THE GROWTH OF ORGANIC SMALL MOLECULE AND INORGANIC HALIDE PEROVSKITE CRYSTALLINE THIN FILMS

By

Pei Chen

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ABSTRACT

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Organic semiconductors have shown exceptional opportunities for manipulating energy in a range of structures in light-emitting diodes, lasers, transistors, transparent photovoltaics, etc. with the presence of excitons at room temperature that distinguishes them from traditional semiconductors. The control over the crystalline order, orientation, layer-coupling as well as defect formation are the key to the fabrication and optimization for improving the performance of organic electronics. In the first part of this thesis, we focus on understanding organic crystalline growth. Organic homoepitaxy growth mode is mapped as a function of vapor phase growth conditions on high quality organic crystalline substrates. Organic-organic hetero-quasiepitaxy is then studied to explore the design rules for ordered alternating organic growth similar to inorganic quantum well structure. A unique organic edge driven case is demonstrated providing new routes to controlling molecular orientation and multilayer ordering. These results could enable entirely new opportunities for enhancing unique excitonic tunability and could also be used as a platform to study organic exciton confinement and strong coupling.

The second part of the thesis is focused on inorganic halide perovskite growth. Hybrid halide perovskites have attracted tremendous attention as an exceptional new class of semiconductors for solar harvesting, light emission, lasing, quantum dots, thin film electronics, etc. However, the toxicity of lead devices and lead manufacturing combined with the instability of organic components have been two key barriers to widespread applications. In this work, we demonstrate the first single-domain epitaxial growth of halide perovskites. This *in situ* growth

study is enabled by the study of homoepitaxy and mixed-homoepitaxy of metal halide crystals that demonstrates the capability of performing reflection high-energy electron diffraction (RHEED) on insulating surfaces. We then focus on tin-based inorganic halide perovskites, $CsSnX_3$ (X = Cl, Br, and I), on lattice-matched metal halide crystals via reactive vapor growth route that leads to singledomain epitaxial films with excellent crystalline order lacking in solution processing. Exploiting this highly controllable epitaxial growth we demonstrate the first halide perovskite quantum wells that creates photoluminescent tunability with different well width. These demonstrations could spark the exploration of a full range of epitaxial halide perovskites and lead to novel applications for metal-halide-perovskite based single-crystal epitaxial optoelectronics. Copyright by PEI CHEN 2019

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KEY TO ABBREVIATIONS

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
α-4Τ	α-quaterthiophene
α-NPD	4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl
AFM	atomic force microscopy
Alq ₃	tris-(8-hydroxyquinolinato) aluminum
AM1.5 G	global standard spectrum
APS	advanced photon source
BL	bilayer (full unit cell thickness)
BSE	backscattered electrons
CBP	4,4'-N,N'-dicarbazole-biphenyl
CuPc	copper(II) phthalocyanine
CsBr	cesium bromide
CsI	cesium iodide
CsSnX ₃	cesium tin chloride (X=Cl), cesium tin bromide (X=Br), cesium tin bromide (X=I)
СТ	charge transfer
DBP	5,10,15,20-tetraphenylbisbenz[5,6]indeno[1,2,3-cd:1',2',3'-lm]perylene
DB-TCNQ	dibenzotetrathiafulvalene-tetracyanoquinodimethane
DFT	density functional theory
DIP	diindenoperylene
DOS	densities of states

DPA	9,10-diphenylanthracene
DB-TCNQ	dibenzotetrathiafulvalene-tetracyanoquinodimethane
EL	electroluminescence
ELO	epitaxial lift-off
F ₁₆ CuPc	copper hexadecafluorophthalocyanine
FIB	focused ion beam
FWHM	full width at half maximum
GGA	generalized gradient approximations
H ₂ Pc	phthalocyanine
HBC	hexa-peri-hexabenzocoronene
HOPG	highly oriented pyrolytic graphite
HSE06	Heyd-Scuseria-Ernzerhof hybrid functional
IR	infrared
Ir(ppy) ₃	fac tris(2-phenylpyridine)iridium
ITO	indium tin oxide
KCl	potassium chloride
L	length of a molecule
L1-L4	layer 1 to 4 in alternating growth structure
LES	lowest energy surface
LiQ	8-hydroxyquinoline lithium
М	molecular weight
MBE	molecular beam epitaxy
МеОН	methanol

MD	molecular dynamics
ML	monolayer (half unit cell thickness)
NaCl	sodium chloride
NIR	near-infrared
NREL	National Renewable Energy Laboratory
NTCDA	1,4,5,8-naphthalenetetracarboxylic dianhydride
NVE	microcanonical ensemble
NVT	canonical ensemble
OLED	organic light-emitting diode
OPV	organic photovoltaics
<i>p</i> -6P	para-sexiphenyl
PL	photoluminescence
PTCDA	3,4,9,10-perylenetetracarboxylic dianhydride
PTCDI-Ph	N,N'-diphenyl-3,4,9,10-perylenedicarboximide
PV	photovoltaics
PVD	physical vapor deposition
QCM	quartz crystal monitor
QE	quasiepitaxial
QT	quaterrylene
RAPD	rapid automated processing of X-ray data
RHEED	reflection high-energy electron diffraction
SAED	selected area electron diffraction
SE	secondary electrons or surface energy

SEM	scanning electron microscopy
SnBr ₂	tin bromide
SnI_2	tin iodide
STEM	scanning transmission electron microscopy
STO	strontium titanate
TCNQ	tetracyanoquinodimethane
TEM	transmission electron microscopy
TTF-TCNQ	tetrathiafulvalene 7,7,8,8-tetracyanoquinodimethane
UV	ultraviolet
UV-Vis	ultraviolet-visible spectroscopy
VASE	variable angle spectroscopic ellipsometry
VASP	Vienna Ab initio simulation package
VIS	visible light
W	width of a molecule
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
ZnPc	zinc phthalocyanine

Symbols

Å	Angstrom, equivalent to 0.1 nm or 10 ⁻¹⁰ m
Α	absorbance, active area in calculating responsivity of a photodetector
A_{ij}	potential depth
a	lattice constant
a_B	exciton Bohr radius
a_L	lattice constant of the adlayer
as	lattice constant of the substrate
b_1^A , b_2^A	real lattice vectors of the adlayer
b_{1}^{S}, b_{2}^{S}	real lattice vectors of the substrate
B_{ij}	atomic interaction distance
С	speed of light
C _{dose}	critical dose
d	thickness of film
Δd	width of the lattice rods
D	self (or tracer) diffusion coefficient
D^*	specific detectivity
D^c	chemical (or collective) diffusion coefficient
D_0	pre-exponential factor in Arrhenius equation for diffusivity
E_{ES}	Ehrlich–Schwoebel barrier
E_g	bandgap
$E_g{}^0$	bulk band gap
E_m	intra-terrace diffusion barrier

Es	diffusion barrier at the step edge
EQE	external quantum efficiency
ΔG	free energy change during nucleus formation
h	Planck constant
ħ	reduced Planck constant
Ι	intensity of the sample beam in UV-Vis measurement, electron beam current in
	RHEED
Ilight	current measured with light illumination
Idark	current measured without light illumination
Io	intensity of the reference beam
J	current density
J _{dark}	dark current density
k	extinction coefficient
k ₀	diameter of the Ewald sphere
k _B	Boltzmann constant
L	luminescence current density
L_z	thickness of the quantum well
М	transformation matrix between adlayer and substrate
<i>M</i> _e	mass of electron
m_e^*	effective mass of the electron
${m_h}^*$	effective mass of the hole
n	the refractive index in Cauchy model, order of planes in Bragg's Law
N_M	multiples of unit cell lattice vector (b_1^A) of the adlayer

N_N	multiples of unit cell lattice vector (b_2^A) of the adlayer
Pincident	incident light power density
p_v	actual vapor pressure during deposition
p_v^{sat}	equilibrium vapor pressure
q	charge of the electron
r	separation distance between atoms in Lennard-Jones potential, radius of the nucleus
R	reflection; responsivity of a photodetector
<i>r</i> _p	reflectivity of p-polarized light
r _s	reflectivity of s-polarized light
Т	transmittance, temperature
$\% T_{Localized}$	fractional localized time
%T <01>	fractional time of a molecule travel along [01] or [10] direction
t	time
<i>t</i> _{damage}	time-to-damage
t_i	initial (guessed) initial thickness in calculating tooling factor
<i>t</i> _f	final (calculated) thickness in calculating tooling factor
TF_i	initial (guessed) tooling factor
TF_f	final (calculated) tooling factor
V	voltage; simple periodic potential in registry modeling
V_0	interatomic potential

α	tilt angle from sample surface normal direction in pole figure measurement
β	rotation angle around sample surface normal direction in pole figure measurement
γsv	free energy of the substrate
$\gamma_{\mathrm{f}s}$	free energy of the interface
γvf	free energy of the epilayer
Δ	phase component of ellipsometric angle
З	permittivity
E _r	relative permittivity, also called dielectric constant
80	vacuum permittivity
θ	angle of the incident beam in XRD geometry, unit cell rotation angle between
	adlayer and substrate
ρ	complex reflectance
λ	wavelength
$\phi_{_{intra}}$	intralayer potential
$\phi_{_{inter}}$	interlayer potential
Ψ	amplitude component of ellipsometric angle

Chapter 1 Introduction

The goal of this chapter is to introduce small organic molecules and inorganic halide perovskites crystalline thin film growth, which are the two major themes discussed in this work.

