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#### INVESTIGATIONS ON INTERFACIAL DYNAMICS WITH ULTRAFAST ELECTRON DIFFRACTION

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#### INVESTIGATIONS ON INTERFACIAL DYNAMICS WITH ULTRAFAST ELECTRON DIFFRACTION

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By

Ryan A. Murdick

#### A DISSERTATION

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

#### DOCTOR OF PHILOSOPHY

Physics & Astronomy

#### ABSTRACT

#### INVESTIGATIONS ON INTERFACIAL DYNAMICS WITH ULTRAFAST ELECTRON DIFFRACTION

By

#### Ryan A. Murdick

An ultrafast electron diffractive voltammetry (UEDV) technique is introduced, extended from ultrafast electron diffraction, to investigate the ultrafast charge transport dynamics at interfaces and in nanostructures. Rooted in Coulomb-induced refraction, formalisms are presented to quantitatively deduce the transient surface voltages (TSVs), caused by photoinduced charge redistributions at interfaces, and are applied to examine a prototypical  $Si/SiO_2$  interface, known to be susceptible to photo induced interfacial charging. The ultrafast time resolution and high sensitivity to surface charges of this electron diffractive approach allows direct elucidation of the transient effects of photoinduced hot electron transport at nanometer ( $\sim 2$  nm) interfaces. Two distinctive regimes are uncovered, characterized by the time scales associated with charge separation. At the low fluence regime, the charge transfer is described by a thermally-mediated process with linear dependence on the excitation fluence. Theoretical analysis of the transient thermal properties of the carriers show that it is well-described by a direct tunneling of the laser heated electrons through the dielectric oxide layer to surface states. At higher fluences, a coherent multiphoton absorption process is invoked to directly inject electrons into the conduction band of SiO<sub>2</sub>, leading to a more efficient surface charge accumulation. A quadratic fluence dependence on this coherent, 3-photon lead electron injection is characterized by the rapid dephasing of the intermediately generated hot electrons from 2-photon absorption, limiting the yield of the consecutive 1-photon absorption by free carriers.

The TSV formalism is extended beyond the simple slab geometry associated with planar surfaces  $(Si/SiO_2)$ , to interfaces with arbitrary geometrical features,

by imposing a corrective scheme to the slab model. The validity of this treatment is demonstrated in an investigation of the charge transfer dynamics at a metal nanoparticle/self-assembled monolayer (SAM)/semiconductor interconnected structure, allowing for the elucidation of the photo-initiated charging processes (forward and backward) through the SAM, by monitoring the deflection of the associated Bragg peaks in conjunction with the UEDV extended formalism to interpret the surface voltage.

The design, calibration, and implementation of a molecular beam doser (MBD), capable of layer-by-layer coverage is also presented, with preliminary investigations on interfacial ice.

With the development of UEDV and implementation of the MBD, continued investigations of charge transfer in more complex interfaces can be explored, such as those pertinent to novel solar-cell device technology, as their quantum efficiencies are usually strongly dependent on an interfacial charge transfer process. As UEDV is inherently capable of probing charge and atomic motion simultaneously, systems that exhibit phenomena that are attributable to strong coupling of the atomic and electronic degrees of freedom are of particular interest for future investigations with UEDV, such as optically induced electronic phase transitions and colossal field switching in functional oxides.

To my family, Aaron, Carrie, John, and Marcia

#### ACKNOWLEDGMENT

First and foremost I would like to acknowledge Dr. Chong-Yu Ruan, Ramanikalyan Raman, and Dr. Yoshie Murooka. I will always think of the four of us as a team, of which I feel very proud to have had a place. Their hard work and dedication with Professor Ruan's energy and leadership allowed for this beautiful lab to be built.

My various mentors along the way: Drs. Bradley Roth, Andrew Goldberg, Norman Birge, Bhanu Mahanti, Ned Jackson, Martin Berz, Andrei Slavin, Ken Elder, Alberto Rojo, and Uma Venkateswaran.

My friends and colleagues from condensed matter: Tzong-Ru Terry Han, Rick Worhatch, Dr. Chris Farrow, Zhensheng Tao, Pampa Devi, Luke Granlund, and Josh Veazey.

I would also like to acknowledge Jim Muns, Tom Palazzollo, and Tom Hudson of the MSU Machine Shop, along with Drs. Reza Loloee, Baokang Bi, Ronald Mickens, and Merlin Bruening for allowing our group to use his ellipsometer.

There are several components to our lab and to this work, from which I would like to acknowledge specific contributions, beginning with R.K. Raman and Aric Pell for the development of the electron guns in our lab; Dr. Yoshie Murooka and R.K. Raman for designing and overseeing the first (Yoshie) and second (Raman) generation sample holders. I would also like to acknowledge Zhensheng Tao for his development and implementation of portions of the formalism in Chapter 5, specifically Section 5.3.2, as well as Richard Worhatch for his contribution to the 'RC-circuit' portion of Chapter 6, and Tzong-Ru Terry Han for his efforts in sample preparation and stage temperature calibrations, and of course, Professor Ruan for his involvement in everything mentioned here, and throughout the entire work.

Finally, my wife Amy, who has loved and supported me, unconditionally, through these trying years.

I am very humbled and grateful to have worked along side of all of you.

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# Chapter 1

# Introduction

#### 1.1 Charge Transfer

The need for a clean energy economy for tomorrow has ushered in a mandate to develop practical solar (carbon neutral) energy capture technologies [1–4]. Charge transfer mechanisms [5–14] and their elucidation lie at the root of novel solar cell technological development [4, 6, 15–51]. An efficient conversion mechanism that reliably competes with internal recombination is the essence of next generation solar cell technology, including dye- [6, 16, 34, 39–43, 43, 44, 48, 52] and quantum dot-sensitized [18, 35] nanoparticles and films, often in conjunction with nanowires for enhanced transport [4, 23, 33, 34, 38], surface plasmon-enhanced harvesting capabilities [20, 23, 25, 30–32, 45, 51, 53], and multiple exciton generation capability [17, 21, 27–29, 33, 47].

Charge transfer is also inherent to semiconductor technology, with steady-state probes at semiconductor/oxide interfaces including conventional steady-state measurement techniques, such as capacitance-voltage (C-V) measurements, Kelvin probes, and X-ray photoelectron spectroscopy [54–59].

The nature of charge transfer, trapping, and detrapping at the Si/SiO<sub>2</sub> interface has gained notable interest as CMOS devices are further integrated in accordance with Moore's law. While the mechanisms associated with tunneling have been studied for years [60–65], it is in the more recent past that gate dielectric oxides have approached the sub-micron to nanometer length scales, which has initiated interest in comparing the various mechanisms associated with leakage currents and tunneling, often concerning the roles of Fowler-Nordheim (FN) and direct tunneling [56, 66–77].

Time-resolved investigations on the Si/SiO<sub>2</sub> interface are commonly done through a contactless approach called electric field induced second harmonic generation (EFISH) [78–100], which is effective in probing the interfacial field as it is a point of broken symmetry; a necessity for SHG. In general, these studies are 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 charge can relax, such that the residual charge level is continuously pumped. This of course depends on the integrity of the interface, or, more directly, the density of interface states.

One of the focal points of this work is a contactless, *time-resolved voltage probing technique* that has been implemented at MSU, extended from ultrafast electron crystallography (UEC) [101–104] and ultrafast electron diffraction (UED) [102, 105–110].

## **1.2 History: Shutters to Short Pulses**

It was predicted in 1931 that the fundamental time scale associated with chemical reactions should be on the order of femtoseconds [111]. Short-pulsed energy excitations had already become a tool used to characterize the lifetime of chemical reactions on the milli- to microsecond time scales by the 1960's, owing to the efforts of Eigen, Porter, and Norrish, who were recipients of the 1967 Nobel Prize in Chemistry [112–116].

The interest in resolving chemical nonequilibrium and transition states continued through the work of Femtochemistry, a technique pioneered by Nobel Laureate Ahmed H. Zewail (1999, Chemistry) [37, 117–121]. In the 'pump-probe' method used by Zewail, a short-duration energy perturbation (usually in the form of an optical pulse) is first introduced to a system of interest. Before the system can return to its original (ground) state, a measurement is taken on the system with another short-duration probe pulse, so as to capture the effects from the pump. Probe pulses can be timed very precisely to arrive at fixed intervals after the pump has initiated the reaction. In the studies of the transient molecular processes, femtosecond pump and probe time resolutions are required. Pump-probe methodology of this general description has been applied to various systems, from gas phase molecular reactions [121], to condensed matter material processes recently, and encompasses many different forms that lead the frontier of time-resolved research today.

The spirit of a fs pump-probe arrangement is to acquire information on matter when it is displaced from equilibrium by electronic excitations. It is thus common for the pump to be an ultrashort laser pulse to initiate various states of excitation (nonequilibrium), while variations come into play with ultrafast probes, depending on applications. One form of probe is a subsequent optical pulse that photoejects electrons from the system, which are then detected in an energy analyzer, known as time-resolved two photon photoemission (TR-TPP) [122–126], which is often coupled with angle-resolved photoemission spectroscopy (ARPES) [127] to examine the carrier energy-momentum relationship (Fermi-surface) in materials. Another form is that of a probing laser pulse that is used to study the reflective or absorptive properties of the system, (transient absorption or reflective spectroscopy) [16, 39, 47, 128–136]. The transient optical responses of the reflected light, (or lack there of) are used to characterize the electronic properties of the photoexcited states. There are also several interesting nonlinear optical techniques that exploit broken symmetries, which can be used as an ultrafast probe. Examples include second-harmonic generation (SHG) and sum-frequency generation (SFG) [80, 85, 90, 92, 97, 137–156], which is highly sensitive to surfaces and interfaces. Another form of probe is that of a low energy infrared (terahertz) pulse that is detected after passing through the excited sample, with the changes in frequency and phase giving a complete measurement of the complex dielectric function, permitting simultaneous studies of carrier relaxation and transport, without the necessity of an electrical contact point with the sample [21, 157, 158].

The essence of pump-probe, which is to function as an effective 'fast camera' to capture these ultrafast events, dates all the way back to the late 1800's and the invention of the first camera to implement a fast shutter speed. Specifically, it was used to answer a question as to whether all four hooves of a horse left the ground at the same time in an individual gallup. Eadweard Muybridge settled this controversy by constructing a camera with a shutter that could open and close approximately 1000 times per second, which was capable of resolving the various stages of a horse's locomotive cycle (Figure 1.1), while it galloped approximately 20 miles per hour (10 m/s). He did this by arranging triggers at various points on the race track that would snap the photo as the horse passed.

A more modern example of a fast detector is that of a streak camera [159–168], which can be employed to measure the temporal profile of an optical pulse, provided the pulse width is longer than  $\approx 100$  fs (lasers are well-below this today). Essentially, a streak camera converts the temporal characteristics of an optical pulse into a spatial profile on a CCD detector, by applying a time varying field to the incoming pulse. Specifically, incoming photons are directed onto a photocathode (preferably with low work function). The electronic emission is accelerated through deflector plates that have a time varying electric field, causing the electron bunch to spray across the CCD detector. The temporal characteristics of the pulse can be deduced from the dispersion



Figure 1.1: The fast camera invented by Muybridge allowed the question to be answered: do all four hooves of a horse leave the ground at the same instant during a gallup? The answer is no. All four legs are off the ground, but not with full extension, which was presumed by many at the time. This sequence was taken 6/19/1878 at a track in Palo Alto, CA. This photograph is property of the Library of Congress Prints and Photographs, Washington, DC 20540.

relationship of detected electrons, which depends on the accelerating voltage, work function of the photocathode, and electric field applied to the deflectors [161]. The time resolution of a streak camera is limited (mostly) by the temporal dispersion of the photoelectron bunch as it is accelerated from the photocathode to the deflection plates. Accordingly, contemporary designs attempt to minimize this distance [161]. Streak cameras have also been implemented for measurement of ultrashort electron pulses [169].

The streak camera, which is literally a fast camera, has not enjoyed the same rapid growth [166, 170] over the past decade as its counterpart, the ultrafast probe, which is more of a figurative fast camera. A fast probe relieves the necessity of having a fast detector, some of which will be discussed in the next section, including the cornerstone technique of this work, ultrafast electron diffraction [102–105, 171–174].

Ultrafast electron diffraction (UED) is an optical pump - diffraction probe technique, spear-headed initially at the California Institute of Technology (Ahmed H. Zewail's group) [102–105, 171–174]. A femtosecond laser pulse excites the sample, while an ultrashort electron pulse serves as the diffractive probe of the crystal structure, at a fixed delay time after the pump arrival. Unlike optical techniques, the diffractive probe is directly sensitive to the atomic configuration of the materials, thus providing crucial information on the nonequilibrium structures of the transient states.

Since its implementation, UED has had numerous accomplishments and remains a robust tool for investigations requiring high spatio-temporal resolution [102–104, 172, 173, 175–177]. Similar developments of ultrafast diffraction techniques using X-rays rather than electrons to probe structure [178–185] have also undergone significant progress, especially with the recent development of femtosecond high brightness coherent X-ray sources from free electron lasers [186–189]. The work here is on the multi-faceted development and expansion of UED at MSU since 2004; specifically, the spawning and development of *measuring transient interfacial electron dynamics*. The technique, ultrafast electron diffractive voltammetry (UEDV), will be presented in Chapter 4.

## Chapter 2

# Ultrafast Electron Crystallography Laboratory at MSU

### 2.1 Introduction

The development of ultrafast electron crystallography (UEC) at MSU aims to combine surface sensitivity, atomic scale spatial resolution, and ultrafast temporal resolution, in order to investigate the ultrafast processes that proceed at nanometer scale surfaces and interfaces. Surface sensitivity is a consequence of the grazing incidence geometry, which, by definition, implies a large transverse momentum component relative to the one normal to the surface. With only ~1% of kinetic energy directed into the depth of the crystal, the beam penetrates only a few sub-surface atomic layers (~ 1-2 nm, depending on incidence angle), thus lending to the surface sensitivity.

Note that surface sensitivity and spatial resolution do not refer to the same thing. High surface sensitivity, indirectly, refers to the level of signal-to-noise (S/N) of scattered electrons arising from their interaction with the surface layer. It is bolstered by a small probe beam cross-section. Spatial resolution, on the other hand, is defined by the Compton wavelength  $(\lambda_e)$ , which is the intrinsic size property of the probing electron, and thus needs not relate to the surface. Consider for example a transmission electron microscope (TEM), which is operated at high accelerating voltages (~ 200 kV) affording high spatial resolution, but the beam can be transmitted throtagh hundreds of atomic layers, and would not be considered surface-sensitive.



Figure 2. 1: Ultrafast electron diffraction geometry at MSU. (a) A schematic of the UEC optical setup. For completeness, both 400 and 800 nm beam lines are shown entering the delay line. In practice one of them will be blocked based on the choice of excitation energy [190]. (b) In the UHV chamber, an optical pulse (of 400 or 800 nm) excites the sample (red), followed by subsequent probing in the form of electron diffraction (blue). The electron pulse is generated from an ultrashort laser pulse striking a silver photocathode (not depicted), negatively biased at -30 kV, which is focused onto the sample. Diffracted electrons are captured on an image intensified phosphor screen and recorded by a CCD camera.

One of the difficulties encountered with the surface sensitive probe is that of the 'velocity mismatch' between the pump and probe, as the former travels at the speed of light (c) and is incident at  $45^{\circ}$ ; the latter at  $\approx 0.34c$  (depending on the accelerating voltage) is incident at a grazing incidence angle. As a result, the ultimate time resolution is limited by the convolution of the two pulses, since their respective arrival times on the surface are different at different points (Figure 2.2) [191]. Baum and
Zewail demonstrated a method using optics, where the wavefront of the pump pulse was tilted relative to the propagation direction, effectively forcing the pump arrival to be consistent with that of the probe at all points [191].



Figure 2.2: The group velocity mismatch problem is demonstrated in parts (a) and (b), the synchronization of the two is inherently confounded by their differing propagation  $\mathbf{speeds}$ . In (c)-(e), the electron beam sees the same pump for all spatial probing points, because of the wavefront tilting of the pump. [191]

To  $\mathbf{overcome}$  the velocity mismatch problem, the approach taken at MSU is to signific **arn**tly reduce the probe size, which limits the spatial area of pump-probe overlap on the surface, thus achieving a high temporal resolution. Through implementation of a short-focal distance electron lens and a set of properly positioned apertures, an electron **probe** as small as 5  $\mu$ m has been demonstrated in studying nanostructures and nanointerfaces [190, 192–194]. Future generation electron guns, which will naturally strive towards even smaller beam cross-sections, will very likely possess the capability of probing a single nanoparticle.

In addition to the importance of the probe characteristics, some of the more technical aspects of UEC, pertaining to instrumentation, pump-probe geometry, frequently occurring measurements and calibrations, and various measures that can be taken to *reduce* sources of error will be outlined in this chapter. It can be thought of as a 'behind-the-scenes' look at what goes into a UEC experiment.

# 2.2 Optical Pump - Diffraction Probe Setup

At MISU, the pump-probe scheme, depicted in Figure 2.1, has a fs-laser pump pulse coupled to an electron beam (or *e*-beam) that probes the crystal structure near the surface via diffraction, as discussed above.

**Diffracted** electrons are collected in a micro-channel plate amplification medium (capable of 10,000 e/e gain), proximity focused onto a phosphor screen, and a CCD camera records the image. Experiments are carried out in an ultra-high vacuum (UHV) system, possessing experimental tools such as a quadrupole mass spectrometer (QMS), detectors for low-energy electron diffraction (LEED), Auger electron spectroscopy, and a spherical energy analyzer, along with several tools for surface preparation, including an argon sputtering gun, a molecular beam doser (design and calibration in Chapter 7), and a load-lock to allow fast sample transfer with no disruption to UHV, all of which is depicted in Figure 2.3. The stage has cryo-cooling capability (down to below 20 K) and five degrees of spatial motion.

A commercial femtosecond laser system (purchased from Spectra Physics), employs a Ti:Sapphire lasing medium to generate ultrashort pulses, at a repetition rate of of ~80 MHz and pulse energy of 2.5 nJ (Figure 2.1). This seed laser is fed into a regenerative amplifier ('Spitfire'), which is pumped by an external laser ('Empower'), to reach a significantly higher pulse energy (up to 2.5 mJ/pulse), with pulse durations of ~ 45 fs and repetition rate of 1 kHz. The principles of femtosecond laser pulse generation, including modelocking and regenerative amplification are presented in Appendix B.



Figure 2.3: The UHV chamber and tools for surface preparation and characterization [190].



Upon exiting the Spitfire, the laser is split into two beam lines (50/50), where one is directed through the delay stage and subsequently to pump the sample, and the other is run through a frequency tripler<sup>1</sup>, such that a 267 nm (4.65 eV) beam is empirited. It is then directed into the UHV chamber where it strikes the electron gun photocathode), held at -30 kV. The photocathode is a thin Ag film of thickness (~ 4 O nm), which has a work function ~ 4.5 eV [195], just below the frequency-tripled exciting pulse energy, to generate photoelectrons with relatively low energy spread. In this enrangement, an ultrashort pulse of electrons of similar duration as the exciting laser pulse [196–199] can be generated at the photocathode, and are accelerated to 30 keV in just 5 mm. A proximity-coupled magnetic lens focuses the electron beam onto the sample. The overall photocathode-to-sample distance is ~5 cm, allowing only a moderate space-charge broadening spread to develop, so as to reach the sub-ps time resolution.

### 2.2.1 Pump-Probe Alignment

Concentric pump-probe spatial overlap is essential prior to beginning an experiment. A stainless-steel shaft with a needle point ( $\approx 75 \,\mu$ m) was built onto the stage (Figure 2.4) for the purpose of pump-probe alignment. The stage position is adjusted such that it can be determined that the electron beam is passing through the needle tip, as shown in Figure 2.4 where an actual image from the CCD of an unfocused beam is displayed. As the electron beam is focused, the beam waist (full-width at half maximum) is smaller than the needle tip size, so the integrated transmission intensity (through the needle) is used to judge the position of the electron beam relative to the needle tip.

Having ensured the passage of the probe beam through the needle tip, the second step is to bring the pump beam through the needle tip as well, thus creating 'pump-

<sup>&</sup>lt;sup>1</sup>The TPH Tripler model was purchased from Minioptic.

probe overlap.' However, allowing the pump laser to directly focus onto the needle tip could actually damage it. For this reason, two diode lasers (adjustable), each with a different vantage point, are used instead to simultaneously pass through the needle tip. Now, the diode lasers overlap at a point in free space, corresponding to a point through which the electron beam is known to pass. The stage is then moved and criented in such a way that the diode laser spots overlap on some metallic flat surface of the stage. The pump laser is then admitted into the chamber with high atternuation (to avoid the possibility of damaging anything inside), and displaced with adjustment mirrors such that it overlaps with the diode spots. This roughly aligns the pump and probe in space. Thus, when the stage is subsequently moved to a point where a diffraction pattern is observed, it can be assumed that the influence of the pump laser is present to some extent.

At this point, the fine adjustments can be made by examining the actual diffraction responses on the sample surface as feedback following additional fine steps of controlling the beams on the surface, as described in Figure 2.5. The first step is to bring the excitation laser beam to a more precise vertical (z in Figure 2.5) alignment position with respect to the probing electron spot on the surface, by way of an adjustment lens to displace the laser spot. By monitoring the corresponding changes in the diffraction pattern as the laser beam is moved through the region (here the laser pulse is timed to arrive before the electron probe pulse), a 'maximum change point' can be identified and the corresponding z-position of the adjustment lens is fixed for the experiment. This results in vertical alignment of the beam spots, as shown in Figure 2.5(c).

Note, the maximum change in the diffraction pattern could be ascertained from various diffraction signatures, such as displacement of spot positions, or drop in Bragg peak intensity; ultimately, depending on the characteristics of the system on which alignment is being executed. Silicon peaks, for example, exhibit very little intensity



Figure 2.4: Coarse alignment. The electron beam and diode lasers from two different vantage points are passed through the needle. This means that the diodes overlap at a point in space corresponding to a known point through which the *e*-beam will pass.

drop, so the position changes are used to align. Also note that aligning the horizontal axes of the two beam spots could also have been done by moving the electron beam instead of the laser beam, but this would necessitate the use of another set of beam deflectors to shift the spot in that direction (which are installed on the gun). The lens here is under planar 2D motor control, which allows for efficient automation of the process. Moreover, deflecting a strongly focused electron beam would cause a change of the crossover size of the beam on the surface and shift the point of interception with the laser beam in the y-direction. Modifications like these introduce undesirable changes to the pump-probe overlap.

The second step of fine adjustment targets alignment of the pump and probe spots horizontally (y) on the surface, by displacing the sample stage in the x-direction. By inspection of the hypothetical example in Figure 2.5(c), the stage would need to move along positive x to compensate the offset. Similar to achieving vertical alignment, the diffraction changes are recorded as a function of the stage position, which is incrementally displaced (every 10-20  $\mu$ m) in the x-direction. However, varying the stage position relative to the electron beam modifies the diffraction pattern. For this reason, at each stage position (x-increment), both ground and excited state patterns are recorded for self-referencing, shown in Figure 2.6(b). The x-position where the maximum difference is observed corresponds to the fully aligned position.

Because of the grazing incidence, motion of the x-goniometer (stage) causes the ebeam footprint to move ~10-fold larger on the surface in the y-direction, or  $\Delta y_{surf} = \Delta x_{stage} / \tan \theta_i$ , where the incidence angle,  $\theta_i$ , is very small. This is in contrast to the pump laser, which has  $1:\sqrt{2}$  correspondence because of the 45° incidence. Taking note of the two alignment steps, the first step moves the laser in free space, while the second step moves the electron footprint on the sample, as it is the stage that is moved.



Figure 2.5: Pump-probe fine alignment. (a) The pump laser (red), incident at  $45^{\circ}$ , incrementally moves vertically (z) along the stage (motion not depicted), with a **Probe** shot (blue) taken at each stop. The maximum change in the diffraction pattern **corresponds** to improving the rough alignment shown in (b) to the partially aligned in (c). The stage goniometer is then adjusted incrementally along the x-direction, at each stop taking diffraction images from the pumped and unpumped sample by **varying** the delay before and after the zero of time. The x-position where maximum **ch** ange was observed corresponds to the fully aligned position in (d).



Figure 2.6: Alignment scans. (a) The first scan of the fine alignment process, showing the **Bragg** peak position change on the CCD screen (inset shows the intensity drop) as the **laser** spot is displaced in increments of 50  $\mu$ m. (b) The second scan of fine alignment, where the stage is stopped every 10  $\mu$ m to take diffraction shots at delays of 500 **ps** (circles) and 700 ps (triangles), and the ZoT is 540 ps. The lens and stage positions were chosen here to be -0.65 and 12.70 mm, respectively.

Why not displace the lens horizontally for the second step to find the overlap? In principle, this can be done (and sometimes is). There are several reasons why it is not advisable. One reason is that it changes the camera distance and thus, the ZoT, as the pump and probe will be overlapped at a different point in free space than before, which is necessarily nearer or further from the camera. Note that vertically displacing the pump laser does not change the ZoT, because the camera distance remains the same, which is why it is safe to do in the first alignment step.

Moving the x-goniometer changes the point where the pump and probe strike the surface, but in free space the point of overlap is unchanged. In the event that the alignment needs to be adjusted during an experiment, as most experiments will sometimes go on for 1-10 weeks, some data sets could have different zeroes of time, hich makes it impossible to be unequivocal when correlating them.

A recent study was conducted by the UEC group where the pump laser induced photoemission yield from a graphite surface, and the background scattering from the diffracted beams could actually be used to 'image' this cloud [200]. There, the pump and probe were *intentionally* misaligned so that the pump laser would strike the surface to the right of the probe pulse. As a result, scattered electrons would be forced to traverse the photoemitted cloud in transit to the CCD. See Reference [200] for details pertaining to the technique and quantification of the photoemission yield.

Another noteworthy point is that of pump-probe interaction, which could happen as the two pulses are engaging the sample. For a post-ZoT delay time, the pump laser pulse could very well encroach the probe pulse in transit to the surface, and exert a ponderomotive force on the electrons in the pulse. Generally speaking, this is not a practical concern as these fields tend to be rather weak, though at high fluences there **are** sometimes some effects. In fact, Hebeisen *et al.* devised a technique to characterize the electron pulse width from these effects [201].

# 2.3 Experimental Measurements and Calibrations

### 2.3.1 Laser Fluence

Fluence is formally defined as the single pulse energy divided by the laser beam crosssectional area, striking the surface. The pulse energy is measured with a power meter<sup>2</sup> at a position in front of the port where the excitation laser enters the UHV chamber. From the power measurement (P), the corresponding pulse energy  $(E_p)$  is given by

$$E_p (J/pulse) = \frac{P (W)}{f_{rep} (Hz)}, \qquad (2.1)$$

where  $f_{rep} = 1$  kHz is the repetition rate of the laser.

All that remains is to know the laser irradiated area on the sample surface,  $A_l$ .

 $\underbrace{\mathbf{Lf}}_{^{2}\text{Spectra-Physics, Model 407 A}} \text{the probe spot size is small compared to that of the pump laser spot, this can}$ 

be deduced by performing the first of the two alignment scans described in Section 2.2, above. As the pump laser is dragged across the surface, the static electron probe (in position) will record increasing dynamical effects as the laser approaches concentricity with the probe, and conversely the dynamics will be quenched as the pump laser continues on its path away from the probe. The probe saw a Gaussian excitation over the motion according to the diffraction patterns recorded along the way; the full-width at half-maximum (FWHM), corresponding to the laser spot size, as shown in Figure 2.7.



Figure 2.7: As the laser spot is brought into the probe area, the response of the Bragg Peak increases until it reaches a maximum. At this point, the pump and probe are Perfectly concentric, followed by the gradual decrease in Bragg peak response as the laser is dragged out of the probe region. The FWHM of this curve is the laser spot size.

The laser strikes the sample at an angle of  $45^{\circ}$ , so the horizontal component • for the spot size is  $\sqrt{2}w$  (w is FWHM). For the elliptically-shaped laser spot, the • a is  $A_l = \pi w^2/\sqrt{8}$ . The viewport window introduces a slight attenuation factor to the laser as it enters the UHV chamber, which has been measured to be 0.806 (transmittance). So the laser fluence is

$$F = 0.806 \left(\frac{E_p}{A_l}\right) = (0.806) \left(\frac{P/f_{rep}}{\pi w^2/\sqrt{8}}\right)$$
(2.2)

### 2.3.2 Pulse Width - Interferometric Autocorrelation

Several different techniques have been developed for sub-ps pulse duration<sup>3</sup> measurement, including (but not limited to) interferometric autocorrelation, frequencyresolved optical gating (FROG) [202], and spectral phase interferometry for direct electric field reconstruction (SPIDER) [203]. The technique employed here is the former [204]. The autocorrelation function is the cross-correlation of a signal with itself, or

$$A(\tau) = \int_{-\infty}^{\infty} E(t)E(t-\tau)dt,$$
(2.3)

where E(t) represents the signal of the fs laser pulse.

Within the framework of autocorrelation, there is more than one method. Essentially, the idea is to find the autocorrelation function,  $A(\tau)$ , measure its width,  $\Delta t_a$ , and then relate it to the pulse width,  $\Delta t_p$ . Very simple relationships, can be derived (trivially) that relate  $\Delta t_a$  to  $\Delta t_p$ , depending on the shape of the pulse (Gaussian, sech<sup>2</sup>, Lorentzian, etc.); some examples are given in Table 2.1.

Conventionally, measuring  $A(\tau)$  is as follows: the pulsed input beam (fundamental) is split (50/50), followed by delaying the twin with respect to the original and then passing them through a doubling crystal, where a second harmonic will be gener ated (SHG). In other words, the two input signals, with fundamental frequency  $\omega_1$ ,

<sup>&</sup>lt;sup>3</sup>Throughout this work, pulse duration and pulse width will be used synonymously. There are  $s_{me}$  cases where it is more intuitive to use one over the other, but they mean the same thing.

Pulse Shape	Signal	$\mathbf{Widths}$
	E(t)	$\Delta t_p / \Delta t_a$
Gaussian	$\exp\left[-2.77\left(t/\Delta t_p ight)^2 ight]$	0.707
Lorentzian	$\left(1+2t/\Delta t_p ight)^{-2}$	0.500
Hyperbolic Sec	$\mathrm{sech}^{2}\left(1.76\ t/\Delta t_{p} ight)$	0.648

Table 2.1: Relationships between the widths,  $\Delta t_p$  and  $\Delta t_a$ , of a signal and its autocorrelation function, respectively.

enter the crystal and a frequency-doubled signal exits,

$$\omega_1 + \omega_1 \Rightarrow \omega_2. \tag{2.4}$$

The amplitude of the SHG signal is  $\propto E^2$ , which is the integrand of Equation 2.3, thus demonstrating the necessity of the doubling crystal. The intensity output can be recorded at various delay times (demonstrating the necessity of a variable delay stage), thereby tracing out the temporal profile of the autocorrelation function,  $A(\tau)$ . Once acquired, its width,  $\Delta t_a$ , is used to deduce  $\Delta t_p$ .

A second way, which is the one employed in the UEC lab at MSU, is to use a single-shot autocorrelator<sup>4</sup>, which eliminates the need for a variable delay stage [ $\geq 05, 206$ ]. Again the fundamental is split into two pulsed beams, with one delayed relative to the other. Here though, the two pulses will enter the nonlinear crystal a t an angle  $\theta$ , with respect to the z-axis, causing them to cross inside at an angle (Figure 2.8). As the pulsed-beams cross each other, they overlap both *spatially and emporally*, provided the beam diameter is much larger than the spatial length of

<sup>&</sup>lt;sup>4</sup>The  $\Delta$  Single Shot Autocorrelator was purchased from Minioptic Technology, Inc.

the pulse,  $c \Delta t_p$ . As shown in Figure 2.8, the SH signal is generated by the crystal and ernitted along the bisecting axis of the two beams (the z-axis in the figure). The signal is proportional to the intensity product of the beams. Since the beams cross at an angle, each overlapping point corresponds to a different 'delay' between the pulses. The signal is summed in time as it reaches the detector (a CCD camera), such that the final shape is Gaussian in space along the y-axis, as depicted in Figure 2.8.



Figure 2.8: Two beams of frequency  $\omega$  enter the doubling crystal at an angle of  $2\theta$ , relative to one another. In the crystal, they overlap spatially and temporally, so that each instant in time represents a different intersection point of the two wavefronts. The SH emission from the crystal ( $2\omega$ ) corresponds to different 'delays' from these intersections, which are integrated in time to make up the autocorrelation signal (red). A filter prevents the two fundamental beams ( $\omega$ ) from entering the detector (faot showrn).

But from this spatial profile, how is the pulse-width deduced? The autocorrelation signal is feed into an oscilloscope, which displays the Gaussian-like profile, with a FWHM,  $\Delta S$  (Figure 2.9) in oscilloscope time units. It is important to note that  $\Delta S$ is not the pulse-width itself, though it is proportional to it. The time axis of the

oscilloscope cannot be true for this input<sup>5</sup>, and therefore must be calibrated. This is done by displacing the mean position of the autocorrelation signal by a known distance, L, with a micrometer inside the device, which rotates the doubling crystal. The micrometer reading has been pre-calibrated against rotation angle, so L can be trusted as the true spatial displacement of the Gaussian. On the oscilloscope, the pulse will move by some time interval,  $\Delta T$  (Figure 2.9). But it is indisputable that the time displacement was L/c, meaning that  $\Delta T$  in oscilloscope time units equals L/c in reality. Thus a calibration factor has been deduced, which is  $L/c\Delta T$ . This **c**alibration must be done every time pulse width is to be measured. The final expression for the (Gaussian) pulse width is

$$\Delta t_p = 0.707 \ \gamma \ \left(\frac{L}{c\Delta T}\right) \ \Delta S, \tag{2.5}$$

where the factor  $\gamma$  is to correct for group velocity dispersion ( $\gamma = 1.8$  for the one used here).

