\sigma$ and deconvoluted it from the reported transient response of VO$_2$ samples, which is on $\lesssim 1$ ps timescale [193, 194]. As shown in Fig. 8.6, the timescale of transient response is reduced with increasing RF power, indicating the compression of the probing electron pulses.

Fig. 8.7 shows the results of RF compression using the values of $\sigma$ extracted from the
Error function fitting. Without RF field, the electron beam (with \(\sim7\times10^4\) electrons per pulse) has developed a pulse duration of 33 ±12 ps (in \(\sigma\)-width) from the source to the sample plane. At an RF power of 210 W, the electron pulse is compressed to 10 ± 4 ps, and at 316 W, the pulse is further reduced to 5 ± 2 ps.

In Fig. 8.7, it is not clear to tell whether the RF compression has reached optimal temporal focusing at 316 W RF power. We note that, according to the analytical Gaussian model prediction [68], 520W RF power is required for optimal temporal focusing at the sample plane with a pulse duration below 1 ps, limited by the phase jitter between the electron pulse and RF field (see Chapter 5). The lowest pulse duration achieved is primarily limited by system instability which we have identified. A periodic breathing motion (\(\Delta \theta\)) of the diffraction pattern was observed, and we correlated the electron pulse arriving time fluctuation at the sample plane to the periodic motion (\(\Delta \theta\)) of the diffraction pattern. According to Eq. 5.10, the observed diffraction pattern position shift (\(\Delta \theta\)) is directly related to the electron pulse energy fluctuation \(\Delta E\) which can be translated to an electron arriving time fluctuation (as shown in Fig. 5.13(b)). The results of the electron pulse arriving time fluctuation are depicted in Fig. 8.8(a), where there is a periodic oscillation with a period of 2.5 minutes. The standard deviation \(\sigma=3.5\) ps of the oscillation is quite consistent with our pulse duration measurement. The oscillation is caused by active temperature regulation of the RF station (the red line in Fig. 8.8(b) is before correction). We improved the temperature stability by adjusting the gain of the temperature control unit (the blue line in Fig. 8.8(b) is after correction). We are currently performing another pulse duration measurement to check the improvement.
Figure 8.8 (a) Electron pulse arriving time fluctuation during the experiment. Zero fluctuation means the electron energy is exactly 100 keV, and due to the phase mismatch, the COM velocity of electron pulse is fluctuated. (b) RF phase stability monitor. The red line shows the phase fluctuation before temperature instability correction and blue line shows the phase fluctuation after the correction.
Chapter 9

Summary and Outlook

To achieve the direct visualization of the ultrafast dynamics, we have developed the RF-enabled high-brightness ultrafast electron microdiffraction system as the first step. The high-brightness electron beam system with a sub-relativistic 100 keV electron beam has successfully achieved a beam intensity $\sim 5 \times 10^6$ electron pulse achieving a transverse emittance $\varepsilon_t \sim 0.167 \mu m$. The high-brightness electron beam system is fully capable to manipulate the electron pulse phase space. With a parallel electron beam, we have achieved $L_t=1.2$ nm, at $N_e=10^5$ and an electron dose $D=5$ electron/$\mu m^2$. With a convergent electron beam, we have achieved that, (1) at $\sigma \sim 3 \mu m$, an electron does $D \sim 2000$ electron/$\mu m^2$ and $L_t \sim 0.5$ nm, and, (2) at $\sigma \sim 5 \mu m$, $D \sim 250$ electron/$\mu m^2$ and $L_t \sim 1.0$ nm (cf. $D$ of conventional UED systems is $\sim 1$ electron/$\mu m^2$ at $\sigma \sim 300 \mu m$). This flexibility of the high-brightness electron beam system enables us to investigate various materials using operational modes emphasizing high spatial and temporal coherence and/or high-density beam optimized for ultrafast electron microdiffraction. Although further optimization for RF compression is required, we have demonstrated the $\sim 10^5$ electron pulse can be compressed down to $\leq 5$ ps pulse duration in our first test. A further RF compression experiment is ongoing to achieve the target of $\approx 200$ fs, set by the RF station stability in our system.

Furthermore, we are able to extend the diffractive voltammetry methodology to investigate molecular charge transport process under a strong field induced by laser at a gold
nanoparticle/molecule/Silicon interface. At the moderate field circumstance, we obtain similar molecular resistivity as the steady-state measurement. While the current applications of diffractive voltammetry are concentrated in cases where the charge transfers are driven in an ensemble of nanosturctures, the mechanisms associated with different microscopic processes can still be discerned through examining the fine voltammetry features, such as the ultrafast charge dynamics in an individual nanoparticle interface. The future application of this methodology lies in a more definitive, site-selected voltammetry study on an individual nanostructured interface, which can be enabled by the development of a high-brightness electron beam system in an ultrafast electron microscope setup capable of zooming in on such features.

The work presented here represents the first step in realizing a high-brightness ultrafast electron microscope. Key steps that are still needed to reach this ultimate goal include further characterizing the correlated beam dynamics in full 6D phase space, and identifying the factors such as aberration and focusability limits in different operation regimes. Interdisciplinary collaboration that pushes the boundaries of ultrafast science, acceleration physics, and beam dynamics toward a more precise and flexible control of beam dynamics is central for furthering the ultrafast imaging technologies using electrons.
APPENDICES
Electron diffraction is one of the most powerful experiment tools for determining the structures. The electron is a low-mass, negatively charged particle, so it can easily be deflected by passing close to other electrons or the positive nucleus of an atom. These Coulomb interaction causes electron scattering, which is the process that makes electron microscope feasible. The wave nature of electrons gives rise to diffraction effect, and this diffraction effect creates electron microscope images or diffraction patterns. Therefore, it is essential to understand both the particle approach and wave approach to electron scattering in order to interpret all the information that comes from electron microscope. Electron scattering from materials is a reasonably complex area of physics, but several references provide a detailed and rigorous treatment of the subject [198, 199, 200, 201, 202]. In following section, a conceptual introduction to the phenomena of diffraction will be introduced.