1.1 Organic Semiconductors

1.1.1 Motivation

The presence of excitons, coulombically bounded electron-hole pairs, in organic semiconductors at room temperature distinguishes them from traditional semiconductors, providing exceptional opportunities for manipulating energy in a range of structures in light



Figure 1.1. Carrier mobility for single crystals, thick films, and monolayer films for various common organic small molecule semiconductors. Figure reprinted with permission.¹

emitting diodes, strongly coupled cavities, lasers, anisotropic transistors, transparent photovoltaics and excitonic switches.²⁻⁷ The degree of crystal ordering for these organic layers has been linked to the efficiency of carrier transport with record mobilities of >30 cm² V⁻¹ s⁻¹ reported for single crystals (**Figure 1.1**), exciton migration,⁸ and emerging photophysics such as singlet exciton fission and polariton lasing.⁹⁻¹⁰ Defects have a large impact on charge transport in organic electronic devices. ¹¹ High defect density in the film will generally lead to large concentration of trap states that hinders the device performance.¹² Control over crystalline order, orientation and layer coupling are therefore critical to optimization and exploitation of exciton dynamics in these materials for next generation electronics. For inorganic semiconductors, quantum wells and quantum dots (i.e. that include many alternating layers) have played important roles in applications such as photodetectors, LEDs, and especially solid-state laser diode.¹³⁻¹⁵ The organic equivalent (**Figure 1.2b**) could have similarly substantial impact but has not been accessible before.



Figure 1.2. TEM for AlGaN/AlN quantum wells for UV laser applications and schematic of multilayer organic single crystalline structure. Figure reproduced with permission.¹³

1.1.2 Review on Small Organic Molecule Crystalline Thin Film Growth

Organic "epitaxy "is different from inorganic epitaxy that is based on lattice matching. The term "quasiepitaxy (QE)" is used to describe this "energetically ordered" growth (explained in **Section 2.3**) QE of organic layers can be achieved on both inorganic and organic substrates.

Various high-quality inorganic crystalline substrates are readily available for organic thin film growth. Many studies have reported on organic-on-inorganic growth systems, including tetracene on SiO₂,¹⁶⁻¹⁷ Ag;¹⁸ pentacene on SiO₂,¹⁹⁻²¹ Au,²²⁻²³ Ag,²⁴⁻²⁵ Cu;²⁶⁻²⁷ diindenoperylene(DIP)

on SiO₂,²⁸⁻³⁰ Au;³¹⁻³² 3,4,9,10 perylenetetracarboxylic dianhydride(PTCDA) on graphite,³²⁻³³ SiO₂,³⁴ GaAs,³⁵ Ag,³⁶⁻⁴¹ Au;⁴²⁻⁴⁴ copper phthalocyanine(CuPc) on graphite, ⁴⁵⁻⁴⁷ Si,⁴⁸⁻⁵⁰ SiO₂,⁵¹⁻⁵² Au,⁵¹ Ag⁵³ and metal halide.^{45, 54-55} Example of organic-inorganic QE are shown in **Figure 1.3**.

One of the obstacles in understanding organic homoepitaxial and organic-organic hetero-QE growth is the lack of high quality organic crystalline substrates. There are reports on the preparation of organic single crystals(substrates), but the sizes are relatively small. Single crystal



Figure 1.3. Examples of organic-inorganic QE growth. High-resolution STM data of (a) pentacene monolayer on HOPG and (b) PTCDA monolayer on the Ag. The unit cell of the adlayers are indicated. Figure reproduced with permission. ^{27, 56}

naphthalene and anthracene sheets(<1cm²) at the liquid–air interface from a mixture of solvents has been reported.⁵⁷ Single crystal naphthalene and anthracene are also prepared from the liquid phase. Kikuchi patterns (explained in **Section 3.2.1**) have been observed by reflection high-energy electron diffraction (RHEED) and were fitted to obtain the mean inner potential.⁵⁸ Needle-like rubrene single crystals (mm² size) were grown using physical vapor transport and used for homoepitaxial growth study.⁵⁹ α -quaterthiophene (α -4T) single crystals grown from solution are used to demonstrate homoepitaxial growth ⁶⁰.



1.5 μm x 1.5 μm

Figure 1.4. Examples of organic-organic QE growth. AFM images of the (a) α -4T on *p*-6P and (b) C₆₀ on single crystal pentacene. Figure reproduced with permission. ⁶¹⁻⁶²

Besides the difficulties in fabricating high quality organic crystalline substrates for subsequent layer growth, obstacles in understanding the organic-organic quasiepitaxy also include the incomplete understanding in the materials selection rules for organic quasiepitaxial growth as well as the limited use of effective in situ real time monitoring techniques. Cases of organicorganic hetero-quasiepitaxial growth systems are infrequent but include quaterrylene(QT) on 62-63 hexa-peri-hexabenzocoronene(HBC) on Au(111), perylene-tetracarboxylicdianhydride(PTCDA)-hexa-peribenzocoronene(HBC)-highly ordered pyrolytic graphite (HOPG), ⁶⁴ rubrene on tetracene, ⁶⁵ rubrene on α -4T, ⁶⁶ α -4T on Rubrene, ⁶⁷ α -4T on tetracene single crystal, ⁶⁸ etc. Example of organic-organic QE are shown in Figure 1.4. Cases of ordered alternating crystalline growth are extremely rare and only include PTCDA/3,4,7,9 naphthalenetetracarboxylic dianhydride(NTCDA) on highly ordered pyrolytic graphite(HOPG), ⁶⁹ 70 dibenzotetrathiafulvalene-tetracyanoquinodimethane(DB-TCNQ)/ NTCDA KBr, on 71 phthalocyanine (H₂Pc)/copper hexadecafluorophthalocyanine $(F_{16}CuPc)$ and zinc phthalocyanine (ZnPc)/ N,N'-diphenyl-3,4,9,10-perylenedicarboximide (PTCDI-Ph) on parasexiphenyl (*p*-6P)on Si/SiO₂.⁷² Clear QE relationships were discovered only in DB-TCNQ/NTCDA and PTCDI-Ph/ZnPc growth systems. It has been suggested that the matching of surface energy is essential in inducing ordered crystalline growth, ⁷⁰ which is one of the predictive material selection criteria in pairing ordered organic growth that is more thoroughly investigated in **Section 4.2**.

1.2 Inorganic Halide Perovskites

1.2.1 Motivation

Hybrid organic-inorganic halide perovskite has the ABX₃ structure where A is an organic cation such as methylammonium ($CH_3NH_3^+$) and formamidinium ($HC(NH_2)_2^+$), B is an inorganic cation which is usually Pb^{2+} and X is halogen anion which can be Cl⁻, Br⁻, and I⁻. This type of perovskites has attracted tremendous attention as an exceptional new class of semiconductors for solar harvesting,⁷³⁻⁷⁵ light emission,⁷⁶ lasing,⁷⁷ quantum dots,⁷⁸ water splitting⁷⁹ and thin film electronics.⁸⁰ Ever since the first report of organic-inorganic perovskite based solar cells with high power conversion efficiency of over 10%,⁸¹ efficiencies of solar cells based on these materials have exceeded 22% only after five years,⁸² however, the toxicity of lead devices and lead manufacturing⁸³⁻⁸⁵ combined with the instability of organic components ^{84, 86-90} have been two key barriers to widespread application. Other barriers include structural defects, ⁹¹⁻⁹² trap states, ⁹³ etc. Tin-based inorganic halide perovskites, such as $CsSnX_3$ (X = Cl, Br, and I), have been considered promising substitutes for their lead analogues since Sn is over 100 times less toxic than Pb and Cs has similar toxicity to Na or K. However, current research on photovoltaic and electronic applications of CsSnBr₃ and CsSnI₃ has, to date, been less encouraging, with solar cell efficiencies of < 5% for solution-processed thin film devices⁹⁴⁻⁹⁵ that are likely limited by the low degree of crystalline ordering.⁹⁶ Indeed, structural ordering has been linked in traditional semiconductors to

a) carrier transport, where mobilities increase from amorphous-Si (1 cm² V⁻¹ s⁻¹)⁹⁷ to single crystalline Si $(1,400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$,⁹⁸ b) recombination rates, where unpassivated grain boundaries act as quenching sites for charge carriers and excited states and c) quantum confinement, which can make even Si an excellent NIR emitter with luminescent efficiency > 60%.⁹⁹ These factors, among others, have motivated the recent interest in halide perovskite single crystal growth.¹⁰⁰⁻¹⁰⁴ Thus, one of the main challenges for enhancing the properties of halide perovskites for high end optoelectronic applications is to obtain epitaxial crystalline films that can also be integrated into heteroepitaxial and quantum well structures. The epitaxial growth is a key step towards realizing 2-dimensional (2D) electron gasses,¹⁰⁵ interface superconductivity,¹⁰⁶ ultra-high mobility strained transistors,¹⁰⁷ magnetoelectric multiferroics,¹⁰⁸ and the observation of fractional quantum hall effects.¹⁰⁹ As shown in previous research on oxide perovskites, numerous phases can be derived from the perovskite structure with even minor changes in the elemental compositions. For example, by removing one-sixth of the oxygen atoms, phase transitions can occur from perovskite to brownmillerite structures.¹¹⁰ Therefore, it is key to gain precise control over the crystal phase, crystalline order, orientation, and interfaces for the optimization of halide perovskite based optoelectronics.

Epitaxial growth has long been utilized to achieve the lowest defect densities and highest performance for applications in lasers, thin film transistors, 2D electron gases, sensors, and highpower devices. The development of inorganic materials such as III-V semiconductors has been extensively accelerated by epitaxial growth. Moreover, studies of epitaxial oxide perovskites have shown that unique properties can occur at the interfaces of different materials including superconductivity, ferroelectricity, and magnetism. These functional properties can be tuned by engineering the symmetries and degrees of freedom of correlated electrons at the interfaces of oxide perovskites, which is associated with the atomic arrangement at the interface.¹¹¹⁻¹¹⁴ Thus, epitaxial growth provides precise interface control and correspondingly yields the potential for interesting new systems such as magnetic superconductors, non-centrosymmetric superconductors and multiferroics.¹¹⁵⁻¹¹⁹ These successes have driven a new focus to control film quality, defect density, strain, and phases of new semiconducting materials that should be applicable to halide perovskites.