#### 2.3.3 **Electron Beam Spot Size**

Measuring the cross-sectional area of the electron beam is carried out using a standard technique called the knife-edge method. With a calibrated and trusted goniometer For stage motion, a knife-edge is clipped on to the stage. Direct beam is a term sed to describe the incident electron beam as it flies directly to the CCD, without Scattering off of the sample (the stage must be moved out of the way prior). Direct beam images are continuously acquired as the knife edge is incrementally brought  $\mathbf{I}$  to its trajectory. As the knife-edge eclipses the beam, the intensity of the direct eam drops. The profile begins at some steady value and then slowly drops to zero, apping out a complementary error function (erfc(x)) as shown in Figure 2.10. The <sup>5</sup>If it were true, then the oscilloscope could be used to measure the pulse width and autocorrelation

ould not be necessary!



Figure 2.9: Signal time axis calibration. The oscilloscope profile of the autocorrelation signal has a spread  $\Delta S$ , which is proportional to the pulse width. When the autocorrelation function is spatially displaced by L, the oscilloscope profile moves by  $\Delta T$ . Moving L and observing  $\Delta T$  is the essence of the calibration (see text).

half-width of this function corresponds to the size of the electron beam. Note, the curve in Figure 2.10 is not a universal for the lab. The beam size can vary due to a number of factors, including changing the current in the magnetic lens that focuses the beam, or the iris diameter for the laser beam as it enters the photocathode. It is very typical to change one or both of these, depending on the requirements of the experiment. Consequently, knife-edge scans are commonly done for each experiment.

### **2.3.4** Rocking Curve

The rocking curve is a standard technique for reflection mode diffraction [207]. Essentially, a rocking curve is a series of diffraction images recorded over some range of incidence angle,  $\theta_i$ . In UEC, it is frequently used as a way to survey the landscape of the crystal prior to beginning the time-resolved experiment [194]. Figure 2.11 shows typical rocking curve, this one performed on a rough Si(111) surface. Full images vere recorded over a range of incidence angles, followed by cropping out a region of interest (ROI) from the each image [Figure 2.11(a)], corresponding to a particular



Figure 2.10: The intensity of the direct beam recorded on the CCD as the knife-edge is incrementally moved in from -15 to +15  $\mu$ m. Inset: Schematic of the knife-edge encroaching the electron beam path [190].

rod in reciprocal space. These cropped portions from each  $\theta_i$  are stitched together in order to synthesize a new image, which is a map of the region as a function of  $\theta_i$ , shown in Figure 2.11(b). The rocking curve map in Figure 2.11(b) was synthesized by cropping a rectangle around the region in each diffraction image corresponding to where the (0,1) is, or would be.

Note that not all peaks appearing in the white boxes in Figure 2.11(a) necessarily Enust be from the same rod (though these are). As the images are scanned through, spots may pop up in that region that are from a different rod. Careful analysis of the spacing between adjacent peaks appearing on the rocking curve maps provides a obust fee dback for identifying the corresponding rods.



Figure 2.11: A compiled rocking curve map, revealing the reciprocal space for Si(11) surface. (a) An example of one of the full diffraction images that are colleven at varying incidence angles. A region of interest is selected from each full image, sleve the white boxes. (b) The rocking curve map, compiled along the (0, 1) reciplentice rod, over incidences of  $0.7^{\circ} < \theta_i < 8.2^{\circ}$ ;  $\theta_S$  is the scattering angle.



# Chapter 3

# **Electron Phonon Interaction**

# **3.1 Two-Temperature Model**

Moving to the theoretical side of UEC, when an ultrafast optical pulse impinges the surface of a metal, the energy is absorbed by the free electrons. If the width of the excitation pulse is shorter than the electron-phonon coupling time, a nonequilibrium is established between the electrons and lattice [208]. The Two-Temperature Model (TTM) [209-213] describes such processes for metallic thin films, given by

$$C_e(T_e)\frac{\partial T_e}{\partial t} = -\frac{\partial q_e}{\partial z} - G(T_e - T_i) + S(z, t), \qquad (3.1)$$

$$C_i \frac{\partial T_i}{\partial t} = -\frac{\partial q_i}{\partial z} + G(T_e - T_i), \qquad (3.2)$$

$$q_{e,i} = -\tau_{e,i} \frac{\partial q_{e,i}}{\partial t} - \kappa_{e,i} (T_e, T_i) \frac{\partial T_{e,i}}{\partial z}, \qquad (3.3)$$

Note the laser heating source term, S(z, t), can be described by a Gaussian in time and an exponential spatial decay into the metal:

$$S(z,t) = \sqrt{\frac{4\ln 2}{\pi}} \frac{(1-R)F}{t_p \delta_s} e^{-z/\delta_s} e^{-4\ln 2\left(\frac{t-t_p}{t_p}\right)^2}.$$
 (3.4)

In the above equations, subscripts e and i represent the electron and lattice subsys-



Figure 3.1: The energy coupling scheme assumed by the TTM. First, the laser pulse is absorbed by the free electrons in the metal, which evolve into a Fermi-Dirac distribution in the first  $\approx 50$  fs. The thermal electrons dump energy into the lattice, causing them to equilibrate after  $\approx 1$  ps (depending on the metal). Both electrons and lattice undergo thermal losses from heat diffusion, the rates of which are largely governed by the thermal conductivity,  $\kappa$  (and strictly speaking the heat capacity and sound speed too).

tems, respectively; T is temperature, q is heat flux, C is heat capacity,  $\kappa$  is thermal conductivity,  $\tau$  is relaxation time, and G is the electron-phonon coupling factor. The optical pulse interacts with the film through parameters  $F, t_p, R$ , and  $\delta_s$ , which represent the fluence, pulse width, reflectivity, and optical penetration depth, respectively. Parameters R and  $\delta_s$  depend on wavelength. The electronic heat capacity and phonon relaxation time are given by [208, 214]

$$C_e = \gamma T_e \tag{3.5}$$

and

$$\tau_i = \frac{3\kappa_i}{C_i v_s^2} \tag{3.6}$$

respectively, where  $\gamma$  is the linear coefficient of heat capacity for the metal and  $v_s$  the speed of sound through the metal.

The TTM is nonlinear (through the temperature dependences of  $C_e$  and  $\kappa_e$ ) and coupled through the term  $G(T_e - T_i)$ , which describes electron-phonon interaction. **Parameter** G is inversely proportional to the electron-phonon coupling time,  $\tau_{ep}$ , or the mean time for electron-phonon scattering. In noble metals, such as Au or Ag, the electron-phonon coupling is quite weak compared to transition metals like Pt or Ni because of the unfilled d-bands associated with the latter. When electrons are excited in a metal with core-level vacancies, it is energetically favorable to try to fill them, which is why the electron-phonon scattering rate will be quite fast relative to that of a noble metal. In a noble metal, electron scattering from atomic sites is more 'random,' since they do not possess the attractive vacancy sites for electrons to rush to fill. This is manifested in smaller values of G for Au/Ag than Pt/Ni (or larger  $\tau_{ep}$ );  $G_{Au} = 2.60 \times 10^{16}, G_{Ag} = 2.80 \times 10^{16}, G_{Pt} = 1.09 \times 10^{18}, \text{ and } G_{Ni} = 1.05 \times 10^{18}, \text{ all } G_{Ni} = 1.05 \times 10^{18$ in units of W m<sup>-3</sup> K<sup>-1</sup> [215]. In principle, G has dependence on electron temperature [216], though it is frequently neglected. For a comprehensive study on the bandstructure and temperature dependence of the various thermophysical properties in the TTM, see Reference [215].

Since the advent of the short-pulsed laser (even before<sup>1</sup>), the TTM has been ubiqitous in its employment because of its time-tested robustness in explaining experinental observables. Examples include melting and ablation [141, 192, 212, 217-224], aser-induced desorption of species from surfaces [225-227], electron-phonon coupling [133, 134, 157, 222, 224, 228-241], nanometer-sized particles [129-135, 192, 230, 231, 33, 242, 243], and general thin-film transport and thermo-mechanical properties [142, 222, 223, 233, 236, 237, 244-247]. It is particularly handy for studying ultra-

<sup>&</sup>lt;sup>1</sup>The inaugural publication of the TTM in 1957 pre-dates the invention of the laser [209]. Interstingly, the authors have a passage where they state: "If the lattice temperature is much less than the temperature of the electrons (hardly a practical case), then ...", today it is very much a practical ase with short-pulsed lasers!

fast laser-induced thermionic emission from metals, as the emission fundamentally depends on the electronic temperature [198, 247, 248].

### **3.1.1** Numerical Solution

Equations 3.1-3.4 are numerically solvable by discretizing them in accordance with the MacCormack method, which, simply stated is a predictor-corrector scheme with predictor gradients reaching forward (upwind) and corrector gradients backward (downwind). Quantities  $T_e$ ,  $T_i$ , and  $q_{e,i}$  are marched forward in time by first calculating an auxiliary value (superscript \*) using a forward difference, with upwind spatial gradients. Assigning n and k to be indices of time and space, respectively, the predictor step is given by

$$T_{e_{k}}^{*(n+1)} = T_{e_{k}}^{(n)} + \frac{\Delta t}{\gamma T_{e_{k}}^{(n)}} \left\{ -\frac{\left(qe_{k+1}^{(n)} - qe_{k}^{(n)}\right)}{\Delta z} - G\left(T_{e_{k}}^{(n)} - T_{i_{k}}^{(n)}\right) + S(z,t) \right\},$$

$$T_{i_{k}}^{*(n+1)} = T_{i_{k}}^{(n)} + \frac{\Delta t}{C_{i}} \left\{ -\frac{\left(qi_{k+1}^{(n)} - qi_{k}^{(n)}\right)}{\Delta z} + G\left(T_{e_{k}}^{(n)} - T_{i_{k}}^{(n)}\right) \right\}; \quad (3.8)$$

dropping the subscripts on the heat flux, both  $q_e$  and  $q_i$  are discretized as

$$q_{k}^{*(n+1)} = q_{k}^{(n)} - \frac{\Delta t}{\tau} \left\{ q_{k}^{(n)} + \kappa \frac{\left(T_{k+1}^{(n)} - T_{k}^{(n)}\right)}{\Delta z} \right\}.$$
 (3.9)

The corrected values of  $T_e$ ,  $T_i$ , and  $q_{e,i}$  are given by

$$\mathbf{T}_{e_{k}}^{(n+1)} = \frac{\left(T_{e_{k}}^{*(n+1)} + T_{e_{k}}^{(n)}\right)}{2} + \frac{\Delta t}{2\gamma T_{e_{k}}^{*(n+1)}}$$

$$\times \left\{ -\frac{\left(qe_{k}^{*(n+1)} - qe_{k-1}^{*(n+1)}\right)}{\Delta z} - G\left(Te_{k}^{*(n+1)} - Ti_{k}^{*(n+1)}\right) + S(z,t) \right\}, \quad (3.10)$$

$$T_{i_{k}}^{(n+1)} = \frac{\left(Ti_{k}^{*(n+1)} + Ti_{k}^{(n)}\right)}{2} + \frac{\Delta t}{2C_{i}}$$

$$\times \left\{ -\frac{\left(qi_{k}^{*(n+1)} - qi_{k-1}^{*(n+1)}\right)}{\Delta z} + G\left(Te_{k}^{*(n+1)} - Ti_{k}^{*(n+1)}\right) \right\}, \quad (3.11)$$

and

$$q_{k}^{(n+1)} = \frac{\left(q_{k}^{*(n+1)} + q_{k}^{(n)}\right)}{2} - \frac{\Delta t}{2\tau} \left\{q_{k}^{*(n+1)} + \kappa \frac{\left(T_{k}^{*(n+1)} - T_{k-1}^{*(n+1)}\right)}{\Delta z}\right\}.$$
(3.12)

By inspection, the final values are the average between prediction steps, and the reevaluated functions, in terms of the predictions, this time with 'downwind' spatial gradients.

Figure 3.2 shows an example calculation for a thin Au film of 100 nm, irradiated by a  $50 \text{ mJ/cm}^2$  pulse at 50 fs, calculated using the numerical scheme presented above with original Fortran source code (Appendix F).

### 3.1.2 Extensions to the Two-Temperature Model

There have been numerous extensions to the conventional TTM. The form presented above in Equations 3.1-3.3 is actually the dual-hyperbolic form proposed by Chen [212]; dual because both electrons and lattice employ the non-Fourier variant for heat flux. This, in and of itself, is an extension from the original parabolic form, where the electron heat flux was taken to be Fourier,  $q_e = -\partial T_e/\partial z$ , and  $q_i$  was neglected together [211]. The non-Fourier heat flux has the form of Equation 3.3, which is



Figure 3.2: An example TTM calculation of the electronic  $(T_e)$  and lattice  $(T_i)$  temperatures on the top surface (z = 0) of a 100 nm Au thin film irradiated with a 50 fs laser pulse of 50 mJ/cm<sup>2</sup>. Inset: depth dependence when the pulse is at maximum inside the film (150 fs).

more physical because it assumes a finite propagation speed for heat diffusion, arising from the first term on the  $RHS^2$ .

Recent theoretical efforts in comparing Boltzmann Transport (BT) to the TTM have shown that the former is more accurate when comparing with experiments [249, 250]. Particularly, when the electron mean free path exceeds the material dimension or the excitation pulse is shorter than the electron thermalization time. In these cases, the TTM will have a tendency to over-estimate the electron temperature. This is largely due to ballistic transport of electrons, which is absent from the TTM. Ballistic transport carries electrons away from the surface much more quickly than a diffusional process. Usually ballistic transport is negligible, but, it must be considered when the excitation fluence is relatively high on a material with weak electron-phonon coupling [228, 229]. An example case would be irradiating a thin film of Au or Ag with sub-100 fs pulse at >50 mJ/cm<sup>2</sup> (by no means is this example all-encompassing).

<sup>&</sup>lt;sup>2</sup>RHS/LHS: right-hand side / left-hand side

In cases such as these, the transport of heat carriers through the film proceeds much more rapidly than what is predicted from strictly diffusional terms. One way around this, without resorting to BT calculations, is to augment the laser source term such that it accounts for ballistic transport [212]. Namely, Equation 3.4 becomes

$$S(z,t) = \sqrt{\frac{\omega}{\pi}} \frac{(1-R) F}{t_p(\delta_s + \delta_b) \left[1 - e^{-L/(\delta_s + \delta_b)}\right]} e^{-z/(\delta_s + \delta_b)} e^{-\omega \left(\frac{t-t_p}{t_p}\right)^2}, \quad (3.13)$$

where  $\delta_b$  is the ballistic range of hot electrons and L is the film thickness.

As emphasized by Wellershoff and colleagues in 1999 [229], an electron temperature is *only* established when thermalization is reached within the electron gas (though electrons and lattice may still be under strong nonequilibrium at this point). One of the inherent short-comings of the TTM is the assumption of an instantaneously thermal electron distribution. In reality, the optical pulse creates a non-thermal population, which degenerates into a Fermi-Dirac (thermal) distribution through electronelectron collisions and, to a lesser extent, electron-phonon scattering.

In 2006, Carpene devised a simple, but effective fix for the treatment of the initial, non-thermal, regime [251]. Without rigorous derivation, the author implemented a phenomenological formalism for calculating the initial non-thermal electron distribution, based on a laser-induced, infinitesimal perturbation to the Fermi-Dirac distribution, which is integrated over the time that the laser pulse interacts with the film. The thermal electron distribution no longer interacts with the laser directly. Instead, the laser heating source term is removed from the rate equation for  $T_e$  and replaced with a term representing the relaxation rate between the non-thermal and thermal electron populations,  $\partial U_{ee}/\partial t$ . Equation(3.1) becomes

$$C_e(T_e)\frac{\partial T_e}{\partial t} = -\frac{\partial q_e}{\partial z} - G(T_e - T_i) + \frac{\partial U_{ee}}{\partial t}.$$
(3.14)

Furthermore, there is no reason to preclude the process of non-thermal electron scattering from phonons. Accounting for this process results in a heating source term for the lattice as well,  $\partial U_{ep}/\partial t$ , making the new rate equation for the lattice

$$C_i \frac{\partial T_i}{\partial t} = -\frac{\partial q_i}{\partial z} + G(T_e - T_i) + \frac{\partial U_{ep}}{\partial t}, \qquad (3.15)$$

with the relaxation rates given by

$$\frac{\partial U_{ee}}{\partial t} = \sqrt{\frac{\omega}{\pi}} \frac{(1-R)F}{t_p} \frac{\alpha e^{-\alpha z}}{(h\nu)^2} \int_{-\infty}^{t} e^{-\omega \left(\frac{t'-t_p}{t_p}\right)^2} H_{ee}\left(t-t'\right) dt', \quad (3.16)$$

$$\frac{\partial U_{ep}}{\partial t} = \sqrt{\frac{\omega}{\pi}} \frac{(1-R)F}{t_p} \frac{\alpha e^{-\alpha z}}{(h\nu)^2} \int_{-\infty}^{t} e^{-\omega \left(\frac{t'-t_p}{t_p}\right)^2} H_{ep}\left(t-t'\right) dt', \quad (3.17)$$

where  $\alpha$  is the linear absorption coefficient, which is equivalent to  $1/\delta_s$  in Equation(3.4), and

$$H_{ee}(t-t') = -\frac{e^{-(\omega_1+\omega_2)(t-t')}}{(t-t')^2} [h^2 \nu^2(t-t') + \varepsilon_F^2 \tau_{ee}(1-e^{-\omega_1(t-t')})]$$
(3.18)

$$H_{ep}(t-t') = -\frac{e^{-(\omega_1+\omega_2)(t-t')}}{(t-t')\tau_{ep}}\varepsilon_F^2\tau_{ee}(1-e^{-\omega_1(t-t')})$$
(3.19)

where  $\omega_1 \equiv \left(h\nu/\varepsilon_F \sqrt{\tau_{ee}}\right)^2$  and  $\omega_2 \equiv 1/\tau_{ep}$ .

When integrated<sup>3</sup>, the physical representation of  $H_{ee}$  is the accumulated proportion of absorbed photon energy that has made the transition from the non-thermal to the thermal electron bath;  $H_{ep}$  for non-thermal electrons energy transitioned to the phonon bath. In the limit of an instantaneously thermal electron distribution (the onventional TTM), both  $H_{ee}$  and  $H_{ep} \to (h\nu)^2 \delta(t - t')$ .

<sup>&</sup>lt;sup>3</sup>Strictly speaking,  $H_{ee}$  and  $H_{ep}$  are integral kernels. More physical meaning can be ascribed to the error integration rather than the quantities themselves.

This formulation by Carpene is termed here the non-thermal Two-Temperature Model (nt-TTM). The additional source term to the lattice means it can be heated sooner, and possibly at a faster rate than with the conventional TTM, depending on the magnitude of G. Consequently, the maximum lattice temperature is routinely calculated higher (and occurs sooner) in the nt-TTM than the TTM. Conversely, the maximum electron temperature is calculated lower and occurs later. This is not surprising, since at any given instant during laser pulse absorption, in the thermal model,  $T_e$  receives 100% of the energy, while in the non-thermal model, the energy is subdivided between the two populations. The non-thermal population will not be entirely depleted of its energy until the pulse has passed. By this time, electronphonon losses are under way and some energy was dumped into the lattice already by the non-thermal electron collisions with phonons, thus precluding any possibility of reaching the same temperature as the maximum predicted in the thermal model.

Carpene's method has been integrated here with the TTM in the form of a subroutine call (Appendix F.1) and has since proven to be well worth the effort, as will be shown in Chapter 5, where non-physical results from calculations are predicted for semiconductors in the sub-50 fs time regime.

At this point, inaccuracies in the conventional TTM have been shown for two major cases, and in both, temperatures were over-estimated. In the first case, a strong ballistic transport regime was activated by the laser because of a high fluence applied to a film with weak electron-phonon coupling. In such a case, the non-physically slow **t** ransport of heat carriers (electrons) from the surface, in the form of diffusion, leads **t** • the large  $T_e$  that is calculated near the surface.

The second instance arises when an instantaneous Fermi-Dirac distribution is assumed prior to the electron-electron relaxation time period. Treating this non-thermal istribution as a thermal one is increasingly problematic as photon energy and electron collision frequency increase, and also with decreasing pulse width. The electron collision frequency is, itself, a transient quantity that increases with temperature. It can be generally inferred that higher fluences increase the likelihood of the TTM description breaking down, as the possibility of under-estimating  $T_e$  based on the laser energy would violate energy conservation, since the TTM already assumes that all laser energy is instantly dumped into the free electron system. In other words, if the laser energy is to be re-partitioned in any way,  $T_e$  cannot possibly receive any more of it than what is already 'assigned' to it in the TTM. In that sense, the TTM provides an upper limit on  $T_e$ , and possesses greater accuracy at lower fluences.

Perhaps the largest upgrade of the TTM was performed by Leonid Zhigilei and co-workers [215, 252–258], where a model was formulated that combined the TTM with molecular dynamics. The TTM was used to describe the bulk continuum and an atomistic approach for the surface layers, based on an embedded atom method (EAM) of molecular dynamics (MD). In this model, the TTM is used to calculate the electron temperature for both regions, and the lattice temperature in the subsurface continuum region. The surface layer lattice temperature is calculated for each simulation cell with the expression

$$T_i^{\text{cell}} = \sum_{n=1}^{N^{\text{cell}}} m_n \left( v_n^t \right)^2 / 3k_B N^{\text{cell}}, \qquad (3.20)$$

where  $v_n^t$  is the thermal velocity of the  $n^{th}$  cell and the forces on the cells are calculated from

$$m_n \frac{\partial^2 \mathbf{r}_n}{\partial t^2} = \mathbf{F}_n + \xi m_n \mathbf{v}_n^t, \qquad (3.21)$$

where  $\xi$  represents the temperature dependent electron-phonon coupling frequency. A schematic of the methodology is given in Figure 3.3 [259].



pressure - transmitting / heat - conducting boundary condition

Figure 3.3: The combined atomistic approach at the surface with the TTM for bulk, formulated by Zhigliei *et al* [259]. Electron-phonon coupling in the atomistic region is expressed through the term,  $\xi m_n v_n^t$ , where  $v_n^t$  is the thermal velocity of the  $n^{th}$ cell and  $\xi$  represents the temperature dependent electron-phonon coupling frequency [259].

#### 3.1.3 Thermal Transport in Nanoparticles

An alternative TTM is employed for nanoparticles under ultrafast laser irradiation. Modeling nanoparticle heat transport differs from the bulk in several ways, such that the fundamental physics of the problem must be reformulated, deviating slightly from the conventional TTM for thin films. In addition, some of the various thermophysical parameters are different, such as G due to the reduced electron-phonon coupling time because of increased scattering with the surface.

When considering optical excitation of a thin film, the area of the film is assumed to be larger than laser spot-size. In addition, the optical penetration depth (typically 10-20 nm) is smaller than the film thickness for most cases, which necessitates the inclusion of thermal gradients into the model. As an example, consider a 2 nm Au manoparticle, which has an optical penetration depth of 15.3 nm. Laser heating of the manoparticle is uniform through the particle. Instead of using the form of an expomential decay over the skin depth, like Equation 3.4, the source term is reformulated in terms of the absorption cross-section,

$$S(t) = \sqrt{\frac{\omega}{\pi}} \frac{F}{t_p} \left(\frac{\sigma_{abs}}{V}\right) e^{-\omega \left(\frac{t-t_p}{t_p}\right)^2},$$
(3.22)

where V is the nanoparticle volume and  $\sigma_{abs}$  is the absorption cross-section of the nanoparticle, which must be calculated from the Mie Theory (see Section 6.3).

For a spherical particle, the surface-to-volume ratio increases as 1/R with decreasing particle size. With the large surface-to-volume ratio, an additional cooling channel for the lattice is activated, as heat can be transferred to its surroundings through the surface. This is particularly true when the nanoparticle colloid is immersed in a solvent, as is commonly the case in optical studies [135, 260]. An additional term can be added to the TTM to describe this cooling, such that Equation 3.2 becomes

$$C_i \frac{\partial T_i}{\partial t} = G(T_e - T_i) - \frac{(T_i - 300K)}{\tau_s}, \qquad (3.23)$$

where  $\tau_s$  represents the characteristic time for lattice cooling. The physics of the energy exchange between the nanoparticle and its surroundings are are buried in  $\tau_s$ . Notice that the diffusion term,  $\partial q_i/\partial z$  has been dropped. Neglecting the electronic diffusion term gives

$$C_e \frac{\partial T_e}{\partial t} = -G(T_e - T_i) + S(t).$$
(3.24)

Equations 3.22-3.24 give the TTM for nanoparticles. To re-cap, the changes are:

$$\frac{(1-R)}{\delta_{s}} \to \frac{\sigma_{abs}}{V} \qquad \qquad \frac{\partial q_{i}}{\partial z} \to \frac{(T_{i} - 300K)}{\tau_{s}} \qquad \qquad \frac{\partial q_{e}}{\partial z} \to 0.$$
(3.25)

Before proceeding, a few notes are considered on the lattice cooling rate. The dependence of  $\tau_s$  on nanoparticle radius, R, can vary based on the nature of the cooling. Namely, the cooling is controlled either by the dissipation rate through the interface or through heat-diffusion in the aqueous environment, surrounding the nanoparticle [261]. To examine the diffusion-limited cooling, consider a spherical nanoparticle at some elevated temperature  $T_p$ , cooling through heat-diffusion:

$$\frac{\partial T_p}{\partial t} = \frac{D}{r} \frac{\partial^2}{\partial r^2} [rT_p(r)], \qquad (3.26)$$

where D is the diffusion coefficient of the solvent. After reducing to 1D form via change of variable, this can be solved analytically with a Laplace transform [262]; the solution being of the form

$$T_p(r,t) \propto f(t) \exp\left(-\frac{r^2}{Dt}\right),$$
(3.27)

Thich yields the characteristic decay time associated with a diffusional process,  $\tau \sim D$ . So if a series of size-dependent measurements of lattice cooling found that the decay time were proportional to  $R^2$ , it could be concluded that the decay was function-controlled. Conversely, if the decay rate of the nanoparticle ensued through the terfacial heat transfer, the temperature is described by [260]

$$\frac{4}{3}\pi r^3 C_p \frac{\partial T_p}{\partial t} = -4\pi r^2 \Gamma T_p, \qquad (3.28)$$

There  $\Gamma$  is defined as the interfacial heat conductance. The solution is an exponential descent with characteristic decay time,  $\tau_s = rC_p/3\Gamma$ ; in other words, linear dependence interface-controlled decay. Re-capping:

> $\tau_s \propto R^2 \Rightarrow$  diffusion-controlled  $\tau_s \propto R \Rightarrow$  interface-controlled.

Hu and Hartland found quadratic dependence for colloidal Au nanoparticles of 4-50 nm in an aqueous solution [135]; linear dependence was found for various metals (Au and Pt) and metal alloys (AuPd) in Reference [260].

### **3.2** Boltzmann Transport in Semiconductors

Ultrafast pulsed laser irradiation is an industry standard for processing silicon-based devices; be it micro-machining, annealing, removal of adsorbates (cleaning), etc. [263]. Consequently, there has been a recent flux of theoretical models to describe the energy transport in semiconductors. The more recent work (since 2005) will be briefly out the timed.

In 2005, Chen and colleagues formulated a self-consistent model for transport dymain is semiconductors subjected to ultrafast laser irradiation, using the relaxationtime approximation of the Boltzmann equation [264]. Model simulations on Si and ce demonstrated strong accuracy in predicting damage thresholds for varying pulseich and fluence, when the lattice temperature was below the melting point (carrierich and gued damage).

With a similar model, in 2007, Korfiatis and colleagues performed a study on demage thresholds in Si, with emphasis on differentiating thermal from non-thermal beased damage, and also the dependence of melting threshold characteristics on wavelength [265]. In 2009, they again simulated damage characteristics associated with Si with an expanded model to account for ablation depth, this time with emphasis on creater formation and morphology [266].

Also in 2009, Qi and Suh developed an extensive model for Si transport with sector al key expansions: (1) the inclusion of thermo-mechanical coupling, (2) multidimensionality, (3) long time scale integration without compromising short time scale presesses. In other words, full treatment of each valid time scale, from electronphonon coupling ( $\sim 1$  ps) to the necessary integration times to examine thermomechanical processes of about 1 ns. The model and its results are published as two parts [267, 268].

Here, the model by Chen and colleagues [264] will be given and solved, as it is frequently invoked in ultrafast laser heating of Si, which is one of the primary topics of this work. It is similar to the Two-Temperature Model (TTM) for metals, presented in Section 3.1, though it involves a third rate equation, in addition to electron and phonon temperature, which is governing equation for carrier generation and recombination. In metals, the carrier density is assumed constant in the TTM. In one-dimensional form, the coupled system of partial differential equations, termed here as the Boltzmann-Transport Model (BTM), is given by

$$\frac{\partial n}{\partial t} = \frac{\alpha I(z,t)}{h\nu} + \frac{\beta I(z,t)^2}{2h\nu} - \gamma n^3 + \theta n - \frac{\partial J}{\partial z},$$
(3.29)

$$C_{eh}\frac{\partial T_e}{\partial t} = (\alpha + \Theta n)I(z,t) + \beta^2 I(z,t)^2 - \frac{\partial W}{\partial z} - \frac{C_{eh}}{\tau_{ep}}(T_e - T_i) - \frac{\partial n}{\partial t}(E_G + 3k_B T_e) - n\left(\frac{\partial E_G}{\partial n}\frac{\partial n}{\partial t} + \frac{\partial E_G}{\partial T_i}\frac{\partial T_i}{\partial t}\right),$$
(3.30)

$$C_{i}\frac{\partial T_{i}}{\partial t} = \frac{\partial}{\partial z}\left(\kappa_{i}\frac{\partial T_{i}}{\partial z}\right) + \frac{C_{eh}}{\tau_{ep}}(T_{e} - T_{i}), \qquad (3.31)$$

$$J = -D\left\{ \left(\frac{\partial n}{\partial z}\right) + \frac{n}{2k_B T_e} \left(\frac{\partial E_G}{\partial z}\right) + \frac{n}{2T_e} \left(\frac{\partial T_e}{\partial z}\right) \right\},\tag{3.32}$$

$$W = (E_G + 4k_B T_e) J - (\kappa_e + \kappa_h) \left(\frac{\partial T_e}{\partial z}\right), \qquad (3.33)$$

where carrier heat capacity is given by

$$C_{eh} = 3nk_B + n\frac{\partial E_G}{\partial T_e},\tag{3.34}$$

and the laser source term is described by

$$I(z,t) = \frac{(\alpha + \Theta n) I_0(t) e^{-(\alpha + \Theta n)z}}{(\alpha + \Theta n) + \beta I_0(t) \left[1 - e^{1 - (\alpha + \Theta n)z}\right]},$$
(3.35)

where  $I_0(t)$  represents the temporal dependence of the laser source, which is given by **the** Gaussian function

$$I_0(t) = \sqrt{\frac{\omega}{\pi}} \frac{(1-R)F}{t_p} e^{-\omega[(t-3t_p)/t_p]^2},$$
(3.36)

and  $\beta$  represent the 1- and 2-photon absorption coefficients respectively;  $\gamma$ ,  $\theta$ ,  $E_G$ , and  $\Theta$  are the Auger recombination coefficient, impact ionization coefficient, band gap ergy, and free carrier absorption cross-section, respectively. Constitutive Equations 3 - 32 and 3.33 represent the carrier current (J) and ambipolar energy current (W), respectively. Parameters are given in Table 3.1, with their empirical functional deendences, if applicable.

## **33** - 2.1 Numerical Scheme

Boltzmann Transport Model (Equations 3.30-3.33) is solved using a staggered Sh (Figure 3.4) [264] with spatial gradients given by central difference. Forward marching is carried out through a 3rd order Runge-Kutta scheme with total Marchine is carried out through a 3rd order Runge-Kutta scheme with total Marchine (TVD) implemented [279-281], with sealed boundaries:

$$J(0, L; t) = W(0, L; t) = q(0, L; t) = 0,$$
(3.37)

and initialization given by

$$n(z,0) = 10^{12} \text{ cm}^{-3}$$
  $T_e(z,0) = T_i(z,0) = 300 \text{ K.}$  (3.38)

Property		Expression
<i>▶i</i> (W/cm K)	[269]	$1585 T_i^{-1.23}$
$C_i ~(J/cm^3)$	[269]	$1.978 + 3.54 \times 10^{-4} T_i - 3.68 / {T_i}^2$
$\kappa_{e,h}~(\mathrm{eV/s}\mathrm{\AA K})$	[270]	$-3.47 \times 10^8 + 4.45 \times 10^6 T_e$
$\tau_{ep}$ (fs)	[128]	$240 \left[ 1 + (n/6.0 \times 10^{20} \text{ cm}^{-3})^2 \right]$
$\gamma ~({ m cm^6/s})$	[271]	$3.8  imes 10^{-31}$
$\mathbf{e}$ (s <sup>-1</sup> )	[272]	$3.6 \times 10^{10} \exp(-1.5 E_G / k_B T_e)$
$\mathcal{D} \ (\mathrm{cm}^2/\mathrm{s})$	[273]	$18(300 \text{ K}/T_i)$
$\mathcal{I}_{G}(\mathrm{eV})$	[274]	$1.16 - 7.02 \times 10^{-4} \frac{T_i^2}{(T_i + 1108)} - 1.5 \times 10^{-8} n^{1/3}$
<b>R</b> (800 nm)	[275]	$0.370 + 5 \times 10^{-5} (T_i - 300 \text{ K})$
R (400 nm)	[275]	$0.541 + 5 \times 10^{-5} (T_i - 300 \text{ K})$
$\frown$ (cm <sup>-1</sup> ) (800 nm)	[265]	$5.02  imes 10^3 \exp(T_i/430)$
$\frown$ (cm <sup>-1</sup> ) (400 nm)	[276]	$5.51  imes 10^4 \exp(T_i/420)$
✓ (cm/GW) (800 nm)	[277]	1.8
Cm/GW) (400 nm)	[128]	10.0
rightarrow (cm <sup>2</sup> )	[278]	$5.1 \times 10^{-18} (T_i/300 \text{ K})$
Tre*		0.19

Table 3.1: Silicon input parameters for the Boltzmann Transport Model.