A.1 Diffraction and Reciprocal Lattice

In the electron microscope, we are mostly interested in scattered electrons which do not deviate far from the incident-electron direction because these electrons includes the information which we seek about the internal structure of the specimen. Other forms of scattering, such as electrons which are scattered through large angle and electrons ejected
from specimen, such as secondary electrons, are also of interest although they are much greater interest in the scanning electron microscope (SEM).

We represent incident and scattered electrons as beams of electrons, which are confined to well-defined paths in the microscope. So the electrons that hit the specimen are called incident beam and electrons scattered by the specimen are diffracted or scattered beams. Electrons going through the specimen are separated into electrons without angular deviation and with measurable angular deviation. In the electron-scattering phenomena, there are the most important terms elastic and inelastic scattering, describing scattering without energy loss and with some measurable energy loss. We can also separate scattered electrons into coherent and incoherent. These distinctions are related since elastically scattered
electrons are usually coherent and inelastically scattered electron are usually incoherent. Let's assume that the incident electron waves are coherent, that is, they are essentially in phase with one another and of a fixed wavelength, governed by the accelerating voltage. Then, coherently scattered electrons are in-phase and incoherently scattered electrons have no phase relationship after interacting with the specimen. The various terms are defined by the following general principles (Fig. A.1):

1. Elastic scattering is usually coherent, if the specimen is thin and crystalline.

2. Elastic scattering usually occurs at relatively low angle\((1^\circ \sim 10^\circ)\), i.e., it is strongly peaked in the forward direction.

3. At higher angles\((\geq 10^\circ)\) elastic scattering becomes more incoherent.

4. Inelastic scattering is almost always incoherent and is very low angle\(< 1^\circ\) scattering.

**A.1.1 Diffraction of Waves and Reciprocal Lattice**

The diffraction depends on the crystal structure and on the wavelength. At wavelengths of incident electron beam, the superposition of the waves scattered elastically by the individual atoms of a crystal results in ordinary refraction. When the wavelength of the electron beam is comparable with or smaller than the lattice constant, we may find diffracted beams in directions quite different from the incident direction.

Consider parallel lattice planes spaced \(d\) apart (Fig. A.2). The electron beam is incident in the plane of the paper. The total path difference for the beams reflected from adjacent planes is \(2d\sin \theta\), where \(\theta\) is measured from the plane (Fig. A.2). Constructive interference of the electron beam from successive planes occurs when the path difference is an integer number \(n\) of wavelength \(\lambda\), so that
According to Bragg law, only certain angle $\theta$ of reflection from all periodic parallel planes will add up in phase to give a strong reflected beam, and this is a consequence of the periodicity of the lattice. Notice that the law does not refer to the composite of the basis of atoms associated with every lattice point. However, the composition of the basis determines the relative intensity of the various orders of diffraction from a given set of parallel planes. We will discuss about this in section 4.1.3.

The Bragg derivation of the diffraction condition Eq. (A.1) gives a neat statement of the condition for the constructive interference of waves scattered from the lattice points. We need a deeper analysis to determine the scattering intensity from the basis of atoms, which means from the spatial distribution of electrons within each cell. We know that a 

$$2d \sin \theta = n\lambda \quad \text{Bragg Law.} \quad (A.1)$$
crystal is invariant under any translation, \( T = u_1a_1 + u_2a_2 + u_3a_3 \), where \( u_1, u_2, u_3 \) are integers and \( a_1, a_2, a_3 \) are the crystal axes. Local physical property of the crystal, such as electron distribution (electron density), \( n(r) \), is invariant under \( T \), \( n(r) = n(r + T) \). This periodicity creates an ideal situation for Fourier analysis. The most interesting properties of crystals are directly related to the Fourier components of electron density. We can represent the periodic electron density \( n(r) \) in three dimensions:

\[
n(r) = \sum_G n_G \exp(iG \cdot r), \tag{A.2}
\]

where \( G \) is a set of vectors which makes \( n(r) \) is invariant under all crystal translation \( T \). The set of Fourier coefficients \( n_G \) determines the scattering amplitude.

To proceed further with the Fourier analysis of the electron density, we must find the vectors \( G \) of the Fourier sum \( n(r) = \sum n_G \exp(iG \cdot r) \). There is a powerful way to find a set of vectors \( G \) with constructing a Reciprocal Space. Reciprocal lattice axis vectors, \( b_1, b_2, b_3 \) are defined as:

\[
b_1 = 2\pi \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3}, \quad b_2 = 2\pi \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3}, \quad b_3 = 2\pi \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3} \tag{A.3}
\]

If \( a_1, a_2, a_3 \) are primitive vectors of the crystal lattice, then \( b_1, b_2, b_3 \) are the primitive vectors of the reciprocal lattice. Each vector is orthogonal to two axis vectors of the crystal lattice. Thus, \( b_1, b_2, b_3 \) have the property

\[
b_i \cdot a_j = 2\pi \delta_{ij} \tag{A.4}
\]

where \( \delta_{ij} \) is Kronecker delta. Points in the reciprocal lattice are mapped by the set of
vectors

\[ G = v_1 b_1 + v_2 b_2 + v_3 b_3, \]  

(A.5)

where \( v_1, v_2, v_3 \) are integers. A vector \( G \) of this form is a reciprocal lattice vector.