1.2.2 Review on Halide Perovskite Epitaxial Growth

While there has been significant research into the epitaxial growth of oxide perovskites, such as the BaTiO₃, SrRuO₃ and LaAlO₃ growth on SrTiO₃(100),^{112, 120-123} single-domain epitaxy has yet to be explored for halide perovskites. This has likely been hindered in large part due to a number of challenges associated with the epitaxial growth of perovskites on dissimilar single crystal substrates including matching of lattice constants, lattice symmetry, coordination, wettability, thermal expansion differences, and bonding character (ionic versus covalent).¹²⁴ There have been only a few reports of even metal halide salt epitaxy,¹²⁵ and only several recent studies of incommensurate van der Waals epitaxy (QE) of halide perovskite micro-sheets,¹²⁶ nanorods,¹²⁷ nanowires,¹²⁸ and nanocrystals¹²⁹⁻¹³⁰ that are accompanied with a high degree of rotational disorder. Limited examples for halide perovskite epitaxy include the growth of hybrid perovskites.

In our work, low-cost alkali halide salts such as NaCl, KBr, KCl, etc. are explored (**Chapter 7 and 8**) as promising substrates for purely inorganic halide perovskite growth which provides the first demonstration of the single-domain thin film epitaxy. These alkali halide substrates provide an ideal range of lattice constants (5.4-6.6 Å) closely matched to those of the halide perovskites (5.5-6.2 Å), with suitable wettability, and congruent ionic bonding. These

examples have confirmed the feasibility of vapor-phase epitaxial growth methods for this group of materials.

1.3 Thesis Outline

The rest of this thesis is arranged as follows: In **Chapter 2**, the theory behind thin film growth is discussed for both epitaxy and quasiepitaxy. **Chapter 3** covers experimental techniques used in this study including diffraction techniques for analyzing crystal structure *in situ* and *ex situ*, thin film morphology, and optical measurements. **Chapter 4** discusses organic homo-epitaxy and hetero-quasiepitaxy (QE). Two methods for fabricating large area organic single crystals are demonstrated. An example of organic homoepitaxy is studied and the growth mode is mapped as a function of growth rate and temperature. The rules for designing ordered alternating hetero-quasiepitaxial growth are then explored. **Chapter 5** discusses a unique organic edge driven growth mechanism discovered in organic hetero-QE. **Chapter 6** discusses the homoepitaxial growth mode study for alkali metal halide crystals which demonstrates the capabilities to perform RHEED on insulating substrates that facilitates the demonstration of inorganic halide epitaxy in **Chapter 7** for CsSnBr₃ **and Chapter 8** for CsSnI₃ where a new pseudomorphic phase is discovered in the latter. **Chapter 9** provides conclusions and outlook for these areas.

Chapter 2 – Background on Thin Film Growth

In this chapter, the growth dynamics for thin film epitaxy are introduced. Conventional inorganic epitaxy is compared with quasiepitaxy of small molecule semiconductors.

2.1 Growth Physics

2.1.1 Elementary Processes

When molecules are deposited onto a substrate, they experience multiple elementary diffusion processes: intra-terrace diffusion, inter-terrace diffusion, nucleation and aggregation as shown in **Figure 2.1**. The most basic process is the intra-terrace diffusion (barrier E_m) when the terrace width is smaller than the mean free diffusion path of the admolecules. This process terminates when the admolecule hits a structural or chemical defect or with other admolecules. The molecule approaching an edge on the substrate encounters a barrier (E_s), which is usually large than E_m . To descend from this step and achieve inter-terrace diffusion, extra diffusion barrier E_{ES} needs to be overcome, known as Ehrlich–Schwoebel barrier.¹³³ When surface diffusivity is



Figure 2.1. The elementary molecule diffusion processes of epitaxial thin film growth. Figure reprinted with permission.¹³²

relatively low, a large E_{ES} will hinder the admolecules from descending and cause more molecules to attach to the upper terrace which promotes 3D growth. At high diffusivity, 2D growth is possibly achieved even with high E_{ES} . In thin film epitaxy, E_{ES} is important for controlling the inter-terrace mass transport and *Em* for intra-terrace mass transport.

2.1.2 Growth Modes

Depending on the strength of adlayer-substrate interactions, four main growth epitaxial modes are commonly observed: Vollmer-Weber(VW) growth (island growth, 3D morphology), Stranski-Krastinov (SK) growth (layer-plus-island growth, change from 2D to 3D morphology after critical thickness), Frank-van-der-Merwe(FM) growth (layer-by-layer growth, 2D morphology), and step glow growth. The schematics for these growth modes along with reflection high-energy electron diffraction (RHEED) oscillation profiles are shown in **Figure 3.6**.¹³²

The classification of the first three growth modes are considered by three macroscopic surface energy: γ_{sv} (free energy of the substrate), γ_{fs} (free energy of the interface), γ_{vf} (free energy of the epilayer).¹³² For an epitaxial film consisting of *n* layers, the FM growth mode occurs when:

$$\gamma_{sv} \ge \gamma_{fs(n)} + \gamma_{vf}, \qquad (2.1)$$

where $\gamma_{fs(n)}$ is the interfacial energy for *n* monolayers. This suggests there is a surface energy gain when the adlayer convers the substrate. In this mode, ad-molecules can diffuse freely in an attempt to completely cover the high energy surface. For homoepitaxy, that is $\gamma_{sv=} \gamma_{vf}$, this condition can be written as $\gamma_{fs} \leq 0$. The VW mode results when:

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf} , \qquad (2.2)$$

In this case, to minimize the nucleated surface area relative to the low energy surface, the admolecules have the tendency for aggregation. Among those growth modes, 3D growth modes (SK and VW) are most frequently observed because of the difficulty to achieve perfect wetting and high diffusivities between organic layers. This is unlike the typical driving force for 3D island growth with traditional epitaxy, which is typically driven by strain. Nonetheless, 1D and 2D growth systems are more intriguing due to their potential in fabricating high quality electronics and quantum wells with low defect density. Step flow growth happens when the terrace width is smaller than the mean free diffusion path of the molecules and the intra-terrace nucleation is largely suppressed, which is usually observed at low flux and sufficiently high temperatures for vicinal(stepped) surfaces of traditional semiconductors such as Si (001), GaAs (001).¹³⁴⁻¹³⁶

2.2 Epitaxy

Epitaxy, by definition, is "growth on a crystalline substrate of a crystalline substance that mimics the orientation of the substrate", i.e. "lattice-matching". Epitaxial growth is achieved for lattice-matched materials and near-equilibrium growth conditions. Because of the former requirement, there is a significant limitation to possible material combinations.

A key parameter for determining the success of a hetero-epitaxial system is the lattice misfit (or lateral strain), f, defined as:

$$f = \left(a_s - a_L\right)/a_L,\tag{2.3}$$

where a_S is the lattice constant of the substrate and a_L is the lattice constant of the unstrained adlayer. If misfit values are too high (e.g. greater than several percent), this leads to poor epitaxial growth with a high degree of peeling, cracking, or 3D islanding past the critical thickness and a high dislocation density below the critical thickness.



Figure 2.2. Schematic diagrams and transmission electron microscopy (TEM) examples of commensurate, pseudomorphic and incommensurate growth in epitaxy.The substrate is shown in blue and the adlayer is shown in grey. Figure reproduced with permission. ¹³⁷⁻¹³⁹

At the highest level, epitaxy can be classified into two categories: homoepitaxy, when the film is deposited on a substrate of the same composition; and heteroepitaxy, when the substrate composition is different from the film. Based on the extent of lattice mismatch, epitaxy can be further classified as commensurate, pseudomorphic, coincident, and incommensurate growth (**Figure 2.2**). Commensurate growth is based on ideal lattice matching between film and substrate. With lattice mismatch, the films can exhibit pseudomorphic or incommensurate growth. In pseudomorphic growth, the film is strained (or structurally distorted) to achieve commensurism. With even larger lattice mismatch, the distortion of pseudomorphic growth causes increasing strain in the film to an extent that relaxation occurs (from monolayers to hundreds of nm) with misfit dislocations generated at the interface.

2.3 Quasiepitaxy (QE)

Distinct from traditional epitaxy, organic "epitaxy" can occur for both chemisorbed materials and weakly binding physisorbing materials, which is known as "quasiepitaxy". This concept is also referred to as "van der Waals epitaxy", however additional forces (such as columbic and ionic forces) can play a role so that the term "quasiepitaxy" is more general. Since it is not strictly lattice matched growth, the term "quasiepitaxy" implies that the films are "ordered, or registered energetically, but not lattice matched". This term is analogous to the concept of "quasicrystals" which means "ordered but not periodical". Quasiepitaxial films have a distinct and reproducible registry of the substrate and adlayer that occurs either along primary lattice vectors or distinct (seemingly arbitrary) rotation angles.

To achieve QE, the intralayer elasticity must be larger than that of the interlayer. This requirement is expressed as ¹⁴⁰

$$\phi_{intra}" >> \phi_{inter}", \qquad (2.4)$$

where ϕ_{intra} is the intralayer potential and ϕ_{inter} is the interlayer potential. ϕ'' is the second spatial derivative of ϕ , which is the elastic constant of the lattice along a certain direction.