Figure 3.4: The spatial discretization mesh used for the Boltzmann Transport model Calculation prescribed by Chen *et al* [264].

Rather than discretizing the entire model, only the essentials of the TVD scheme  $\mathbf{x}$  represented for an arbitrary equation,  $\partial \phi / \partial t = L[\phi, \phi; z, t]$ . Using time and space  $\mathbf{x}$  dices, n and k, respectively, the TVD scheme is given by computing two auxiliary  $\mathbf{x}$  teps and then the updated value in terms of the auxiliary values:

$$\phi^{(1)} = \phi^{(n)} + \Delta t L(\phi^{(n)}, t^{(n)}), \qquad (3.39)$$

$$\phi^{(2)} = \frac{3}{4}\phi^{(n)} + \frac{1}{4}\phi^{(1)} + \frac{1}{4}\Delta t L(\phi^{(1)}, t^{(n)} + \Delta t), \qquad (3.40)$$

$$\phi^{(n+1)} = \frac{1}{3}\phi^{(n)} + \frac{2}{3}\phi^{(2)} + \frac{2}{3}\Delta tL\left(\phi^{(2)}, t^{(n)} + \frac{\Delta t}{2}\right).$$
(3.41)

This method for the time-stepping is different than the one prescribed by Chen *al.* for this model, which was a forward difference. The reason for this is that the merical 'stiffness' of this system was found to increase as the excitation pulse was *cle* shorter, more intense, or more energetic  $(t_p \downarrow, F \uparrow, \lambda \downarrow)$ . In general, the *ulation* requirements here exceed those used in Reference [264], which is likely why *the* method they prescribed did not hold up for most of the cases considered here. *addition*, the 3rd order RK scheme allows for the choice of a slightly larger time
step than used by Chen and colleagues  $(5 \times 10^{-20} \text{ s})$ , which cuts down computation time.

An example calculation is given in Figure 3.5, depicting the depth dependence of the electronic temperature,  $T_e$ , for several selected times prior to 1 ps. In general, the *s*patial gradients are only steep enough to be active in the early times ( $\leq 1$  ps), when the laser pulse is being absorbed by the film. The 45 fs pulse is completely absorbed **int** to the film by 250 fs. In other words, the laser source term given in Equation **3**.35 has zero amplitude by this time. The depth dependences of lattice temperature **a...** d carrier density are given in Figure 3.6. Example calculations depicting temporal **d e** pendences are presented in Section 3.2.2.

The carrier density, n, reaches its maximum concurrently with the laser pulse (mear  $\approx 135$  fs) and changes very slowly compared to  $T_e$ . This is why only 45 fs and 1 ps curves are plotted for n in Figure 3.6; those of 250 and 500 fs are nearly identical to 1 ps. It is not a surprise because the carrier density speed should be less than that of the electron thermal energy. The thermal energy propagates through carrier collisions, which is more efficient than actually displacing carriers, as they will identical before traveling very far. A simple calculation confirms this (in addition the BTM calculations in Figures 3.5 and 3.6). A rough estimate of the carrier density speed is given by  $v_n \sim \alpha D \approx 450$  m/s. A similar estimate can be made for the electronic thermal propagation speed,  $v_T \sim \alpha(\kappa_e/C_{eh}) \approx 2500$  m/s, nearly an culations show the difference between chemical and heat diffusion speeds.

Note, the lattice temperature was not mentioned (because it is still ramping up), its speed is much slower than that of the electrons because the heat capacity of lattice is more than 1000 times greater than that of the electrons, while their the mal conductivities rarely differ by more than a factor of 10 (both are functions of temperature).



**Theorem 1** gure 3.5: The depth dependence of the electronic temperature,  $T_e$ , plotted at 50, **100** for  $t_p = 45$  fs, **100** fs. Here, the thickness  $L = 60 \ \mu m$ , the pulse duration  $t_p = 45$  fs, **100** d the fluence  $F = 35 \ mJ/cm^2$ .



is gure 3.6: The depth dependence of the lattice temperature,  $T_i$ , plotted at 50 fs ( $d_i$ ), 250 fs (green), 500 fs (blue), and 1 ps (orange), for  $L = 60 \ \mu m$ ,  $t_p = 45$  fs,  $d_i F = 35 \ mJ/cm^2$ . Inset: Carrier density, n, plotted as a function of depth (y-is is log); n reaches maximum at  $\approx 140$  fs, which is 5 fs after the laser pulse is at  $E_{auxtion}$  and  $t_p$  set to 45 fs; initiated 3 pulse widths before time zero, shown  $E_{auxtion}$  3.36).

### 3.2.2 Non-thermal Regime

The nonequilibrium regime associated with the internal relaxation of the electron gas to a Fermi-Dirac distribution was treated by implementing the formalism of Carpene [251], as was done in Section 3.1.2 for the TTM. The formalism is essentially the same; the laser source term is removed from Equation 3.30, and replaced by  $\partial U_{ee}/\partial t$ , which is identical to Equation 3.16, and a source term is added to the lattice (Equation 3.31), which is  $\partial U_{ep}/\partial t$  from Equation 3.17. An additional step, beyond Carpene's model must also be taken with the BTM. Namely, that is to subdivide the carrier density into thermal and non-thermal populations. To do this, a dimensionless quantity representing the proportion of carriers that have made the transition from non-thermal to the thermal population is defined, P(t), given by<sup>4</sup>

$$P(t) \equiv \frac{\int_0^t H_{ee}(t-t')dt'}{(h\nu)^2}.$$
(3.42)

figure a matter of convenience, the RHS of Equation 3.29 is defined as  $\tilde{F}(n,t)$ . The termal population of electrons,  $\tilde{n}(t)$ , is given as

$$\frac{\partial \tilde{n}}{\partial t} = P(t) \ \tilde{F}(n,t)|_{n \to \tilde{n}}, \tag{3.43}$$

it the Equation 3.29 now representing the non-thermal population. Furthermore, in Let  $\mathbf{i}$  be last two terms in Equation 3.30, the *n* and  $\partial n/\partial t$  parts are replaced by their Let  $\mathbf{i}$  be remained counterparts,  $\tilde{n}$  and  $\partial \tilde{n}/\partial t$ . This formulation is termed here the non-thermal Let  $\mathbf{i}$  be remained to the interpart of the interp

To appreciate the importance of proper treatment of the non-thermal regime, it is seful to examine it along-side the conventional model, which is done in Figure Note that the units of  $H_{ee}$  are [Energy]<sup>2</sup>/[time], so P(t) can be thought of as the square energy of incident photons to the converted-thermal energy, at time t.



**i** gure 3.7: An example calculation for the nt-BTM performed on silicon. The fluence, wellength, pulse width, and thickness are 35 mJ/cm<sup>2</sup>, 800 nm, 45 fs, and 50  $\mu$ m, spectively. Inset: Zoomed-in view of the first 500 fs. 3.8. Focusing on the thermal case for a moment, it is striking that the electronic temperature ramps up dramatically (to  $\approx 1800$  K) in Figure 3.8 when only the front tail of the laser has entered the film (6% of maximum). The reason for this is that the carrier heat capacity,  $C_{eh}$ , increases approximately linearly with n (see Equation 3.34), and the temporal profile of the carrier density follows that of the laser (see Figure 3.9, inset). When the electrons receive just a small portion of laser energy, the temperature is drastically raised because the heat capacity is still 'waiting' for n to reamp up. At this instant, it is still 8 orders of magnitude lower than what it will be  $\mathbf{v}$  hen n reaches maximum<sup>5</sup>.



Sure 3.8: A comparison of the BTM and nt-BTM. The fluence, wavelength, pulse th, and thickness are  $35 \text{ mJ/cm}^2$ , 800 nm, 45 fs, and  $50 \mu \text{m}$ , respectively. Inset: med-in view of the first 500 fs. The laser temporal profile is shown in orange. For thermal case,  $T_e$  reaches 1800 K with the laser at only 6% of its maximum. Inset: tice temperature,  $T_i$ .

The early rise of  $T_e$  was noted by Chen and colleagues in Reference [264], however they did not ment on the physical validity of the observation.

But is this physically valid? The answer is no, because it occurs over a time period that precedes the electron-electron scattering time. The temperature could not exhibit such changes in the absence of electron scattering events. Strictly speaking, even the use of the word 'temperature' is incorrect, since it is an ill-conceived quantity prior to electron thermalization. Notice that the nt-BTM result has not yet responded during this time. Furthermore the BTM over-estimates temperature by 37% for the **case** considered in Figure 3.8. The importance of properly treating this small window **of** time is abundantly clear, as accuracy is sacrificed otherwise.

### **3.2.3** Quasi-Fermi Levels

Under nonequilibrium conditions in a semiconductor, the electron and hole concentrations require separate descriptions for their respective occupation levels, termed Quasi-Fermi levels,  $\phi_c$  (subscript c, carrier, means it could be electron or hole). With the carrier temperature,  $T_c$ , and density,  $n_c$ , evaluated,  $\phi_c$  can be calculated by imlicitly solving

$$n_c = N_c(T_c) \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x}}{1 + \exp(x - \eta_c)} \, dx, \qquad (3.44)$$

**Solution** There  $N_c(T_c)$ , the effective density of states, is expressed as

$$N_c(T_c) = 2 \left[ \frac{m_c^* k_B T_c}{2\pi\hbar^2} \right]^{3/2},$$
(3.45)

 $\mathbf{T}_{\mathbf{r}}$  d the scaled reduced Fermi level,  $\eta_c$ , is expressed for electrons (e) and holes (h) (in  $\mathbf{r}_{\mathbf{r}}$  is of  $k_B T_c$ ) as

$$\eta_e = \frac{\phi_e - E_C}{k_B T_e},\tag{3.46}$$

and

$$\eta_h = \frac{\phi_h - E_V}{k_B T_e}.\tag{3.47}$$

In principle, it is straight-forward to supplement the Boltzmann Transport algorithm with the calculation of the quasi-Fermi level. However, since  $\phi_c$  cannot be isolated in Equation 3.44, it must be determined numerically. It is convenient to define a quantity representing the quasi-Fermi level relative to the conduction band  $edge^{6}$  since it is more intuitive (termed the reduced Fermi level):

$$\mu_e^* = \phi_e - E_C. \tag{3.48}$$

Solving Equation 3.44 for  $\eta_e$  is performed via the Newton-Raphson method [282], which has the general form

$$x^{l+1} = x^l - \frac{f(x^l)}{f'(x^l)},$$
(3.49)

where f(x) = 0 (it is the RHS minus the LHS of the equation to be solved).

For the case here, it is convenient to begin with the following definitions:

$$A \equiv \frac{n_e(t)}{N_e(T_e)},\tag{3.50}$$

$$F_{\nu}(\eta_e) \equiv \frac{1}{\Gamma(\nu+1)} \int_0^\infty \frac{\sqrt{x}}{1 + \exp(x - \eta_e)} \, dx, \qquad (3.51)$$

$$f(\eta_e) \equiv A - F_{1/2}(\eta_e).$$
 (3.52)

Equation 3.51 are the familiar Fermi integrals; exploiting their simple differentiarules, the derivative of Equation 3.52 is

$$f'(\eta_e) = -F'_{1/2}(\eta_e) = -F_{-1/2}(\eta_e). \tag{3.53}$$

is At this point, the subscript c is dropped and only the quasi-Fermi level associated with electrons nsidered (holes are discarded).

By inspection of Equations 3.44 and 3.52, any  $\eta_e$  such that,  $f(\eta_e) \neq 0$ , must be incorrect. While not correct, evaluating the function and its derivative at this value produces a new value that is closer to to the correct one (the essence of the Newton-Raphson method). The correct  $\eta_e$  can be found by successive iteration:

$$\eta_e^{(l+1)} = \eta_e^{(l)} - \frac{f(\eta_e^{(l)})}{f'(\eta_e^{(l)})}.$$
(3.54)

While simple, this method is quite powerful. Calculation of  $\eta_e$  is performed at each time step within the Boltzmann Transport PDE<sup>7</sup> solving program. Since  $\eta_e$ does not change significantly from one time step to the next<sup>8</sup>, the initial guess of  $\eta_e$ on successive time steps is fairly close to the converged value. Mathematically, that is to say that the losses incurred in calculation speed from adding this iterative section to the BT solver are minimal because  $\Delta t$  is chosen, such that

$$\frac{|\eta_e(t+\Delta t)-\eta_e(t)|}{|\eta_e(t)|} \ll 1.$$
(3.55)

Thus faster converging methods, which would require higher order derivatives, The unnecessary here. The transient behavior of the quasi-Fermi level displays large fifterences between the cases when the non-thermal regime is treated correctly and hen it is assumed thermal (Figure 3.9).

PDE: partial differential equation.

Convergence requires that time steps are chosen small, such that no quantities change too rapidly the course of one step.



igure 3.9: The quasi-Fermi level is plotted for both the BTM (green) and nt-BTM blue). Compared to all other quantities,  $\mu_e$  exhibits the largest difference between the two models because it depends on both  $T_e$  and  $n_e$ . The nt-BTM is more physical the Fermi gas should be nearly degenerate before electron scattering commences, thich the nt-BTM closely resembles. The BTM curve actually drops below the lence band edge, which is non-physical. Inset: The carrier density, plotted for both odels with the laser temporal profile shown in orange.



# 3.3 Discussion

A comprehensive introduction to the Two-Temperature Model, which is frequently invoked for data analysis, has been presented. For example, the thermal expansion coefficient for most materials is well-established [195, 283]. With Debye-Waller analysis of the Bragg peak motion, the lattice temperature of the system can be measured with UEC. The TTM provides a convenient secondary check on the value.

The model for nanoparticles has been used in conjunction with the Mie scattering formalism to explain recent UEC experimental observations pertaining to Ag nanoparticles, which is not included in this work, but can be found in Reference [193]. The full Mie scattering formalism shall be presented in Section 6.3 with example temperature calculations for Ag and Au.

The Boltzmann Transport model for silicon is the most frequently employed of all the models presented in this work. Results from the nt-BTM will be invoked in Chapters 4 and 5.

# Chapter 4

# Ultrafast Electron Diffractive Voltammetry

## 4.1 Introduction

To most scientists, the word 'diffraction' carries with it the connotation of resolving structures. Rightfully so, since diffraction, in its various forms, has been the work horse for resolving crystal structures and lattice constants for most of the last century. When a coherent electron beam is scattered off the crystal planes, such as with UEC, a natural question that arises is, should one be concerned with electrostatic interactions with local fields near the surface; specifically, those not having to do with the inner (crystal) potential. As will be demonstrated in this chapter, the answer is yes; particularly in RHEED<sup>1</sup> or LEED<sup>2</sup> geometries, where the incident beams have small momentum components normal to the crystal. In general, electric fields near surfaces have their strongest components normal to the surface, since this is where the **symmetry** is broken (there is no reason for charge to separate in-plane unless there **is a** boundary, crack, defect, etc.).

<sup>&</sup>lt;sup>1</sup>**RHEED**: reflective high energy electron diffraction.

<sup>&</sup>lt;sup>2</sup>LEED: low energy electron diffraction.

Traditionally, the charge-based deflection of the electron beam has been regarded as an artifact or source of systematic error for electron crystallography measurements [284]. However, with careful analysis, the electron beam can be used as a charge-sensitive probe, and it is generalizable to complex geometries and interfacial structures. Furthermore, since it is the pump laser pulse that is responsible for generating the near-surface field(s) (more on this later), the technique is inherently time-resolved. Over the past two years, Ultrafast Electron Diffractive Voltammetry (UEDV) has emerged as a formidable technique for measuring phenomena associated with charge separation near surfaces [107, 194, 285]. In addition, there have been similar efforts to use an electron beam to measure charge-based phenomena, though not diffractive. Miller and colleagues conducted a pump-probe study where an optically ablated plume was probed with an electron beam. The electric field was quantified based on the deflection of the direct beam spot on the CCD screen [286]. In 2009, Park and Zuo conducted a similar experiment, where they flew the direct beam over the sample and monitored the deflection arising from pump-induced surface charging [287].

Historically, the available measurement techniques for surface potentials have been sparse. Cowley proposed a novel method for surface potential measurement using a nanometer-sized probe in a STEM [288]. With this, the central spot of the microdiffraction pattern will stretch and warp, which can be analyzed to determine some properties of the surface potential. Sufficiently large, flat crystal faces are necessary. Gold, being inert, was a model system, on which the technique was employed successfully for the (111) surface [289]. It is not a direct measurement of surface potential, since it requires careful analysis of the streaking lengths (associated with the central spot) calculated from a modified image barrier model, and also an *a-priori* presumption of the functional form of the potential.

More recently, Spence and colleagues considered the possibility of Convergent-Beam Low Energy Electron Diffraction (CBLEED) to map the potential associated with a surface dipole layer. There, a nanometer-sized probe was proposed in conjunction with CBLEED rocking curve measurements to deduce the surface potential [290]. With the convergent-beam geometry, many orders can be recorded at once in the reflection rocking curve due to the small probe (nm). The associated intensity variations are sufficiently sensitive to surface dipole layer parameters, such that the surface potential could be accurately deduced from multiple scattering calculations. Calculation of the LEED patterns with the inclusion of a surface potential (superimposed on the crystal inner potential), would allow for simulation of an observed CBLEED pattern. It is important to note that this was a proposal for a developing a CBLEED apparatus, accompanied with multiple scattering calculations. The measurements for the surface dipole layer depend on accurate knowledge of the imaginary part of the inner potential (pertaining to multiple scattering and other electron extinctions [207]). Due to contemporary advances in items such as energy filters, cooling stages, CCD detectors, and most notably, convergent-beam geometry, determination of the multiple scattering effects from raw diffraction patterns has become realizable<sup>3</sup> [291]. Spence and colleagues concluded that CBLEED was worthy of further development based on measurements of multiple scattering phenomena, formerly unavailable, coupled with calculation of the patterns.

# 4.2 Coulomb Refraction

The term 'surface potential' has a long standing history in semiconductor physics as pertaining to a space-charge region (SCR), arising from depletion (majority carrier concentration at the surface is less than the bulk level), accumulation (majority carrier near surface is greater than in bulk), or inversion (minority carrier concentration

<sup>&</sup>lt;sup>3</sup>In Reference [290], these advances were termed as a 'minor revolution.'

exceeds that of the majority carrier). The fields measured by UEDV can and do pertain to an SCR, but it is not the only constituent when the system is driven far from its equilibrium with the pump laser. The primary sources of the pump-induced field near the surface will be discussed in detail, but for now, note that the potential measured by UEDV is not limited to that associated with an SCR. Before exploring the field sources, the measurement technique will first be detailed along with the formalism for quantifying the 'Coulomb refraction' of the scattered beams.

Refraction, a term typically reserved for photons as they propagate through different media, can be used analogously to describe electron propagation through crystalline media, where the index of refraction is given by [292, 293]

$$n_e = \sqrt{\frac{V_0 + eV_s}{V_0}},$$
(4.1)

with  $V_0$  and  $V_s$  being the accelerating and surface voltages, respectively. The case of an incident electron beam with kinetic energy  $K = eV_0$  impinging a crystal at an angle  $\theta_i$  with respect to the surface plane is depicted in Figure 4.1. Under normal conditions, where there is no field near the surface, it scatters from the crystal planes and exits the surface at an angle  $\theta_0$ . The addition of a constant electric field in the probe volume augments the trajectory. The incident electron is refracted deeper into the crystal than it otherwise would have been; the diffracted electron traveling to the surface (exiting) is impeded by the electrostatic forces (from  $V_s$ ), such that it exits at an angle  $\theta'_o$ , which is shallower than  $\theta_o$ . The surface potential,  $V_s$ , is generally small compared to the inner potential,  $U_{IP}$ , such that both the refracted and unrefracted beam paths scatter through the same Bragg angle,  $\theta_B$ . In other words, the intrinsic momentum transfer that the crystal exerts on the beam is conserved. Accordingly, the Bragg condition remains intact, regardless of the presence of a field, which implies

$$\sin\theta_o + \sin\theta_i = \sin\theta'_o + \sin\theta'_i = N_{hkl}\frac{\lambda_e}{d_{hkl}}.$$
(4.2)



Figure 4.1: Two different electron trajectories shown; one with no surface potential present (light-gray) and the augmentation of the trajectory due to a surface potential,  $V_s$  (black). The magnitude of the surface potential can be deduced from the vertical displacement of the peak on the CCD screen.

From the characteristics of the trajectory with and without a field present, a relationship can be formulated between the shift in the trajectory and the surface potential, effectively quantifying the Bragg peak shifts.

#### 4.2.1 Slab Model

Using Equation 4.2, and invoking all of its assumptions, a relationship can be formulated for  $V_s$  in terms of experimentally known quantities,  $\theta_i$  and  $\theta_o$ , as is done here for a simple slab geometry like the one depicted in Figure 4.1. Assuming a constant electric field with no tangential components, the energy gained or lost by propagating through  $V_s$  should be solely reflected in the vertical momentum, such that

$$p_{z'_i}^2 - p_{z_i}^2 = 2m_e(K' - K) = 2m_e V_s \tag{4.3}$$

and

$$p_{z_0'}^2 - p_{z_0''}^2 = 2m_e(K' - K) = 2m_e V_s, \qquad (4.4)$$

where  $K' = e(V_0 + Vs)$  and the vertical momenta are given by

$$p_{z_i'} = p_x \tan \theta_i', \tag{4.5}$$

and

$$p_{z_i} = p_x \tan \theta_i, \tag{4.6}$$

with analogous relationships for  $\theta'_o$  and  $\theta''_o$ . Using  $p^2/2m_e = eV_0$ , Equation 4.3 becomes

$$\tan^2 \theta_i' = \tan^2 \theta_i + \frac{\chi}{\cos^2 \theta_i},\tag{4.7}$$

where  $\chi \equiv V_s/V_0$ , and Equation 4.4 becomes

$$\tan^2 \theta'_o = \tan^2 \theta''_o + \frac{\chi}{\cos^2 \theta''_o},\tag{4.8}$$

Using the Bragg condition (Equation 4.2), from Equations 4.7 and 4.8, the quantities  $\theta'_i$  and  $\theta'_o$  can be suppressed in favor of  $\theta_i$  and  $\theta''_o$ , to give

$$\Delta_B = \sin^{-1} \sqrt{\frac{D^2 - \chi}{1 + D^2} - \theta_0},\tag{4.9}$$

where

$$D = \frac{\tan(\theta_o + \theta_i) - \sqrt{\tan^2 \theta_i + \chi/\cos^2 \theta_i}}{1 + \tan(\theta_o + \theta_i)\sqrt{\tan^2 \theta_i + \chi/\cos^2 \theta_i}},$$
(4.10)

and the shift in the outgoing angle,  $\Delta_B \equiv \theta_o - \theta''_o$ . A useful exercise for investigating the parameter space is to calculate the Bragg peak shift,  $\Delta_B$ , over a series of varying angles  $\theta_i$  and  $\theta_o$ , which is shown in Figure 4.2. By inspection, it is immediately clear that the larger shifts are expected for small  $\theta_i$  and  $\theta_o$ . In other words, the maximum shifts are expected for the lowest order peaks observed, at the shallowest incidence angles. This is consistent with expectations, as the electrons that are propagating nearly parallel to the surface will spend more time in the field, and should be deflected more as a result.



Figure 4.2: The parameter space of Equation 4.9 for  $V_s = 3.0$  V. Small values of both  $\theta_i$  and  $\theta_o$  imply a small momentum component normal to the surface, which means the effect from the field is more pronounced, as reflected in the larger peak shifts,  $\Delta_B$ .

With additional algebra, and substituting back in for  $\chi$ , an expression can also be formulated that gives the surface potential,  $V_s$ , as a function of  $V_0$ ,  $\theta_i$ ,  $\theta_o$ , and the observable Bragg peak shift,  $\Delta_B$ , by inverting Equation 4.9, which is

$$\frac{V_s}{V_0} = \frac{\left(\theta_o \Delta_B - \theta_i \theta_o + \Delta_B^2 / 2\right)^2 - \theta_i^2 \left(\theta_o + \Delta_B\right)}{\left(\theta_i + \theta_o\right)^2}.$$
(4.11)

This expression has several assumptions: (1) The electric field at the surface is homogeneous, has negligible tangential components, and spans the entire depth of the probe region. (2) The spot size of the probing electron beam is much smaller than that of the excitation laser, such that there are no edge effects from the field as the beam enters or exits the crystal. Accordingly, the transverse momentum components remain unchanged for all cases considered. (3) The effect of  $V_s$ , does not interfere with the inner potential ( $V_{IP}$ ) from which usual electron scattering commences, such that the Bragg angle,  $\theta_B$ , is conserved in the presence of  $V_s$ . In other words, the intrinsic manner of the diffraction is unchanged.

### 4.3 Generation of Near-Surface Fields

The electric field, which is responsible for Coulomb refraction, arises from a photoinduced charge separation from the pump laser. However, this description is still rather vague when considering the possible ways in which charge can separate. In this section, the aim is to clearly identify the different constituents of the measured transient surface voltage (TSV) and discuss their respective roles in Coulomb refraction.

### 4.3.1 Field Constituents

A qualitative assessment of the various field sources shall be outlined first. The work function for most materials is ~4-5 eV, and the excitation laser employed here can be operated at energies of 1.55 (800 nm) or 3.10 eV (400 nm)<sup>4</sup>. For both energies, the 2-photon absorption cross-section is non-negligible (longer wavelengths result in increased multiphoton absorption events [277, 278, 294, 295]). Clearly, the 3.1 eV excitation pulse is capable of directly ejecting electrons through multiphoton emission. While 3-photon processes have rather small cross-sections at 800 nm [294, 295], which would be necessary to directly overcome the work function in most materials, 2-photon

<sup>&</sup>lt;sup>4</sup>In principle, the frequency-tripled 267 Hz beam could also be used to pump the sample, though, to date, it has only been used for photo-electron generation with the electron gun

processes with an 800 nm excitation are quite common, especially with moderate to high laser intensities [277].

Multiphoton absorption in conjunction with the wide Fermi distribution associated with a hot electron distribution makes thermionic emission also quite plausible [247, 248, 296–298]. Generally speaking, a photoemitted charge distribution, denoted here as  $\sigma_{vsc}$ , should be considered in the TSV measurement [200]. Its contribution can be suppressed (or enhanced), depending on the system, excitation fluence, pulse-energy, and pulse-width. The effect of vacuum emission is depicted schematically in Figure 4.3.



Figure 4.3: Mechanisms associated with vacuum emission. (a) Multiphoton absorption can supply sufficient energy for an electron to overcome the work function. (b) With thermionic emission, the quasi-Fermi level need not be above the work function, as the width of the Fermi distribution is sufficiently broad because the electrons are hot. As the tail rises above the work function, electrons are emitted into the vacuum.

Another possibility is that of a space-charge region established in the bulk due to the electronic occupation of surface states [81, 126, 299]. When a semiconductor, such as silicon, is irradiated with an ultrafast laser, electron-hole pairs are generated in the bulk. Under normal circumstances, these electrons and holes will relax to their respective band edges (conduction or valence) and recombine [300]. Should there be an abundance of available surface states in the system (e.g. because the surface is oxidized [107, 122, 301] or due to a reconstruction [126, 302]), it is plausible that a portion of the highly excited electrons may find a lower energy cost in occupying these states than relaxing to the conduction band minimum, thus establishing a potential gradient, as the bulk responds to the lost charge. The lifetime of surface or trap states [87, 107, 126] plays a crucial role in determining the bulk response. This lifetime is affected by the coupling strength between surface and bulk evanescent states, tunneling (or leakage) currents [87, 90, 303], etc. This sub-surface field should be considered in TSV measurements, particularly in a system with poor screening.

Another possible contribution to the field is that of the surface dipole layer. [36, 54, 194, 290, 304–310], which arises from the charge relaxation associated with the termination of crystal structure at surfaces. The surface dipole layer is central to the fundamental mechanisms in processes such as chemisorption of self-assembled monolayers on metals and semiconductors [49, 54, 311], charge transfer at metalsemiconductor heterojunctions [312], dye-sensitized solar cells [313], organic light emitting diodes (OLEDs) [314], and even molecular patterning [315]. A static dipole is known to form at the Si/SiO<sub>2</sub> interface due to charge transfer induced by a difference in electronegativity between Si atoms and SiO<sub>2</sub> molecules [306]. The surface dipolar field region can be enhanced by further charge separation from photoexcitation, where an upper surface sheet is occupied by one charge and the lower by the counter charge [194]. A summary of the TSV that the incident electron beam sees as it scatters from the crystal is shown in Figure 4.4. The Coulomb force is proportional to the strength of the electric field, so the measured TSV comes from field-integration along its trajectory through the photo-induced field region (laser excited region), or

$$TSV = \int_{z_0}^{z_1} E_z(z) dz,$$
 (4.12)

where  $z_1$  is the position at which the electron beam enters the field region, and  $z_0$  the position of the diffractively probed region (both are shown in Figure 4.4). The TSV

could be expressed more generally by summing from each constituent, the changes of the net potential near the surface, or

$$TSV = \Delta V_{IP} + \Delta V_{dp} + \Delta V_{sc}(\theta_i) + \Delta V_{vsc}(\theta_i, \theta_o, \alpha_{vsc}), \tag{4.13}$$

where the aspect ratio of the vacuum space charge region,  $\alpha_{vsc} = (z_{vsc} - z_0)/L$ , changes as the photoemitted electron disk moves away from the surface [194, 200, 287],  $\Delta V_{IP}$  describes the change in the inner potential,  $\Delta V_{dp}$ , the change in potential arising from a change in the strength of the interfacial dipole,  $\Delta V_{sc}$ , the sub-surface bulk space-charge region,  $\Delta V_{vsc}$ , the potential associated with emitted charge density,  $\sigma_{dp}$ , and L the associated length of the laser spot on the surface.

### 4.4 Quasi-3D Structure

As mentioned in Appendix A.0.3, suppression of the spatial coordinate normal to the surface that the electron beam samples (e.g., RHEED or LEED geometry) will result in the elongation of the reciprocal lattice. To fully illustrate the point, consider the limiting case of an infinitesimally thin surface, where a 2D array of vertical rods extending from  $-\infty$  to  $\infty$  would result. Elongation of the reciprocal lattice can be understood through the standard relationship between Fourier complements:  $\Delta k_z \Delta z = 2\pi$ , which gives rise to the Scherrer criterion for estimating the length scales of crystallites [316]. In practicality, it is inevitable that a finite sub-surface periodicity will be sampled by the electron beam. A possible ramification of which is that the reciprocal lattice degenerates into modulated rods, as shown in Figure 4.5. This is particularly common when the surface is rough, giving a finite, in-plane persistence length for diffraction [207], or if the surface has steps or ripples, which effectively results in a spread of  $\theta_i$  over the electron footprint on the surface.



Figure 4.4: Transient surface potential diagram introduced by various sources of photoinduced charge separations (see text) near the  $Si/SiO_2/OH$  interface. The transient surface voltage (TSV) determined using the electron diffractive approach comes from the electric field integration over the region traversed by the incident and diffracted electron beams.

Convergent beams also have a spread in the incidence angle over the beam spot (by definition, since the impinging beam is conical) in addition to the small spot size, which paradoxically yields more information than a larger spot size [207, 290, 317, 318]. In fact, for any diffraction-limited probe, the size of the angle-resolved cone of scattering generated for each Bragg order increases as the probe size is reduced [290].

In Figure 4.5, the dark grey spots on the CCD screen represent the modulated spot pattern on the reciprocal lattice rods, with the pattern corresponding to the true lattice spacing. In fact, when the surface is sufficiently rough or when the crystallographic orientation of the sample is randomized, such as the powder diffraction from nanoparticles or quasi-polycrystalline diffraction from highly-oriented pyrolytic graphite (HOPG), more than one Bragg peak can appear simultaneously at a fixed  $\theta_i$ , as shown in Figure 4.6(b)-(d). The reliable appearance of the 3D Bragg diffraction over a finite  $\Delta \theta_i$  ensures persistent tracking of the 3D crystalline property (lattice parameters and associated potential) as laser-induced perturbations arise within the crystal.