Every crystal structure has two lattices associated with it: the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal. A microscope image is a map of the crystal structure in real space. Two lattices are related by the definitions Eq. A.3. Thus when we rotate a crystal in a sample holder, we rotate both the direct lattice and the reciprocal lattice.

A.1.2 The Ewald Construction in Reciprocal Space

The set of reciprocal lattice vectors \( G \) determines the possible reflection of incident waves. In Fig. A.3, the difference in phase factors is \( \exp[i(k - k') \cdot r] \) between beams scattered from volume elements \( r \) apart. The wavevectors of the incident and outgoing beams are \( k \) and \( k' \), respectively. We suppose that the amplitude of the wave scattered from a volume element is proportional to the local electron density \( n(r) \). The total amplitude of the scattered wave in the direction of \( k' \) is proportional to the integral over the crystal of \( n(r) dV \) times the phase factor \( \exp[i(k - k') \cdot r] \).

In other word, the amplitude of the electric or magnetic field vectors in the scattered electromagnetic wave is proportional to the following integral which defines the quantify \( F \) that we call the scattering amplitude:

\[ F = \int dV n(r) \exp[i(k - k') \cdot r] = \int dV n(r) \exp[-i\Delta k \cdot r], \]  

(A.6)

where \( k - k' = -\Delta k \), or \( k + \Delta k = k' \). \( \Delta k \) is scattered vector which is the change in
Figure A.3 The phase angle difference of incident beam is $\mathbf{k} \cdot \mathbf{r} = 2\pi \sin \varphi / \lambda$ and the path difference at $O$ and $\mathbf{r}$ is $r \sin \varphi$. For diffracted beam, the phase angle difference is $-\mathbf{k'} \cdot \mathbf{r}$. The total phase angle difference is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$, and the beam scattered from $dV$ at $\mathbf{r}$ has the phase factor $\exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}]$ relative to the beam scattered from a volume element at the origin $O$. 

Crystal Specimen
wavevector.

When we put Eq. A.2 of \(n(r)\) into Eq. A.6, then we can get the scattering amplitude

\[
F = \sum_G \int dV n_G \exp[i(G - \Delta k) \cdot r]. \tag{A.7}
\]

When \(\Delta k = G\), the exponential in Eq. A.7 vanishes and \(F = V n_G\). This means that scattering amplitude \(F\) is negligible when \(\Delta k\) differs significantly from any reciprocal lattice vector \(G\).

In elastic scattering process, the magnitudes of \(k\) and \(k'\) are equal with energy conservation law, and two conditions, \(k^2 = k'^2\) and \(\Delta k = G\) gives us diffraction condition (If \(G\) is a reciprocal lattice vector, then \(-G\) is also a reciprocal lattice vector.):

\[
2k \cdot G = G^2. \tag{A.8}
\]

The condition \(\Delta k = G\) of diffraction theory can be expressed in another way called Laue equations. This different representation is important because it gives us the geometrical information. Take the scalar product of both \(\Delta k\) and \(G\) with \(a_1, a_2, a_3\). Then we get

\[
a_1 \cdot \Delta k = 2\pi v_1, \quad a_2 \cdot \Delta k = 2\pi v_2, \quad a_3 \cdot \Delta k = 2\pi v_3, \tag{A.9}
\]

These equations imply a geometrical interpretation: the first equation represents that \(\Delta k\) lies on a certain cone about the direction of \(a_1\), second lies about \(a_2\) and third one lies about \(a_3\). Therefore, \(\Delta k\) must satisfy all three equations, and it must lie at the common line of intersection of three cones. Ewald construction helps us visualize the nature of the accident that must occur in order to satisfy the diffraction condition in three dimension,
Figure A.4 Ewald sphere construction: The points are reciprocal lattice points of the crystal. The vector \( \mathbf{k} \) is drawn in the direction of the incident beam, and the origin is chosen such that \( \mathbf{k} \) terminates at any reciprocal lattice points. We draw a Ewald sphere of radius \( k = 2\pi/\lambda \) about the origin of \( \mathbf{k} \). A diffracted beam will be formed if Ewald sphere intersects any other reciprocal lattice points. The Ewald sphere as drawn intercepts a point connected with the end of \( \mathbf{k} \) by a reciprocal lattice vector \( \mathbf{G} \). The diffracted beam is in the direction \( \mathbf{k}' = \mathbf{k} + \mathbf{G} \). The angle \( \theta \) is the Bragg angle of Fig. A.2.
\[ \Delta k = G. \]

We now construct the sphere of radius \( k \). The sphere is known as the sphere of reflection so called Ewald sphere. The key point is that when the Ewald sphere intersects the reciprocal lattice points, the diffraction condition, \( \Delta k = G \) in Eq. A.8, is satisfied. Then combine the concepts of the reciprocal lattice, and Ewald construction to picture how the intensity of each diffracted beam varies as we tilt the specimen or the electron beam. We can see the position of a diffraction peaks move when the Ewald sphere is moved relative to the reciprocal lattice. Also, if any points in the reciprocal lattice intersect the surface of the Ewald sphere, the set of planes corresponding to the points must satisfy the diffraction condition, Eq. A.8, and hence that the planes will diffract strongly.