2.3.1 Energetic Considerations

Energy minimization is used for describing optimal quasiepitaxial configurations at equilibrium conditions. Due to the rotational degrees of freedom and shallow potential landscape, this organic adlayer will rotate in-plane to minimize the total energy of this adlayer-substrate system. The adlayer lattice vectors are related to the substrate lattice, generally, via the transformation matrix:

$$\begin{bmatrix} b_1^A \\ b_2^A \end{bmatrix} = \mathbf{M} \begin{bmatrix} b_1^S \\ b_2^S \end{bmatrix} = \begin{bmatrix} \frac{b_1^A \sin(\alpha - \theta)}{b_1^S \sin(\alpha)} & \frac{b_1^A \sin(\theta)}{b_2^S \sin(\alpha)} \\ \frac{b_2^A \sin(\alpha - \theta - \beta)}{b_1^S \sin(\alpha)} & \frac{b_2^A \sin(\theta + \beta)}{b_2^S \sin(\alpha)} \end{bmatrix} \begin{bmatrix} b_1^S \\ b_2^S \end{bmatrix}, \quad (2.5)$$

where real lattice vectors of the adlayer are expressed in b_1^A , b_2^A and b_1^S , b_2^S for the substrate, and α ,

 β and θ are defined in **Figure 2.3a**.



Figure 2.3. Schematic modes of epitaxy and quasiepitaxial overlayer alignments. (a) Schematic of molecular overlayer alignment showing real lattice vectors of the adlayer (b_1^A, b_2^A) and substrate (b_1^S, b_2^S) . Schematic modes of overlayer alignments showing (b) commensurate growth (epitaxy), (c) incommensurate growth (quasiepitaxy) and (d) point-on-line coincidence (quasiepitaxy).

For a two-layer organic stacking system, the equilibrium spatial configuration is described by the van de Waal potential energy and electrostatic interaction summed through every atomatom combination in respective layers. The sum of the van de Waal potential is expressed as:

$$\Theta = \frac{1}{n_a} \sum_{i}^{n_a} \sum_{j}^{n_s} A_{ij} \left(\left(\frac{B_{ij}}{r_{ij}} \right)^{12} - \left(\frac{B_{ij}}{r_{ij}} \right)^6 \right),$$
(2.6)

where A_{ij} is the potential depth, and B_{ij} is the atomic interaction distance, *r* is the separation distance between atom *i* and *j* and Θ is the ensemble surface energy density ⁷⁰. To accurately model and predict the in-plane registry, lattice parameters of the adlayer on a substrate needs to be experimentally measured. Before modeling the in-plane registry, the equilibrium separation distance needs to be calculated. To ensure that the global minimum is obtained, the full system energy is then calculated in the following procedure: 1) Fix the adlayer at certain rotation angle, defined as the angle between one of the two real lattice vectors of the adlayer (b_1^A) and substrate (b_1^S) (**Figure 2.3**). 2) Locate the energetic minimum as a function of adlayer-substrate distance, 3) Translate the adlayer across the substrate unit cell to find the energetic minimum, and 4) repeat steps 1-3 for each rotation angle. Thus, a plot of the minimum energy at every rotation angle can identify/predict the overall equilibrium adlayer-substrate registry.

To reduce the complexity of the calculation, a simplified model is also applied using a simple periodic potential (V):¹⁴¹

$$V = V_0 \cos(2\pi x / a) \tag{2.7}$$

where V_0 is the interatomic potential, x is the position, a is the lattice parameter. The dimensionless geometric potential (V/V_0) is used to describe the relationship between the adlayer and the substrate which is defined as:
$$\frac{V}{V_0} = \frac{1}{N_N N_M} \left(2N_N N_M - \frac{\sin(\pi N_M M_{11})\sin(\pi N_N M_{21})}{\sin(\pi M_{11})\sin(\pi M_{21})} - \frac{\sin(\pi N_M M_{12})\sin(\pi N_N M_{22})}{\sin(\pi M_{12})\sin(\pi M_{22})} \right) (2.8)$$

where M_{ij} are the matrix elements of M in Equation 2.4, and $N_M x N_N$ are the total number of unit cells in the overlayer with N_M and N_N corresponding to multiples of b_1^A, b_2^A respectively. The V/V_0 ratio can have certain values depending on the adlayer-substrate alignment: 1 for incommensurate structures, 0 for commensurate structures, and values between 0 and 1 for coincident registry (Figure 2.3b-d). This geometric model has successfully predicted registry for a number of overlayer-substrate systems.^{70, 141} An example is shown in Figure 2.4. This method is useful for doing quick analysis; however, it oversimplifies the interatomic potentials and ignores the difference in molecular constituents since it gives the same prediction for different materials with the same lattice constant.



Figure 2.4. Example of V/V_{θ} analysis for zinc phthalocyanine (ZnPc) on deactivated Si(111)-B surface. The geometry potential model shows the first minima at $\theta = 28\pm0.5^{\circ}$ and gives V/V_{θ} value of ~ 0.7 indicating a QE relationship. The simulated azimuthal rotation angle matches well with experimental value of $\theta = 27\pm2^{\circ}$ shown in the STM topography image. Note that the presence of two-dimensional Moiré pattern highlights the incommensurate nature of the substrate and adlayer common to quasiepitaxial systems. Figure reprinted with permission.⁴⁸

2.3.2 Kinetic Considerations

In the previous section, the adlayer-substrate interaction is only discussed in terms of energetic minimization, but there are also kinetic aspects involved.

Materials deposited onto a substrate experience several diffusion processes. There are two different types of diffusion coefficients: the chemical (or collective) diffusion coefficient (D^c) and self (or tracer) diffusion coefficient (D). Chemical diffusion happens when there is a concentration gradient in the system while self-diffusion happens spontaneously without a gradient and can take place under equilibrium conditions¹⁴². Thus, in a very low molecular density case, $D^c=D$. D is defined with the Arrhenius equation below:

$$D = D_0 \exp(\frac{-E_m}{k_B T}), \qquad (2.9)$$

where D_0 is a pre-exponential factor, E_m is the diffusion barrier. Typical values for E_m are in the range of 1-50meV. Classical diffusion defines the mean square displacement from the starting position as being proportional to time as:

$$\left\langle \left(r(t)\right) - \left(r(0)\right)^{2} \right\rangle = 2\nu Dt, t \to \infty,$$
 (2.10)

Where the angular brackets denote an ensemble average over the equilibrium state in the system. For the 2D surface diffusion case, v = 2. (v = 1 for 1D diffusion, v = 3 for 3D diffusion). This equation is used for simulating surface diffusivity discussed in **Section 9.1**.

The change in the free energy ΔG during nucleus formation is described as ¹⁴³

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_{\nu} + 4\pi r^2 \gamma , \qquad (2.11)$$



Figure 2.5. The plot of free energy change ΔG as a function of *r*. ΔG (red line) is balanced by the volume free energy change (green line) and interfacial energy change (blue line) due to formation of solid phase.

where ΔG_{ν} is the change in the chemical free energy per unit volume for condensation (gas to solid), *r* is the radius of the nucleus and γ is the interfacial energy per unit area. The relationship between ΔG_{ν} and r is plotted in **Figure 2.5**. The equilibrium radius of the nucleus or critical radius is described as $r^* = -2\gamma/\Delta G_{\nu}$. At critical radius, the critical free energy change is $\Delta G^* = (16/3) \pi \gamma^3 / (\Delta G_{\nu})^2$, which is the barrier to nucleation. This critical radius represents the stability point where the cluster becomes stable by adding more molecules. For a 2D cluster, **Equation 2.11** can be written as

$$\Delta G = -\frac{1}{a^2} \pi r^2 \Delta G_{\nu} + 2\pi r \gamma', \qquad (2.12)$$

where *a* is the lattice parameter, $\gamma' = 2\gamma_{vf} + \gamma_{fs} - \gamma_{sv}$ and $\Delta G_v' = k_B T \log((p_v - p_v^{sat}) / p_v^{sat})$. p_v^{sat} is the vapor pressure at equilibrium related to growth temperature and p_v is the actual vapor pressure during deposition as function of deposition rate. Thus, the 2D nucleation rate r_n can be expressed as ¹⁴⁴

$$r_{n} = \frac{D}{a^{2}} \sqrt{\log(1 + (p_{v} - p_{v}^{sat}) / p_{v}^{sat})} \exp(-\frac{E_{m}}{k_{B}T} - \frac{-\pi(\gamma / k_{B}T)^{2}}{\log(1 + (p_{v} - p_{v}^{sat}) / p_{v}^{sat})}), (2.13)$$

This equation can give insight into when nucleus formation is favorable. When 2D nucleation rate is small enough (close to zero), new nucleus will stop to form, and the existing nuclei will grow larger from nuclei and step edges.

2.4 Key Issues with Inorganic Halide Perovskite Growth

The epitaxial growth of inorganic halide perovskites is based on lattice matching, thus finding the ideal substrates that provide the minimal lattice mismatch is a key step. Also, phase study (phase control, phase stability, etc.) is crucial to perovskites epitaxy. The stoichiometry determined by the precursor ratio during reactive vapor growth can have an impact on the achieved phase, which emphasizes the importance of precise growth rate control. Furthermore, for quantum well (QW) applications, the growth of smooth crystalline perovskite layers is necessary. An ultralow deposition rate (~0.01nm/s) can help the precursors fully react at the substrate to better achieve smoother films.

2.5 Key Issues with Organic Thin Film Growth

Organic quasiepitaxy is entirely distinct from traditional epitaxy in terms of the size, crystal structure and bonding interactions.¹⁴⁵ First, organic molecules are usually large and have more degrees of freedom (e.g. molecular rotation). Without typical adlayer-substrate crystallographic relationships, the organic thin film nucleation is largely influenced by the energetic interaction between the molecules and the substrate surface. Also, unit cell sizes for organic materials are also typically much larger than for inorganic crystals. Finally, the bonding between organic molecules and substrates can consistent of a range of interactions (covalent, ionic, van der Waals), but are

predominately van der Waals in nature. Therefore, compared to inorganic materials, kinetic process for organic materials often occur at much lower temperatures.

Chapter 3 – Experimental Techniques

In this chapter, various experimental techniques for thin film preparation and characterization used throughout this thesis are described in detail. Characterization techniques are discussed including diffraction methods, morphology, and optical measurement.