### 4.4.1 Robustness of the TSV Formalism

To experimentally examine the interference along the reciprocal lattice rods, a rocking curve is acquired, which is the measured diffraction intensity over a range of  $\theta_i$ (introduced in Section 2.3.4). This is carried out in the ultrafast electron crystallography (UEC) experimental setup [190] by tilting the sample plane while the direct beam remains fixed, which defines  $\mathbf{s} = \mathbf{s}_0 - \mathbf{s}_i = 0$ , at position C in the diffraction image (Figure 4.5). Here, rocking analysis over three types of crystal is presented: a smooth silicon (111) surface [107, 194], 2 nm gold nanoparticles [192], and HOPG [108, 194], as described in Figure 4.7 [194]. The periodicity of the (111) modulation in the reciprocal lattice rods was examined by collecting the intensities frame by frame in the  $\theta_i$ -scan over the (0,3) reciprocal lattice rod. By stitching together



Figure 4.5: The Ewald construction in the reflection geometry. The incident beam  $\mathbf{s}_i$  impinges the crystal at a glancing angle,  $\theta_i$ . A finite sub-surface periodicity is sampled by the beam, causing a vertical interference pattern to form on the reciprocal lattice rods (the white spots on the rods and grey spots on screen), illustrating the potentially quasi-3D nature of the diffraction pattern (see text). The bright peaks on the screen (white) represent the points where the reciprocal lattice interference spots intersect the Ewald sphere. If  $\theta_i$  is increased (or decreased), the Ewald sphere rocks about point O while the rods remain stationary, causing the Laue circles to cross different parts of the reciprocal lattice for examination with diffraction. The dashed circle represents the zeroth order Laue zone (ZOLZ).



Figure 4.6: Diffraction patterns from (a) a smooth Si (111) surface, (b) a Si(111) surface with prominent step edges, (c) metallic nanoparticles, (d) HOPG. The patterns shown in (b)-(d) exhibit quasi-3D features, while (a) does not. Determining the plausibility of Coulomb refraction-based shifting can be bolstered when several peaks from the same reciprocal lattice are co-present on a single diffraction pattern, as this allows for a direct comparison in a single shot, rather than rocking the sample to find the next order on the rod.

the intensity scan along the rod over the given range, shown as a compiled rocking map in Figure 4.7(a), the evolution of the projected Bragg peaks in the diffraction image with changing  $\theta_i$  as the Ewald sphere cuts across different sections of the rod, could be elucidated. For the (0,3) rod, the trajectory of the Ewald sphere cut evolves diagonally across the compiled rocking map, with the periodic intensity increasing over nearly evenly spaced  $\theta_i(\theta_0)$ , which obeys the Bragg relationship,

$$\sin\theta_i + \sin\theta_o = N_{111} \frac{\lambda_e}{d_{111}},\tag{4.14}$$

where  $N_{111}$  denotes the diffraction order and  $d_{111}$  is the interlayer separation (3.135 Å for Si). As  $\theta_i$  increases, so does the sub-surface periodicity sampled by the beam, as it penetrates deeper with an increased momentum component perpendicular to the surface. This reduces the range  $\Delta \theta_i$  for which the Bragg peaks can be observed, thus reflecting the complementary (Fourier) relationship. For a stepped surface, the

domain structures produce 3D features, yielding multiple Bragg peaks to appear at one crystal orientation, as shown in Figure 4.6(b). In the diffraction obtained from HOPG (single-shot pattern in part (d) of Figure 4.6), this extension becomes nearly continuous, as shown in the rocking curve map in Figure 4.7(c). Following this quasi-3D extension, shown in the rocking curve maps, the associated changes introduced in the atomic and electronic degrees of freedom caused by photoexcitation can be monitored.



Figure 4.7: Compiled rocking map for Si(111) (a), Au nanoparticles of size 2 nm (b), and HOPG (c). These maps are obtained by stitching together scattered intensity patterns along the normal direction over a range of incident angles ( $\theta_i$ ). The corresponding scattering angle ( $\theta_S$ ) for the intensity pattern is also shown. In (a), the Ewald sphere cut from the (0,3) rod is traced out in the diagonal, as each Bragg peak is present for only a small angular range, while in (b) and (c) the diffraction is powder-like, in which multiple peaks are co-present over an extended range of electron incidence.

The first case chosen to demonstrate robustness is that of a single incidence angle with multiple peaks on the same rod, exhibited here by a Si(111) surface with a chemically grown oxide layer (see Section 5.2.1), with prominent step edges [107, 194]. Here, three peaks along the (0,0) rod were clearly visible at an incidence angle of  $\theta_i = 6.8^{\circ}$  (Figure 4.8 inset). Using the formalism from Section 4.2.1, the changes in momentum transfer were converted to surface voltage, which is presented in Figure 4.8. Note that the (0,0,24) and (0,0,27) peaks agree on the value of the maximum transient surface voltage for the fluences presented. The incidence angle for these two peaks was, of course, the same, since they were co-present on the same diffraction image. The (0,0,24) peak shifted more than the (0,0,27) as is shown in Figure 4.8(a), which is expected from Equation 4.11, where smaller values of  $\theta_o$  (and  $\theta_i$ ) predict larger shifts ( $\Delta_B$ ) for a given voltage (Figure 4.2).

At this point, the focus is shifted to investigating the TSVs obtained from different points on different Laue circles. Various reciprocal lattice rods can be examined in an experiment by rotating the sample in-plane (denoted by angle  $\phi$ ), shown schematically in Figure 4.9. Combining the  $\phi$  and  $\theta_i$  operations, it is possible, in principle, to determine the 3D atomic lattice structure. The rocking curve for a smooth Si(111) surface is shown in Figure 4.7(a). Unlike the case above with the stepped-surface, the higher orders are present only as incidence angle  $\theta_i$  is also increased, which is also an indication of the superior surface integrity.

The objective here was to analyze the Bragg peak motion from multiple peaks on this rod, compare them to each other, as well as another peak from a different rod. This was to see if the agreement is robust as incidence angle and diffraction order are varied (previously only the variations associated with the latter were examined). In principle, the TSV formalism should remain equally valid as different rods than the (0,0) are examined.

Peaks (0,1,24), (0,1,24), and (0,3,24) were found at incidence angles of  $6.24^{\circ}$ , 4.70°, and 4.15°, respectively. The dynamics of each were elucidated by performing pump-probe experiments under a fluence of  $64.3 \text{ mJ/cm}^2$ , pulse width 45 fs, with a near infrared pump wavelength of 800 nm. Figure 4.10 compares the transient surface potential delay scans for the three peaks. The two peaks from the (0,1) rod show strong agreement, with a small deviation from the (0,3,24) peak. The deviation could come from other sources of TSV that cannot be described by the idealized dipolar slab model, which may possess an angular dependence.



Figure 4.8: (a) The momentum transfer  $\Delta s$  as a function of time for the (0,0,24) (red) and (0,0,27) (blue) peaks. As expected, the lower order peaks shift more than those of higher order, consistent with the TSV formalism. Inset: the diffraction pattern from the fixed crystal orientation used throughout this pump-probe experiment. The (0,0,30) peak is present in this pattern, shown by the top-most peak. The signal-tonoise for this peak was rather weak to follow dynamically, so it was excluded. (b) The transient surface voltage (TSV) for the listed fluences. The two different orders are in close agreement for all fluences. [107]



Figure 4.9: Schematic experimental geometry of ultrafast electron crystallography, showing the different angles of rotation,  $\theta$  and  $\phi$ , the former associated with a rocking curve, the latter with an in-plane rotation (a). In part (b), the Ewald sphere intersects the (0,3) rod. An in-plane rotation ( $\Delta\phi$ ) about the (0,0) rod causes the (0,3) rod to move away out of the intersection and the (0,1) rod to move in.

An area worthy of future consideration would be the examination of a TSV correction factor based on the position of the Bragg peak along the 'perimeter' of the Laue circle. The agreement for the two very different  $\theta_i$  suggests that the TSV change is largely caused by the finite-depth potential drop across the SiO<sub>2</sub> dipolar layer as the electron beam crosses it, *en route* to the diffracting Si(111) planes. At this fluence, the Si(111) lattice spacing is expected to change at most 0.011% ( $\approx 3.4 \times 10^{-4}$  Å), corresponding to a maximum temperature rise of 40 K, calculated from a Boltzmann transport model [264] (Section 3.2), and the linear thermal expansion coefficient [283], thus offering less than 1% contribution to the observed  $\Delta_B$ .



Figure 4.10: The TSV deduced from examining the (0,1) and (0,3) reciprocal rods for the Si(111)/SiO<sub>2</sub>/OH interface, with a fixed laser fluence of 64.3 mJ/cm<sup>2</sup>. The incidence angles for the (0,3,24), (0,1,21), and (0,1,24) peaks are  $6.24^{\circ}$ ,  $4.70^{\circ}$ , and  $4.15^{\circ}$ , respectively.

A relatively high fluence was chosen for these experiments so the delay scan for each of the three peaks could be carried out quickly. Lower fluences require more acquisitions at each delay so the change in peak position can be resolved from the noise level, which is not the case for high fluences, where the dynamical effects are easily discernible, thus requiring fewer delay cycles as fewer frames are necessary to average out the noise.

Here, each experiment required a 3-frame average for each delay, where each frame consisted of approximately 4000 shots (pumped and probed 4000 times per frame, implying a 4 second acquisition time with the 1 kHz repetition rate), meaning that the experiment on each peak lasted about 30-40 minutes. Over the course of several hours, the laser is quite reliable, making it very safe to presume that the three experiments were performed under identical pump conditions. As an additional check, the pump fluence was checked before and after the experiment, as was the alignment condition; neither exhibited any change.

The situation becomes increasingly complicated as the fluence decreases, as the peak shifting is generally on the order of tenths of pixels, sometimes less (the highest experimental resolution achievable by the author is a 0.06 pixel change in peak position, on Si at a fluence of  $\approx 12.5 \text{ mJ/cm}^2$ ). The 'dynamical coordinates' for nearly all other systems, respond considerably stronger to pump excitation than silicon. For example, with HOPG, peaks will shift  $\sim 20$  pixels under moderate to high fluences. Even low fluences respond with 5-10 pixels. It is not unusual over the course of  $\sim$ 8-12 hours, for the laser, electron beam, or stage to drift slightly, thereby changing the alignment condition. If present, these artifacts must be carefully monitored and extracted.

### 4.5 Coulomb Refraction vs. Lattice Expansion

Based on Equations 4.9 and 4.11, the field-induced shifts can be evaluated to understand the trend of  $\Delta_B$  under different incidence angles, diffraction orders, and surface potentials, and a comparison can be made for the dependence of the structure-related shifts,  $\delta_B$ . At a given  $V_s$ ,  $|\Delta_B|$  generally decreases more rapidly for larger diffraction orders ( $\theta_o$  values), as demonstrated in Figure 4.11.

The opposite is true for thermal expansion, where the shift,  $\delta_B = -\theta_B \cdot \delta a/a$ , is proportionally magnified for the higher orders ( $\theta_B$ ). Indeed, larger diffraction cones<sup>5</sup> respond more strongly to a lattice expansion,  $\delta a$ . Further comparison of the relative changes of  $\Delta_B$  and  $\delta_B$  in two contrasting regimes shows that for smaller  $\theta_i$  and N,  $\Delta_B$  tends to dominate over  $\delta_B$ , as shown in Figure 4.11(a), simulated for  $\theta_i = 1.25^{\circ}$ and  $N \sim 2$  over a nominal  $V_s$  range of  $\sim 1$  V.

For larger  $\theta_i$  and N, the trend will reverse, as demonstrated in Figure 4.11(b), where  $\theta_i = 5.05^{\circ}$  and  $N \sim 8$ , comparing to a nominal structural change at the level of 0.5%, which corresponds to lattice heating of the order of 500 K for solids. To separate  $\Delta_B$  from  $\delta_B$  experimentally, it is thus beneficial to examine both high and low angle regimes, i.e. low  $\theta_i$  and N for TSV determination, and high  $\theta_i$  and Nfor structural changes [194]. In fact, this is another reason why peak (0,0,30) was not presented in Figure 4.8, as it was not an ideal candidate for TSV measurement. An additional method (not presented here) involves a Fourier phasing algorithm for isolating the TSV effects from structural changes in graphite [108, 190, 194].

### 4.6 Beyond the Slab Model

Recall from Section 4.2.1 that one of the underlying assumptions of the slab model is that the field has negligible tangential components. The large laser spot size com-

<sup>&</sup>lt;sup>5</sup>A diffraction cone is described by joining the vertices of vectors  $s_i$  and  $s_o$ .



Figure 4.11: The total peak shift,  $\Delta_B$ , calculated for varying degrees of lattice expansion (blue) and surface voltage. For a fixed voltage, the associated shift is less prominent for higher orders of diffraction ( $\theta_0$ ). This is in contrast to the structural based shift,  $\delta_B$ , where the higher orders are more strongly affected.

pared to that of the electron beam validates the assumption of a homogeneous field perpendicular to the surface, since this is what the e-beam sees. Essentially, the electron beam enters and exits from the top surface of the charged capacitor slab, and knows nothing of the edge effects (Figure 4.12).



Figure 4.12: The electron beam diameter being much smaller than that of the laser is an underlying assumption for the validity of the formalism presented in Section 4.2.1, where the TSV is not affected by the tangential components of the field, because the electron beam enters and exits from the top of the 'capacitor.' The aspect ratio of the capacitor is exaggerated for clarity. Realistically, the height and width are of the orders of 1 nm and 100  $\mu$ m, respectively.

In principle, extending the UEDV technique to less 'friendly' field geometries should be possible, as the charged probe will respond to the fields through which it propagates. The question lies in the interpretation of the resulting diffraction patterns. To quantitatively evaluate the various systematic factors that may affect proper deduction of the TSV, and to treat the TSV beyond simple geometries, the formalism described in Equations 4.9 and 4.11 can be extended to consider Coulomb refraction in various, non-planar geometries. It will be demonstrated that extension to an arbitrary shaped potential (depicted in Figure 4.13), is realizable with the surfacesensitive probe.

The primary justification of this approach hinges on the fact that the effect of a surface potential, whatever its shape may be, is to contribute much less change (proportionally) to the tangential momentum components than those perpendicular to the surface. This is plausible because the electron beam has nearly 100% of the accelerating voltage (30 kV) in its horizontal momentum. As a result, any tangential field components (which tend to be rather weak compared to the longitudinal one) are expected to have only marginal effects on the high energy momentum components in that direction.



Figure 4.13: General refraction geometry for a grazing incidence electron beam. The effective bending of the incident(exiting) beam, caused by the local field associated with  $V_s$  in the nanostructures, differs depending on the entry(exit) point  $z_1^i(z_1^o)$ . Since the relative change of the transverse momentum remains small, the slab model can be extended to treat arbitrary geometries through a correction factor,  $\Theta(\alpha, \theta)$ , that depends on position (through  $\alpha$ ) and angle (see text).

Rather than constructing a new formalism from first principles, a correction factor is imposed onto the slab model for both the incoming and outgoing electron wave vectors, given by  $\Theta_i(\theta_i, \alpha)$  and  $\Theta_o(\theta_o, \alpha)$ , such that Equations 4.7 and 4.8 become

$$\tan^2 \theta_i' = \tan^2 \theta_i + \Theta_i(\theta_i, \alpha) \frac{\chi}{\cos^2 \theta_i}, \qquad (4.15)$$

and

$$\tan^2 \theta'_o = \tan^2 \theta''_o + \Theta_o(\theta_o, \alpha) \frac{\chi}{\cos^2 \theta''_o}.$$
(4.16)

Analogously, Equation 4.9 becomes

$$\Delta_B = \sin^{-1} \sqrt{\frac{D^2 - \Theta_o(\theta_o, \alpha)\chi}{1 + D^2} - \theta_0},$$
(4.17)

where

$$D = \frac{\tan\left(\theta_i + \theta_o\right) - \sqrt{\tan^2 \theta_i + \Theta_i(\theta_i, \alpha)\chi/\cos^2 \theta_i}}{1 + \tan(\theta_i + \theta_o)\sqrt{\tan^2 \theta_i + \Theta_i(\theta_i, \alpha)\chi/\cos^2 \theta_i}}.$$
(4.18)

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

$$\chi = \left\{ \left[ (c+2)\Theta_{i}(\theta_{i},\alpha) - c\Theta_{o}(\theta_{o},\alpha) \right] \right.$$

$$\pm \sqrt{\left[ (c+2)\Theta_{i}(\theta_{i},\alpha) - c\Theta_{o}(\theta_{o},\alpha) \right]^{2} - 4ab[\Theta_{o}(\theta_{o},\alpha) - \Theta_{i}(\theta_{i},\alpha)]^{2}} \right\}$$

$$\left. \left. \right/ b[\Theta_{o}(\theta_{o},\alpha) - \Theta_{i}(\theta_{i},\alpha) \right]^{2},$$

$$(4.19)$$

where
$$a = \frac{\left(\theta_o \Delta_B - \theta_i \theta_o + \Delta_B^2 / 2\right)^2 - \theta_i^2 \left(\theta_o + \Delta_B\right)^2}{\left(\theta_i + \theta_o\right)^2},\tag{4.20}$$

$$b = \frac{1}{\left(\theta_i + \theta_o\right)^2},\tag{4.21}$$

and

$$c = \frac{2\theta_i^2 + 2\theta_i\theta_o - 2\Delta_B\theta_o - \Delta_B^2}{(\theta_i + \theta_o)^2}.$$
(4.22)

If  $\Theta_o(\theta_o, \alpha) = \Theta_i(\theta_i, \alpha)$ , then  $\chi = a$ . The + or - is chosen in Equation 4.19 based on the sign of  $(c+2)\Theta_i - c\Theta_o$ ; + is used if the quantity is  $\leq 0$ , - is used if it is > 0.

### 4.6.1 Correction for Finite-Slab Geometry

With the general formalism laid out, the attention is turned to non-planar geometries. The first example is similar to the slab geometry, but with the *e*-beam propagating out the side of the 'capacitor,' rather than exiting from the top. This could occur experimentally if the electron beam diameter were as large, or larger than the laser spot. In this scenario, surely some of the incoming electrons would sample the tangential field components from the capacitor.

To investigate the deviation from the slab model, a simulation is performed where the electron is propagated through a parallel plate capacitor with a fixed nominal voltage, and then analyzed in the far field to determine the 'measured' voltage when it is no longer under the influence of the capacitor. Comparing the far-field voltage to the nominal one gives the correction factor. Of particular interest here, are the cases where the electron exits the capacitor from the side, rather than the top. An approximation can be made a - priori that the correction factor is

$$\Theta(\theta, \alpha) \approx \begin{cases} \theta/\alpha & \text{if } \theta < \alpha, \\ 1 & \text{if } \theta \ge \alpha. \end{cases}$$
(4.23)

If this simple approximation for the correction is assumed to be true, it can immediately be noted that the divergence of  $\Delta_B$  as the diffracted electron beam approaches the shadow edge ( $\theta_o$  approaches 0) is suppressed by this correction factor. Note, in Equation 4.9,  $\Delta_B$  diverges as  $\theta_o \rightarrow 1$ , whereas  $\Delta_B \rightarrow \sin^{-1} \sqrt{D^2/(1+D^2)}$  in Equation 4.17 because  $\Theta_o \rightarrow 0$  as  $\theta_o \rightarrow 0$ .

The real correction factor is obtained through the following procedure. A parallelplate capacitor is simulated with vacuum dielectric between the plates ( $\epsilon = \epsilon_0$ ), which are 2*h* apart and 2*a* wide, and charged such that there is a 10 V potential difference between the plates. The plate at y = h is held at a voltage,  $V_{plate} = -5$  V, and the bottom plate (y = -h) is held at +5 V. The top-right quadrant is depicted in Figure 4.14(a), which by symmetry, is actually sufficient to solve the problem (y = 0is grounded).



Figure 4.14: Correcting the TSV for a finite slab. (a) The potential is calculated for the mesh, followed by launching an electron at an angle  $\theta$  from the origin (x = y = 0), and using the change in kinetic energy, deduced from  $\theta'$  to get the probed voltage,  $V_s^*$ . The aspect ratio,  $\alpha = h/a$ , is varied to examine different exit points. (b) Simulation results for the correction factor,  $\Theta(\theta, \alpha)$ , as a function of aspect ratio,  $\alpha$ , show that for smaller launch angles, the correction factor is well-approximated by Equation 4.23.

Using the figure as a guide, the electron is launched at an angle  $\theta$  from the capacitor center (x = y = 0), with kinetic energy  $eV_0 = 30$  keV, thus defining the momentum components as  $p_x = \sqrt{2m_eV_0} \cos \theta$  and  $p_y = \sqrt{(2m_eV_0)} \sin \theta$ .

A  $5 \times 5 \text{ mm}^2$  mesh with variable spacing (finest near the edges of the capacitor) is constructed to resolve the field. Dirichlet boundary conditions are set at the mesh limits y = 0 and 5 mm, and x = 5 mm, where the potential is fixed at 0 V. The solution is symmetric about the y-axis (the x = 0 boundary is reflective). The upper limits of the mesh were found to be sufficiently large compared to the capacitor dimensions (for all capacitor sizes considered) such that the potential could be set to 0 V at the right and top limits of the mesh, with no loss of accuracy.

With all boundaries defined and the nominal capacitor voltage set, the potential at all x and y node points was calculated (uniquely) by iteratively solving Laplace's equation at each node point until convergence was reached [319]. Once the electrostatic potential had been determined, the equations of motion were solved for an electron propagating through the field<sup>6</sup>. When the electron reached x = 5 mm, the calculation was stopped and the hypothetical 'measured' voltage,  $V_s^*$ , is determined from the ratio of momentum components in the far field, or

$$\frac{V_s^*}{V_0} = \tan^2 \theta' - \tan^2 \theta \approx \theta'^2 - \theta^2, \qquad (4.24)$$

where  $\theta'$  is the arctangent of the momentum components in the far-field, and a smallangle approximation was assumed. Any difference between  $V_s^*$  and  $V_{plate}$  is an indication of a source of error in the TSV measurement. The correction factor can now be properly defined from the simulation results, as

$$\Theta(\theta, \alpha) = \frac{V_s^*}{V_{plate}}.$$
(4.25)

<sup>&</sup>lt;sup>6</sup>These calculations were carried out using the Trak Charged Particle Toolkit from Field Precision.

The results are shown in Figure 4.14(b), where the aspect ratio of the capacitor,  $\alpha = h/L$ , is varied so that the effects associated with the different exit points can be analyzed. The edge-effects are increasingly important for the smaller angles and larger aspect ratios. This makes sense, since an electron launched at a shallow angle, in a capacitor where the top plate is rather far away (large  $\alpha$ ), will ride along the symmetry boundary of the capacitor until it exits, which means that it would have flown through a region of very small potential. The closer it gets to the top plate, the more potential, close to the nominal value, it would have experienced.

Conversely, the higher orders (large  $\theta$ ) will have a greater likelihood of flying out the top of the capacitor, even when  $\alpha$  is large, which is why  $\Theta$  deviates from 1.0 much more slowly at  $\theta = 3.5^{\circ}$  than at  $\theta = 1.5^{\circ}$  or  $2.5^{\circ}$ . As expected, edge effects, or those associated with a field possessing a non-negligible tangential component, are expected to be more pronounced with larger diffraction cones. This is consistent with physical intuition, since the larger diffraction cones have smaller horizontal momentum components.

# 4.6.2 Correction at the Nanoparticle/SAM/Semiconductor Interface

The second scenario is that of an array of metallic nanoparticles, immobilized on a semiconductor substrate via self-assembled molecular (SAM) chains. This nanoparticle/SAM/semiconductor interconnect occurs frequently in UEC [190, 192–194], and is addressed in greater detail in Chapter 6. Here, the emphasis is on determining the accuracy of TSVs in measuring the associated fields with charge that has been transferred to the nanoparticle, such that it is fixed at a nominal voltage. Since this chapter is on the topic of the measurement technique, the nanoparticle data on charging and discharging are withheld until Chapter 6. Only the measurement correction factors shall be derived here. Similar analysis is performed for this geometry to that of the slab correction, this time setting the potential of the nanoparticle to the nominal voltage of -5 V. The nanoparticle sits on a 1 nm dielectric slab ( $\epsilon_r = 2.5$ ), representing the self-assembled linker chain. Beneath it is a grounded metal slab representing photoexcited silicon. The equations of motion were solved for various nanoparticle sizes, and at different launch points along the height of the linker molecule. The results are shown in Figure 4.15. Here, the aspect ratio is redefined as the ratio of SAM thickness (h) to the nanoparticle diameter (D),  $\alpha = h/D$ ; h = 1 nm for all cases simulated.



Figure 4.15: (a) The calculated potential for the case of a 20 nm metallic nanoparticle, charged to -5 V, with a 1 nm thick, dielectric layer ( $\epsilon = 2.5$ ) atop the Si substrate. (b) The correction factor as a function of aspect ratio (SAM to nanoparticle) is calculated by resolving the trajectory from the electric forces. The solid points are the simulated data; the lines are from the approximation  $\Theta = h/D$  (see text). Inset: The correction factor as a function of launch angle  $\theta$  for three different launch positions along the SAM.

#### 4.7 Discussion

A general formalism of electron diffractive voltammetry has been constructed, that is suitable to deduce surface potentials for arbitrary geometries. This chapter emphasized the measurement technique, with a general description of the various field constituents near the surface, including vacuum emission, surface charging, bulk spacecharge, and surface dipole layers. In addition, their effects were contrasted with those associated with lattice expansion, which are also buried in the Bragg peak motion. Notable differences were identified in their respective behaviors, which were quantified in various experimental regimes, such as deep/shallow incidence and low/high diffraction orders.

When operated in proper regimes, UEDV possesses the unique capability of monitoring 'site-specific<sup>7</sup>, charge dynamics with ultrafast time resolution, thereby making the determination of electrical conductance possible from the transient I-V characteristics associated with various nanoscale materials and interfaces, evidenced here from the studies of charging dynamics at the semiconductor/oxide interface, and on a semiconductor/molecule/metal nanoparticle interconnect. In contrast to optical spectroscopic techniques [5, 6, 320], whose lifetime measurements of the charge transfer states provide a quantitative measurement of the electronic coupling matrix elements, the time scale determined with the voltammetry methodology is a transport time scale integrated over all possible channels of charge transfer, with both forward and backward channels considered. Therefore, these two approaches provide a strong complement to one another.

<sup>&</sup>lt;sup>7</sup>Here, the term site-specific is used to imply a characteristic length scale for nanostructures, which can be as small as a few nm.

# Chapter 5

# Carrier Transport at the $Si/SiO_2$ Interface

## 5.1 Introduction

The nature of charge transfer, trapping, and detrapping at the Si/SiO<sub>2</sub> interface has gained notable interest as CMOS devices are further integrated in accordance with Moore's law. As the dielectric oxide layer necessarily becomes thinner, leakage currents become a non-negligible hindrance in transistor performance, an effect that was formerly not present with thicker oxides. Leakage currents commonly lead to interfacial fields as carriers occupy defect and surface states. These fields, measurable with UEDV, provide additional insights into the intricacies associated with interfacial charge transfer.

On the most basic level, the field arises from charge separation at the interface as carriers are transported from the bulk to the surface. The nature of the field is influenced by many variables, including, but not limited to, dopant (type and concentration), defect state density, surface roughness, oxide thickness, the strength of surface-bulk coupling, etc. In addition, the charge rearrangement mechanisms remain non-trivial, be it via direct or field-induced (Fowler-Nordheim) tunneling [303, 321, 322], internal photoemission (IPE) as the quasi-Fermi level of hot electrons (holes) is raised above the conduction (valence) band offset, which usually involves some sort of multiphoton absorption effects. 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.

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 [78–100].

Photoelectron spectroscopic methods have been effective in elucidating the interfacial electronic structures [323, 324], as well as monitoring the surface state populations directly [122, 126, 299]. Bulk carrier dynamics in Si have been studied extensively on the pico- to femtosecond time scales with a variety time-resolved techniques [104, 126, 128, 136, 286, 300, 325].

The focus here is to investigate the charge injection processes during charge rearrangement (field generation), and in doing so, provide additional clarity to the source(s) of the field, using the recently developed technique of ultrafast electron diffractive voltammetry (UEDV) [107, 194, 285], discussed in Chapter 4. Under ultrafast laser irradiation, a fraction of the valence band (VB) electrons are promoted to the conduction band (CB), followed by charge rearrangement at the interface, depending the nature of the excitation (laser intensity, energy, duration, etc.), as will be demonstrated in this chapter. This chapter will summarize the general results on interfacial hot carrier transport that have been ascertained from Si/SiO<sub>2</sub> experimentation, specifically UEDV.

## 5.2 Experimental Methods

#### 5.2.1 Surface Preparation

Preparation of silicon wafers follows a modified RCA procedure [326]. Si(111) wafers<sup>1</sup> of *p*- and *n*-type are cleaned in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (7:3) for 10 min at 90 °C, followed by immersion in room temperature NH<sub>4</sub>F (40% in H<sub>2</sub>O for 6 min) to remove the native oxide. An ultrathin oxide layer is deposited by immersion in HCl/ H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1:1:5) for 10 min at 90 °C, followed by further cleaning in NH<sub>4</sub>OH/ H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1:1:6) for 10 min at 90 °C. Oxide thicknesses are measured with an ellipsometer. For the experiment here, an *n*-type wafer was chosen with thickness  $19.8 \pm 2.0$  Å.

The sample was immediately transferred to the UHV chamber via load-lock. The optical pulse width was measured prior to beginning the experiment to be  $40.8\pm3.2$  fs, using the autocorrelation method described in Section 2.3.2. The laser spot footprint on the surface, which is elliptical, was measured to be  $6.96\pm0.63\times10^5 \ \mu\text{m}^2$ , using the method in Section 2.3.1. Laser fluences were measured before and after each delay scan, as the laser power can slightly fluctuate over the course of a day. When they were different, an assessment was made as to when the laser power had dropped (or risen) based on the electron counts. A weighted average was computed between the before and after fluences, according to the proportion that the scan was deemed to have spent at each fluence.

These experiments were carried out at ~  $6.0 \times 10^{-9}$  torr. The sample stage was brought to within ~1 mm of the electron gun, as to minimize space-charge broadening effects (a camera is positioned to look directly at the sample surface through a con-flat viewport flange, which allows visible verification of the alignment). The direct electron beam was measured using the knife-edge method (Section 2.3.3) to be  $22.1 \pm 1.3 \ \mu$ m, corresponding to an *e*-beam footprint on the sample with elliptical

<sup>&</sup>lt;sup>1</sup>Silicon wafers, purchased from *Silicon Inc.*, Boise, ID

area of  $5.29 \times 10^3 \ \mu m^2$ , which is about a factor of 13 smaller than the pump laser footprint.

#### 5.2.2 Pump-Probe Alignment

After most delay scans, the pump-probe alignment was re-checked with the alignment scans described in Figures 2.5 and 2.6, from Section 2.2.1, which is standard practice for pump-probe investigations of Si when applying the laser energy and fluences used here, as it does not exhibit a large response to the pump laser since the optical penetration depth at 800 nm is  $\approx 4 \ \mu$ m.

Re-alignment is imperative if an overall drift in the position of Bragg peaks was observed, which happens approximately 20% of the time when a delay scan exceeds 10 hours (most likely to occur with low fluences). It may also be necessary to discard the data if an assessment cannot be made as to when the alignment was lost. An alignment check usually takes about 40 minutes, and if possible, is performed at the desired fluence of the next experiment. However, in the interest of conserving laser run time, if the dynamical changes at the next fluence are known to be quite small, a higher fluence may be chosen to align the pump and probe so that the next experiment can begin swiftly. For example,  $F = 64.3 \text{ mJ/cm}^2$  was used to align the scans for fluences of 13.6, 17.1, and 17.4 mJ/cm<sup>2</sup>, as the changes in the spot position are quickly resolvable at that fluence.

#### 5.2.3 Data Analysis

The diffraction patterns for each delay are fit according to the intrinsic properties of the crystal (lattice constant, crystal orientation), and the physical geometry of the UHV chamber (camera distance, incidence angle, beam angles, crystal rotation, accelerating voltage, etc.), such that the theoretical spot pattern matches well with the observed one. This is essentially a geometry problem of first calculating the Ewald sphere intersections with the reciprocal lattice, which can be deduced from the accelerating voltage and incidence angle (which give the radius and orientation of the Ewald sphere) and the unit cell with the corresponding lattice constant of the material to calculate the reciprocal lattice. The intersections are projected in space by the camera distance to give the calculated spot pattern on the screen, which was all programmed in a home-built crystal fitting program. Fitting each pattern with a Gaussian for the diffraction peak at each delay, a plot is generated of momentum transfer s vs. time, each of which is converted to a TSV delay scan using the formalism from Chapter 4, specifically Equation 4.11. The process is illustrated in Figure 5.1, where the Gaussian peak fit is shown on a raw diffraction image in panel (a). The spot position in pixels (the mean of the Gaussian) can be directly converted into momentum transfer coordinates using the fit parameters of the ground (pre-excited) state, leading to the plot in panel (b). Finally, using the UEDV formalism, s(t) is converted to TSV (inset).

Each TSV plot is fitted with an empirical function describing charge injection and decay, given as

$$V_s = V_{fit} \left[ 1 - \exp(-t/\tau_i) \right] / (1 + t/\tau_c), \tag{5.1}$$

such that the charge injection  $(\tau_i)$ , relaxation  $(\tau_c)$ , and maximum amplitude voltage  $(V_{fit})$  characteristics can be extracted. The results are shown in Figure 5.3.