A.1.3 Frouier Analysis of The Basis: Structure Factor and Atomic Form Factor

When the diffraction condition \( 2k \cdot G = G^2 \), Eq. A.8 is satisfied, the scattering amplitude Eq. A.6 for a crystal of \( N \) cells can be written as

\[
F_G = N \int_{cell} dV n(r) \exp[-iG \cdot r] = NS_G. \tag{A.10}
\]

The quantity \( S_G \) is called the structure factor and is defined as an integral over a single cell, with \( r = 0 \) at one corner. It is useful to write the electron density \( n(r) \) as the superposition of electron density function \( n_j \) associated with each atom \( j \) of the cell. If \( r_j \) is the vector to the center of atom \( j \), then the function \( n_j(r - r_j) \) defines the contribution of that atom to the electron density at \( r \). The total electron density at \( r \) due to all atoms in the single
cell is the sum

\[ n(r) = \sum_{j=1}^{s} n_j(r - r_j) \]  

(A.11)

over the \( s \) atoms of the basis. The decomposition of \( n(r) \) is not unique because we cannot always say how much charge density is associated with each atom.

The structure factor defined by Eq. A.10 can be written as integral over the \( s \) atoms of a cell:

\[ S_G = \sum_j \int dV n_j(r - r_j) \exp(-iG \cdot r) \]

(A.12)

\[ = \sum_j \exp(-iG \cdot r_j) \int dV n_j(\rho) \exp(-iG \cdot \rho), \]

where \( \rho = r - r_j \). Now we can define the atomic form factor as

\[ f_j = \int dV n_j(\rho) \exp(-iG \cdot \rho), \]

(A.13)

integrated over all space. If \( n_j(\rho) \) is an atomic property, \( f_j \) is an atomic property. We combine Eq. A.12 and Eq. A.13 to obtain the structure factor of the basis in the form

\[ S_G = \sum_j f_j \exp(-iG \cdot r_j). \]

(A.14)

Using the definition, \( r_j = x_j a_1 + y_j a_2 + z_j a_3 \) of \( j \)-th atom, Eq. A.14 can be transformed into

\[ S_G(hkl) = \sum_j f_j \exp(-2\pi i(h x_j + k y_j + l z_j)). \]

(A.15)

The \( f_j \) is physical quantity of the scattering power of the \( j \)th atom in the unit cell. The
value of $f_j$ involves the number and distribution of $j$th atomic electrons, and the wavelength and angle of scattering of the incident beam. The scattered electrons from a single atom takes account of interference effects within the atom. We defined the atomic form factor in Eq. A.13 ($r_j = 0$; a single atom). If we assume that electron distribution is spherically symmetric, then we can derive a single atomic form factor:

$$f_j = 2\pi \int dr r^2 d\cos \alpha n_j(r) \exp(-iGr \cos \alpha)$$

$$= 2\pi \int dr r^2 n_j(r) \frac{e^{iGr} - e^{-iGr}}{iGr}$$

$$= 4\pi \int dr n_j(r) r^2 \frac{\sin Gr}{Gr}.$$  \hspace{1cm} (A.16)

The electron density is uniformly concentrated at the center, then $f_j = 4\pi \int dr n_j(r) r^2$ is equal to the number of atomic electrons, $Z$. Therefore, $f_j$ is the ratio of the scattered amplitude of actual electron distribution.
Appendix B

Experiment Setup of Ultrafast Electron Diffraction

Ultrafast electron diffraction (UED) technique is pump-probe method which is the most appropriate experiment to study photo-induced ultrafast dynamics of atomic structure and charge transfer. [28, 203, 40, 96, 34, 30, 95, 29, 25, 204] UED employs timed sequences of femtosecond laser pulse to initiate the reaction and ultrashort electron pulse generated by the femtosecond laser pulse to probe the transient dynamics of atomic structure and charge carriers. This sequence of pulse is repeated, timing the electron pulse to arrive before and after irradiation. A series of the snapshots of diffraction patterns at different time delay can be inverted to reveal the four-dimensional transient structure dynamics.

With ultrafast electron microscope system, I have also built the UED system in the same chamber shown in Fig. B.1(b). Two systems driven by the same femtosecond laser can be operated independently. Moreover, the 40 kV electron pulse relative timing to 100 kV UEM electron probe can be controlled with another delay stage of 266 nm laser. So 40 kV electron beam can be used for the pump to excite the sample.

In the UED experiment setup, the pump laser is focused onto the sample at the center of the UHV chamber. The pulsed electron source is generated through photoemission from a 40 nm thickness silver cathode, accelerated to 40 keV, collimated and focused onto the
Figure B.1 Ultrafast electron diffraction experiment geometry with ultrafast electron microscope system. (a) A schematic diagram of the UEC optics setup. Both 400 and 800 nm beam lines are shown entering the delay line, but one of them is blocked based on the choice of excitation. The time delay between pump laser pulse and electron probe is controlled by delay stage adjusting traveling path length. Also, pulse shaper is shown in the diagram, but it has not been tested yet. (b) In UHV specimen chamber, the 100 kV UEM column beam goes from top down, and 40 kV UED electron beam goes horizontally. The pump laser lands on the sample with $45^\circ$ tilting.
Figure B.2 Schematic picture of the femtosecond laser source: (1) femtosecond seed pulse (Mai-Tai), (2) amplifier for femtosecond pulse (Spitfire), (3) continuous wave pump laser for amplification (Empower).

sample. The probe is scattered from the sample and the signal is collected at the other end of the UHV chamber using an intensified CCD camera which is capable of single-electron detection.

**B.1 The Femtosecond Laser System**

The femtosecond laser source is composed of 3 separated sub-systems shown in Fig. B.2: Mai-Tai, Spitfire, and Empower. These three units operate together to generate the final amplified pulsed laser. To generate high power femtosecond pulse laser, there are two separated stages; (1) pulse generation in Mai-Tai, (2) amplification with Spitfire and Empower.