3.1 Physical Vapor Deposition (PVD)

3.1.1 Thermal Evaporation

Thermal evaporation is a common method of physical vapor deposition (PVD). A simplified evaporator diagram is shown in **Figure 3.1**. It is one of the simplest forms of PVD and typically uses a resistive heat source to evaporate a solid material in a vacuum environment to form a thin film. The materials are heated in baffled tungsten boats producing a high vapor pressure stream. The evaporated material traverses the vacuum chamber and coats the substrate. The required deposition pressure to assure ballistic (line of sight) deposition is usually in the range of 10^{-6} torr, which is achieved by a two-stage pumping process: a rough mechanical pump to 10^{-2} torr and a cryopump further to 10^{-6} torr.

The deposition rate (usually 0.01 - 1 nm/s) is monitored using quartz crystal monitors (QCM) above each source. Quartz crystals resonate at specific frequencies that depend on the total volume of thin film deposited on them. QCMs are calibrated to relate the thickness arriving on the QCM to the thickness on the substrate by the ratio called the tooling factor (TF). The equation below is used to calculate the calibrated tooling factor (*TF_i*):

$$\frac{t_i}{TF_i} = \frac{t_f}{TF_f},\tag{3.1}$$



Figure 3.1. Evaporator diagrams. (a) A simplified diagram of thermal evaporation chamber with one source (left). The labelled parts are: (1) source boat, (2) copper contacts, (3) source shutter, (4) quartz crystal monitor (QCM), (5) substrate shutters, (6) substrate, and (7) rotation stage. During deposition, source and substrate shutters are open (right). (b) Schematic showing the positioning of the six evaporation sources and three QCM sensors located at the bottom inside the custom Angstrom Engineering EvoVac deposition system. The substrate stage is above these sources. (E-beam and sputtering components are also equipped in the system.)

where t_i is the initial measured thickness based on the initial guess of the tooling factor TF_i and t_f is the thickness measured on a reference substrate (usually undoped single-crystalline Si) using

ellipsometry or atomic force microscopy (AFM). Each QCM can be used until the lifetime drops below 80%-90% range.

Co-deposition of two or three materials can be achieved by assigning each to a different QCM. Every source is tooled separately on a Si wafer using ellipsometry prior to the co-deposition. Note that the real thickness of the film grown on Si can be different from growth on other substrates (particularly for alkali halide crystals, for example) due to different wetting conditions. To achieve the desired stoichiometry (molar ratio), the rate (volumetric) ratio for each precursor needs to be calculated from the molar mass and density. For reactive co-deposition, the thickness of the reacted film needs to be measured by cross-sectional SEM as ellipsometry is not feasible on the optically transparent crystalline substrates utilized in this work.

Deposition control is accomplished using the Inficon SQS-242 deposition software (**Figure 3.2**). The deposition process starts with preconditioning (Ramp 1/Soak 1/Ramp 2/Soak) followed by a shutter delay for the growth rate to stabilize at the set rate. Then the substrate shutter is opened, and the substrate stage rotation is enabled to achieve uniform growth across the substrate. The software will control the output power to the source using closed loop PID control with feedback from the assigned crystal sensor.



Figure 3.2. Inficon SQS-242 deposition software interface during a two-source co-deposition (shown in manual mode).

3.1.2 Electron-beam (E-beam) Evaporation

Electron-beam (E-beam) is another PVD technique used in this work. In E-beam deposition, the target materials are bombarded with electron beam created by a charged tungsten filament. The electrons are accelerated by the high voltage that is applied between the hearth and the filament. The focusing and the alignment of the electron beam is controlled by a strong magnetic field. The schematic of the E-beam deposition process is shown in **Figure 3.3.** The chamber pressure requirement is 10⁻⁵ torr and 10⁻³ for some modern systems. Compared with thermal evaporation, E-beam has many advantages. First, the E-beam material utilization efficiency is high which reduces cost. For example, gold is deposited using E-beam for fabricating cavities for cavity-melt

deposition (CMD) discussed in **Section 4.1.1.1**. Second, much higher heating temperature can be reached so that higher deposition rates (up to 1-2nm/s) can be achieved. Third, because the electron beam is only confined at the source material, the contamination from nearby components are largely reduced leading to higher purity of the deposited materials.



Figure 3.3. Schematic of the E-beam deposition process.

3.2 In situ Diffraction Technique: Reflection High-energy Electron Diffraction (RHEED)

3.2.1 RHEED Introduction

Reflection high-energy electron diffraction (RHEED) is a powerful technique to study the evolution of surface structures. It has been successfully used in monitoring the growth of semiconductor thin films, ¹⁴⁶ metals, ¹⁴⁷⁻¹⁴⁸ and complex oxides.¹⁴⁹⁻¹⁵⁰ A schematic of the RHEED technique is shown in **Figure 3.4**. A high-energy electron beam, typically 10–30 keV, is directed at the film surface at grazing incident angle (1~3°), and the resulting diffraction pattern is captured by a CCD camera. Because of the small incident angles, the electron penetration depth is at the monolayer scale (0.5-1.0nm), making it a particularly surface sensitive technique.

With such low penetration depth, the electron wave density in the normal direction is not sampled for perfectly smooth films or crystals. In this case, the 3D reciprocal lattice devolves into

a 2D array of infinitely long lattice rods. The intercept of the Ewald sphere with these rods corresponds to an allowed diffraction condition and streaked patterns are formed. However, for rough crystalline samples, the normal-direction electron density is sampled because of multiple small features on the sample surface. Reciprocal lattice points emerge and lead to spotty features of the RHEED patterns. Typical diffraction patterns are shown in **Figure 3.5** corresponding to different surface crystallinity. Because high energy electrons are used in RHEED, the diameter of the Ewald sphere (k_0) is orders of magnitude larger than most reciprocal lattices (i.e. 20keV electrons, $k_0 = 785$ nm⁻¹), which means we can see the Ewald sphere as a plane cutting the reciprocal lattice.



Figure 3.4. RHEED schematics. (a) Typical RHEED geometry. (b) Photo of the RHEED system installed in an evaporation vacuum chamber (Angstrom Engineering EvoVac Evaporator). (c) Ewald sphere construction with RHEED. The Ewald sphere has a width of Δk_0 due to the variance of the electron beam energy. The lattice rods have a width of Δd due to the structure factor width and crystalline defects. Figure reproduced with permission.¹⁴⁵

Kikuchi patterns in RHEED images can be seen in the case of thick single crystals. The formation of a Kikuchi lines is a two-step scattering process. First, electrons from the incident beam collide elastically (losing a small amount of energy) with the bulk sample and randomize the directions of their wavevectors. Then, if the energy loss is small, the resulting electron distribution can then be rescattered inelastically and isotropically from crystal planes leading to Kikuchi diffraction lines. These Kikuchi lines move in a continuous and coincident manner when the crystal is rotated, which is a feature often used to align the azimuthal direction of the crystal with respect to the incident electron beam.



Figure 3.5. Example RHEED patterns. A smooth crystalline surface generally shows streaked patterns while a rough crystalline surface generally shows spotty patterns. Ring patterns indicate 3D-disorder (or crystalline powder) and a diffuse halo pattern indicates the surface is amorphous. Figure reproduced with permission.¹⁴⁵



Figure 3.6. Growth mode with the RHEED intensity signal vs. time.The typical RHEED oscillation profiles are plotted below each growth mode schematic. Figure reproduced with permission.¹⁵¹

Growth modes can be deduced from RHEED oscillations represented by the intensity of RHEED specular beam versus growth time. **Figure 3.6** shows an illustration of the various growth modes with RHEED oscillations. In the 2D growth mode, the periodic formation and coalescence of 2D nuclei lead to the intensity oscillation (**Figure 3.6c**). Generally, one period of RHEED oscillation corresponds to one molecular layer or atomic layer¹⁵². In reality, the second layer would start to form before the growth of previous layer is fully complete, thus an overall decreasing in oscillation intensity is often observed. 3D growth will show a rapid damping in amplitude (**Figure 3.6a**). For step flow mode, the growth is viewed as steps traveling across the surface. With a relatively stable step density, the intensity will eventually reach a constant (**Figure 3.6e**).

3.2.2 Electron Beam Damage

Materials suffer damage after long exposure to high-energy electrons.¹⁵³ The time-todamage (t_{damage}) of a material is defined as:

$$t_{damage} = C_{dose} A/(qI) \tag{3.2}$$

where C_{dose} is the critical dose in units of C/cm², *A* is the electron beam area, *q* is the charge of the electron, and *I* is the electron beam current. In general, a minimum for the critical dose exists for a certain beam energy (around 0.1-5keV) for many organic molecules. From the equation, a direct way to increase the time before the film is damaged is to decrease the electron beam current. In the following chapters, *in situ* RHEED is demonstrated using ultralow current only in the nA range to capture images via a detector system with low f -number lenses and sensitive detectors, eliminating damage/charging even on organic and insulating layers over the measurement time (over several hours). This enables the monitoring of organic small molecule growth and perovskite growth on insulating halide crystals.⁴⁷

3.3 Ex situ Diffraction Technique

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most important tools for characterizing structures, phases, texture, and other structural parameters such as average grain size, crystallinity, strain, and crystal defects. XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at certain angles from each set of lattice planes within the material.