The two main features of the TSV results are: (1) The time scale for charge separation ( $\tau_i$ ) here is characterized by charge injection into the surface states of SiO<sub>2</sub>, has two separate time scales. At the lower fluences ( $F < 20 \text{ mJ/cm}^2$ ), the injection time,  $\tau_L \approx 100 \text{ ps}$ , while the higher fluences ( $F > 20 \text{ mJ/cm}^2$ ) the injection time is significantly shorter, as  $\tau_H \approx 65 \text{ ps}$ . (2) The fluence dependence of the TSV can be very well described by a quadratic relationship,  $TSV = aF + bF^2$ , where  $a = 1.016 \times 10^{-2} \text{ (mJ/cm}^2)^{-1}$  and  $b = 8.803 \times 10^{-4} \text{ (mJ/cm}^2)^{-2}$ . The crossover from  $\tau_L$  to  $\tau_H$  as F increases is very consistent with the corresponding TSV rise



Figure 5.1: (a) The diffraction peak is fit at each delay scan with a Gaussian (blue), followed by converting the camera pixel coordinates to s-coordinates (b) using the unit cell, lattice constant, camera distance, etc. (see text). The momentum transfer (s) at each delay is then converted to transient surface voltage using Equation 4.11. The orange lines in (a) are intensity line scans from within the guided area (magenta).



Figure 5.2: UEDV data with fitting curves given by Equation 5.1, zoomed in to early times to show the contrasting  $\tau_i$  as fluence increases. The panels that have insets are showing the full time scale.

observed here. The crossover from linear (aF) to quadratic  $(bF^2)$  contributions as the main source of the TSV appears near  $F \approx 20 \text{ mJ/cm}^2$ , as shown in Figure 5.3.

This crossover behavior in the fluence dependence in  $\tau_i$  and the maximum amplitude TSV near 20 mJ/cm<sup>2</sup> can be explained through the following simple analysis of the respective proportions of the total TSV mediated by the 1- and 2-photon absorptions. Consider the simple picture of electron-hole pair generation through optical excitation, with 1- and 2-photon absorption present (neglecting Auger recombination, diffusion, and depth dependence):

$$\frac{\partial n}{\partial t} = \frac{\alpha I_0(t)}{h\nu} + \frac{\beta I_0(t)^2}{2h\nu}.$$
(5.2)

Integrating over time gives

$$\int_{-\infty}^{\infty} \left(\frac{\partial n}{\partial t}\right) dt = \int_{-\infty}^{\infty} \left(\frac{\alpha I_0(t)}{h\nu}\right) dt + \int_{-\infty}^{\infty} \left(\frac{\beta I_0(t)^2}{2h\nu}\right) dt, \tag{5.3}$$

which is equivalent to

 $n_{total} =$ 

$$\frac{\alpha}{h\nu} \cdot \sqrt{\frac{4\ln 2}{\pi}} \cdot \frac{(1-R)F}{tp} \int_{-\infty}^{\infty} e^{-4\ln 2\left(\frac{t-t_p}{t_p}\right)^2} dt +$$
(5.4)  
$$\frac{\beta}{2h\nu} \cdot \frac{4\ln 2}{\pi} \cdot \frac{(1-R)^2 F^2}{t_p^2} \int_{-\infty}^{\infty} e^{-8\ln 2\left(\frac{t-t_p}{t_p}\right)^2} dt,$$

where the first and second lines are the 1- and 2-photon yields, respectively. Simplifying Equation 5.5, the ratio of 2- to 1-photon yields can be expressed as

$$R_{(2:1)} = \sqrt{\frac{\ln 2}{2\pi}} \cdot \frac{\beta}{\alpha} \cdot \frac{(1-R)F}{t_p}, \qquad (5.5)$$

or  $\approx 0.332 \cdot \frac{\beta(1-R)F}{\alpha t_p}$ , thus revealing the pulse width dependence. Additionally, a dependence on fluence and the ratio of 2- to 1- photon absorption coefficients,  $\beta/\alpha$  is revealed.

Using the parameters for Si of  $\alpha = 2.27 \times 10^3 \text{ cm}^{-1}$  and R = 0.37, with the pulsewidth measured during the experiment of  $t_p = 40.8$ , assuming that  $R_{(2:1)} = 1$  when the 2-photon overtakes linear absorption processes, a measured value of the 2-photon absorption coefficient,  $\beta$ , can be deduced from the fluence threshold observed in these experiments. Assuming the measured fluence threshold here could lie between 18-22 mJ/cm<sup>2</sup>, this corresponds to  $\beta = 7.5 - 9.1 \text{ cm/GW}$ , which is within the range of values found in the literature, as is shown in Table 5.1.

As will be discussed in the following sections, the linear dependence of  $\tau_i$  on Fat lower fluences can be explained based on a thermally-mediated electron tunneling process across the SiO<sub>2</sub> layer, in which the rise of the quasi-Fermi level in Si is linearly proportional to F. However, as the 2-photon absorption overtakes the 1-photon as the primary mechanism in generating carriers in Si, a coherent (2+1) photo-absorption process will lead to photoinjection of electrons into the SiO<sub>2</sub> the conduction band, thus leading to a more efficient way of injecting charges to the surface of SiO<sub>2</sub>.

# **5.3** Photoinduced Surface Charging (Injection)

# 5.3.1 Direct Tunneling

this section, direct tunneling of electrons from Si through the oxide is considered
0, 61, 67, 68, 303, 329]. The oxide acts as a tunneling barrier for the excited plasma
the silicon sub-surface region. From the frame of reference of a standard heterojunction investigation of ultrathin oxide tunneling, the situation here is atypical, in

	β	$F_{50/50}$	λ	$t_p$	Method	
/(c	===n/GW)	$(mJ/cm^2)$	(nm)	(ps)		
	50.0	3.3	625	0.1	Sokolowski-Tinten et al. (2000)	
					pump-probe reflectivity [136]	
	<b>1</b> .5	109.4	1064	4-100	Boggess et al. (1986)	
					pump-probe transmissivity [278]	
/	⊒.8	91.1	850	0.2	Bristow et al. (2007)	
					pump-probe transmissivity [277]	
١	<b>3</b> 8.0	4.3	625	0.08	Esser et al. (1990)	
$\vdash$					pump-probe transmis./reflectiv. [327]	
$\backslash$	<b>9</b> .0	18.2	800	0.130	Korfiatis et al. (2007)	
					imposed theoretically [265]	
	6.8	24.1	800	0.028	Sabbah & Riffe (2002)	
					pump-probe reflectivity [328]	
$\langle$	8.2	20.0	800	0.045	Murdick et al. (2009)	
					UEDV	

Table 5.1: Some of the measurements of the 2-photon absorption coefficient ( $\beta$ ) for Si found in the literature. Few studies exist that have measured this parameter. Avelength varies between 625-1064 nm for the studies listed and pulse duration m 28 fs to 100 ps, possibly explaining the wide range of values for  $\beta$ .



Figure 5.3: Injection time (top) and the maximum amplitude voltage (bottom), both as a function of fluence. Both plots show the onset of a faster and stronger source of voltage after ~ 20 mJ/cm<sup>2</sup>. The fluence-dependent TSV can be fitted with a quadratic equation  $(aF + bF^2)$ , in which the quadratic component  $(bF^2)$  overtakes the linear one (aF) near 20 mJ/cm<sup>2</sup>, coinciding with the crossover behavior in  $\tau_i$  at the same fluence.

that there is no applied voltage, contacts, or measured current. Rather, the voltage is the result of optical excitation.

Optical voltage generation occurs because the quasi-Fermi level of the substrate is raised due to the photoexcitation of (hot) carriers, in conjunction with a finite tunneling probability, which is directly attributable to its nanoscale thickness. While electronic injection to deep trap states at the interface will contribute to the overall TSV, as revealed from optical pump-probe studies [81, 85], its contribution is negligible on shorter time scales (hundreds of ps) due to the relatively low density of deep trap states compared to the surface charge density accumulated through tunneling. Deep trap states tend to have longer lifetimes ( $\gtrsim$  ns) which are not observed here.

Note that Fowler-Nordheim tunneling is not applicable here because the quasi-Fermi level of Si would have to rise by at least the conduction band offset between Si and SiO<sub>2</sub> ( $\approx 3.2 \text{ eV}$ ), such that it would lie in the triangular part of the barrier. An excitation like this would cause carrier-induced damage before this could occur. Moreover, the tunneling *is the source* of the voltage here, whereas with FN tunneling, an applied field induces the tunneling.

An approximation can be made assuming a parallel-plate capacitor, with the voltage drop across the dielectric oxide  $V_b = e\tilde{\sigma}L/\epsilon_0\epsilon_{ox}$ , which confirms the order of magnitude to be 10-100 mV, using a surface state density,  $\tilde{\sigma} = 10^{12}$ - $10^{13}$  cm<sup>-2</sup> [330], L = 1 nm, and  $\epsilon_{ox} = 2.1$ .

With the calculation of the quasi-Fermi level  $(\mu_e)$  and electronic temperature  $(T_e)$  from the models introduced in Section 3.2, the tunneling current through the oxide can be calculated from [60, 61, 67, 68, 303]

$$i(t) = \frac{4\pi e}{\hbar} lS \int D_1(\varepsilon) D_2(\varepsilon) \left| \tilde{M}_{12}(\varepsilon) \right|^2 \left[ f_1(\varepsilon, \mu_1) - f_2(\varepsilon, \mu_2) \right] d\varepsilon,$$
(5.6)

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where  $D_1(\varepsilon)$  represents the 3D density of states in the Si bulk,  $D_2(\varepsilon)$  is the 2D density of states at the Si/SiO<sub>2</sub> interface, l is the wave function decay length into Si, S is the sample area excited by the pump laser,  $f_1$  and  $f_2$  are the Fermi functions at the Si/SiO<sub>2</sub> and SiO<sub>2</sub>/vacuum interfaces, respectively, and  $M_{12}(\varepsilon)$  are the matrix elements of the transmission, given by [60, 67, 68]

$$\tilde{M}_{12} = -\frac{\hbar^2}{2m} \int_0^L \left( \psi_1^* \nabla \psi_2 - \psi_2 \nabla \psi_1^* \right) dz,$$
 (5.7)

where  $\psi_1$  and  $\psi_2$  are the wave functions on the left  $(z \leq 0)$  and right sides  $(z \geq L)$  of the barrier, respectively (see Figure 5.4).

For a trapezoidal barrier, the wave function in each region is given by [70] (assuming no incident wave from the right)

$$\psi(z) = \begin{cases} A \exp(ik_1 z) + B \exp(-ik_1 z) & \text{for } z \leq 0, \\ C \exp(\int_0^z k_b(z')dz') & \\ +D \exp(-\int_0^z k_b(z')dz') & \text{for } 0 < z < L, \\ G \exp(ik_3 z) & \text{for } z \geq L, \end{cases}$$
(5.8)

where

$$k_1 = \sqrt{\frac{2m_1\varepsilon}{\hbar^2}},\tag{5.9}$$

$$k_b(z) = \sqrt{\frac{2m_2[V(z) - \varepsilon]}{\hbar^2}},\tag{5.10}$$

$$k_3 = \sqrt{\frac{2m_1[\varepsilon + eV_b]}{\hbar^2}},\tag{5.11}$$

$$u = \int_0^L k_b(z) dz, \qquad (5.12)$$

$$D_1(\varepsilon) = \frac{m_1}{\pi^2 \hbar^3} \sqrt{2m_1 \varepsilon}, \qquad (5.13)$$

$$D_2(\varepsilon) = \frac{\tilde{N}}{\sqrt{2\pi\sigma_{\varepsilon}}} e^{-(\varepsilon - \varepsilon_F)^2 / 2\sigma_{\varepsilon}^2},$$
(5.14)

 $V(z) = \Phi_0 - eEz$ ,  $\Phi_0$  is the conduction band level offset between the Si and SiO<sub>2</sub>,  $m_1$  and  $m_2$  are the effective masses of the silicon and oxide, respectively ( $m^*$  is approximated as  $m_1$  for tunneled electrons). The electric field in the barrier is  $E = -V_b/L$ , where L is the oxide thickness. The simple picture in Figure 5.4(c) depicts the stationary states associated with Equation 5.8. The transmission matrix elements can be found by inserting Equation 5.8 into 5.7. After applying the boundary conditions

$$\psi(0^{-}) = \psi(0^{+}), \ \frac{1}{m_1} \left(\frac{d\psi}{dz}\right) \Big|_{0^{-}} = \frac{1}{m_2} \left(\frac{d\psi}{dz}\right) \Big|_{0^{+}}$$
$$\psi(L^{-}) = \psi(L^{+}), \ \frac{1}{m_2} \left(\frac{d\psi}{dz}\right) \Big|_{L^{-}} = \frac{1}{m_1} \left(\frac{d\psi}{dz}\right) \Big|_{L^{+}}, \tag{5.15}$$

and properly normalizing, the matrix elements are found to be

$$|M_{12}(\varepsilon)|^2 = \frac{\hbar^4}{m^2 l^2} \left(\frac{k_1 + k_3}{k_1 - k_3}\right)^2 \sin^2\left(\frac{(k_1 - k_3)L}{2}\right) T(\varepsilon), \tag{5.16}$$

where  $T(\varepsilon)$  is the transmission probability  $(|G|^2/|A|^2$  in Eq. 5.8), given by [70]

$$T(\varepsilon) = \frac{\left(2\frac{k_1k_b^L}{k_b^0}\right)^2}{\left\{\left(k_3 + \frac{k_1k_b^L}{k_b^0}\right)\cosh u\right\}^2 + \left\{\left(\frac{m_2k_1k_3}{m_1k_b^0} - \frac{m_1k_b^L}{m_L}\right)\sinh u\right\}^2}.$$
 (5.17)

The total accumulation of tunneled charge at time t,

$$Q_{tun}(t) = \int_0^t i(t') dt'.$$
 (5.18)

allows the voltage drop across the barrier,  $V_b$  to be deduced from the total capacitance,  $C_{tot}$ , which consists of two series capacitors: electrostatic ( $C_E$ ) and quantum ( $C_q$ ) [331], given by



Figure 5.4: (a) A band diagram depicting the Si/SiO<sub>2</sub>/vacuum interface. (b) Schematic of the energy diagram with relevant quantities used for the tunneling calculations. Electrons that tunnel through the oxide to the SiO<sub>2</sub>/vac interface, cause the quasi-Fermi level  $\mu_2$  to raise, making the barrier take on a trapezoidal shape. The electronic density of states is shown in light-grey for the silicon (D<sub>1</sub>) and the SiO<sub>2</sub>/vac interface (D<sub>2</sub>). The difference between the two levels,  $\Delta \mu$  (dark grey band) is the primary factor in determining the tunneling current. For a given energy ( $\varepsilon$ ), when  $\Delta \mu$ ,  $D_1(\varepsilon)$ , and  $D_2(\varepsilon)$  are all  $\neq 0$ , then there will be a tunneling current through the SiO<sub>2</sub>. (c) Probability amplitude schematic; the wave functions with amplitudes (A, B, C, D, G) are used to compute the tunneling matrix elements,  $M(\varepsilon)$ .

$$C_E = \frac{\epsilon_0 \epsilon_{ox} S}{L} \tag{5.19}$$

and

$$C_q = e^2 D_2(\varepsilon_F) \tag{5.20}$$

respectively, where  $\epsilon_{ox}$  is the relative permittivity of SiO<sub>2</sub>, and  $D_2(\epsilon_F)$  is given by Equation 5.14.

Note that  $C_q$  becomes particularly important as the length scale of the insulating dielectric decreases, such as the case here. With the thicker oxides of the past, quantum capacitance effects could be neglected since  $C_q \gg C_E$ , and thus the voltage drop across the 'quantum capacitor' was negligible. The voltage drop across the barrier due to optically-induced tunneling is then

$$V_b(t) = \frac{Q_{tun}(t)}{C_{tot}},\tag{5.21}$$

where  $C_{tot} = C_Q C_E / (C_Q + C_E)$ .

The goal is to investigate the role of tunneling on the slow  $\tau_i$  observed for low fluences. Accordingly, the charge relaxation (long time) portion of the experimental curves, which is deemed to be due to a different mechanism, is maintained by imposing the relaxation factor from Eq. 4.3 onto the simulated  $V_b$ , such that  $V_s = V_b \left(\frac{1}{1+t/\tau_c}\right)$ . The simulated  $V_s$  is fitted with the injection factor from Eq. 4.3,  $V_{fit} \left[1 - \exp\left(-\frac{t}{\tau_i}\right)\right]$ , the results of which are shown in Figure 5.5, for parameters  $S = 6.96 \times 10^{-7} \text{ m}^2$ ,  $m_1 = 0.19m_e$ ,  $m_2 = 0.5m_e$ , L = 1.0 nm,  $\Phi_0 = 3.125 \text{ eV}$ ,  $\tilde{\sigma} = 2.75 \times 10^{13} \text{ cm}^{-2}$ , w = 0.35 eV,  $\varepsilon_F = -0.373 \text{ eV}$ , and l = 1.0 Å; [84]. The density of states at the SiO<sub>2</sub>/vacuum interface and the barrier thickness and height were used as fitting parameters. The tunneling current was most sensitive to L and  $\Phi_0$ , which enter through the transmission probability,  $T(\varepsilon)$ .



Figure 5.5: The characteristic time associated with surface charging,  $\tau_i$ , as a function of excitation fluence. The simulated  $\tau_i$  assumes that the TSV is constituted solely from the voltage drop across the oxide barrier, calculated from Equation 5.21.

Note, one of the assumptions of the calculation is that the relaxation of tunneled electrons to lower lying levels on the right side of the barrier is assumed to occur faster than the time scales associated with the tunneling events through the barrier.

From the results of this calculation, shown in Figure 5.5, it seems plausible that direct tunneling is a dominant mechanism for voltage generation at low fluences. Moreover, the role of tunneling rapidly diminishes as fluence is increased to moderate or high levels, indicating that another mechanism seemingly over-powers the tunneling as the primary source of the TSV generation, which will be investigated in the next section.

#### 5.3.2 Coherent (2+1) Absorption (2-Photon + Free Carrier)

The quadratic dependence of  $\tau_i$  on fluence is interpreted as a coherent absorption process, where a significant fraction of the population lying at the 2-photon level (~ 1.5 eV above the CB edge) begins to dephase through scattering with other electrons that have been elevated to that level. The ability to promote an electron to the SiO<sub>2</sub> conduction band depends on the dephasing time of the hot electrons generated by 2-photon absorption and the initial point in momentum space in the non-thermal regime, as will be detailed later, the electron dephasing time ( $\tau_{ee}$ ) is inversely proportional to the hot electron density.

Presented below is self-consistent analysis of 1- and 2-photon absorption, with a 'lossy' term for electron-electron scattering,  $\tau_{ee}$ . From this fraction, the probability of an additional photon absorption is calculated, thus arriving at the effective absorption cross-section describing the '2+1' yield. Note that it is not the same as 3-photon absorption, where three coherent photons would be absorbed simultaneously, and a cubic dependence would be expected in the TSV (3-photon absorption is negligible at wavelengths this short).

From the 2+1 population, the net charge transfer to the surface is quantified via injection of photoelectrons into the conduction band of  $SiO_2$ , leading to surface charging. This process of electron transport from Si to  $SiO_2$  is called internal photoemission (IPE) (internal because the electrons are not at the vacuum level). A schematic of the process is shown in Figure 5.6. This process is found to have quadratic dependence and a sufficiently high yield to describe the TSV magnitudes observed here.

Recall from Equation 3.36, the Gaussian expression describing the temporal character of laser interaction with Si,

$$I_0(t) = \sqrt{\frac{4\ln 2}{\pi} \frac{(1-R)F}{t_p}} \exp\left[-4\ln 2\left(\frac{t-3t_p}{t_p}\right)^2\right].$$
 (5.22)

The spatial dependence assumes an exponential decay into the substrate

$$I(z,t) = I_0(t)e^{-z/\delta_e f f}$$
(5.23)



Figure 5.6: Coherent absorption, characterized by a consecutive 2- and 1-photon absorption with electron scattering dephasing.

ġ, (Ľ 2 f;; where the effective optical penetration depth is given by

$$\delta_{eff} = \frac{1}{\alpha + \Theta n} \ln \left[ \frac{e(\alpha + \Theta n) + \beta I_0}{\alpha + \Theta n + \beta I_0} \right].$$
(5.24)

The 2-photon absorbed population is described by

$$\frac{\partial N_{2ph}}{\partial t}(z,t) = \frac{\beta I(z,t)^2}{2h\nu} - \frac{N_{2ph}(z,t)}{\tau_{ee}},\tag{5.25}$$

where  $\beta$  is the 2-photon absorption coefficient, just as in Section 3.2, and the second term on the RHS describes the ensuing electron-electron relaxation,  $\tau_{ee}$ , given by [332]

$$\frac{1}{\tau_{ee}} = \frac{ne^4}{\pi\epsilon^2 \sqrt{8m^* E^3} m^{*1/2}} L(E_k, q_0), \qquad (5.26)$$

where

$$\begin{split} L(E_k, q_0) &= \log\left(1 + \frac{8m^*E_k}{\hbar^2 q_0^2}\right) - \frac{1}{1 + \hbar^2 q_0^2/8m^*E_k} \\ &- \frac{\pi}{2} \left\{1 - \frac{\left(\hbar^2 q_0^2/2m^*E_k\right)\left(1 + \hbar^2 q_0^2/8m^*E_k\right)}{1 + \left(\hbar^2 q_0^2/2m^*E_k\right)\left(1 + \hbar^2 q_0^2/8m^*E_k\right)}\right\}, \quad (5.27) \end{split}$$

and  $q_0 = 1/\lambda_D$ , where  $\lambda_D$  is the Debye length, given by  $\lambda_D = \sqrt{\epsilon k_B T_e/ne^2}$ .

The free-carrier absorption  $N_{fca}$ , which is the 2+1 absorbed population, is calculated from

$$\frac{\partial N_{fca}}{\partial t}(z,t) = \Theta N_{2ph}(z,t) \frac{I(z,t)}{h\nu}, \qquad (5.28)$$

where  $\Theta$  is the free-carrier absorption cross-section [278].

Of the electron population that has gained sufficient energy to overcome the barrier for IPE, the total accumulation is given by,

$$N_{ipe}(t) = \int_0^t \int_0^\infty N_{fca}(z, t') \eta(z, t') dz dt',$$
(5.29)



Figure 5.7: Results from the 2+1 photon calculations using the formalism above, showing a quadratic dependence in the internal photoemitted yield.

where the transport efficiency,  $\eta(z, t)$ , represents the fraction of the 'eligible' population,  $N_{fca}$ , that can be transported and satisfy momentum conservation.

As can be seen in the above figures, the dependence is indeed quadratic. The processes involved in the 2+1 transport are outlined in Table 5.2. At this point, the characteristic length associated with this charge separation cannot be determined with certainty, however, at densities on the order of  $10^{14}$  cm<sup>-2</sup>, the magnitude of the IPE yield is certainly sufficient to generate the TSV magnitudes observed in the experiments here.

## 5.4 Surface-Bulk Coupling (Relaxation)

It was previously shown [107] that the decay behavior of the TSV at the Si(111)/SiO<sub>2</sub> interface compares well with the surface state dynamics on a vacuum-cleaved Si(111)- $(2 \times 1)$  surface, revealed by a photoemission study [126] (Figure 5.8), where the surface

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Fluence (a.u.)	2-photon	$ au_{ee}$	Photon Flux	2+1 Yield
1	1	1	1	1
2	4	1/2	2	4
0	0	1 /0		0
3	9	1/3	3	9

Table 5.2: The underlying processes associated with 2+1 absorption, all of which are occurring within the duration of the optical excitation pulse. For an arbitrary fluence (column 1), the 2-photon yield will increase quadratically (column 2), but this population will experience a loss from electron-electron scattering (column 3), which has linear dependence on fluence. The probability of absorbing a third photon is linear with the photon flux, still illuminating the surface (column 4). The net effect is the 2+1 yield, which goes as  $N_{2+1} \propto \left(F^2 \times F^{-1} \times F = F^2\right)$  – quadratic (column 5).

recombination observed was said to be due to a strong coupling between the surface states and bulk evanescent states.

In Figure 5.8, the TSV has been rescaled to match with the amplitude of the data extracted from Reference [126]. A striking similarity in the relaxation rates is clear. If the observed field here were because of charge transfer to deep trap states, the time scale for the TSV to decay would be on the order of ns- $\mu$ s or possibly longer, and the observed 100 ps would not make sense. There would also be a residual charging effect since deep trap state occupation is largely irreversible. No residual effect was observed. Since it is known that the generated TSV involves the surface (bulk Dember fields are far too weak to deflect the beam to this extent), it is very reasonable to presume the same strong surface-bulk coupling as in Reference [126], ultimately dictating the decay rate of the field.

Further evidence of the strong role played by carrier dynamics on the surface recombination is revealed by the power-law decay of the TSV, shown in Figure 5.9(a),



Figure 5.8: Transient surface state population measured by photoemission [126] (diamonds) compared with the measured TSV (triangles) (rescaled;  $F=72 \text{ mJ/cm}^2$ ), demonstrating very similar decay rates.

where an exponent near -1 (-0.93  $\pm$  0.03) is ascribed to the characteristic decay of surface charges, with a time constant of 100 ps. If the field decayed because 1D diffusion the power would be -1/2. The -1 power arises from a phenomenological model for bipolar drift recombination, which is illustrated in Figure 5.9(b)-(d). The relaxation of electrons occupying surface states is rate-limited by the bulk carrier dynamics. The nonequilibrium space-charge layer, with initial separated charge density  $\sigma_0$ , is modeled as two separate slabs, separated by a distance  $l_{e-h}$  in a dielectric medium ( $\epsilon_{Si} = 11.8$  for Si), shown in Fig. 5.9(c). The power-law characteristics are manifested in the simple rate equation

$$\frac{d\sigma(t)}{dt} = \frac{\sigma(t)}{\tau_r},\tag{5.30}$$

with the space-charge recombination time  $\tau_r = l/\mu E$  depending on the transient field E, which is directly related to the surface charge  $\sigma(t)$ . Its solution  $\sigma(t) = \sigma_0/(t/\tau_c + 1)$  has a characteristic time scale  $\tau_c = l\epsilon/\mu\sigma_0$ , which is the time for the TSV to drop by 50% from its initial value, and corresponds to the induction period in the log-log plot of the solution, as described in Figure 5.9(d). For  $t >> \tau_c$ , the  $t^{-1}$  behavior emerges, similar to what is observed experimentally (Figure 5.9). To compare with the experimental results, a linear decay of the surface potential barrier ( $V_s$ ) is assumed over the space-charge layer  $l_{e-h}$ , and determine the size of the induced space-charge regime to be  $l \approx 400$  nm (using carrier mobility,  $\mu=100$ cm<sup>2</sup>/V·s according to Reference [264], the measured  $\tau_c$  of ~100 ps, and  $V_s$  of 2 V), which is in agreement with the laser penetration depth in Si.



Figure 5.9: (a) Log-log plot of the TSV with a linear fit to the long time data. (b) A schematic of the space-charge region. (c) A schematic of the bipolar (two-slab) drift model in (c) is implemented to describe the recombination. (d) Carrier drift causes the surface charge,  $\sigma_0$  to diminish with a characteristic time  $\tau_0$ , after which,  $\sigma_0$  falls as  $t^{-1}$  obtained from the slab model.

## 5.5 Discussion

Using UEDV, the fundamental nature of the mechanisms associated with surface voltage generation at the  $Si/SiO_2$  interface have been investigated. With careful analysis of the charge transfer processes, the UEDV data clearly separate two distinctive regimes of charge rearrangement. The first is associated with a low intensity excitation regime, showing a linear dependence on fluence. In Section 5.3.1, analysis on the direct tunneling of electrons through the oxide correlated well with the UEDV observations, thereby providing strong evidence that it is the underlying mechanism of TSV generation in this regime. The primary charge transfer process occurring in this regime involves electron tunneling from Si to the surface states of SiO<sub>2</sub>.

The second mechanism involves charge transfer to unoccupied states in the SiO<sub>2</sub> conduction band, through an absorption process that relies on a coherent, 2+1 optical absorption. Note that the energy offset from the valence band edge of Si to the CB edge of SiO<sub>2</sub> is  $\approx 4.3$ -4.5 eV, indicating that 2-photon absorption alone is insufficient for significant electron transport to SiO<sub>2</sub> (in the form of IPE). The analysis of a coherent, 2+1 photon absorption process was demonstrated here to constitute a significantly high yield and shorter injection time, consistent with observations. More importantly, the 2+1 absorption (with electron dephasing) explains the quadratic trend observed experimentally, rather than a cubic one.

#### 5.5.1 Thermionic and Photoinduced Emission

As discussed in Section 4, when performing UEDV experiments, one of the most essential features that must be extracted from the data is the source of the electric field. The robustness of TSV determination in Si/SiO<sub>2</sub>, which is mostly independent of electron penetration depth (controlled by the incidence angle,  $\theta_i$ ; see Figure 4.10), indicates that the main source of TSV comes from the fixed length voltage drop across the SiO<sub>2</sub> barrier. However, a weak  $\theta_i$  dependence is found at short times, which contributes approximately 10% of the TSV.

Sources of  $\theta_i$ -dependent TSVs include the vacuum and bulk space charge regions,  $\Delta V_{vsc}$  and  $\Delta V_{sc}$ , respectively. In the case of  $\Delta V_{sc}$ , the threshold is the flatband photovoltage of approximately 300 mV [310]. The vacuum space charge region,  $\Delta V_{vsc}$ , established by the formation of a vacuum emitted electron cloud above the surface, stems from several possible emission pathways, such as thermionic, direct photoemission, or field-induced, which leads to a time-dependent electric field above the surface.

Thermionic emission occurs when the tail of the Fermi-Dirac distribution rises above the vacuum level (Figure 5.10). As the process evolves, a space-charge cloud develops, which serves as a hindrance to further electron emission. Riffe and colleagues formulated a simple addition to the Richardson-Dushman equation to account for the space-charge effect [248]. The expression gives the number of emitted electrons,  $N_{esc}$ , per unit time that will fly outward from the surface,

$$\frac{dN_{esc}}{dt} = \pi R_1 R_2 C_1 k_B^2 T_e^2 \exp\left(-\frac{\varepsilon_F - \mu + W + ae^2 N_{esc}/R_1}{k_B T_e}\right),$$
 (5.31)

where  $C_1 = 4\pi m/h^3$ ,  $R_1$  and  $R_2$  represent the semi-major and minor radii of the (elliptical) excitation laser, respectively. The Fermi energy, chemical potential<sup>2</sup>, and work function are represented by  $\varepsilon_F$ ,  $\mu$ , and W, respectively. The last term in the numerator of the exponential in Equation 5.31 was introduced by Riffe and colleagues to account for the space-charge effect[248]. The factor, a, is a geometrical factor characterizing the emitted electron distribution (in units of  $[4\pi\varepsilon_0]^{-1}$ ). For a spheroid, thin-disc, or thin ellipsoid, a = 1.2, 1.7, and 1.95, respectively.

<sup>&</sup>lt;sup>2</sup>For a metal the chemical potential should be used, whereas with semiconductors the quasi-Fermi level should be used for both electrons and holes, such as here with Si.



Figure 5.10: Thermionic emission at an  $Si/SiO_2$  interface. The work function is exceeded by the fraction of electrons occupying states in the upper tail of the Fermi-Dirac distribution (shaded region). As the excitation pulse is absorbed by the surface, the accumulated yield from the tail can lead to a non-negligible charge density cloud above the surface.

Here, the thermionic emission source is neglected because of the low photon energy (1.55 eV) resulting in a low theoretical yield of photoelectrons, and more so because of the crystallographic probe used to measure the TSV, which has been shown previously to be most strongly affected by sub-surface fields [194]. For non-crystallographic methods where the direct electron beam has been used to probe photoelectrons, see References [200, 286, 287].

#### 5.5.2 Dielectric Enhancement of the Interface Dipole

Prior to photo-excitation, a static dipole forms at the  $Si/SiO_2$  interface because of an abrupt difference in the electronegativity in the Si and  $SiO_2$  atoms,[36, 306, 333] inducing an interface potential given by

$$V_{dp} = \frac{e\rho^* l_d N_s}{\left(\epsilon_{Si} + \epsilon_{ox}\right)/2},\tag{5.32}$$

where  $\rho^*$  is the amount of partial charge transfer from Si to SiO<sub>2</sub> (depending on the electronegativity offset),  $l_d = 1.67$  Å is the distance of transition associated with
the interface[324, 333] (the Si-O bond length),  $N_s$  is the planar density of Si atoms  $(7.833 \times 10^{14} \text{ bonds/cm}^2 \text{ for Si-111})$ , and  $\epsilon_{Si}$  and  $\epsilon_{ox}$  are the relative permittivities of the Si and SiO<sub>2</sub>, equal to 11.8 and 2.1, respectively. Taking  $\rho^* = 0.22$  electrons per bond,[333] the potential of the static surface dipole is estimated to be  $V_{dp} = 749$  mV.

The hot carrier plasma initiated by photo-excitation causes a sharp change to the dielectric properties of silicon as the free carrier response acts to lower the permittivity.[136] In 2000, Sokolowski-Tinten and von der Linde demonstrated with pump-probe reflectivity measurements that the effect is well-described by the Drude model for a damped plasma. Under photo-excitation, the dielectric function takes the form

$$\epsilon^* = \epsilon_{Si} + \Delta \epsilon_{fcr}, \tag{5.33}$$

where the free carrier permittivity change,  $\epsilon_{fcr}(\omega, n)$ , is expressed according to the Drude model

$$\epsilon_{fcr} = -\left(\frac{\omega_p}{\omega}\right)^2 \frac{1}{1+i\frac{1}{\omega\tau_D}},\tag{5.34}$$

 $\tau_D$  is the Drude damping time[136] of 1.1 fs,  $\omega_p$  is the plasma frequency, given by  $\omega_p = \sqrt{e^2 n / \epsilon_0 \epsilon_{Si} m_{opt}^*}$ , where *n* is the carrier density, and  $m_{opt}^*$  is the optical effective mass, measured to be[136]  $\approx 0.18 m_e$ .