The low power (~ nJ/pulse) seed pulse laser output is generated by two lasers, continuous wave (CW) diode-pumped Nd:YVO$_4$ laser and a mode-locked Ti:Sapphire pulsed laser, which are enclosed in two separate chambers.

The Nd:YVO$_4$ gain medium in CW pump chamber lases at 1024 nm which is frequency-doubled to 532 nm in a non-critically phase matched Lanthanum Triborate (LBO) crystal.
in order to match the absorption spectrum of Ti:Sapphire in the pulsed output chamber. The Ti:Sapphire gain medium which is pumped by the CW diode-pumped laser generates femtosecond pulse which is active mode–locked to produce 45 fs laser pulse with 600 mW average power at the pulse repetition rate of 84 MHz. This corresponds to \( \sim 7 \) nJ/pulse.

These seed pulses enter the Spitfire where they are first stretched in time using a 4-pass stretcher grating. This is done to avoid non-linear effects, such as self-focusing that can set in at high laser peak-power and possibly damage the optical components. The stretched pulse is then allowed to enter the amplifier cavity consisting of a Ti:Sapphire gain medium which is pumped by a Q-switched Nd:YLF laser (Empower) that provides \( \sim 20 \) W pulsed output at 10 kHz repetition rate. Since Nd:YLF lases at 1053 nm, the output is upconverted to 527 nm in an LBO crystal to match Ti:Sapphire absorption peak. This intense 20 W laser sets up the population inversion in the Ti:Sapphire crystal, following which, the seed femtosecond laser pulses from the Mai-Tai are allowed to enter the amplifier cavity. The seed laser picks up gain each time it passes through the pumped Ti:Sapphire gain medium and builds up in strength over multiple cavity round trips. Once the population inversion in Ti:Sapphire has been completely consumed and no further amplification is possible, the amplified pulse is directed out of the cavity into a pulse compressor where it is compressed back to femtosecond duration. The final pulse train exiting the system posses the following characteristics: 45 fs, 800 nm center wavelength, 0.4 mJ/pulse and 10 kHz pulse repetition rate.

**B.2 40 kV Pulsed DC Elecron-Gun**

The pulsed electron source for a probe in UED experiment is shown in Fig. B.3. Ultrafast electron pulse is generated by irradiation of 266 nm (4.6 eV) femtosecond laser pulse on a
semi-transparent silver film (∼40 nm thickness, work function of silver: ∼4.4 eV). The film is thermally evaporated onto a transparent sapphire substrate. Photoemission electron pulse generated by femtosecond laser pulse preserves the ultrashort time duration of the incident laser pulse. This electron pulse is accelerated to 40 kV in the gap between the cathode and the anode (gap distance ∼6 mm), and it enters the central bore of a magnetic pole pieces through 100µm aperture to make the beam align into the optical axis of the magnetic lens. 1500 Au mesh is mounted in front of the anode hole, in order to prevent the field penetration through the anode hole which might cause irreversible beam emittance growing. The magnetic lens pole piece is made of soft-iron with solenoidal current carrying coils in its interior. The magnetic lens pole generates the non-uniform magnetic field and the electron pulse is spatially focused by this non-uniform field. The focused electron pulse exits the pole piece through 2nd aperture which can be changed, 50 ∼ 200µm. After magnetic lens, two pairs of deflector rods controls the electron pulse direction towards the sample at the center of the chamber.

To develop a short-pulse electron gun, the challenge is how we can overcome the inherent repulsion among electrons in a pulse, by the collective space-charge effect. This space charge effect tends to broaden the temporal resolution of the electron pulse in the drift region as it propagates to the sample. There are several approaches to overcome the space charge effect: (1) short flight distance [84], (2) radio-frequency compression of electron pulse [205, 60], (3) high acceleration voltage in relativistic regime [58], (4) single-electron mode [56] where the space charge effect is eliminated, (4) electron pulse self compression [206]. We use the second approach for our UEM system, but, for UED system, use the first approach, a short flight distance gun by designing a universal electron gun in which the distance is ≤ 7 cm.
Figure B.3 Universal electron gun design. (a) Zoom-in of the electron gun head part, (b) actual image of the fully assembled universal electron gun before installation into the chamber, (c) overall layout of the electron gun including the gun chamber with 6” conflat flange.
Moreover, 40 kV universal electron gun is fully independent unit which can be mounted in any chamber having the 6” conflat flange port (shown in Fig. B.3). The major purpose of the new 40 kV electron gun is constructing the universal electron gun as a complete unit, which can be mounted into any type of chambers. So practical challenge for designing the electron gun is how we can install all the parts, high voltage (HV), electrical wires for deflectors, and the water cooling line for a magnetic lens, into one complete unit, and at the same time, how can we make a short distance from the electron gun cathode to a sample, in order to minimize the space charge effect of the electron pulse. As shown in Fig. B.3, the gun head part (a blue box in Fig. B.3(a)), including cathode head, anode, magnetic lens, deflectors is outside of the electron gun chamber because it will be inside of the target chamber where the electron gun and a sample are mounted (shown in Fig. B.1(b)). The electron gun chamber is mounted to the target chamber through the 6” CF flange, and the electrical wires for deflector rods and thermocouple to monitor magnetic lens temperature, and the water cooling tubes are installed through six of the 1.33 inch CF flanges at the side ports of specially designed 6 inch CF flange. Also, high voltage feedthrough is mounted at one of 4 ports (three 4.5 inch ports and one 2.75 inch port) in a gun chamber (shown Fig. B.3(c)), and the high voltage pin is directly connected to the cathode body without any additional connector. So we can avoid the arcing problem because all the sharp edges are berried completely. Another technical issue is the potential problem of arcing in a silver film on cathode and the MACOR rods to isolate cathode from the ground. This arcing problem can be easily solved with recoating the 40 nm silver film on the cathode and replace the MACOR rods, so we have to implement the way to replace them easily, instead of unmounting a whole electron gun. So the cathode and MACOR rods are designed easily.
Figure B.4 Performance characterization of the 40 kV universal electron gun. (a) Analog-to-digital unit (ADU) measurement: CCD camera response of a single electron event is about 175 intensity of one pixel. (b) the number of electron per pulse with the measured ADU as a function of a different magnetic lens focusing strength. The reason for the increase in the number of electron with stronger focusing is more electrons able to pass through the 100 µm aperture because of stronger focusing. (c) the beam size at the sample location and the CCD camera as a function of a different magnetic lens focusing. (d) divergence angle of the electron beam with different focusing strength. The divergence angle is calculated by the beam sizes at the sample and CCD camera with the camera distance between the sample and CCD camera.
disassembled through the 8 inch CF flange at the bottom, shown in Fig. B.3(c).