The typical Bragg-Brentano XRD geometry is shown in **Figure 3.7**. Bragg's law describes the diffraction condition for constructive interference, which is expressed as:

$$2d_{hkl}\sin\theta = n\lambda \tag{3.3}$$

where *d* is the interplanar spacing between parallel planes of atoms in the family (hkl), θ is the angle of the incident beam with respect to these planes, *n* is an integer, λ is the characteristic wavelength of the X-rays. Cu K α ($\lambda = 1.5406$ Å) is frequently used on labscale X-ray instruments



Figure 3.7. XRD geometry. Two beams with identical wavelength and phase approach a crystalline solid and are scattered from separate atomic planes. There is constructive interference (in-phase) from this scattering at the angle define by Bragg's law.

but monochromatic synchrotron sources were also utilized in this work (λ : 0.0619870 nm) at the Argonne National Laboratory Beamline 24-ID-C. The Advanced Photon Source (APS) at Argonne National Laboratory used a hot cathode heated to ~1100°C to produce electrons and then accelerated to relativistic speeds in a linear accelerator. Further acceleration is performed in booster synchrotron which is a racetrack-shaped ring of electromagnets and 7 GeV can be reached within half a second.¹⁵⁴⁻¹⁵⁵

3.3.2 Pole Figure

Pole figure measurements are used to study the orientation distribution of crystallographic lattice planes and texture analysis via stereographic projections. To collect pole figures, the crystal structure of the sample needs to be well known so that the diffraction angle (2θ) corresponding to the *hkl* pole can be set for the scan. The diffracted intensity is collected by varying two geometrical

parameters: the tilt angle from sample surface normal direction (α) and rotation angle around sample surface normal direction (β). The collected data is plotted as a function of α and β . (Figure 3.8)



Figure 3.8. Sphere of fixed-length scattering vector and stereographic projection. The tilt angle from sample surface normal direction is α and the rotation angle around sample surface normal direction is β .

In-plane pole figure measurement is a pole figure measurement performed using the inplane arm. This method has two major advantages over the conventional pole figure measurement. First, diffraction from lattice planes perpendicular to the sample surface can be detected, which allows a complete mapping from $\alpha=0^{\circ}$ to 90° (rather than being limited to about 70°). Second, the sample is maintained horizontal in the case of a horizontal sample goniometer meaning this method



Figure 3.9. Example of pole figures. (a) Example pole figures for a randomly oriented sample, a textured polycrystalline sample that is (111)-fiber oriented and a single crystalline sample with a (111) surface. (b) Measured and simulated KCl (111) pole figure for KCl (100) substrate.

does not require the sample to be tilted, which eliminates the trouble of clipping the sample to the stage to prevent them from falling.

Examples of pole figures are shown in Figure 3.9a. The pole figure for a randomly oriented sample only has a uniform intensity of distribution due to the lack of preferred orientation. A textured polycrystalline sample that is (111)-fiber oriented will show strong distribution for {111} and {220} in a ring shape. The single crystalline sample with a (111) surface orientation shows strong intensity of distribution from $\{111\}$ and $\{220\}$. If the 2θ position for the pole figure scan is set the same as the surface orientation of the crystalline sample, a strong distribution will be located at the center ($\alpha=0^{\circ}$). Typically, distributions at the center or edge ($\alpha=90^{\circ}$) are not ideal for pole figure scans because the symmetry obtained from non-surface orientations are more interesting compared to the known distribution from the surface plane and the signal on the edge is usually not strong. An allowed 2θ position other than the surface orientation with strong peak intensity and clear symmetry is usually chosen for pole figure scan. For example, KCl (111) at $2\theta=24.49^{\circ}$ is chosen for the pole figure scan of KCl (100) substrate. A fourfold symmetry is shown in **Figure 3.9b.** It is also emphasized that pole figure measurements can only be obtained when the crystal structure of the film is well known so that the 2θ position for a pole can be precisely set for the scan.

3.3.3 Rocking Curve

Rocking curves are primarily used to study defects such as dislocation density, mosaic spread, curvature, misorientation, and inhomogeneity. This method is performed by rocking the thin-film sample while the detector is kept a fixed 2θ angle to record diffraction intensities from the preferentially oriented lattice planes. ¹⁵⁷ The degree (or distribution) of preferred orientation is estimated from the full width at half maximum (FWHM) of the rocking curve profile. The FWHM for a single crystalline sample are at 0.001° range, such as 0.003° for Si(220)¹⁵⁸ and 0.0082° for Strontium titanate (STO) (002)¹⁵⁹. Organic crystalline samples such as pentacene(001) show FWHM values between 0.08° to 0.09° for the thin film phase and 0.22°for the bulk phase.¹⁶⁰ An example of a rocking curve scan is shown in **Figure 3.10b**.



Figure 3.10. Rocking curve measurement geometry and an example rocking curve scan of (004) for Si (Ge) on Si. Figure reprinted with permission.¹⁵⁶

3.4 Thin Film Morphology Measurements

3.4.1 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a versatile and powerful microscopy technology for studying surfaces at the nanoscale. It has the advantage of imaging almost any type of surface, including polymers, ceramics, composites, glass, and biological samples and overcomes the drawback of scanning tunneling microscope (STM) imaging which is limited to conducting or semiconducting surfaces.

The typical AFM set-up is shown in Figure 3.11. AFM uses a low spring constant cantilever to image the sample surface. At one end of the cantilever, a sharp tip is fabricated using semiconductor processing techniques. The cantilever moves backward and forward above and cross the sample surface. The force exerted on the tip varies with the difference in the surface height and thus leads to the bending of the cantilever. A laser beam gets constantly reflected from the top of the cantilever towards a position-sensitive photodetector. The deflection is tracked and used to calculate the actual position of the cantilever. In this way, AFM records a threedimensional image of the surface topography of the sample under a constant applied force (nN range) without causing any damage to the sample surface. Most commercial AFM instruments can reach a vertical resolution as low as 0.01 nm for more rigid cantilevers and the lateral resolution is related to the tip condition, but it is usually lower.¹⁶¹ Common scan modes are contact mode, non-contact mode and tapping mode. In contact mode, contamination to the tip often happens and leads to distortion to the image. Non-contact mode generally has lower resolution. Tapping mode is most widely used to achieve higher resolution without causing destructive damage to the sample surface.



Figure 3.11. Typical set-up of AFM. The laser beam is reflected off the back of the tip onto a quadrant photodiode. The deflection of the cantilever is measured as it tracks the surface to obtain the sample topography.

3.4.2 Scanning Electron Microscope (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces topography images of a sample by scanning the surface with a focused beam of electrons (**Figure 3.12**). The resolution of the SEM is can go to 1nm. Both backscattered electrons (BSE) and secondary electrons (SE) can be used for SEM imaging. In the most common SE imaging mode, SE emitted by atoms excited by the electron beam are detected using an Everhart-Thornley detector. The number of SE detected depends on the topography of the sample. When the incident electron enters the sample, SE are produced from the emission of the valence electrons of the constituent atoms in the specimen. Due to low energy (<50 eV) of the SE, those generated deeper are absorbed while those on the surface are emitted, thus SE are very surface sensitive. The incident angle of the electron beam will affect the amount of emission and therefore creating brightness differences in an SEM image. Nonconductive specimens collect charge when scanned by the electron beam, thus they are usually coated with gold, gold/palladium alloy, etc. via sputtering.



Figure 3.12. Basic construction of a SEM system.

3.5 Thin Film Optical Measurements

3.5.1 Ultraviolet-visible Spectroscopy (UV-Vis)

Ultraviolet-visible (UV-Vis) spectroscopy can be used to measure the transmission in the UV-visible-infrared region of the electromagnetic spectrum of thin films coated on substrates or solutions contained in cuvettes. The schematic of a dual-beam spectrometer is shown in **Figure 3.13**. A beam of light from a visible and/or UV light source (wavelength from 300nm to 1900nm) is separated into its component wavelengths by a diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. The sample beam passes through the thin film sample or a cuvette containing a solution of the compound being studied in a transparent solvent. The reference beam passes through nothing for absolute thin film measurements or an identical cuvette containing only the solvent. Note that for thin film transmission measurements, reference samples (e.g., clear glass slides) should not be utilized since the reflection from the glass/air interface cannot be properly separated by simple

subtraction. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam is defined as I_0 and the intensity of the sample beam is defined as *I*. Absorption may be presented as transmittance ($T = I/I_0$) or absorbance ($A = \log I_0/I$).



Figure 3.13. Schematic of a UV-Vis spectrometer configured to measure transmission for a thin film sample.

3.5.2 Variable Angle Spectroscopic Ellipsometry (VASE)

Variable angle spectroscopic ellipsometry (VASE) is a technique used to characterize thin film thicknesses and optical constants. It measures the change in polarization of reflected light. A monochromatic beam of light is polarized and sent through a fiber optic directed at a thin film sample on a reflective surface. The light reflected off the sample is collected at a detector, and, based on the phase difference and light attenuation of the reflected light, the ellipsometric angles Ψ (amplitude component) and Δ (phase component) can be calculated:¹⁶²

$$\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$$
(3.4)

where ρ is the complex reflectance, r_p and r_s are the reflectivity of p- and s-polarized light, respectively, Ψ and Δ are a polar description of the ratio of reflectance for p- and s-polarized light. A Cauchy model is used to fit the *d* (film thickness), optical constants *n* and *k* (refractive index and extinction coefficient) represented as:¹⁶²

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$$
(3.5)

$$k(\lambda) = A_k e^{B_k(\frac{hc}{\lambda}) - C_k}$$
(3.6)

To reduce the model to three fit parameters, only the spectroscopic region with no absorption is used (k=0). Thus, from the measured Ψ and Δ for a wavelength range, n and d can be fitted. The measured thickness can be used to calculate the tooling factor (discussed in **Section 3.1.1**) of thermally evaporated material such as organic semiconductors, charge transfer (CT) compounds, alkali metal halides, halide perovskites, etc.

Chapter 4 – Organic Homoepitaxial and Hetero-quasiepitaxial Growth

This chapter focuses on understanding the homoepitaxial and hetero-quasiepitaxial (QE) growth of classical organic semiconductors. For homoepitaxial growth, two methods for fabricating single crystalline substrates were developed and the homoepitaxy of 9,10-diphenylanthracene (DPA) was studied. This is the first demonstration of studying homoepitaxial growth of organic crystals using RHEED. For hetero-QE growth, various organic-organic growth pairs with low and high energy mismatch of lowest energy surface (LES) were explored to understand the design rules for ordered organic crystalline structures.