In Eq. 5.32, the permittivity of the interface is represented by the average of Si and SiO<sub>2</sub>, implying that for a sufficiently dense plasma generation, the free carrier response can enhance the interfacial potential. The carrier density, n, will rise nonlinearly with increasing fluence, as the generation due to multiphoton absorption  $\propto F^2$ , which means the TSV should also, since  $\Delta \epsilon_{fcr} \propto \omega_p^2 \propto n$ .

To calculate the effect of the free carrier response on surface dipole enhancement (SDE), the transport model from Section 3.2 is invoked to calculate the plasma frequency, which, in turn gives  $\Delta \epsilon_{fcr}$ , and thus the effect of SDE. The SDE factor is estimated by substituting Equations 5.33 and 5.34 into Equation 5.32, simulated over the course of the plasma generation. Results from the SDE calculations could not account for the magnitude of the TSV observed here, nor the trend. For the highest fluences, the estimated SDE is ~100 mV. Thus, it is concluded that SDE effects are negligible here.

### 5.5.3 Future Investigations / Open Questions

In addition to the UEDV experiments described in this chapter, experiments were also performed for a series of 400 nm excitation fluences, as shown in Figure 5.11, with fluences ranging from 1.7 to 20.4 mJ/cm<sup>2</sup>. While similar injection times as the 800 nm experiments were found, with distinctive  $\tau_H$  (~50 ps) and  $\tau_L$  (~100 ps) at high and low fluences, respectively, the corresponding TSV is much higher in the case of 400 nm, which could be due to the increased abundance of direct band gap transitions. Furthermore, unlike the quadratic fluence dependence found at 800 nm, the dependence at 400 nm is approximately linear, as the initial creation of free carriers can be achieved now by 1-photon absorption, rather than 2-photon absorption.

As UEDV continues to evolve in the coming years, specifically with data pertaining to vacuum space charge by applying the new charge-imaging probe geometry from Reference [200], it is likely that the hot electron dynamics within the materials that lead to TSVs as well as photoemission can be fully elucidated. Another interesting experiment might be to test both pump energies on a direct band gap semiconductor like gallium arsenide, or a wide band gap like TiO<sub>2</sub>, and compare the injection times. Additional experiments were also performed on p-type Si(111) and a Si(100) sample with heavy doping ( $\rho \sim 0.01 \ \Omega \cdot cm$ ). Neither showed major differences in the TSV dynamics. As expected, the TSVs observed by UEDV are not affected by the majority carrier concentration at the ground state because the bulk of the TSV is due to photoexcitation from a high intensity optical source. Regardless of where the Fermi level lies in the gap, both are going to respond the same way to femtosecond laser excitation. However, additional insights pertaining to tunneling could possibly be gained by examining the low fluence regimes of n- and p-types with heavy doping in both, such that the Fermi level is pinned near CB or VB edge. There, it would be expected that the p-type would show a lesser TSV from tunneling, as the quasi-Fermi level would start from ~ 1 eV below that of the n-type.

Performing the same experiments at low temperatures ( $\leq 100$  K) would be beneficial in that it would suppress the linear absorption, allowing only the effects from 2-photon absorption to contribute to the TSV, due to the depletion of the phonon population which is necessary to assist indirect transitions. Such experiments were carried out, but inconclusive as the diffraction signal dropped unexpectedly after the stage was cooled, rendering any conclusions ambiguous.

A preliminary pulse-width dependence experiment was conducted for a *n*-type  $Si(111)/SiO_2$  sample, shown in Figure 5.12. As the pulse width of the excitation laser is shortened, the TSV response increases. While this is consistent with the interpretation of the (2+1)-induced process, in which an enhanced transient optical field at shorter pulse duration promotes 2-photon absorption (see Equation 5.5), the degree to which consecutive 1-photon absorption is affected by electron-electron relaxation (also enhanced), is not yet fully resolved. A full experiment where both fluence and pulse width are varied should serve to provide additional insights to the relationship between multiphoton absorption and the TSV.



Figure 5.11: UEDV data at 400 nm excitation. (a) The TSV response at different fluences. The ZoT was determined to be 540 ps. (b) Fit results for 800 nm (red) and 400 nm (blue) data (800 is the same as in Section 5.3; shown here for a baseline). Parameters  $\tau_i$  and TSV (inset) are plotted against laser fluence. Both 400 and 800 nm experiments show distinctive fast ( $\tau_H$ ) and slow ( $\tau_L$ ) injection times for high and low fluence regimes, respectively, yet the TSV dependence on F is linear for 400, and quadratic for 800 nm excitations, respectively.



Figure 5.12: A pulse width dependence was observed for the transient surface voltage. Blue, green, and red correspond to ~41, 72, and 90 fs, respectively. The fluence dropped slightly as the pulse width was made shorter ( $F = 44.6 \text{ mJ/cm}^2$  for the 41 fs pulse and 49.0 mJ/cm<sup>2</sup> for the 90 fs pulse).

# Chapter 6

# Charge Transfer in Surface-Supported Nanoparticles

### 6.1 Introduction

The scope of nanoparticle research spans many disciplines with *vast* possibilities of incorporation into practical use, including nanoelectronics [334–340], photovoltaics [15, 17–19, 22, 26, 29, 33–35, 40–43, 46, 48, 50], and even quantum-dot based lasers [341–346]. 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 [347–349]. Metallic nanoparticles have also been invoked in biomedical imaging [350, 351]. 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 beating the diffraction limit for spatial resolution [352–355]. It has been observed that the same near-field optical-enhancement ('lensing') effect can be used for creating nano-sized features on substrates [356–358].

Monodisperse metallic nanoparticles (Figure 6.1) can be deposited on Si substrates (a) by way of self-assembled aminosilanes (b) [190, 359, 360]. The aminosilane chains, which are anchored to the Si substrate, immobilize the nanoparticles through the formation of van der Waals bonds.



Figure 6.1: (a) A sample of Au nanoparticles immobilized on a functionalized Si substrate. (b) The chemical form of the APTMS linker molecule. (c) Schematic of an electron beam scattering from the ordered self-assembled monolayer chain and the corresponding diffraction pattern. [190, 194].

The 2D nanoparticle ensemble shown in Figure 6.1(a) is an ideal prototype for UEC [192, 193]. In fact, a special implementation of UEC, called ultrafast electron nanocrystallography (UEnC) has recently emerged, where the technique has been optimized for the study of nanoscale structures (e.g. metallic nanoparticles, quantum dots, nanointerfaces, etc.) [190, 192]. When an ensemble of nanoparticles is sampled by the electron beam, a powder diffraction pattern results, as is shown in Figure 6.2(a), which is constituted from the many different crystal faces (b) 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 that is sufficiently ordered, such that very clear diffraction spots from the linker molecules are present in the patterns [Figure 6.2(a)].



Figure 6.2: Small-angle diffraction pattern obtained from the Au nanoparticle / SAM / semiconductor interface. (a) The raw diffraction image shows powder diffraction from the Au nanoparticles as well as a vertical array of spots at the center (arrows), corresponding to the self-assembled linker molecules. (b) Scattering intensity as a function of momentum transfer (s), where radial averaging has been performed around each ring perimeter, followed by a subtraction of the diffractive background (incoherent scattering), yielding the peaks shown in the plot. The peaks identified are consistent with fcc polycrystalline structure with a lattice constant equal to that of Au (a = 4.080 Å).

Here, the charging dynamics will be examined for an interfacial structure consisting of the interconnected nanoparticle/SAM/semiconductor geometry discussed here, shown in Figure 6.1. Observations of the near-field lensing effect will also be presented briefly. First, the sample preparation procedures will be covered, followed by a brief overview of the Mie theory, which is central to the topic of photoinduced charge transfer and near-field effects in nanoparticles. 6. E Š. T 3 £. 2 ċ. Ŀ þ

### 6.2 Sample Preparation

The nanoparticles that have been studied by the UEC group at MSU are always adsorbed on a substrate, never in solution, because the experiments are done in UHV. The particles must be well isolated on the surface, to avoid multiple scattering effects, as scattered electrons from one nanoparticle could interact with another nanoparticle *en route* to the CCD, ultimately destroying the signal to noise. Au and Ag solutions are purchased in monodisperse colloidal form. Individual nanoparticles are negativley charged via citrate ligation, such that they tend to remain monodisperse if the pH is not altered. Spin-coating this solution onto Si wafers is one option, though from experience, it tends to give a very low yield of nanoparticle coverage. Furthermore, with the nanoparticles in direct contact with the Si, the long-term stability of the samples might be affected by the atomic diffusion between the nanoparticles and the substrate. Moreover, the strong diffraction signal from the crystalline Si substrate might overwhelm the overall signal, rendering the diffraction signal from the nanoparticle undetectable.

Functionalization of the Si substrate with a self-assembled aminosilane layer is used to effectively control the areal densities of adsorption, as well as to provide a buffer layer that is sufficiently thick, to suppress the diffraction signal from the underlying substrate. Depending on the aminosilane that is chosen, the nanoparticles will be raised from the substrate by approximately 1 nm. Specifically, the linker molecules implemented in the UEC lab include [3-(2-Aminoethylamino)propyl]trimethoxysilane (APTMS), (3-Aminopropyl)trimethoxysilane (APTES) and 2-[2-(3-Trimethoxysilyl propylamino)ethylamino]ethylamine (APES), which self-assemble to about 0.8, 1.0, and 1.2 nm in thickness, respectively. The inclusion (or omission) of NH-groups along the chain allow its length to be adjusted; from shortest to longest, there are zero, one, and two NH-groups on the chains of APTES, APTMS, and APES, respectively<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup>Aminosilanes are ordered from Sigma-Aldrich.

Preparation of wafers follows similar recipes to those in References [338, 359, 360], which is schematically outlined in Figure 6.3. Silicon wafers are first cleaned using traditional acid/peroxide based cleaning techniques [326]. The usual cycle is immersion in  $H_2SO_4/H_2O_2$  ('pirahna') (7:3) for 10 min at 90 °C, NH<sub>4</sub>F (40% in H<sub>2</sub>O for 6 min), NH<sub>4</sub>OH/ H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O ('base piranha') (1:1:6) for 10 min at 90 °C, and HCl/ H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O (1:1:5) for 10 min at 90 °C. Between each step wafers are rinsed in deionized water for 10 min. After the cleaning, a hydroxylated surface results, shown in Figure 6.3(a).

Surface functionalization with the aminosilanes is the next step. In this step, the silane head attaches to the -OH groups on the Si surface. The general procedure for APTMS is to immerse all wafers into a solution containing 5 mL of APTMS and 1 mL of acetic acid, dissolved in 480 mL of H<sub>2</sub>O [Figure 6.3(b)], for 60 minutes, followed by a rinse and dry N<sub>2</sub> cycle [Figure 6.3(c)], then baking at 120° in an oven with pure N<sub>2</sub> gas to complete Si-O bond formation. Upon immersion in the Au nanoparticle solution (Au colloid, ethanol, H<sub>2</sub>O at 1:1:2), individual Au nanoparticles become immobilized as they form van der Waals bonds with the protonated NH<sub>3</sub><sup>+</sup> sites. A rinse and dry cycle follows, and the sample is ready to be imaged in an SEM. Note the 1:1:2 ratio for colloid/ethanol/water can be varied and different surface coverage densities will result, which is shown in Figure 6.4.

Further control of dispersion is achieved by altering the pH of the APTMS solution in the functionalization step, which varies the density of -NH<sub>2</sub> anchoring sites [361]. For example, raising the amount of acetic acid from 1 mL will indirectly result in an increased surface coverage density [362], which is demonstrated in Figure 6.4, where the pH of 7.0 and 2.0 result in nanoparticle areal densities of 70 and 300  $\mu$ m<sup>-2</sup>, respectively.



Figure 6.3: The stages of sample preparation. (a) A modified RCA process leaves a clean, hydroxylated Si surface. (b) Immersion of wafers in APTMS and acetic acid, dissolved in deionized water functionalizes the surface, followed by a rinse/dry cycle (c), and subsequent immersion in colloid solution (d) (described in text), and a final rinse/dry step (e) [190].



Figure 6.4: The effect of varying the ethanol/water ratio on surface coverage. All panels have 1 mL of colloid solution. The ratios of H<sub>2</sub>O to ethanol are given in the upper-right corner of each panel. The hydrophobicity is reduced as the ethanol concentration is increased, which effectively enhances the mobility of the nanoparticles in solution [190].



Figure 6.5: The effect of varying the pH of the solution during aminosilane functionalization. Adding small amounts of acetic acid increases the density of anchoring sites (NH $_3^+$ ) for the negatively charged nanoparticles, hence the increased coverage. Panels (a) and (b) have areal densities of 70 and 300  $\mu$ m<sup>-2</sup>, respectively. Note, sample (b) would give convoluted signal, as the nanoparticles are overly dense, scattered electrons would be intercepted by adjacent nanoparticles before arriving to the CCD. [190]

#### 6.3 Surface Plasmon Resonance / Mie Theory

A gold colloid solution is red (Figure 6.6). Why? In 1908, German physicist Gustav Mie aimed to answer this question and did. The answer lies in the way that the nanoparticles scatter light. Mie proved this by solving Maxwell's equations for electromagnetic radiation interacting with small metal spheres (assuming bulk dielectric functions), subject to the appropriate boundary conditions [363].



Figure 6.6: A 20 ml bottle of Au nanoparticles with average diameter of 9.6 mm  $\pm$  10%. The red color has to do with the way light is scattered and absorbed by the nanoparticles. The nanoparticles are monodisperse (non-aggragated) due to surface functionalization with citrates. A sharp change in pH (toward basic) would cause them to agglomerate and the solution would turn blue because of the new average nanoparticle size.

When light impinges a metal, the free electrons can be excited into collective oscillatory motion about the heavy ionic core. This occurs when the conditions are met for surface plasmon resonance (SPR), which depends on the dielectric properties of the metal as well as the size. Usually these oscillations are found in the deep ultraviolet spectral region, but for some materials, particularly noble metals, the absorption properties are strongly influenced by interband transitions, the sum effects of which lead to a red-shifting of the SPR. Figure 6.7 shows an example of excitation of the dipolar mode of of a metallic nanoparticle. The term 'surface' in SPR can be made clear from this figure; while the electrons are oscillating about the positive ionic core, the restoring force arises from the *surface* polarization, which flips every half oscillation.



Figure 6.7: The oscillating dipolar mode of a metallic nanoparticle. The incoming wavefront has an electric field **E** that induces a collective oscillation of the free electron gas about the positive ionic core. Polarization arises because of the net charge difference created near the surface, which causes the restoring force for the polarization to flip. Here, the period of oscillation is *T*. This figure was re-drawn from *Reference* [564].

The intensity losses of the wavefront due to absorption and scattering from a volume of nanoparticles with number density N, are given by

$$\Delta I_{abs}(z) = I_0(1 - e^{-N\sigma}abs^z) \tag{6.1}$$

and

$$\Delta I_{sca}(z) = I_0 \left( 1 - e^{-N\sigma_{sca} z} \right), \tag{6.2}$$

respectively [364].

The absorption cross-section,  $\sigma_{abs}$ , accounts for heat generation within the nanoparticle. The scattering cross-section,  $\sigma_{sca}$ , describes scattering from the nanoparticles, or changes in the propagation direction. A third quantity known as the extinction cross-section is defined as

$$\sigma_{ext} = \sigma_{sca} + \sigma_{abs}. \tag{6.3}$$

The results from Mie's calculations are [364, 365],

$$\sigma_{ext} = \frac{2\pi}{|\mathbf{k}|^2} \sum_{l=1}^{\infty} (2l+1) \operatorname{Re}(a_l + b_l), \qquad (6.4)$$

$$\sigma_{sca} = \frac{2\pi}{|\mathbf{k}|^2} \sum_{l=1}^{\infty} (2l+1)(|a_l|^2 + |b_l|^2), \tag{6.5}$$

with

$$a_{l} = \frac{m\psi_{l}(mx)\psi_{l}'(x) - \psi_{l}'(mx)\psi_{l}(x)}{m\psi_{l}(mx)\eta_{l}'(x) - \psi_{l}'(mx)\eta_{l}(x)},$$
(6.6)

$$b_{l} = \frac{\psi_{l}(mx)\psi_{l}'(x) - m\psi_{l}'(mx)\psi_{l}(x)}{\psi_{l}(mx)\eta_{l}'(x) - m\psi_{l}'(mx)\eta_{l}(x)},$$
(6.7)

where  $m = \tilde{n}/n_m$  is the ratio of the complex index of refraction,  $\tilde{n}$ , to the real refractive index of the surrounding medium,  $n_m$ . The prime indicates differentiation with respect to the argument. The dimensionless parameter x, defined as  $x = |\mathbf{k}|R$ , characterizes the size, with R being the nanoparticle radius, and  $k = 2\pi/\lambda$ , where  $\lambda$ is the wavelength of the incoming light. Functions  $\psi_l$  and  $\eta_l$  are the Riccati-Bessel functions, which are presented in Appendix E. Each l value in the sum gives a different order of multipole excitation within the nanoparticle.

When the wavelength of incoming light is reasonably large compared to the nanoparticle ( $\lambda \gtrsim 20R$ ), only the dipolar, l = 2 term is significant, and the extinction cross-section reduces to

$$\sigma_{ext} = 9 \frac{\omega}{c} \varepsilon_m^{3/2} V \frac{\varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2},$$
(6.8)

where  $V = (4\pi/3)R^3$  is the nanoparticle volume. Notice that in Equation 6.8, the spectral features ( $\epsilon$ ) of the extinction cross-section do not depend on particle size, though clearly the amplitude does through V. But the width and position of the plasmon are unaffected. Does this mean that the spectral features become indepen-

dent of size as nanoparticles shrink? The answer is no. Not only because there exists ample experimental evidence to the contrary [242, 364, 366–368], but also because the assumption of bulk dielectric function becomes invalid at sizes this small ( $\leq 20$  nm). Essentially, this would be equivalent to saying that the band structure is the same for nanoparticles and bulk, which is, of course, not true. Apart from this, the Mie formulation has been extremely successful in describing the optical spectra. Rather than abandoning it all together, remedying this short-coming is considerably simpler than some of the alternatives.

One possible remedy is to start from the beginning, as Mie did, solving Maxwell's equations, but this time properly accounting for all of the possible fields and excitations at the retarded (or advanced) times and construct a *non-local* dielectric response function. In general, this option is quite difficult and not analytically solvable. For an in depth discussion, see pp. 72-75 of Reference [364]. Another option, which is widely invoked, is to formulate an effective, size-dependent dielectric function in terms of the bulk function, and stick with the Mie formulation. In other words, modify the bulk dielectric function to reflect the necessary size-dependence.

Before formulating the phenomenological size-dependent dielectric function, it is worthwhile to pause and examine the key differences between bulk metals and nanoparticles. Naturally, the surface-to-volume ratio is greatly enhanced in the latter. If the electron mean free path<sup>2</sup>,  $l_{\infty}$ , exceeds the particle size, surface scattering becomes a limiting factor for electron relaxation, meaning that proper treatment of the surface scattering must be implemented. Given that, plasmons in a nanoparticle generally dephase more quickly than in bulk.

The Drude dielectric response of free electrons in a metal is given by [369],

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega},\tag{6.9}$$

<sup>&</sup>lt;sup>2</sup>Subscript  $\infty$  refers to bulk.

where  $\gamma$  represents the phenomenological damping constant and the plasma frequency is,

$$\omega_p = \sqrt{\frac{ne^2}{\varepsilon_0 m^*}},\tag{6.10}$$

where n is the volume density of electrons in the metal and  $m^*$  their effective mass. For bulk,  $\gamma = \gamma_{\infty}$ , and  $\gamma_{\infty}$  is the sum of electron-electron and electron-phonon scattering rates, as those are the two primary processes that provide damping for the excited free electron gas. The finite size effect enters the formalism through the damping parameter,  $\gamma$ . Specifically, the damping will now have two terms, one comprising bulk scattering events ( $\gamma_{\infty}$ ), and an additional term for surface scattering, such that the net damping factor (now size-dependent) becomes

$$\gamma(R) = \gamma_{\infty}(\omega) + A \frac{v_F}{R}, \qquad (6.11)$$

where A is essentially a fitting parameter that will depend on the metal and  $v_F$  is the Fermi velocity. This means the net dielectric function, now size-dependent, becomes [364]

$$\varepsilon(\omega, R) = \varepsilon_{\infty}(\omega) + \omega_p^2 \left( \frac{1}{\omega^2 + \gamma_{\infty}^2} - \frac{1}{\omega^2 + \gamma(R)^2} \right) + i \frac{\omega_p^2}{\omega} \left( \frac{\gamma(R)}{\omega^2 + \gamma(R)^2} - \frac{\gamma_{\infty}}{\omega^2 + \gamma_{\infty}^2} \right).$$
(6.12)

Since the bulk dielectric functions for noble metals are rather well-tabulated [370–372], parameter A from Equation 6.11 is frequently used as an experimental fitting parameter, allowing for the formalism presented here for the dielectric function modifications to be used in conjunction with the Mie theory [242, 368, 373–389].

Recently, the importance of parameter A has been recognized and expanded in the literature, due to past experimental observations of its dependence on the surrounding medium,  $\epsilon_m$ , [390, 391]. Pinchuk and colleagues have expanded A into two parts, noting that it encompasses an elastic scattering component from the surface,  $A^{size}$ , and an interfacial damping component from adsorbate-induced resonance states,  $A^{interface}$ , such that  $A = A^{size} + A^{interface}$  [392-395].

### 6.3.1 Example Calculations of Mie Scattering with TTM

A program was written to convert the material dielectric functions to the size-dependent one and solve the corresponding scattering cross-sections, which couples nicely to the TTM presented in Section 3.1.3. The logical steps will be briefly laid out here.

The nanoparticle size R and bulk material index of refraction,  $\tilde{n} = n + i\kappa$ , are read in along with the corresponding wavelength  $(\lambda)$ , bulk mean free path  $(l_{\infty})$ , Fermi velocity  $(v_F)$ , plasma frequency  $(\omega_p)$ , empirical scattering parameter (A), and surrounding medium index of refraction  $(n_m)$ . The bulk damping constant is calculated from  $\gamma_{\infty} = v_F/l_{\infty}$ , and the size-dependent damping function from Equation 6.11. Using the Fresnel relationships, the real and imaginary parts of the dielectric function are constructed from  $\varepsilon_1 = n^2 - \kappa^2$  and  $\varepsilon_2 = 2n\kappa$ , respectively. The corrected function,  $\varepsilon(\omega, R)$  is evaluated by adding  $\omega_p^2 \left[ \left( \omega^2 + \gamma_{\infty}^2 \right)^{-1} - \left( \omega^2 + \gamma(R)^2 \right)^{-1} \right]$  to the real part, and  $i \frac{\omega_p^2}{\omega} \left( \frac{\gamma(R)}{\omega^2 + \gamma(R)^2} - \frac{\gamma_{\infty}}{\omega^2 + \gamma_{\infty}^2} \right)$  to the imaginary part. Now, size-dependent n and  $\kappa$  can be computed from

$$n = \sqrt{\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1}{2}},$$
(6.13)

and

$$\kappa = \sqrt{\frac{(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1}{2}},\tag{6.14}$$

followed by a call to a subroutine that takes the new n and  $\kappa$ , along with  $n_m$  and  $\lambda$ , and returns  $\sigma_{ext}$ ,  $\sigma_{abs}$ , and  $\sigma_{sca}$  [365]. Using the indices of refraction for Au and Ag from Johnson and Christy (1972) [370], Figure 6.8 shows several example calculations,

where efficiency factors are defined as  $Q_{abs} = \sigma_{abs}/\pi R^2$ , and analogously for  $\sigma_{sca}$ and  $\sigma_{ext}$ .



Figure 6.8: Example Mie Scattering calculations. (a) Absorption factor for 20 nm Au and Ag nanoparticles. The inset shows the scattering factor  $(A = 1 \text{ and } n_m = 1.33)$ . (b) The electron and lattice temperature of Ag (solid) and Ag (dashed) irradiated by a 400 nm, 50 fs, pulse at 5 mJ/cm<sup>2</sup>, where  $\sigma_{abs}$  was used instead of R and  $\delta_s$  (see Section 3.1.3). (c) Absorption factor for 40 nm Ag nanoparticle as a function of the refractive index of the surrounding. Shown are vacuum (1.0), water (1.33), and common value for nanoparticle ligands (2.5), clearly indicating the strong dependence of the SPR position. (d) Surface scattering factor A is varied for  $Q_{abs}$ , which mostly affects the SPR width.

It is interesting to see how Au and Ag, both of which are fcc noble metals with similar bulk electric and chemical properties, behave so differently because of SPR excitation. For example, in Figure 6.8(a), Ag will absorb much more than Au at wavelengths near 400 nm, which is reflected in the temperature rises, as shown in the TTM calculation in part (b). Had the excitation been closer to the SPR for Au ( $\approx$  525 nm), the trend would reverse and Au would become hotter.

Electron 'spill-out,' which is due to the extension of the electronic wavefunction beyond the surface, can also be an important effect [364, 396–398]. In classical electrodynamics, the nanoparticle surface, r = R, is treated as a 'hard boundary'. That is to say that the electron charge density abruptly changes from -en inside the metal, where n is the volume density of electrons, to zero outside the nanoparticle  $(r \rightarrow R^+)$ . This is usually valid, but in reality, the change in electron density is not abrupt, it decays outside the metal over a distance comparable to the Fermi wavelength [399]. If the metal is large in dimension, hard boundary treatment is valid. However, the spill out distance can be as high as tenths of nanometers, which in some cases, is not much smaller than the nanoparticle itself. Material property changes associated with electron spill out can include reduced screening effects leading to stronger electronphonon coupling [400], and changes in SPR position and width [401, 402].

In the beginning of this section it was asked why Au nanoparticles are red. Figure 6.9 has the answer.

The Mie formalism presented here with the TTM from Section 3.1.3 has been successfully implemented as secondary checks on lattice temperature for UEnC studies, most notably, Ag nanoparticles [193], where it assisted to preclude a thermallymediated channel for fragmentation at low fluence (not presented here). With the general Mie picture in mind, some of the interesting observations associated with nanoparticle charging will be presented.



Figure 6.9: The normalized scattering factor for Au nanoparticles of 10 nm diameter, showing a strong peak near 650 nm, which will appear red in the visible spectrum.

### 6.4 UEDV Investigations on Molecular Transport at the Nanoparticle / Molecules / Substrate Interface

As mentioned, the molecular wires that take part in the immobilization (aminosilanes) tend to order very well beneath the nanoparticles. So much so, that their structures are clearly resolvable from electron diffraction [190, 192], as was shown in Figure 6.2.

The fortuitous discovery of SAM diffraction peaks<sup>3</sup> in conjunction with the extension of UEDV to arbitrary geometries (Section 4.6.2), 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

<sup>&</sup>lt;sup>3</sup>It actually came as a surprise to see the diffraction peaks from the SAM in the first studies of Au nanopartices in the UEC lab.

which, a charge transfer process will ensue depending on the relative offset between the transient Fermi levels of the two systems. Quantifying this process would provide an additional technique for the investigation of molecular transport, an area of notable interest [403–408]. The diffraction peaks associated with the SAM are the most suitable for studying the charge transfer process, as the powder diffraction pattern (Debye-Scherrer rings) from the Au can exhibit strong Debye-Waller changes [182, 185, 192] in intensity and position due to the formidable structural changes, which only serve to complicate the isolation of the TSV. The potential associated with these nanostructures can be determined from an extended slab model, with an angular-dependent correction factor ( $\Theta$  from Section 4.6.2) to model the relevant angular shifts observed in the diffraction.

Specifically, the transient voltage of a 20 nm gold nanoparticle, caused by photoinduced 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 Å<sup>-1</sup> (orders N = 1 to 3), which is depicted in Figure 6.10. For small-angle diffraction ( $\theta \leq 2^{\circ}$ ), the dispersion in  $\Theta$  due to the position-dependent refraction effect can be ignored, as shown in the inset of Fig. 4.15(b). In other words, the same correction factor,  $\Theta$ , can be applied to all three of the diffraction orders from the SAM.

The total transient shift  $\Delta_B$  in Figure 6.10(b) includes two charging mechanisms: one is due to the voltage drop across the Si/SiO<sub>2</sub> surface ( $V_s$ ), and the other is the drop across the SAM ( $V_M$ ), (recall the TSV 'voltmeter' in the Figure 4.4). A simple RC-circuit is adopted to conceptualize the transport properties associated with this interface (Figure 6.11). To isolate the voltage drop across the linker molecule, the contribution to  $\Delta_B$  from  $V_s$  must be subtracted out. Typically, the  $\Delta_B$  associated with a bare Si/SiO<sub>2</sub> surface has an exponential down turn followed by a power-law



Figure 6.10: UEDV applied to the Semiconductor/SAM/Nanoparticle interface. (a) A ground state diffraction pattern of this system, which exhibits the characteristic Debye-Scherrer rings for the polycrystalline Au nanoparticles, co-present with the diffraction peaks associated with the linker molecules. The latter, extracted from the full pattern, are also shown in part (b) (inset). (b) The total transient shift,  $\Delta_{B_1}$ , observed from the (001) diffracted beam (circled), which is that of N = 1 (s = 2.75 $A^{-1}$ ) from the aminosilane linker molecule (chemical structure shown in inset).

recovery (recall from Chapter 5). The temporal evolution of the TSV for Si/SiO<sub>2</sub> is well-fit by the empirical functional form given by Equation 5.1.



Figure 6.11: The equivalent circuit diagram to describe the charging and discharging dynamics in the semiconductor/SAM/nanoparticle interconnected geometry. Subscripts 'M' and 'S' describe the linker molecule and Si/SiO<sub>2</sub> surface, respectively. Their associated resistances, capacitances, and voltage drops are denoted by R, C, and V, respectively. The resistances of the bulk  $(R_{bulk})$  and vacuum gap  $(R_{vac})$  are considerably larger than  $R_M$  and  $R_S$ , such that both  $\rightarrow \infty$ .

The presence of an additional upward swing followed by a fast exponential downward swing can be discerned with careful analysis, which is shown in Figure 6.12. Whatever the relaxation mechanism of  $V_M$ , it does not appear to be a power-law decay like that associated with  $V_s$ , which is governed by the long carrier relaxation in the silicon bulk. This is useful in separating the two contributions, which is done by fitting with Equation 5.1 in the long-time relaxation regime and also with the data near the ZoT. From this well-constrained fit,  $\tau_c$  is found to be 33.5 ps, similar to that in Si(111)/SiO<sub>2</sub>-only substrate, while  $\tau_i$  is significantly shorter (22.6 ps), reflecting the abundance of new acceptor states provided by SAM/Au functionalization, enhancing the rate of surface charge transfer. Subtracting out  $V_s$ , the voltage drop across the SAM,  $V_M$ , shows distinctive exponential charging and discharging characteristics, associated with the hot electron transport through the SAM, which can be analyze  $\mathbf{C}$  to yield the respective molecular RC time  $(\tau_{RC})$ , as shown in Fig.6.12(b). Upon fitting  $V_M(t)$ , it is found that the transient resistance,  $R_M = 1.92 \text{ M}\Omega$  for the charging stroke, followed by 4.5 M $\Omega$  at the onset of the discharging stroke, and then rising to 26.6 M $\Omega$  over the slower arm of the discharging stroke, with  $C_M$  set to  $2.92 > 10^{-18}$  F for all. The capacitance was determined from the field modeling of the interface described in Section 4.6.2.

It is rather interesting to compare the molecular resistance,  $R_M$  values above, to the steady-state values determined by Sato and colleagues, for the same linker molecule [360]. They reported  $R = 12.5 \text{ M}\Omega$ , obtained by applying a bias voltage across the molecular interface, using a 10 nm Au nanoparticle (implying a SAM coverage area ~ 4 times smaller). The smaller injection resistance obtained using the ultrafast photo-initiated voltammetry setting, as compared to the recovery  $R_S$  or the steady-state data, can be understood from the hot electron transport picture, in which the hot carriers initiated by photoexcitation are given more access to a broader range of unoccupied acceptor states and a reduced interfacial potential barrier (hence



Figure 6.12: (a) The refraction shift observed by following the (001) diffracted beam (at s = 2.75 Å) from the SAM described in Fig. 6.1. The solid points represent the raw diffraction shifts arising from the SAM  $(V_M)$  and the Si/SiO<sub>2</sub> surface  $(V_S)$ (continuous line) (see text). The inset shows the early time evolution of the TSV shift theat has a significant  $V_M$  contribution, deviating from the smooth transition of  $V_S$  described by Equation 5.1. (b) The voltage drop across the SAM,  $V_M$ , which was determined by first subtracting the contribution  $V_S$  from  $\Delta_B$ , followed by applying Equation 4.19. The fit shows a rise time  $\tau_i = 5.6$  ps and a biexponential decay with time scendes 13.1 and 77.7 ps.

the low  $\leftarrow$ r resistance to transport of 1.92 MΩ). As the carriers cool, these channels are less active, reflected by the higher resistance of 26.6 MΩ.

#### 6.5 Near-Field Lensing: Nano-cavity Patterning

#### 6.5.1 Near-Field Enhancement

What is near-field enhancement? Perhaps a better question is why? In fact, a glance at Figure 6.7 may help clarify. As the nanoparticle has a strong proclivity to absorb near SPR wavelengths, the incident light begins driving the conduction electrons into oscillation about the ion core, such that surface charge piles up on the poles (equal and opposite), oscillating sign every  $\pi/\omega$ . In other words, it is acting like an antenna. This oscillation interacts with the peripheral electromagnetic radiation, drawing it into the nanoparticle. By peripheral radiation, this means photons that were on a course to fly by the nanoparticle in the absence of this interaction. This is why it is sometimes referred to as a lensing effect.