The performance of the universal 40 kV electron gun is comparable with our old system, and the number of electrons per pulse is even higher up to a factor of five. To characterize the electron pulse of this 40 kV electron gun, we quantify the number of electrons per pulse and magnetic lens focusing strength with measuring the electron beam size (shown Fig. B.4). To count the number of electron, we operate the electron gun in a single electron mode by reducing the 266 nm laser intensity to extremely low levels. This enabled the detection of isolated single electron events at the CCD. Measuring the detector response over multitude of such recorded events allowed us to determine the average detector response per single electron event, and, as shown in Fig. B.4(a), a single electron signal of CCD camera corresponds to $\sim 175$ of signal intensity. Based on this estimate, we obtained a maximum probe pulse intensity of $5 \times 10^3$ electrons per pulse, though normal operating conditions range in the $4 \times 10^3 \sim 5 \times 10^3$ range. While this is not sufficient for single shot diffraction acquisition, which typically requires $\sim 10^6$ electrons per pulse, it is sufficient for multi-shot diffraction investigations. The beam size is also critical from experimental point of view because it significantly reduces the detrimental effects of velocity mismatch [206] which causes the reduction in the temporal resolution. The electron beam size in our old system is about 30 $\mu$m and the electron beam size of new universal electron gun is also about 30 $\mu$m in experimental condition, where the electron beam is close to parallel beam. Therefore, new universal electron performance is sufficient for independant UED experiment, and the UED experiment with the electron gun can be run in any types of chambers.

\textbf{B.3 Image Acquisition System: Charge Coupled Device(CCD) Camera}
For a diffraction acquisition system, a highly sensitive device capability to detect a single electron event is necessary to detect weak diffraction signals. To achieve the high sensitivity, we are using PI-MAX from Princeton instrument operating at -20°C which is implemented with image intensifier from Hamamatsu. The image intensifier is composed more than 10^6 individual miniature electron multipliers with an excellent input to output spatial geometric accuracy, in order to amplify weak diffraction signals with a high spatial resolution. The construction of the system is shown in Fig. B.5. There are several stages through which the signal represented by the incident electron proceeds to achieve amplification, and eventual detection.

As shown in Fig. B.5, 60 nm thickness aluminum film to block the background photon signals which come from the pump laser or room light is coated on the optical face-plate of the image acquisition system, CCD camera. The penetration depth of visible wavelength photon in Al is ∼ 15 nm, while that of 40 kV electron beam is about several µm range. Therefore, most of the ambient background photon are blocked by this Al film. The electrons penetrating through the Al film strike a phosphor screen and generates the visible range photon. These photons are focused by a 2:1 ratio optical taper which is a bundle of optical fibers on the CCD camera intensifier window. Then the photons are converted back into electrons at the front of image intensifier by photo-cathode. The generated photoelectrons are accelerated and enters the micro channel plate (MCP). The MCP is composed more than 10^6 micro-channels which are individual miniature electron multipliers. The electron amplification is achieved by sequential secondary electron generation. The amplified electrons strike another phosphor to convert the electrons to much larger number of photons. These amplified photons are detected by CCD camera. A special absorptive layer
Figure B.5 Structure of charge coupled device (CCD) camera design. (a) Schematic illustration of CCD camera structure: in front of CCD camera, we have the optical taper to focus a signal in large area into small CCD camera input window (2:1 ratio). On the optical taper face, we have an optical face-plate, and the 60 nm aluminum film and phosphor film are coated on the face-plate surface. The Al film screens the background photon from room light and pump laser. The phosphor film converts the electron signal to photon to amplify the intensity. Red box indicates the intensifier. (b) the schematic diagram of the MCP in intensifier. MCP is composed of more than $10^6$ micro-channels which are individual miniature electron multipliers. (c) design of the fully assembled CCD camera.
absorbs any of the light that might leak through the semi-transparent photocathode, while
the aluminum reflection layer seeks to block any light generated near the phosphor screen
from returning to the photocathode. Each MCP can provide an amplification of up to 1000
times, and an image intensifier can have up to 3 MCPs between the photocathode and the
phosphor screen, thus allowing a gain of up to $10^9$. Finally, the amplified signal, in the
form of light photons is incident on the CCD screen, where it is detected in the usual way.
Moreover, each MCP which is 6 $\mu$m diameter independent electron multiplier allows the
accurate spatial resolution of the amplified signals.
Appendix C