4.1 Organic Homoepitaxial Growth

4.1.1 Organic Single Crystal Substrate Growth

4.1.1.1 Cavity-melt Deposition (CMD) Method

Cavity-melt deposition (CMD) was utilized to fabricate crystalline substrates of controlled thickness over several cm² substrates which can be used for subsequent homo-epitaxial or hetero-QE vapor growth of organic films. Schematics of the CMD process are shown in **Figure 4.1**. Bare glass substrates were cleaned prior to deposition of four metal spaces via e-beam deposition. The cleaning process includes sonicating bath in soap, deionized water, and acetone (~3 min for each step) and then rinsing in boiling isopropanol (~5 min). Dried substrates were then loaded into the deposition chamber with a patterned mask shaping the area of the metal spacers. A thin Ti layer (5nm) and then a thick Au (350nm, can be increased to create thicker cavities) layer were deposited on each substrate. The thin Ti layer bonds strongly with the glass substrate. When the substrates with Ti/Au metal spacers were then assembled (by pressing) together to form a cavity, top Au layer from both pieces make contact and a strong Au-Au bond is formed. Cavities with fixed gap (~500-

1000nm) were transferred into quartz boats loaded with organic materials and then confined by two tight-fitting quartz sleeves so that the cavities can be kept in an organic vapor environment during crystal growth. The sleeves were then placed into a long quartz tube that was sequentially evacuated and filled with N₂.



Figure 4.1. CMD process for fabricating single crystalline organic substrates. (a-d) Schematics for CMD process, (e) Photo of the assembled cavities, (f) Photo of the assembled cavities placed in molten organic material in a 3-zone furnace.

Both the melting and cooling process were done in a programmable PID controlled 3-zone tube furnace. Temperature was first raised to 10-15°C below the melting temperature of the organic material. The melting process can initiate at several degrees below the melting temperature. Maintaining this temperature for 5-10 mins can fully liquify the material while avoiding overheating. Liquified material is drawn into the cavity via capillary forces. This temperature was maintained for ~5 min until the powdered organic material fully melted. The boats were then slowly cooled at a rate of 1°C/h. When the temperature reached 2/3 of the melting point, a faster

cooling process to room temperature started at a rate of 10°C/h. Cavities were then separated by razor blades to expose the organic crystalline film as organic substrates for vapor growth.

Using this method, various organic crystalline substrates were successfully prepared. XRD patterns and cross polarized optical images of the fabricated organic substrates are shown in **Figure 4.2**. The cross polarized optical imaging is a direct way to visualize the grains and grain boundaries. Anthracene (001), α -N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (α -NPD) (101), perylene (100), triphenylene (200) and DPA(020) organic substrates are successfully fabricated showing single crystalline growth with only one preferred orientation. The fluoranthene substrate is polycrystalline. The melting points and CMD results of the materials explored are summarized in **Table 4.1**. Various parameters (pressure, temperature, cooling rate, purity of the material, etc.) can be optimized in order to prepare true single crystalline organic substrates.



Figure 4.2. XRD patterns and cross polarized optical images of the organic crystalline substrates prepared using CMD. The black square marked the Au (111) peak (from the metal spacers) at 2θ =37.18°.

Material	Melting Point (°C)	CMD Results
Anthracene	215	Crystalline
Rubrene	315	Amorphous
DPA	248	Crystalline
Perylene	276	Crystalline
α-NPD	279	Crystalline
β-NPD	150	Amorphous
Pyrene	145	Crystalline
Triphenylene	198	Crystalline
Fluoranthene	111	Crystalline

Table 4.1. List of organic materials for CMD.

4.1.1.2 Vapor Growth Method

The drawback of using CMD to fabricate organic single crystalline substrates for organic homoepitaxy or hetero-quasiepitaxy lies in the difficulties of performing *in situ* and real-time RHEED characterization because the glass substrates used for cavities create heavy charging when electron beam is directed onto the surface. Furthermore, this method is unable to provide thickness control < 500nm and is unable to support growth of more than one layer. To overcome the charging problem, a vapor growth method was also developed to create small bulk single-crystals as substrates that could be mounted on conductive surfaces. The vapor growth of DPA single crystals (lateral length up to 1.5 cm) was demonstrated as an example. DPA is a promising candidate for device applications as high mobilities have been reported up to 34 cm² V⁻¹ s⁻¹.¹⁶³

The source boat containing DPA powder was placed in a long quartz sleeve at the high temperature zone. A short one-side opened quartz sleeve was placed on the low temperature zone for crystal collection. This separated short sleeve makes it convenient to remove the crystals. Another one-side opened quartz sleeve was placed at the end of high temperature zone to confine



b



Figure 4.3. Vapor growth method for fabricating single crystalline organic substrates. (a) Schematics for vapor growth of DPA crystals. The open ends of the inner sleeves are indicated by dashed lines. (b) Photo of the vapor growth in a 3-zone furnace.

the organic vapor during heating. All the inner sleeves were placed in a long quartz tube that can be evacuated and filled with N₂. This long quartz tube was then enclosed in a programmable PID controlled 3-zone tube furnace. The high temperature zone is set to $10-15^{\circ}$ C below the melting point of the organic material. The melting point of DPA is 245-248°C, so in this case, the high temperature zone was set to ~223°C, which fully melts the materials if maintained for 5-10min. The low temperature zone is set to $10-15^{\circ}$ C below the high temperature zone. When the DPA fully melted in the boat, the inner sleeves were filled with DPA vapor and crystallization initiates on the inner walls of the sleeve in the low temperature zone. The temperature was maintained until enough crystals were formed or the boat containing the molten DPA became empty.

4.1.2 Homoepitaxial Growth of 9,10-Diphenylanthracene (DPA)

Homoepitaxial growth of DPA was performed in our custom thermal evaporation chamber (Angstrom Engineering) equipped with reflection high energy electron diffraction (RHEED) system (STAIB Instruments) shown in **Figure 4.4a**. The DPA single crystal substrate was prepared using the vapor growth method discussed in **Section 4.1.1.2**. Due to the fragility of the crystals, they were carefully attached to the growth stage using a tiny drop of ionic liquid (1-ethyl-3-methylimidazolium dicyanamide, Sigma Aldrich) instead of conductive carbon tape used for thicker metal halide single crystal substrates used in **Chapter 7 and 8**. The ionic liquid is important to reduce charging and to reduce stress on the crystal, and it has a low vapor pressure to prevent outgassing.



Figure 4.4. Schematic of DPA homoepitaxial growth.

(a) Schematics for homoepitaxial growth of DPA crystals. (b) Crystal structure of DPA (monoclinic, a = 0.94 nm, b = 2.03 nm, c = 1.00 nm, $\alpha = 90.00^{\circ}$, $\beta = 113.00^{\circ}$, $\gamma = 90.00^{\circ}$. ¹⁶⁴ (c) Cross polarized optical images for single crystal DPA substrate (area: ~15mm²).

Cross polarized optical images were taken using a simple rotational polarize and analyzer kit (360° rotation) prior to loading in the evaporator. Out-of-plane XRD and rocking curve measurements were performed using a Rigaku SmartLab XRD instrument with a Cu K α source at 40 kV and 44 mA and using a Ni filter. Atomic force microscopy (AFM) was performed in contact mode for *ex situ* film morphology characterization. A silicon tip coated in Ti/Ir was used for the AFM measurements (Asylum Research).



Figure 4.5. Structural characterization of the DPA single crystal substrate. (a) XRD, (b) rocking curve analysis and (c) Rotation dependent RHEED of the of DPA single crystal substrate prepared using vapor growth method.

XRD characterization is performed on the DPA substrates prepared using vapor growth to understand the growth orientation shown in **Figure 4.5a**. Only (020) peaks, corresponding to its LES, are seen from the scan indicating the substrate is single crystalline which is consistent with the cross polarized optical images showing single grain with no grain boundaries, twinning, or grain rotations (**Figure 4.4c**). Rocking curve scans for DPA (020) is shown in **Figure 4.5b**. The FWHM is 0.15° which is larger than traditional semiconductors such as 0.003° for Si(220). ¹⁵⁸ The broadening of the FWHM from the mosaics (misorientation of crystallites) should not exist due to the single-crystalline nature of the sample. One possible explanation to this broadening is the limited thickness/volume of the sample. Rotation dependent RHEED patterns and the emergence of clear Kikuchi patterns that vary along different azimuthal angles demonstrate the single crystalline nature of the DPA substrate crystal (**Figure 4.5c**). Kikuchi patterns in RHEED are usually observed from bulk single crystalline samples with minimal defects and grains. This finding is the second demonstration of Kikuchi lines for organic crystals.⁵⁸ Because charging was



Figure 4.6. RHEED for DPA homoepitaxy of 20nm at 75°C. (a) RHEED pattern transition. (b) Specular intensity change vs growth time.

still an issue with these small crystals, we were unable to obtain real-time RHEED oscillation data despite great success with alkali metal halide crystal homoepitaxy described in **Chapter 6**. Nonetheless, growth modes were still observable via ex-situ AFM. The AFM line scan of the bare DPA substrate exhibits steps with ~ 2nm height equal to the thickness of two monolayers of DPA (020) (**Figure 4.7a**). The growth mode diagrams for DPA homoepitaxy was mapped as a function of growth rate and temperature. At moderate temperatures (room temperature) and 0.05nm/s



Figure 4.7. AFM images of DPA homoepitaxy. (a) Bare DPA substrate and homoepitaxial growth (20nm) performed at (b) room temperature, 0.05nm/s, (c) low temperature (-120°C), 0.05nm/s and (d) room temperature, 1nm/s.