Near-field ablation of Si was observed by surprise in the UEC lab in 2006. Upon SEM imaging some over-exposed samples of surface-supported Au nanoparticles from UEC experiments, Dr. Yoshie Murooka found a surprisingly strong presence of nanocavities on the Si substrate, shown in Figure 6.13. Interestingly, this cavity formation occurred at laser fluences that were below the damage threshold of the Si.



Figure 6.13: Femtosecond laser induced nano-cavity formation. (a)-(b) are from one sample, (c)-(d) from another.

Recently, Obara and colleagues have shown that near-field focusing is responsible for these effects, and can be used to selectively ablate portions of the substrate lying beneath the nanoparticles. The process is depicted schematically in Figure 6.14.

The mechanisms behind the near-field focusing effect are well-understood on a theoretical level, and the technique has been demonstrated for nano-cavity formation



Figure 6.14: A schematic of near-field lensing under the assumption of UEC geometry (pump laser incident at  $45^\circ$ . The lens that is shown is fictitious, but captures the essence of the near-field antenna. The extinction cross section  $\sigma_{ext}$  is the ratio of the incident power to the total intensity scattered and absorbed.

to dept **L**s as small as tens of nanometers [181, 409], though the widths of the nanocavities **produced** from this method are usually quite large ( $\sim 1 - 1.5 \times D$ ,  $D \gtrsim 100$  nm). **Driven** by the interests in making sub-10 nm nano-cavities, options are being explored in the UEC lab to exploit the near-field effect in 2-5 nm nanoparticles. First, the properties that make a good 'lens' are briefly highlighted, through simple analysis, follwed **by** a proposed experimental direction.

Briefly, the formalism of the field enhancement is examined. Conversion of incident far-field  $\mathbf{r}$  adiation to the near-field is characterized by the near-field efficiency,  $Q_{nf}$ , given by

$$Q_{nf} = 2\sum_{l=1}^{\infty} \left\{ |a_l|^2 \left[ (l+1)|h_{l-1}^{(2)}(x)|^2 + l|h_{l+1}^{(2)}(x)|^2 \right] + (2l+1)|b_l|^2 |h_l^{(2)}(x)|^2 \right\}$$
(6.15)

where  $h_l^{(2)}(x)$  denotes Hankel functions of the second kind,  $a_l$  and  $b_l$  have the same definitions as in Equations 6.6 and 6.7, respectively, and x = kR, with  $k = 2\pi n_m/\lambda$  [410]. The dielectric properties of the material enter through  $a_1$  and  $b_l$ . Note that Equation 6.15 is not the field enhancement factor itself, however it is proportional to it.

Consider the following comparison between Ag and Au 40 nm diameter particles, in a dielectric medium with index of refraction  $n_m = 1.5$ , and parameter A from Equation 6.11 is given as 1 for both cases. Figure 6.15 shows the near-field efficiency with scattering and absorption efficiencies also depicted for each. While the silver has a reach stronger effect, to attribute it to the SPR absorption alone would be incorrect. The near-field effect is present with particles that are strong absorbers (for the antenna 'lensing' effect) and strong scatterers. Strong absorption alone is insufficient (if the particle absorbed everything and scattered nothing, there would be no field outside to do the ablating). The ' $E^2$ -power' that is doing the drilling is actually scattered radiation from the incident field (pump laser), the amount of which, is greatly enhanced because of the dipole oscillation antenna effect. In fact, because the surface plasmons in silver are damped so quickly (~ 5 fs), Au is actually considered to be a more ideal candidate for near-field ablation [356, 409, 411], if the wavelength is near infrared, where the scattering properties are 600 times larger than the absorption in the near-field [409].

Plech and colleagues recently reviewed the field of femtosecond laser effects on plasmonic structures [181]. In Figure 6.16 (reproduced from Reference [181]), they showed that as particle size is reduced such that it is  $\lambda \gg R$ , the scattered fields resemble those depicted. ).

Interestingly, Eversole and colleagues showed that by tilting the angle of incident **radiation** by 45°, much stronger ablation effects were observed, namely, in the thresh-



Figure 6.15: The efficiency factors,  $Q_{abs}$  (blue),  $Q_{sca}$ (green), and  $Q_{nf}$  (red), for 40 nm Ag (a) and Au (b) embedded in a dielectric medium with index of refraction  $n_m=1.5$ .



Figure 6.16: Shown are the effects of particle size on the scattered near-field [181]. The UEC geometry is similar (in polarization), but tilted to  $45^{\circ}$  incidence.

old [409]. This is actually the same geometry as the UEC system, with the pump laser incident at  $45^{\circ}$ .

An interesting, yet simple experiment would be to test on small nanoparticles (2-5 nm) with the pump laser at nearly planar incidence, which would tilt the direction of scattered radiation in the small particle limit in Figure 6.16, such that it is directed normal to surface. One hindrance is that near-field effects are smaller with smaller nanoparticles. But a size-selective study could be carried out, beginning with 10-20 nm sizes to observe the effects. Moreover, while the near-field enhancement may be smaller, the lightning rod effect will be larger since it only has to do with small features (specifically potential gradients near small features) and is not a resonance phenomenon. The nanoparticles would ideally be spin-coated onto the surface to minimize the distance between nanoparticle and surface.

# Chapter 7

## **Molecular Beam Doser**

### 7.1 Introduction

Interfacial water plays a crucial role in all of life, as it is involved in a vast array of biological, chemical, and physical processes [412–415]. Arguably, the most widelyemployed technique to date to characterize the ultrafast processes associated with interfacial water has been nonlinear vibrational spectroscopy, based on second harmonic and sum frequency generation (SHG and SFG) [416–418]. The identification of site-specific spectroscopic responses from these techniques provide very rich information on the structural and dynamic behavior of this important substance.

Recently, it has been demonstrated that the transient structural dynamics of nanometer scale water/ice bilayers on surfaces can be effectively resolved by UEC [103, 177].

Recent work by Tian *et al.* reveals that at the water/vacuum interface and water/molecule interface, a strong interfacial field is present, suggesting a significant charge redistribution at the interface and that the environment is highly basic [419]. The charge transfer mediated by water and ice is central to many photochemically active processes including ozone depletion and photocatalysis. To investigate the charge transfer dynamics across nanometer thick water/ice structures adsorbed to substrates, a UHV molecular beam doser (MBD) was developed that is capable of layer-by-layer growth of interfacial water. This doser system is coupled to the UEC stage, which has cryo-cooling capabilities, down to  $\leq 20$  K, allowing gas-phase vapor to condense into ice very efficiently upon exposure. This chapter serves to demonstrate the design, calibration, and implementation of the molecular beam doser, along with some preliminary data from the inaugural experiments with interfacial water at MSU.

Dosing, which is a common technique in surface science, is to expose a sample to a gas in situ and allow the gas to adsorb onto the surface [420, 421]. To do this, one option is to back-fill the vacuum chamber with the gas the experimenter wishes to expose, monitoring its partial pressure as a means of quantitative exposure [85]. However, this is not a viable option here for several reasons. First, the photocathode, situated inside the vacuum chamber, is in close proximity to the sample ( $\sim 5$  cm), is held to an accelerating voltage of -30 kV during experiments, A sudden influx of gas molecules could easily be ionized by this voltage, possibly resulting in an arc discharge, which could be devastating to the multitude of electronics in the vicinity. Secondly, a sharp increase in pressure can take days to pump out, particularly for the case of water. Moreover, displacement of impurities on the chamber wall could reduce the purity of the gas that is to be dosed. There is also a risk of damage to the mass  $s_{\rm Pectrometers}$  and ionization gauges, due to the interaction of the back-filled H<sub>2</sub>O Eas with the sensitive thermionic emitters, which are inherent to these devices. To **avoid** these problems, it is necessary to expose the sample to the gas in a controlled, **Quantitative manner**.

#### 7.2 Design Methodology

The MBD, was designed with the following criteria in mind: (1) the effusion rate must be slow and controlled as to allow for quantitative gas deposition, (2) the dosing must be uniform over the surface, (3) the dosing head must be in close proximity to the sample as to minimize the gas not sticking to the sample and it must be retractable as to not interfere with experiments that do not require dosing, (4) dosing must have rapid shutoff capability, and (5) it must be all metal construction because of the presence of a high voltage electron gun, which could otherwise charge it up. Slow effusion is achieved through the use of a pinhole orifice, which dramatically impedes the flow, while uniform dosing is ensured via a microcapillary array at the end of the dosing gun (Figure 7.1). This component was fabricated by drilling micron-sized holes in a square of copper shim-stock with the femtosecond laser, similar to Reference [422] (see Section 7.4).



Figure 7.1: Schematic view of the doser reservoirs. Gas is admitted into the system to a pressure  $P_G$ . The pinhole orifice prevents the intra-doser pressure,  $P_D$  from rising significantly, from its original pressure prior to dosing, P. Here, P is the pressure of the main chamber and S is the pumping speed

#### 7.3 Pinhole Orifice

Flow restriction is the key to controlled dosing because the gas being introduced to the system is 9-10 orders of magnitude higher in pressure than UHV. To do this, a pinhole orifice is employed in the form of a 1/4" VCR<sup>1</sup>, deformable, stainless-steel gasket<sup>2</sup>, which is compressed between a VCR double-male<sup>3</sup> and VCR double-female<sup>4</sup> (Figure 7.2).



Figure 7.2: A laser-drilled, stainless steel gasket, deformed between a VCR doublefemale and double-male operates as a flow restrictor. The clearance hole has a 2  $\mu$ m diameter and was drilled at the center of the gasket.

The conductance of an orifice whose diameter is small compared to its length (as is the case here, 2:600  $\mu$ m) is given by the expression [423]

$$C = \frac{\frac{D^2}{4}\sqrt{\frac{\pi RT}{2m}}}{1 + \frac{3L}{4D}},$$
(7.1)

where D is the pinhole diameter, L the orifice length (gasket thickness), R is the ideal gas constant, and m and T are the molecular weight and temperature, respectively, of the gas. For  $D = (2.0 \pm 0.2) \ \mu\text{m}$ ,  $L = (0.6 \pm 0.1) \ \mu\text{m}$ ,  $m = 28 \ \text{amu}$ , and  $T = 300 \ \text{K}$ , the conductance is calculated to be  $C = (1.7 \pm 0.6) \times 10^{-9} \ \text{L/s}$ .

To compare this calculated result with a measurement, the pinhole gasket was calibrated with N<sub>2</sub> gas in the load-lock (Figure 7.3), prior to installing it with the doser (Figure 7.3). To calibrate, on one side of the pinhole a volume, V, was purged with N<sub>2</sub> gas to a static pressure,  $P_0$ , and subsequently pumped through the pinhole until it equilibrated with the load-lock pressure (UHV). The time constant associated

<sup>&</sup>lt;sup>1</sup>VCR: variable compression ratio.

<sup>&</sup>lt;sup>2</sup>Stainless-steel VCR gasket with a 2  $\mu$ m hole drilled in the center, purchased from Lenox Laser. <sup>3</sup>Swagelok, part number SS-4-VCR-6-DM.

<sup>&</sup>lt;sup>4</sup>Swagelok, part number SS-4-VCR-6-DF.
with the decay of N<sub>2</sub> pressure,  $\tau$ , is related to the conductance by

$$C = \left(\frac{mP_0V}{\rho RT}\right)\frac{1}{\tau},\tag{7.2}$$



Figure 7.3: Dry nitrogen gas is pumped through the pinhole. (a) The left volume is purged with N<sub>2</sub> until it reaches  $P_0$ . The right volume (load-lock) is continuously pumped by a turbo molecular pump (pumping speed S), such that it is maintained at  $\approx$  mid-10<sup>-8</sup> torr. The time taken for  $P_0 \rightarrow P$  is used to measure the conductance, along with the gas and geometric properties  $(P_0, V, T, m)$ . The pressure rise in the load-lock from the influx of N<sub>2</sub> is negligible. (b) The measured pressure in time during the pumping shows that under these conditions, it takes  $\approx$  20 hours for the pressures to equilibrate to the load-lock base pressure.

where  $\rho$  is the mass density of the gas  $(1.251 \ g/L)$ . After purging the volume,  $V \approx (6.0 \pm 1.2) \times 10^{-6} \text{ m}^3$  with N<sub>2</sub> to  $P_0 = (14 \pm 2)$  Torr, the exponential decay time associated with the pump-down was measured to be  $\approx (7.2 \pm 2.0) \times 10^4$  s, corresponding to a conductance of  $(1.1 \pm 0.7) \times 10^{-9}$  L/s, which is depicted in Figure 7.3(b). The calculated result from Equation 7.1 is in agreement with the measurement. Note that the decay is exponential because the gas is in the molecular flow regime, meaning that the mean free path of the gas molecules is large compared to the dimensions of its container. Put more simply, the gas molecules rarely collide with each other, they are much more likely to collide with the surrounding walls. If the flow were viscous, Equation7.2 would no longer apply. For more on comparing molecular with laminar flow, see Reference [423].

#### 7.4 Microcapillary Array

As mentioned in Section 7.1, the MBD must be of all-metal construction because of the presence of an electron beam. Microcapillary arrays, conventionally made of glass, are available for purchase but they are rather expensive and would need to be sputter-coated with a metal to not charge up. Rather than doing this, fabricating it with the femtosecond laser was found to be simpler and more cost-effective. Copper shim-stock was purchased from McMaster-Carr of thickness 0.002" ( $\approx$  50.8 µm) and mounted to a home-built, 2D micrometer controlled stage. The laser was deflected outside of the UHV chamber and focused onto the shim-stock, then raster-scanned along the shim-stock, exposing it to pulses of  $\approx$  200 mJ at each stop, resulting in clearance holes of  $\approx$  25 – 40 µm diameter, spaced 500 µm apart (Figure 7.2).



Figure 7.4: Scanning electron micrograph images of the microcapillary array. The resulting holes from laser drilling were  $\approx 25.40 \ \mu m$  in diameter, spaced 500  $\mu m$  apart, and conical through the thickness.

The microcapillary array is held in place by pressing it between two pieces that comprise the doser head (Figure 7.5). The pieces are fastened by machine screws; the pressure exerted by the screws dictates the goodness of seal. Ideally, all gas molecules entering the doser head will exit through the MCA holes. But since the locking mechanism for the MCA is a press-fit, the leak through the sides needs to calibrated beforehand as well.



Press MCA against doser cap

Figure 7.5: Holding mechanism for the microcapillary array. The microcapillary array is simply pressed between the two pieces shown that are fastened by 4 # 0.80 machine screws, leaving the possibility of gas leaking through the sides. However, flow through the array holes is unimpeded, so should be favored

To first order, it is conceivable that most of the gas will exit the MCA, since it is porous. Quantifying the leak rate through the sides involves a similar procedure to that of the pinhole orifice calibration (Section 7.3). Two tests are run with dry nitrogen gas: the first is where it is pumped through the MCA (Figure 7.6), the second through an undrilled 'blind' piece of copper shim-stock with the same dimensions as the MCA. The blind piece only permits gas through the sides, while the MCA has this channel in parallel with the MCA holes.

With the MCA in place, the total conductance (which encompasses both the sides and the holes conducting in parallel) is given by

$$C_{tot} = C_{side} + C_{holes} = \left(\frac{mP_0V}{\rho RT}\right)\frac{1}{\tau_1}.$$
(7.3)



Figure 7.6: Schematic of the two setups used to investigate the rate of side leak. (a) With no holes drilled (blind), the shim-stock *only* permits passage through the sides. (b) This configuration permits gas through the MCA holes and the sides (parallel conductances). The time associated with pumping gas through each configuration allows for the side leak rate to be determined (see text).

When the blind piece is in, the total conductance is only that of the gas leaking from the sides, given by

$$C_{side} = \left(\frac{mP_0V}{\rho RT}\right)\frac{1}{\tau_2},\tag{7.4}$$

indicating that the ratio of the side leak to the total conductance with both channels working in parallel is

$$\frac{C_{side}}{C_{tot}} = \left(\frac{mP_0V}{\rho RT}\right) \cdot \left(\frac{\rho RT}{mP_0V}\right) \cdot \frac{\tau_1}{\tau_2},\tag{7.5}$$

such **th** at the proportion escaping through the array holes is

$$\frac{C_{side}}{C_{tot}} = 1 - \frac{\tau_1}{\tau_2}.$$
(7.6)

The measured values for  $\tau_1$  and  $\tau_2$  were 1.4 and 35.1 seconds, respectively (Figure 7.7). Inserting these values into Equation 7.6 gives the ratio of 0.96, meaning that 96% of the gas effuses through the holes of the MCA and the doser will work as intended.



Figure 7.7: A direct comparison of the 'pump-through' times associated with a blank piece of shim-stock and the drilled piece. Their difference gives the leak rate through the sides, which is found to be ~ 4% (see text).

#### 7.5 Operation

Extreme caution must be taken when administering a gas at a pressure that is 9-10 orders of magnitude higher than that of the volume into which it is being admitted, especially when the gas is water. This section describes the dosing procedure and the steps that must be taken to guard against undesirable – potentially catastrophic incidents.



Figure 7.8: A full schematic view of the molecular beam doser.

A **full** schematic of the MBD, with all of its functioning parts is depicted in Figure 7.8. To simplify the explanation of the dosing procedure, the four valves used in dosing are narried in Figure 7.8 (*Evac*, *Dose*, *Purge*, and *Steady-State*). The atmosphere side of **the** MBD is referred to as the gas-handling system (GHS). Using Figure 7.8 as a guide, operation of the MBD is as follows. First, pump the GHS: with *Purge* and *Dose* closed, open *Evac* and *Steady-State* (this is actually the steady-state condition for the dosing system). Second, admit water vapor into the GHS by closing *Evac* and *Steady-State* (has no consequence at this step, but it needs to be closed eventually), and opening *Purge* (*Dose* remains closed). The vapor pressure is monitored on the manometer. When a stable backing pressure is reached, *Dose* may then be opened to commence exposure.

When the sample is adequately dosed, the flow is quickly stopped by closing *Purge* and opening *Evac*, which evacuates the GHS and any gas that has not yet passed through the pinhole<sup>5</sup>. Finally, the non-operational condition is restored once *Dose* is closed and *Steady-State* is re-opened, with *Evac* remaining open<sup>6</sup>.

As pointed out by Huffstetler and Leavitt, it is necessary to uniformly heat the outside of the GHS with heating tape to prevent water condensation on the inner walls, which gives rise to unstable backing pressures and introduces difficulties in evacuating the GHS [424]. In this case, spatial constraints forced the use of 1/4" tubing for the GHS (1/2" tubing was preferred and is more common). This makes the issue of heating the GHS more delicate, as the high surface-to-volume ratio increases the likelihood of gas adsorption on the GHS inner walls.

The tubing on the UHV side of the MBD is necessarily heated to a higher temperature than the GHS to prevent condensation on its inner walls as well as to offset the **possibility** of Joule-Thomson cooling (throttling) as the gas passes through the pinhole. Because of the all-metal construction of the doser, conventional heating methods, such as NiCr wire could not be used unless the wire were sheathed such to be electrically insulated from the doser. A much simpler solution was found to be simply **p**assing an electrical current through the stainless steel tubing on the UHV side of the MBD (typical current/voltages  $\approx 6-10$  A at 1-3 V); the resistance, while low ( $\approx 0.25 \Omega$ ), is large enough to where resistive heating is sufficient to hold the walls at a sufficiently high temperature (5-10° higher than the GHS). A thermocouple is employed to monitor this temperature. The GHS temperature is monitored by correlating the manometer pressure with the temperature associated with its value on the **pressure-temperature** diagram for the vapor pressure of water, and also via pyrometer as a secondary check. Optimal dosing conditions are usually chosen to be

<sup>&</sup>lt;sup>5</sup>A negligible volume of gas on the UHV side of the pinhole will still be dosed.

<sup>&</sup>lt;sup>6</sup>Typical operation is to allow the MBD to be continuously pumped for about an hour, with the MBD heating slightly raised from the dosing level to minimize wall adsorption.

with backing pressure near 42-48 Torr, which corresponds to a water vapor temperature in the GHS of 35-40°C, though the stainless steel walls of the GHS are routinely measured with an optical pyrometer to be higher under such conditions (70-80°C), which is expected as its thermal conductivity is quite low (for a metal), such that the static condition has the walls hotter than the vapor inside.

The last operational point, which cannot be over-stressed, is that heating of the reservoir in which the water is contained can be done, but it is crucial that the gashandling system walls are warmer than the water container. Heating the water supply has benefits, as the water vapor will flow out more rapidly upon exposure to vacuum pressure. However, the GHS has a high surface-to-volume ratio and the flow rate *out* of the GHS is governed by the pinhole. Increasing the influx of water vapor, while resulting in a higher dosing rate, drastically increases the likelihood of condensation on the GHS walls, even when they are heated. The point is most easily illustrated by considering the various possibilities, given in Table 7.1.

Supply Temp.	GHS Temp.	Dosing Rate	Risk of Condensation	
ambient	warm	slow	low	
ambient	$\mathbf{hot}$	slow	low	
warm	warm	fast	moderate	
hot	warm	faster	high	
warm	hot	fast	low	

Table 7.1: A comparison of the various conditions that can be used to dose. Either of the scenarios in the first two rows works fine, but the bottom line scenario is optimal.

### 7.6 Tests with $H_2O$

Calibration of the various conductance and leak rates associated with the pinhole and MCA are outlined in their respective sections above. Here, the MBD has been moved to its final working place in the UHV chamber.

During a dosing experiment, the sample stage is cooled to  $\sim 20$  K. If, for some reason, the dosing rate were to become much faster than anticipated, the sample stage would act as a cold trap and it is unlikely that the global pressure of the chamber would rise considerably, if at all, since the doser is in close proximity to the sample-holder. This could leave the experimenter with a false sense of security. When the cooling is stopped and the temperature is rising to ambient, vacuum contamination could occur as the water sublimates from the sample stage. Furthermore, a sudden spike in the pressure introduces the possibility of arc discharge from the high voltage used by the electron gun, even if the spike is short-lived. These effects, which are considered in the next section, serve as the final pre-cautionary test prior to attempting substrate dosing.

#### 7.6.1 Thermal Desorption Test

To test how well (or unwell) the UHV pressure holds up during dosing conditions, a 'mock' dosing experiment was held. A silicon wafer with chemically grown oxide (see Section 5.2.1) was placed in the UHV chamber. The sample-holder was cooled, such that the stage read a temperature close to 20 K.

Dosing commenced for 2 hours, at which point the cryo-cooler responsible for maintaining the low temperature of the sample-holder, was switched off. Pressure was recorded in real time as the sample-holder warmed to ambient temperature, a plot of which is shown in Figure 7.9. Water desorption occurred near a stage temperature of 150 K. The reason it is bifurcated is most likely that water was dosed onto the

various copper surfaces of the stage in addition to the Si wafer. The two will have different energies of adsorption. A quadrupole mass spectrometer (QMS) could be employed to identify the peaks below 100 K, but the focus here was to determine the net rise in chamber pressure from dosed water desorption. If it were the case that too much water had been dosed, this would risk damage to the QMS, which is more costly than the ion-gauge used for the measurements here.

Warming from 55 to 280 K took about 6 hours. Note that within 2 minutes of switching the cryo-cooler off, the stage warms from 20 to ~40 K. The pressure rose nearly an order of magnitude from water desorption, which lasted all of 10 minutes, and was then pumped out very effectively. More importantly, the sublimated water did not cover a significant amount of surface area in the chamber, since the baseline pressure is completely recovered in a matter of hours with no baking. The net result of this test is that the MBD is safe for UHV use. A rise to mid-10<sup>-8</sup> for a few minutes is non-problematic. Furthermore, it comes at the conclusion of the experiment, when any dosed water would have been sublimated by then anyway (so the experiment would be over).

Recall in the introduction of this chapter there were five requirements to be met; slow effusion, uniform coverage, rapid shutoff, metal construction, and retractability. All have been discussed at this point except for the last one, which is accomplished by using a standard linear motion feedthrough, or 'push-pull.' Due to spatial constraints and a limited number of unoccupied chamber flanges, the inlet from the GHS and the motion feedthrough had to come through two different ports<sup>7</sup> (Figure 7.10). Both ports were CF-2.75", which means that the inner diameter is a mere 1.1", which would have made it impossibly tight to put the push-pull in the same flange, when trying to run in a 1/4" flexline for the gas, which has a female nut that is nearly an inch, thermocouple wire, electrical wire for the heating.

<sup>&</sup>lt;sup>7</sup>This **'two-flange'** problem could have been circumvented if a 0.450" or larger flange had 00 been available.



Figure 7.9: UHV chamber pressure as a function of sample-holder temperature. As the sample-holder warms, various species desorb from the Si surface, hence the rise in global pressure. The bifurcated peak at  $\approx 150$  K is water desorption.

The doser sits at the same height as the sample on the stage in the experimental position. The push-pull is fastened to an OFHC copper piece, on which the MBD sits securely in place, as all parts are rigid. However, this requires that the tubing inlet from the GHS, responsible for supplying the doser with water, *cannot* be rigid. Flexible stainless steel tubing of 1/4" diameter with VCR terminations was ordered to custom specs from *Finemech Inc.* to meet this constraint.

### 7.6.2 Preliminary Testing of H<sub>2</sub>O on Si

Prior to dosing, the water in the ballast was taken through three consecutive freezepump-thaw cycles to improve the purity of the water. The water supply ballast was immersed in a liquid nitrogen container to freeze the water inside. The dissolved gas tends to be expelled from water when it freezes. The *Purge* valve is then opened (Figure 7.8) to allow unoccupied volume inside the ballast to be pumped of impurities.



Figure 7.10: The final CAD drawings of the MBD and GHS. Upper right: motionfeedthrough in the form of a push-pull is connected to a rigid copper piece, on which the MBD sits. The flexible stainless steel tubing is seen dangling from the MBD head. Bottorn center: a snapshot of the actual GHS (the ballast is not shown). The CAD drawing (blue) does not depict the flexible tubing.

The *Pzerge* valve is closed and the water is allowed to thaw, followed by repeating the cycle several times.

The first surface to be dosed was the Si(111)/SiO<sub>2</sub> (hydrophilic) surface. The UHV system began at high-10<sup>-9</sup> Torr. The sample stage was cooled down to  $\approx 20$  K, which made the pressure drop even lower, to  $5.5 \times 10^{-9}$  torr. Water was admitted to the gras-handling system, which was warmed with heating tape to approximately  $35^{\circ}$ C, such that the backing pressure was  $\approx 45$  torr. The ballast was mildly heated 2- $3^{\circ}$ C above ambient. The stainless steel hosing inside the vacuum chamber was heated by running a steady DC current of 9.1 A at 2.4 V. Calibrations have shown that the point of contact for the thermocouple that reads stage temperature is actually colder than the sample itself, as it sits in a well-shielded area. All temperatures from this point on refer to the calibrated sample temperature rather than the stage.

Dosing commenced for 60 minutes when the sample reached 95 K. Diffraction patterns during dosing displayed ring-like signatures, evident of a polycrystalline structure. After dosing for 60 minutes, the cryo-cooler was switched off, and ground state diffraction patterns were continuously recorded throughout the warming of the stage, some of which are shown in Figure 7.11, beginning with 118 K. At approximately 145 K, the ice begins to sublimate and the rings sharpen as the temperature increases, becoming completely desorbed near 156-158 K. At 150-155 K, the diffraction images show characteristics of a cubic ice layer [103], before rapidly sublimating, allowing the silicon peak beneath to show, which can first be seen at  $\sim$ 156 K.



Figure 7.11: Ground state diffraction patterns of an ice layer adsorbed to Si(111)/SiO<sub>2</sub>. The cryo-chiller for the stage was turned off after the pattern in the 118 K shot was taken. Repeated shots were taken as the stage warmed to 160 K, where all remaining water had clearly sublimated. At 145-150 K, it can be seen that the Debye-Scherrer rings become substantially sharper, signifying that the water has sublimated down to the last bilayer.

It is tricky to maintain the sharp Debye-Scherrer rings by switching the cryocooler back on once they are visible to reverse the temperature trend, due to the poor thermal conductance between the crystat and sample holder (it has been found to take 15-20 minutes to reverse the temperature rise and begin to cool). However, the structure can be annealed with ample time to chill the stage back down before sublimation. Figure 7.12(a) shows water at 118 K, with no annealing, while part b shows the annealed structure on Si following pulsed laser irradiation of 66 mJ/cm<sup>2</sup> for 15 mins at 1 kHz with 45 fs pulses. The cryo-cooler was then switched back on, and the bilayer rings can now be studied however desired. The Debye-Scherrer rings are identified in Figure 7.13.



Figure 7.12: Laser annealing water on Si. (a) The usual water structure near 118 K, the rings are rather broad. (b) The ice structure following laser irradiation with 66  $mJ/cm^2$  for 15 mins at 1 kHz with 45 fs pulses.

Also in Figure 7.13 is the intensity from the gated region as a function of the ambient temperature during stage warming. At each acquisition during the warm-up, the maximum intensity was chosen from this box and plotted against temperature. Note, the two downward spikes at 125 and 140 K are artifacts due to the slight adjustments of the stage that were necessary to account for thermal expansion of the stage itself as it warmed. In the initial stages of the warm-up, the diffraction pattern has to be





Figure 7.13: The Debye-Scherrer rings are identified for the annealed water structure. The maximum intensity from the gated region (red dashed box) is plotted as a function of the ambient temperature during the warming cycle (inset), where the 'M' shape can be seen as the water goes through sublimation.

'chased' a bit by adjusting the goniometer to keep the pattern optimal, but it subsides by 140 K, at which point it remains fairly stable throughout, needing only minor adjustments that actually become quite predictable with experience. The behavior of the curve from 150-159 K (the'M' shape in the curve) is highly reproducible.

At this point, the interpretation of the 'M' shape in the intensity/temperature plot (Figure 7.13) is as follows. The first peak is due to a well-ordered ice bilayer, from which, the top monolayer begins to desorb, and the diffraction intensity begins to drop. Prior to desorbing, the remaining monolayer has a reconstruction of sorts as it relaxes into a commensurate layer, again, resulting in an increase in the diffraction intensity. This is short-lived as, finally, the last monolayer desorbs and the intensity drops to zero from the  $H_2O$  structure.

#### 7.7 Discussion

A molecular beam doser was designed, assembled, and installed in the UEC lab at MSU. Following the dosing procedure recipe outlined here, any substrate that is loaded into the UHV chamber can be dosed. Silicon was tested as a prototype and in principle the dynamics of the interfacial water could have been investigated, however this has already been done for this system [103].

Other experiments that come to mind are single crystal TiO<sub>2</sub> films [425], which have considerable interest in their interaction with water [426, 427] because TiO<sub>2</sub> is a photocatalyst[428]. When placed in water, directing UV light onto TiO<sub>2</sub> causes it to cleave impurities that are adsorbed to its surface. The harmless products, usually CO<sub>2</sub> and H<sub>2</sub>O, desorb, meaning that TiO<sub>2</sub> effectively purifies water under sunlight. Recent studies with time resolved photoemission have elucidated interesting properties of the interfacial electronic structure at the TiO<sub>2</sub>/H<sub>2</sub>O interface[124], and charge transfer coupled to atomic motion at the TiO<sub>2</sub>/CH<sub>3</sub>OH interface [123].

### Chapter 8

## Summaries & Discussion

The most important aspect of this work is the development of ultrafast electron diffractive voltammetry (UEDV) and its successful application in measuring the transient dynamics of interfacial charge transfer, as demonstrated through the studies of hot electron processes (generation and surface charging) at the  $Si/SiO_2$  interface, and molecular transport across a nanoparticle/molecule/semiconductor interconnect. Additionally, the transient near-surface field determined by UEDV can be directly combined with the photoemission dynamics obtained by ultrafast electron projection imaging [200] to provide a more complete understanding of electron dynamics in photoexcited materials.

UEDV is complementary to a cohort of other approaches that are sensitive to the surface electron dynamics, such as photoelectron [123–125] and surface-field enhanced nonlinear spectroscopy [81, 85, 153]. The site-specific and charge-sensitive characteristics of electron diffractive approach allows the transient effect of electron transport to be elucidated, while spectroscopic techniques provide information on the energetics and rates of electronic relaxation and accumulation in surface charging dynamics.

The ultrafast time resolution and high sensitivity to nanoscale charging of the UEDV approach, allows the identification of two distinct charge transfer mechanisms

near the surface of Si/SiO<sub>2</sub>, distinguished by the fluence dependence of their respective injection times (Figure 5.3) of surface charging. To understand the origins of these charge transfer behaviors, theoretical modeling of Boltzmann transport near the Si surface is implemented, with appropriate treatment of the early time nonthermal regime and calculation of quasi-Fermi levels to take into account the transient hot electron states, all of which is presented in Chapter 3. This analysis leads to the conclusion that the observed linear TSV response at lower fluences is due to a thermally-mediated tunneling process, which ensues as the quasi-Fermi level of electrons is raised, followed by direct tunneling through the oxide, for which calculation follows the formalism in Section 5.3.1. Photoexcitation of carriers determines the quasi-Fermi level, while the electron temperature dictates the width of the Fermi distribution, both of which are factors in the tunneling calculation (see Equation 5.6).