Formalism of diffracted voltammetry under small angle condition

C.1 Slab model UEDV formalism can simplified by applying small angle approximation: \( \theta_i \) & \( \theta_o \ll 1 \), and \( \chi \ll 1 \). Under these conditions, Eq. (6.8) is reduced to:

\[
D = \frac{[\theta_o + (1-a)\theta_i] - [(1-a)\sqrt{\theta_i^2 + \chi}]}{1 + [\theta_o + (1-a)\theta_i][(1-a)\sqrt{\theta_i^2 + \chi}]} \sim [\theta_o + (1-a)\theta_i] - [(1-a)\sqrt{\theta_i^2 + \chi}]. \tag{C.1}
\]

Also, \( \Delta B \) is modified as

\[
(\Delta B + \theta_o)^2 \sim D^2 - \chi. \tag{C.2}
\]

By combining Eq. (C.1) & Eq. (C.2), we can get the following equation:

\[
(\Delta B + \theta_o)^2 = [\theta_o + (1-a)\theta_i]^2 + (1-a)^2\theta_i^2 + a(a-2)\chi - 2(1-a)[\theta_o + (1-a)\theta_i]\sqrt{\theta_i^2 + \chi}. \tag{C.3}
\]

Solving Eq. (C.3) for \( \chi \), we arrive at the following relationship:

\[
\chi = \frac{B}{2a^2(a-2)^2} \pm \sqrt{\left[\frac{B}{2a^2(a-2)^2}\right]^2 - \frac{C}{a^2(a-2)^2}}, \tag{C.4}
\]
where

\[ B = 4(a - 1)^2(\theta_i^2 + \theta_o^2) + 4(a^2 - 2a + 2)(1 - a)\theta_i\theta_o + 2a(a - 2)(\Delta_B^2 + 2\Delta_B\theta_o), \quad (C.5) \]

\[ C = [(\theta_o + (1 - a)\theta_i)^2 - (\Delta_B + \theta_o)^2]^2 + (1 - a)^2\theta_i^2[(1 - a)^2\theta_i^2 - 2(\theta_o + (1 - a)\theta_i)^2]. \quad (C.6) \]

Simplification can be made for different \( a \) value. For \( a = 0 \), Eq. (C.3) can be simplified as:

\[ (\Delta_B + \theta_o)^2 = [\theta_o + \theta_i]^2 + \theta_i^2 - 2[\theta_o + \theta_i]\sqrt{\theta_i^2 + \chi}, \quad (C.7) \]

so the inversion can be made analytically:

\[ \chi = \frac{\frac{1}{2}\Delta_B^2 + \Delta_B\theta_o - \theta_o\theta_i)^2 - \theta_i^2(\Delta_B + \theta_o)^2}{(\theta_o + \theta_i)^2}. \quad (C.8) \]

which is equivalent to Eq. (1) in the previous study.[40]

If \( \Delta_B \ll \theta_i \& \theta_o \), Eq. (C.8) can be further linearized:

\[ \chi = -2\frac{\theta_o^2\theta_i}{(\theta_o + \theta_i)^2}\Delta_B. \quad (C.9) \]

For \( a = 1 \), Eq. (C.3) can be simplified as:

\[ (\Delta_B + \theta_o)^2 = \theta_o^2 - \chi, \quad (C.10) \]

yielding a TSV formalism:

\[ \chi = -\Delta_B(\Delta_B + 2\theta_o). \quad (C.11) \]
If $\Delta B \ll \theta_i \& \theta_o$,

$$\chi = -2\theta_o \Delta B.$$  \hspace{1cm} (C.12)

For $a = 2$, implying $\theta_i = \theta_o$ in RHEED geometry, we can reduce the general formalism to

$$(\Delta B + \theta_o)^2 = \theta_i^2.$$  \hspace{1cm} (C.13)

Therefore, the surface scattered diffraction change, $\Delta B$, is independent of $\chi$. In other words, the measured $\Delta B$ in experiments is not affected by TSV.

**C.2 Beyond slab model** Small angle approximation can also be made for TSV determination beyond the slab model, formulated in Eqs. (??) to (??). For $\Theta_o(\theta_o, \alpha) \neq \Theta_i(\theta_i, \alpha)$, the surface potential, $V_s$ from $\Delta B$, can be written for small angles as

$$\chi = \left\{ [(c + 2)\Theta_i(\theta_i, \alpha) - c\Theta_o(\theta_o, \alpha)] 
\right.$$  

$$\pm \sqrt{[(c + 2)\Theta_i(\theta_i, \alpha) - c\Theta_o(\theta_o, \alpha)]^2 - 4ab[\Theta_o(\theta_o, \alpha) - \Theta_i(\theta_i, \alpha)]^2} \right\}$$

$$\sqrt{b[\Theta_o(\theta_o, \alpha) - \Theta_i(\theta_i, \alpha)]^2},$$  \hspace{1cm} (C.14)

where

$$a = \frac{(\theta_o \Delta B - \theta_i \theta_o + \Delta_B^2/2)^2 - \theta_i^2 (\theta_o + \Delta B)^2}{(\theta_i + \theta_o)^2},$$  \hspace{1cm} (C.15)

and

$$b = \frac{1}{(\theta_i + \theta_o)^2},$$  \hspace{1cm} (C.16)
and

\[ c = \frac{2\theta_i^2 + 2\theta_i\theta_o - 2\Delta_B\theta_o - \Delta_B^2}{(\theta_i + \theta_o)^2}. \]  

(C.17)
Appendix D

Magnetic Annealing Procedure

The magnetic lens material is low carbon soft-iron including chemical composition
(C/Mn/P/S/Si/Al/N: 0.01/0/18/0.005/0.005/0.1/0.004 %) from CMI Specialty Products, Inc.. After fabricating the magnetic lenses, the parts are annealed with following procedure to maximize the magnetic property which is recommended by the company:

1. Anneal the fabricated parts up to 1544°F.

2. Hold at 1450 - 1550°F for 1-2 hours.

3. Cool to 1450°F in 1 hour in vacuum.

4. Cool to 1350°F in 1 hour in vacuum.

5. Cool to 1250°F in 1 hour in vacuum.

6. Cool to 1150°F in 1 hour in vacuum.

7. Cool to 900°F in 1 hour in vacuum.

8. Cool 200°F/hr to 300°F in atmosphere to prevent warpage of thin complicated parts.

9. Air cool to ambient.
Appendix E

Optimization of Pierce Geometry

Electron Gun

As discussed in section 4.2, the combination of Pierce gun and CML1 provides the initial convergence of photoemitted electron beam, which is then subject to the space-charge-driven expansion of the photoelectron pulse. The performance of the prescribed Pierce geometry will depend on the electron density present. The conventional Pierce geometry has the highest field present at the edge of the cone-shaped anode, which limits the achievable extraction field at the cathode surface. Based on the experimental feedback, we may consider different cathode and anode geometry for providing higher extraction field at the cathode surface while maintaining the necessary self-focusing effect for compensating the space-charge-driven beam divergence. Fig. E.1 shows ray tracing simulation using different gap distances to compare the self-focusing power based on non-interacting electrons. We found that if we reduce the gap distance by 20%, we can increase the extraction field strength by 45%, whereas the self-focusing power, as measured by the divergence angle at crossover, can be reduced by more than a factor of 2. In comparison, increasing the gap distance by 20% leads to a 20% increase of self-focusing power, and a 20% decrease of extraction field. The self-focusing power should be tuned to the strength of the space-charge-driven expansion associated with high-intensity beam. Since the cathode is easily
Figure E.1 (a) Schematic illustration of a non-interacting photoemission electron generation on a cathode: $R$ is the initial location where the electron is generated and $\theta$ is the divergence angle caused by the focusing field of Pierce gun geometry. (b) Field Precision simulation result of the electron divergence angle at different initial position ($R$) at various gap distances between the cathode and anode: a gap distance of the current design is 20 mm and the surface extraction field is 2.2 MV/m field, and 20% smaller gap distance, 16 mm, generates 45% higher extraction field, 3.2 MV/m.
changeable in our set up, we may use different cathode geometry for generating different density beams.
Appendix F

List of Initials and Acronyms

<table>
<thead>
<tr>
<th>ADU</th>
<th>Analog-to-Digital Unit</th>
<th>AGM</th>
<th>Analytical Gaussian Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB</td>
<td>Conduction Band</td>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CML</td>
<td>Condenser Magnetic Lens</td>
<td>CFEG</td>
<td>Cold Field Emission Gun</td>
</tr>
<tr>
<td>COM</td>
<td>Center Of Mass</td>
<td>DWF</td>
<td>Debye-Waller Factor</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme Ultra Violet</td>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>FEL</td>
<td>Free Electron Laser</td>
<td>FMM</td>
<td>Fast Multiple Method</td>
</tr>
<tr>
<td>HFEG</td>
<td>Hot Field Emission Electron Gun</td>
<td>HGN</td>
<td>Hollow Gold Nano-shell</td>
</tr>
<tr>
<td>HHG</td>
<td>High Harmonics Generation</td>
<td>HOPG</td>
<td>Highly Oriented Pyrolytic Graphite</td>
</tr>
<tr>
<td>LDP</td>
<td>Laser Driven Plasma</td>
<td>LSPR</td>
<td>Localized Surface Plasmon Resonance</td>
</tr>
<tr>
<td>MCP</td>
<td>Micro Channel Plate</td>
<td>mRDF</td>
<td>modified Radial Distribution Functions</td>
</tr>
<tr>
<td>NP</td>
<td>Nano-Particle</td>
<td>Obj.ML</td>
<td>Objective Magnetic lens</td>
</tr>
<tr>
<td>PE</td>
<td>Photo-Emission</td>
<td>REED</td>
<td>Reflective High-energy Electron Diffraction</td>
</tr>
<tr>
<td>Acronym</td>
<td>Abbreviation</td>
<td>Acronym</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------</td>
<td>---------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>RF</td>
<td>Radio–Frequency</td>
<td>ROI</td>
<td>Region OF Interest</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembly Monolayer</td>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SPR</td>
<td>Surface Plasmon Resonance</td>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TTM</td>
<td>Two Temperature Model</td>
<td>TSV</td>
<td>Transient Surface Voltage</td>
</tr>
<tr>
<td>UED</td>
<td>Ultrafast Electron Diffraction</td>
<td>UEM</td>
<td>Ultrafast Electron Microscope</td>
</tr>
<tr>
<td>VC</td>
<td>Valence Band</td>
<td>VC</td>
<td>Virtual Cathode</td>
</tr>
<tr>
<td>VCO</td>
<td>Voltage Control Oscillator</td>
<td>X–FEL</td>
<td>X-ray Free Electron Laser</td>
</tr>
<tr>
<td>ZOT</td>
<td>Zero Of Time</td>
<td>6D</td>
<td>Six Dimension</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


[35] Z Tao, T Han, SD Mahanti, PM Duxbury, F Yuan, C-Y Ruan, K Wang, and J Wu. Decoupling of Structural and Electronic Phase Transitions in VO2.


[113] EI Goldman, NF Kukharskaya, and AG Zhdan. The Effect of Imaging forces in Ultra Thin Gate Insulator on the Tunneling Current and Its Oscillations at the Region of