In contrast, a consecutive 2- and 1-photon absorption process (2+1) leading to a direct injection of charge into the SiO<sub>2</sub> conduction band is invoked to explain the more rapid and quadratic rise of the TSV at higher fluences. This picture is supported by incorporating Boltzmann transport with the (2+1) formalism presented in Section 5.3.2, confirming that the rapid dephasing of the 2-photon generated hot carriers limits the free carrier absorption process, thus leading to the specific quadratic dependence that was observed.

UEDV holds tremendous potential in the possible application to some of the novel solar cell designs, such as dye- and/or quantum dot-sensitized films (or nanocrystals), where the interfacial charge transfer mechanisms are central to the quantum efficiency, and generally speaking, occur on an ultrafast time scale [39]. Another interesting avenue of application that explores the capability of the ultrafast transient field determination at interfaces is to investigate the local field switching caused by electron phase transitions, as a phase shift in the electron wave can be introduced as it traverses through an extended electric and magnetic field. The correlation between the atomic and electronic degrees of freedom has been a long-standing problem in studying strongly correlated electronic systems [429–431]. The growth of local charge instability and/or lattice distortion[173, 430, 432, 433] has recently been revealed to appear prior to its colossal electronic switching (phase transition) into different functional states in these systems. The simultaneous determination of the transient field and structural dynamics, which are inherently measurable with UEDV, is proposed as a tool for researching the complex intermediate phases in electronic phase transitions involving structural changes.

## Appendix A

### **Principles of Electron Diffraction**

#### A.0.1 Bragg's Law

Scattered electrons from adjacent crystallographic planes will interfere constructively when their path difference is an integer multiple of the electron wavelength,  $\lambda_e$ , which leads to the Bragg condition (Figure A.1),

$$m\lambda_e = 2d\sin\theta. \tag{A.1}$$



Figure A.1: Bragg Scattering. The path difference between two adjacent lattice planes is  $d\sin\theta$ .

For a crystal with lattice constant a, and a Bragg plane with Miller indices  $\{h, k, l\}$ , the lattice spacing for an arbitrary cubic system can be found from the relation

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$
(A.2)

which leads to a relationship between the lattice constant, a, and the Bragg peak  $m_{axima}$ .

$$\left(\frac{m\lambda}{2a}\right)^2 = \frac{\sin^2(\theta_{hkl})}{h^2 + k^2 + l^2}.$$
(A.3)

#### A.O.2 The Reciprocal Lattice

Regardless of the type of diffraction probe (X-ray, neutron, electron, etc.), the reciprocal space is the natural coordinate system to describe probe interaction with the crystal. Consider the functional form of Equation A.3, the measurable quantity,  $\theta_{hkl}$ , is related to the *reciprocal* of the lattice parameter, *a*. This point provides merely a small example of the essence of diffraction: put simply, diffraction measurements are taken in reciprocal space. For a Bravais lattice described by

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \tag{A.4}$$

the **cor**responding reciprocal lattice is defined such that the primitive vectors of the direct space,  $\{a\}$  and those of the reciprocal space,  $\{b\}$  satisfy the relationship

$$\mathbf{b}_{j} \cdot \mathbf{a}_{i} = 2\pi \delta_{ij},\tag{A.5}$$

from which, the individual primitive vectors of reciprocal space can be stated as

$$\mathbf{b}_1 = 2\pi \frac{(\mathbf{a}_2 \times \mathbf{a}_3)}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)},\tag{A.6}$$

$$\mathbf{b}_2 = 2\pi \frac{(\mathbf{a}_3 \times \mathbf{a}_1)}{\mathbf{a}_2 \cdot (\mathbf{a}_3 \times \mathbf{a}_1)},\tag{A.7}$$

and

1

$$\mathbf{b}_3 = 2\pi \frac{(\mathbf{a}_1 \times \mathbf{a}_2)}{\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)}.$$
 (A.8)

The (hkl) plane will be perpendicular to vector  $\Delta \mathbf{s}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ , with the spacing between adjacent (hkl) planes given by

$$d_{hkl} = \frac{2\pi}{|\Delta \mathbf{s}_{hkl}|}.\tag{A.9}$$

In reflection mode geometry, the probing electrons sample only a few, sub-surface, atomic planes. Consequently, it is convenient to define a planar geometry in direct space as

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2. \tag{A.10}$$

Note, the primitive vectors here will not necessarily be the same as those in Equation A.4. They depend on the crystal cut of the surface being investigated. Taking the direction normal to the surface to be  $\hat{z}$ , the reciprocal lattice is described by

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \hat{\mathbf{z}}}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{\mathbf{z}})} \tag{A.11}$$

and

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_1 \times \hat{\mathbf{z}}}{\mathbf{a}_2 \cdot (\mathbf{a}_1 \times \hat{\mathbf{z}})}.$$
 (A.12)

Note that a primitive vector  $\mathbf{a}_3$  is not present in Equation A.10, meaning that if a third primitive vector for the reciprocal lattice were to be defined, it would have a magnitude tending toward  $\infty$ . This nonetheless corresponds to something physical. In fact, the reciprocal lattice for an infinitesimally thin (ideal) surface is not a 3D array of points, but rather a 2D array of rods, with each rod extending from  $-\infty$  to  $\infty$ . This point will be discussed further in Section (A.0.3).

#### A.0.3 Ewald Construction

The Ewald Construction is a convenient and elegant tool to determine which scattering planes will give rise to constructive interference, based on the incident wave vector (direction and magnitude), the reciprocal lattice, and the scattered wave vectors. Consider a coherent electron beam incident on a crystal surface,  $s_i$ , which makes an angle  $\theta_i$  with the plane of the surface. The diffracted wave vectors,  $s_f$ , have magnitude equal to that of  $s_i$ ,

$$|\mathbf{s}_i| = |\mathbf{s}_f|,\tag{A.13}$$

that is to say that elastic scattering is one of the underlying assumptions of the Ewald Construction. The momentum transfer, s, must lie in the reciprocal lattice for constructive interference,

$$\mathbf{s} = \mathbf{s}_f - \mathbf{s}_i = \mathbf{K}_m. \tag{A.14}$$

where  $K_m$  is the a vector of the reciprocal lattice, through which the  $m^{\text{th}}$  diffracted beam passes. The Ewald sphere, depicted in Figure A.2 can be thought of as an ensemble of all candidate momentum transfers, such that energy and momentum are conserved. Should one of these candidate momentum transfers line up with a reciprocal lattice vector,  $K_m$ , constructive interference will result.

For glancing incidence, the beam penetrates only a few superficial layers. Suppressing this longitudinal degree-of-freedom in direct space (z) causes elongation of its reciprocal space conjugate  $(K_z)$ . As a result, the reciprocal lattice goes from a 3D array **of** points to a 2D array of rods, which is depicted in Figure A.3(b).



Figure A.2: The Ewald construction. A 2D cross-section of the Ewald sphere is shown, representing all possible momentum transfer candidates, s. Constructive interference occurs only when s lies in the reciprocal lattice, shown by the black dots.



Figure A.3: The Ewald construction as periodicity is suppressed in the longitudinal direction. Panel (a): the Ewald sphere intersecting a 3D array of reciprocal lattice points. Long range order is present in all directions. Panel (b): when the electron beam samples only superficial (surface) layers, the reciprocal lattice points are elongated in the direction normal to the surface, resulting several families of planes of reciprocal lattice plane. Constructive interference will occur when a passes through one of the rods.

There are several cases where the longitudinal reciprocal lattice dimension becomes elongated. Figure A.4 shows three examples, Low Energy Electron Diffraction (LEED) [434], Transmission Electron Microscopy (TEM) [435], and Reflection High Energy Electron Diffraction (RHEED) [207], which is the geometry used in the UEC <sup>lab</sup> at MSU. It may be puzzling why the term RHEED is not used to describe the tech-<sup>ni</sup>que employed in this work. Typically, RHEED implicitly carries the connotation of <sup>m</sup>olecular beam epitaxy (MBE), which is not part of UEC. Furthermore, it is quite

<sup>COD</sup>mon for a RHEED/MBE group to invoke time-dependent plots in publications, <sup>W</sup>dere the characteristic time scales are representative of the rate for molecular layer growth (minutes). A term like 'Time-Resolved RHEED' could potentially mislead readers, since the time-resolved here refers to femtoseconds. The decision to not use the term RHEED is to avoid this confusion, especially since RHEED/MBE pre-dates UEC by many years.

In Figure A.4(b), the reciprocal lattice associated with TEM, or any transmission geometry, may not necessarily be rods, as it will depend on the sample thickness. The accelerating voltages used in TEM are typically 100-200 kV, which has the implication that thicker samples, of order ~100 nm can be penetrated by the beam. In transmission mode UEC, accelerating voltages are typically 55-60 kV, with film thicknesses on the order of 20-50 nm. For example, Harb and colleagues used Si films of thickness 30 and 50 nm with an accelerating voltage of 55 kV [325]; Nie et al. used used 20 nm films of Al with 60 kV in Reference [436]. A 20 nm Si(001) film will have  $\approx$ 150 lattice planes, which constitutes long-range order. Consequently, the rods in Figure A.4b would need to be 'discretized.' Conversely, it is quite common for TEM samples to consist of only several atomic layers, in which case the rod picture is accurate. It is of little consequence, since most  $s_f$  vectors tend to be parallel to the rocts in transmission geometry.



Figure A.4: Typical Ewald constructions (not to scale) for the cases of LEED (a), transmission geometries such as TEM (b), and reflection mode geometries, such as RHEED (c). The size of the respective Ewald spheres will be much different for these three cases, depending on the accelerating voltage. Generally speaking, LEED would have the smallest, followed by RHEED, followed by TEM. Ensemble wave vectors  $s_f$ are drawn opaque. All interior angles here are  $\theta_S$ .

Figure A.4 demonstrates the convenience and power of using the Ewald construction. Specifically, robust predictive power regarding the likelihood of satisfying diffraction conditions for a given accelerating voltage, lattice, and geometry, is available prior to running the experiment, simply by drawing a correctly scaled picture. For example, the large Ewald sphere in a TEM will have many intersections with the reciprocal lattice, implying many diffraction spots. For LEED, the Ewald sphere is relatively small (because of the low accelerating voltage implying a small magnitude of  $s_i$ ), Thearing less intersections. However, the low accelerating voltages guarantee only superficial penetration, meaning that for all intents and purposes, the rods stretch from ( $-\infty$ ,  $\infty$ ). Furthermore, the cone describing the flux of scattered electrons,  $s_f$ , will subtered a reasonably large solid angle, thereby sweeping out all intersections within.

### Appendix B

# Femtosecond Laser Pulse Generation

When the first working laser came into fruition in 1960, it was described as "a solution looking for a problem" [437]. In UEC, it is employed in similar spirit. Namely, it serves as a means to excite the sample by introducing an intense perturbation that exists only for only tens of femtoseconds. This is how a system is 'kicked' into nonequilibrium in UEC (and in many other time-resolved techniques). The short duration of the laser pulse is achieved through a technique called modelocking, followed by a regenerative amplification process to make these short burts more intense; both will be described below.

### B.0. Modelocking

Consider two flat mirrors separated by a distance L, with light of wavelength,  $\lambda$  bouncing back and forth from the mirrors  $(L \gg \lambda)$ . This is a simple example of an optical cavity. The waves will interfere in the region between the mirrors such that standing modes are created, with each independently oscillating mode separated from an adjacent mode by frequency,  $\Delta \nu = c/2L$ . This alone represents the cavity

mode structure. The insertion of a gain or lasing medium (e.g. a crystal such as Ti:Sapphire, Nd:YAG, LBO, etc.) into the optical cavity, causes the selection of a range of energies, in the frequency domain to remain, while the rest are annihilated (Figure B.1). In this scenario, the phases of these modes are not coupled or 'locked' together. In fact, releasing them from the cavity would result in a continuous-wave (CW) laser, in which frequency fluctuations, would lead to beating effects, resulting in a mode-averaging such that the output intensity is nearly constant.



Figure B.1: Panel (a) The frequency range (bandwidth) for an arbitrary lasing medium, (b) standing waves created in an optical cavity, (c) the superposition of (a) and (b), which is the laser output. The lasing medium selects only those cavity modes that fall within its bandwidth.

Modelocking is a technique that enforces a fixed phase between a cavity mode and its surrounding modes. There is a variety of ways to do this; the case outlined here will be active modelocking with an acousto-optic modulator (AOM). The gain medium, Ti:Sapphire, has a bandwidth of  $\approx 300$  nm, centered around 800 nm of (Figure B.2). The AOM, positioned in the laser cavity, sinusoidally modulates the amplitude of **intra-cavity modes.** For a mode with frequency,  $\nu$ , modulating its amplitude with **frequency**  $\nu'$  will result in symmetric sidebands at  $\nu \pm \nu'$ . If the frequency of **modulation** is chosen such that it coincides with the characteristic  $\Delta \nu$  associated **with** the cavity, the central mode and the sidebands, which are driven in phase, **correspond** to cavity modes. The result is that the central mode and its sidebands **are** phase-locked. This operation is continued on the sidemodes until the entire cavity **corres**ists of modes with a fixed phase relationship, which are separated in the time **domination** by  $\tau = 2L/c$ , where  $\tau$  is the time for one round trip through the cavity. The **term** poral width of each pulse (pulse-width) is inversely proportional to the number **of modes** which are oscillating in phase, N, and the mode separation,  $\Delta \nu$ . Assuming **a Corres** such a shape with N modes, the minimum achievable pulse-width is

$$t_p = \frac{0.44}{N\Delta\nu}.\tag{B.1}$$



Figure B.2: The normalized absorption and emission spectra for Ti:Sapphire. Absorption occurs from about 400 to 650 nm; emission from 600 to 1050 nm [438].

In the UEC lab at MSU, a continuous wave laser (Spectra-Physics; Millennia<sup>®</sup>) outputs a beam at 532 nm, which is used to pump the modelocked Ti:Sapphire laser (Spectra-Physics; Tsunami<sup>®</sup>).

The Ti:Sapphire is the most commonly used lasing medium for ultrashort pulse generation because of its wide gain bandwidth and its broad absorption band in the blue to green range (Figure B.2), which has the implication that it can be pumped by a wider variety of lasers. A wider bandwidth leads to a shorter pulse, but it also leads to an enhancement in group velocity dispersion (GVD). GVD occurs because the index of refraction is frequency-dependent<sup>1</sup>, which results in different frequencies having different transit times through the cavity. For a positive GVD<sup>2</sup>, the lower frequencies (red) lead the higher ones (blue), and vice-versa for a negative chirp. The expression given in Equation B.1 is said to be the transform-limited value of the pulse-width. In actuality,  $t_p \geq 0.44/N\Delta\nu$ . GVD is one of the primary reasons why the pulse-width may be greater than the transform-limited value. However, pulsebroadening due to GVD can be reversed. In the Tsunami, velocity dispersion is offset by a series of prisms to compensate the effect.

#### **B.0.5** Regenerative Amplification

The beam outputted from Tsunami has a repetition rate of  $\approx 80$  MHz, a wavelength near 800 nm, and is < 80 fs in duration, with each pulse carrying  $\approx 2-3$  nJ. Upon exiting the Tsunami, the beam, which will be referred to as the seed laser from now on, enters an amplifier, called the Spitfire<sup>®</sup>. Like the Tsunami, the Spitfire has a Ti:Sapphire crystal in the optical cavity, however, its purpose is not the same<sup>3</sup>. The population inversion in the Spitfire is created by an external laser called the

 $<sup>{}^{1}</sup>$ GVD is not solely caused by the Ti:Sapphire rod, but also the intra-cavity optical components. For all materials, the index of refraction is frequency-dependent.

<sup>&</sup>lt;sup>2</sup>This can also be called a positive 'chirp.'

<sup>&</sup>lt;sup>3</sup>The Spitfire can actually operate as a laser instead of a regenerative amplifier. In fact, this is part of its optimization procedure. The primary purpose is as an amplifier though.

Empower<sup>®</sup> which outputs a 527 nm pulsed<sup>4</sup> beam at 1 kHz. The intensity of the Empower is ultimately what controls the level of amplification.

When a Ti:Sapphire crystal is irradiated with an intense laser beam, the beam will have a tendency to 'self-focus' as it travels through the crystal [439]. Consider the scenario where the number of photons in a pulsed beam, which is conserved, is travelling enveloped in a beam whose area is shrinking from the self-focusing effect. The concentrated energy per unit area, or fluence of the beam will continuously increase as the beam traverses the crystal, which can quickly overwhelm the crystal and ultimately damage it. To use the Ti:Sapphire crystal to amplify the pulse, it is first necessary to decrease the duration of the seed pulse, or stretch it, to avoid damaging the crystal. When an ultrashort pulse is stretched, its peak intensity is reduced. This allows for safe passage through the Ti:Sapphire crystal where it is amplified. Upon passage through the crystal, the amplified pulse is still longer than what the Tsunami fed in, so the third task for the Spitfire is to compress the pulse back down to ultrashort, thus completing the regenerative amplification cycle. This process is called Chirped-Pulse Amplification (CPA) because stretching the pulse in the time domain is equivalent to introducing a frequency chirp. To reiterate, the three stages are (Figure B.3): (1) stretch the seed laser to keep it from damaging the Ti:Sapphire crystal, (2) pass it through the Ti:Sapphire crystal and allow amplification (the crystal being pumped by Empower) (3) compress the pulses back down. The Spitfire output is what will eventually pump the sample. Its repetition rate is controlled by Empower. Note, from Tsunami to Spitfire, the conversion was



<sup>&</sup>lt;sup>4</sup>The repetition rate of the Empower is user controlled between 50 Hz and 10 kHz. Increasing the rep. rate will decrease the energy per pulse.

High repetition rate lasers are frequently (pardon the pun) employed in pumpprobe studies, sometimes putting them at a disadvantage. Consider how often a laser with repetition rate of 80 MHz will pump a a sample: every 12.5 ns. Some systems are not completely relaxed in 12.5 ns (which will be discussed further in Chapter 5). For now, just note that 1 kHz is beneficial in that it does not run the risk of pumping the residual level associated with some effect, unless that effect has not relaxed by 1 ms and it allows for much higher degrees of excitation to a system since it is amplified.

が一次に



Figure B.3: The seed pulses are stretched (in time) prior to amplification as to not damage the Ti:Sapphire crystal, followed by amplification in the Ti:Sapphire crystal. Finally they compressed back down after amplification. [440]

## Appendix C

# Thermophysical Properties of Selected Metals

	Au	Ag	Cu	Pt	Al	Ni	
$\overline{C_i}$	2.49	2.47	3.45	2.86	2.42	3.95	$\left(\times 10^{6} \mathrm{J} \cdot \mathrm{m}^{-3} \mathrm{K}^{-1}\right)$
$\kappa_i$	317	429	401	716	237	907	$(W \cdot m^{-1} K^{-1})$
$ au_{m{i}}$	36.4	39.2	15.4	70.7	7.1	18.9	(ps)
$\gamma$	67.6	62.5	71.0	748.1	91.2	1077.4	$(J \cdot m^{-3} K^{-1})$
G	2.5	2.8	10.0	110.0	31.0	105.0	$(\times 10^{16} \text{ W} \cdot \text{m}^{-3} \text{K}^{-1})$
R	0.93	0.96	0.96	0.72	0.87	0.69	
$\delta_s$	12.7	14.5	12.1	12.8	7.5	14.5	(nm)

Table C.1: The thermophysical properties for gold, silver, copper, platinum, aluminium, and nickel. The values of  $\delta_s$  and R are given at 800 nm (1.55 eV). Acquiring them for other wavelengths is quite simple by just gathering the complex index of refraction values (n and  $\kappa$ ) from the various physical and chemistry handbooks [195], and using  $\delta_s = \lambda/4\pi\kappa$ . Experimentally gathered reflectivities are available in Reference [195].

## Appendix D

# Complex Index of Refraction for Au and Ag

	А	u	$\mathbf{A}\mathbf{g}$		
λ (nm)	n	κ	n	κ	
1938	0.240	14.080	0.920	13.780	
1610	0.560	11.210	0.150	11.850	
1393	0.430	9.519	0.130	10.100	
1216	0.350	8.145	0.090	8.828	
1088	0.270	7.150	0.040	7.795	
984	0.220	6.350	0.040	6.992	
892	0.170	5.663	0.040	6.312	
821	0.160	5.083	0.040	5.727	
756	0.140	4.542	0.030	5.242	
705	0.130	4.103	0.040	4.838	

Table D.1: The complex index of refraction  $\tilde{n} = n + i\kappa$  for Au and Ag at various wavelengths, from Johnson and Christy (1972) [370] (continues on next page).

	А	u	Ag		
λ (nm)	n	κ	<u>n</u>	<u>κ</u>	
660	0.140	3.697	0.050	4.483	
617	0.210	3.272	0.060	4.152	
582	0.290	2.863	0.050	3.858	
549	0.430	2.455	0.060	3.586	
521	0.620	2.081	0.050	3.324	
496	1.040	1.833	0.050	3.093	
471	1.310	1.849	0.050	2.869	
451	1.380	1.914	0.040	2.657	
431	1.450	1.948	0.040	2.462	
413	1.460	1.958	0.050	2.275	
397	1.470	1.952	0.050	2.070	
382	1.460	1.933	0.050	1.864	
368	1.480	1.895	0.070	1.657	

Table D.2: Au and Ag complex index of refraction (continued from previous page).
	Au		Ag	
λ <b>(nm)</b>	n	κ	n	κ
354	1.500	1.866	0.100	1.419
343	1.480	1.871	0.140	1.142
332	1.480	1.883	0.170	0.829
320	1.540	1.898	0.810	0.392
311	1.530	1.893	1.130	0.616
301	1.530	1.889	1.340	0.964
292	1.490	1.878	1.390	1.161
284	1.470	1.869	1.410	1.264
276	1.430	1.847	1.410	1.331
269	1.380	1.803	1.380	1.372
262	1.350	1.749	1.350	1.387
255	1.330	1.688	1.330	1.393

Table D.3: Au and Ag complex index of refraction (continued from previous page).

<u>λ (nm)</u>	Au		Ag	
	<i>n</i>	κ	<u>n</u>	κ
249	1.330	1.631	1.310	1.389
243	1.320	1.577	1.300	1.378
237	1.320	1.536	1.280	1.367
231	1.300	1.497	1.280	1.357
226	1.310	1.460	1.260	1.344
221	1.300	1.427	1.250	1.342
216	1.300	1.387	1.220	1.336
212	1.300	1.350	1.200	1.325
207	1.300	1.304	1.180	1.312
203	1.330	1.277	1.150	1.296
199	1.330	1.251	1.140	1.277
195	1.340	1.226	1.120	1.255
192	1.320	1.203	1.100	1.232
188	1.280	1.188	1.070	1.212

) ,\_\_

Table D.4: Au and Ag complex index of refraction (continued from previous page).

## Appendix E

## **Riccati-Bessel Functions**

The Riccati-Bessel functions  $\psi_l(x)$  and  $\chi_l(x)$  are given in terms of the conventional Bessel functions of the 1st and 2nd kinds,  $J_{\alpha}(x)$ , and  $Y_{\alpha}(x)$ , respectively:

$$\psi_l(x) = \sqrt{\frac{\pi x}{2}} J_{l+1/2}(x), \tag{E.1}$$

$$\chi_l(x) = -\sqrt{\frac{\pi x}{2}} Y_{l+1/2}(x),$$
 (E.2)

and

$$\eta_l(x) = \sqrt{\frac{\pi x}{2}} \left( J_{l+1/2}(x) - iY_{l+1/2}(x) \right) = \psi_l(x) + i\chi_l(x).$$
(E.3)

The first and second Bessel functions are

$$J_{\alpha}(x) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m! \,\Gamma(m+\alpha+1)} \left(\frac{x}{2}\right)^{2m+\alpha} \tag{E.4}$$

and

$$Y_{\alpha}(x) = \frac{J_{\alpha}(x)\cos(\alpha\pi) - J_{-\alpha}(x)}{\sin(\alpha\pi)}.$$
 (E.5)

Derivatives satisfy the convenient relationship

$$Z'_{\alpha}(x) = Z_{\alpha-1}(x) - \frac{\alpha Z_{\alpha}(x)}{x}, \qquad (E.6)$$

where  $Z_{\alpha}$  could be  $J_{\alpha}$  or  $Y_{\alpha}$ . If  $\alpha$  is integer, the following relationship is also valid:

$$Z_{-\alpha}(x) = (-1)^{\alpha} Z_{\alpha}(x).$$
(E.7)

## Appendix F

# Two-Temperature Model Computer Program

! \_\_\_\_\_\_ ! This program solves the Two-Temperature Model for metals 1 with non-Fourier heat transfer for the heat flux. \_\_\_\_\_ ŗ ! UNITS: MKS ļ ! COMPILES: Fortran 90, (f90, f95, gfortran, g95, ifort, etc.) 1 CALLS: nrtype.f90 ! 1 CODED BY: Ryan A. Murdick (5/20/2006) 1 ! (rmurdick@gmail.com) ļ \_\_\_\_\_ USE nrtype; IMPLICIT NONE

REAL(DP),ALLOCATABLE :: Te(:),Ti(:),Qe(:),Qi(:),

- \* TeStar(:),TiStar(:),QeStar(:),QiStar(:)
  REAL(DP) F,lambda,tp,tm,ds,R,Ki,Ci,Ce,Ke,G,tau\_i,tau\_e,
- \* gam,gauss,T0,dt,dz,thick,time,t,tt,z,zz,S,C(50)
  INTEGER(I4B) n,k,nt,nz

İ

MATERIAL (Au)

! (input these)

!	
	Ki=317.0_DP
	Ci=2.5D6
	tau_i=38.7D-12
	tau_e=40.0D-15
	G=2.6D16
	gam=70.0_DP
!	DIMENSIONS / RUN TIME
!	

190

```
thick=100.0D-9
nz=101
time=5.0D-12
dt=5.0D-17
! (leave these alone)
dz=thick/(nz-1)
nt=NINT(time/dt)+1
ALLOCATE(Te(nz),TeStar(nz),Ti(nz),TiStar(nz),Qe(nz),
* Qi(nz),QeStar(nz),QiStar(nz))
```

```
! INITIALIZE
```

```
!
        T0=298.0_DP
    DO k=1,nz
      Te(k)=T0
      TeStar(k)=T0
      Ti(k)=T0
      TiStar(k)=T0
      Qe(k)=0.0_DP
      QeStar(k)=0.0_DP
      Qi(k)=0.0_DP
      QiStar(k)=0.0_DP
    ENDDO
!
    SPEED-UP CONSTANTS
ļ
```

C(1)=sqrt(gauss/PI\_D)\*(1-R)/(tp\*ds)\*F

C(2)=1.0\_DP/ds C(3)=gam/tp\*\*2 C(4)=1.0\_DP/dz C(5)=-dt/dz C(5)=-dt/dz C(6)=dt\*G C(7)=dt/dz/Ci C(8)=dt\*G/Ci C(8)=dt\*G/Ci C(9)=1.0\_DP-dt/tau\_i C(10)=Ki\*dt/tau\_i/dz C(11)=dt/tau\_i/dz C(11)=dt/tau\_i/dz C(12)=Ki/dz C(13)=2.0\_DP\*dt\*Ki/dz\*\*2/Ci IF(C(13) >= 1.0\_DP) PRINT\*, 'Unstable Courant'

OPEN(unit=20,file='T\_time.dat')

```
! SOLVE
! ------
! (begin time loop)
D0 n=1,nt
    t=(n-1)*dt
    ! (begin space loop)
D0 k=2,nz-1
    z=(k-1)*dz
    S=C(1)*DEXP(-C(2)*z)*DEXP(-C(3)*(t-tm)**2)
```

! Predictor Step

|------Ce=gam\*Te(k)TeStar(k)=Te(k)+(C(5)\*(Qe(k)-Qe(k-1))-C(6)\*(Te(k)-Ti(k))+dt\*S)/Ce\* TiStar(k)=Ti(k)-C(7)\*(Qi(k)-Qi(k-1))+C(8)\*(Te(k)-Ti(k))\*  $QeStar(k)=Qe(k)*(1.0_DP-dt/tau_e)$  $+C(5)*Ke/tau_e*(Te(k)-Te(k-1))$ \* QiStar(k)=Qi(k)\*C(9)-C(10)\*(Ti(k)-Ti(k-1))Ke=Ki\*TeStar(k)/TiStar(k) ! Corrector Step 1-----Ce=gam\*TeStar(k)  $Te(k)=0.5_DP*(Te(k)+TeStar(k))$ +(C(5)\*(QeStar(k+1)-QeStar(k)))\* -C(6)\*(TeStar(k)-TiStar(k))+dt\*S)/Ce)\*  $Ti(k)=0.5_DP*(Ti(k)+TiStar(k))$ -C(7)\*(QiStar(k+1)-QiStar(k))\* +C(8)\*(TeStar(k)-TiStar(k))) \*  $Qe(k)=0.5_DP*(QeStar(k)*(1.0_DP-dt/tau_e)+Qe(k))$ +C(5)\*Ke/tau\_e\*(TeStar(k+1)-TeStar(k))) \*  $Qi(k)=0.5_DP*(QiStar(k)*C(9)+Qi(k))$ -C(10)\*(TiStar(k+1)-TiStar(k)))\* Ke=Ki\*Te(k)/Ti(k)ENDDO ! (spatial loop done)

```
! Boundary Conditions
|-----
Te(1)=Te(2)
Ti(1)=Ti(2)
TeStar(1)=TeStar(2)
Te(nz)=Te(nz-1)
TeStar(nz)=TeStar(nz-1)
Ti(nz)=Ti(nz-1)
TiStar(nz)=TiStar(nz-1)
tt=t*1.0D12
WRITE(20,*) tt,Te(1),Ti(1)
ENDDO
! (time loop done)
CLOSE(20)
STOP
END
```

#### F.1 Non-Thermal Electrons Subroutine

```
_____
!
!
     This subroutine calculates non-thermal electron
i
     scattering channels. Call from a TTM or Boltzman
     transport program, just replace your laser source
!
!
     like in Carpene (2006)
!
     _____
                   _____
1
     UNITS: MKS (careful not to use eV for energy!)
!
```

ļ COMPILES: Fortran 90, (f90, f95, gfortran, g95, ifort, etc.) ! CALLS: nrtype.f90, and your favorite integration ! Ł subroutine (Simpson's rule, etc.) Replace the calls to INTEGRATE below. ! ! ! CODED BY: Ryan A. Murdick (7/17/2009) (rmurdick@gmail.com) ! 1 ! NOTES: Make sure your source heating term has ! gaussian shape with max at ! three pulse-widths. This is not checked for 1 SUBROUTINE NON\_THERM (t,dt,ll,tp,Ef,h\_nu,Tau\_ep,wp, \* NN, Ree, Rep) USE nrtype; IMPLICIT NONE ! INPUT/OUTPUT DECLARATION (GLOBAL) 1 REAL(DP), INTENT(IN) :: t, tp, Ef, h\_nu, Tau\_ep, dt INTEGER(I4B), INTENT(IN) :: NN,11 REAL(DP), INTENT(OUT) :: Ree, Rep ! BEGIN LOCAL DECLARAION ! REAL(DP),ALLOCATABLE :: arg1(:),arg2(:)

REAL(DP) beta, Tau0, wp, tm, Tee, c1, c2, c3, c4,c5,c6,tt,P,Hee,Hep,sml,h\_nu2 \* INTEGER(I4B) nt,i ! \_\_\_\_\_ Tau0=128.0\_DP/(PI\_D\*\*2\*3.0\_DP\*\*0.5\_DP\*wp) tm=3.0\_DP\*tp beta=4.0\_DP\*DLOG(2.0\_DP) !h\_nu2=h\_nu-1.1\_DP\*e h\_nu2=h\_nu c1=1.0\_DP c2=h\_nu2\*\*2/Ef\*\*2/Tau0+1.0\_DP/Tau\_ep c3=h\_nu2\*\*2/Ef\*\*2/Tau0 c4=Ef\*\*2\*Tau0 c5=h\_nu2\*\*2 sml=1.0D-20 ! Since the pulse is only defined from ~ 0 to 5\*tp, ! we can safely integrate Hee(t-tt)\*P(tt) from 0 to t, ! ļ even though mathematically it should be -infinity to t Integrate 5 pulse-widths (-2.5:2.5) tp ! ! (Sufficient for Gaussian) ļ dt=5.0\_DP\*tp/(1.0\_DP\*NN) ! Set the upper integration limit "t" was read in by the routine, make sure !

```
!
       nt reflects t.
ļ
       nt=NINT(t/dt+1.0)
       PRINT*,11
Į.
       ALLOCATE(arg1(11), arg2(11))
!
       *****
       INTEGRATE {P(tt) H(tt), tt = 0..t}
!
!
       (tt is the dummy integration variable)
I.
       _____
       DO i=1,11
         tt=(i-1)*dt
        P=DEXP(-beta*(tt-tm)**2/tp**2)
        Hee=-DEXP(-(t-tt)*c2)/(t-tt+sml)**2*(
          c5*(t-tt)+c4*(1.0_DP-DEXP(c3*(t-tt))))
    *
         arg1(i)=P*Hee
        Hep=-DEXP(-(t-tt)*c2)/((t-tt+sml)*Tau_ep)*
         c4*(1.0_DP-DEXP(c3*(t-tt)))
    *
        arg2(i)=P*Hep
ļ
        IF(ll<=10) PRINT*,'ll,i,Hee',ll,i,Hee</pre>
       ENDDO
       CALL INTEGRATE(arg1,11,dt,Ree)
       CALL INTEGRATE(arg2,11,dt,Rep)
       [Ree/(hv)<sup>2</sup>] is dimensionless
!
!
                                ______
       DEALLOCATE(arg1,arg2)
ł
                     ......................
```

END SUBROUTINE NON\_THERM

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