growth rate, AFM images after growth reveal parallel step features indicative of a step-flow growth mode. The step width and density after the growth remains similar to the original substrate. Line scans shows a uniform step height of ~1nm across the surface which corresponds to one monolayer of DPA (020) (Figure 4.7b). These trends are reminiscent of traditional semiconductor growth where step flow growth occurs at low flux and high temperature growth conditions but is in contrast to the low temperature growth required for improved quasiepitaxial growth of organic semiconductors like 3,4,9,10-perylenetetracarboxylic dianhydride(PTCDA).¹⁶⁵ For vicinal surfaces of traditional semiconductors such as Si (001), GaAs (001), step flow growth is observed at sufficiently high temperatures.¹³⁴⁻¹³⁶ Alkali halide homoepitaxy shows step flow growth at high temperatures as well (discussed in Chapter 7). The fact that step flow growth is seen for DPA at room temperature suggests a sufficient surface mobility (and low enough flux) for the molecule to move to the step edge before nucleating within the terrace. At high flux conditions (high rate growth of 1nm/s at room temperature), this step flow growth develops into Frank-Van der Merwe layer-by-layer (2D) growth, with nucleation occurring within terraces (Figure 4.7d). At lower temperature (-120°C) and 0.05nm/s growth rate, 3D islands start to form leading to non-uniform coverage and larger step height. This indicates a transition to Stranski-Krastanov layer-plus-island growth (Figure 4.7c) which is caused by decreased surface diffusivity of the DPA molecule at low temperature.

4.2 Ordered Organic-organic Hetero-quasiepitaxial (QE) Growth

For alternating hetero-QE growth, we utilize the same deposition and *in situ* RHEED set up shown in **Figure 4.1a.** We focus on looking at various organic molecules (listed in **Table 4.2**) paired with NTCDA to study the design rules for ordered alternating growth of organic crystalline layers. NTCDA and the paired material is deposited alternating onto a single-crystal KBr (100) substrate freshly cleaved prior to the growth. An alternating growth structure containing two growth cycles is used in this study shown in **Figure 4.8i**. Out-of-plane XRD and AFM characterization were utilized to measure the stacking orientation and growth features respectively.

Table 4.2. Calculated surface energies (SE) of lowest energy surface (LES) for a range of organic crystals including NTCDA and materials for paired alternating growth.

Isolated surface energies of different planes were calculated with Materials Studio v7.0 (Morphology module) using the equilibrium method with the universal force field. The materials are listed in the order of increasing SE difference with NTCDA (100). The values for acenes agree with reported values. ¹⁶⁶⁻¹⁶⁷

Material	LES	SE (J m ⁻²)	SE Difference with NTCDA (100) (%)
NTCDA	(100)	0.085	N/A
DBP	(010)	0.076	9.3
C_{60}	(111)	0.101	20.7
Tetracene	(001)	0.101	20.7
Pentacene	(001)	0.104	23.1
Coronene	(101)	0.064	24.0
CuPc	(200)	0.058	30.6
CuPc	(002)*	0.069	17.4
β-perylene	(100)	0.133	58.7

*Second lowest energy surface.

A range of surface energy systems with different energy mismatch between their LES are studied to understand the design rules for ordered organic-organic crystalline hetero-QE growth and the role of this mismatch plays in growth modes. Specific combinations for energy- 1) matched, 2) mismatched-low, and 3) mismatched-high are explored. Pair growth of NTCDA with the chosen small molecules are explored in the order of increasing energy difference of their LES with NTCDA(100): 5,10,15,20-tetraphenylbisbenz[5,6]indeno[1,2,3-cd:1',2',3'-lm]perylene (DBP) (energy-matched), C₆₀, tetracene, pentacene (energy mismatched-low), coronene, copper phthalocyanine (CuPc) and perylene (energy mismatched-high). XRD is performed after one growth circle to determine the crystalline orientation of the film. Despite the small energy mismatch between LES of DBP and NTCDA, the L3 for DBP growth pair is polycrystalline with ring-like RHEED pattern and L4 is completely amorphous with diffuse halo pattern (**Figure 4.8b**). This suggests DBP cannot support multilayer ordering pairing with NTCDA.

The energy mismatched-low set shows ordered crystalline growth for at least two pairs. After the second growth circle, the L4 for C_{60} , tetracene, pentacene all show clear rotational dependent RHEED patterns indicating good in-plane order. AFM shows that the L2 for C_{60} set is smooth and the grain size as well as orientation is maintained after L4 (**Figure 4.10a, g**). RHEED patterns suggest smooth crystalline growth for both L2 and L4 of C_{60} set. Both the L2 and L4 for



Figure 4.8. In situ RHEED patterns of the alternating growth pairs. (a) the bare KBr substrate, (b-h) alternating growth of NTCDA with DBP, C_{60} , tetracene, pentacene, coronene, CuPc and perylene, (i) schematic of bottom-up alternating growth. (L is short for layer). Crystal structure of the KBr substrate and molecular structures of the growth materials are shown (C: gray; H: white; O: red; N: blue, K: purple; Br: maroon and Cu: pink).


Figure 4.9. XRD patterns of the alternating growth pairs. X-ray diffraction characterization of the bare KBr substrate(K), NTCDA growth on KBr(K/N) and growth of DBP, C_{60} , tetracene, pentacene, coronene, CuPc and perylene on NTCDA. All the materials show crystalline growth from the LESs on NTCDA (100) surface (except for DBP that grows amorphously). The pentacene (001) peak is not shown in the XRD scans, but this LES growth direction is confirmed by RHEED.

tetracene set show needle-like growth from the AFM, where the preferred alignment of grains is

more obvious for L4(Figure 4.10b, h). For pentacene, AFM shows that L4 has two preferred



Figure 4.10. AFM images of crystalline alternating growth pairs. $20 \text{nm of } (a,g) C_{60,}$ (b,h) tetracene (c,i) pentacene (d,j) coronene (e, k) CuPc (f, l) perylene growth on NTCDA after the first (L1-L2) and second (L3-L4) growth circle.

orientation perpendicular to each other (**Figure 4.10i**). Each of the tetracene and pentacene layers show clear spotty RHEED patterns indicating the rough crystalline surface.

The energy mismatched (high) set show little ordering beyond one pair suggested by the RHEED for L4. For coronene set, L2 shows needle-like growth but the orientation is random (**Figure 4.10d**), which agrees with the ring patterns observed over the streaks in RHEED (**Figure 4.8f**). Non-needle-like grains are seen for L4 (**Figure 4.10j**) and crystalline features from RHEED faded into a diffusive halo pattern (**Figure 4.8f**). AFM shows one major grain alignment for L2 of CuPc set and RHEED shows spotty patterns indicating a rough crystalline surface (**Figure 4.10e**). However, the L4 of CuPc shows random grain orientation (**Figure 4.10k**) and shows a corresponding diffuse ring feature from RHEED (**Figure 4.8g**). For the perylene set, the L4 AFM features look similar to pentacene (**Figure 4.10l**) but the RHEED pattern shows rings, indicating a polycrystalline structure is developed (**Figure 4.8f**).

In sum, these results indicate that multilayer order is indeed likely supported by surface energy matching, requiring a matching in the range of 10-20%. This is likely a good starting point for designing organic-organic multilayer structures moving forward and strengthens the hypothesis that surface energy matching is a key criteria on ordered multilayer growth (in contrast to lattice matching in traditional epitaxy).⁷⁰

4.3 Conclusion

In this chapter, methods for fabricating organic single crystalline substrates were developed including CMD and vapor growth. The CMD has the advantage of area and thickness control but brings difficulties for RHEED due to the charging issues. The vapor growth shows the capability of fabricating free standing organic single crystalline substrates up to ~1cm in length which is used for demonstrating homoepitaxy of DPA, which is the first application of RHEED to organic homoepitaxial growth by using ultra low currents and the second demonstration of Kikuchi patterns from organic crystals. Moreover, a series of organic growth pairs with low and high energy

mismatch of LES were explored to elucidate design rules for ordered alternating crystalline growth and suggests that the ideal range for energy mismatch between LES is 10-20%.

Chapter 5 – Uncovering a New Growth Mode: Edge-Driven Organic-on-Organic Quasiepitaxy

In this chapter, we demonstrate the ordered alternating hetero-quasiepitaxial growth of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and diindenoperylene (DIP) crystalline films on single-crystal substrates from the bottom up exploiting a new edge-interaction driven mechanism. Each layer is shown to grow with a well-defined quasiepitaxial registry regardless of the incommensurate unit cells, where the multilayer pair growth is maintained for multiple cycles. While there is a close surface energy matching between the lowest energy surface (LES) of DIP and NTCDA, it is a non-lowest energy plane of DIP that is formed in the multilayer structure. While surface energy matching of the lowest energy surface is likely to play an important role in many other organic-organic systems, the ability to grow this multilayer system with sustained ordering provides an intriguing new mechanism in organic-organic quasiepitaxy. Epitaxial superlattice structure has had significant importance in inorganic quantum wells and quantum dots applications, such as photodetectors, light emitting diodes, and solid state laser diodes.^{14, 168-173} The organic equivalent could have similarly substantial impact but has not been widely accessible previously. Thus, this new growth mode for achieving quasiepitaxial multilayers could provide novel pathways to fabricate highly ordered organic superlattices with tunable orientation for enhanced excitonic electronic devices.

5.1 Experimental

Vapor deposition of each material was performed in the multi-source thermal evaporator described in **Section 3.1.1**. Growth was carried out under a base pressure less than 3×10^{-6} torr at a rate of 0.03 nm/s at room temperature on freshly cleaved single-crystal KBr (100) substrates. The deposition temperature was monitored with a thermocouple integrated into the substrate holder

that was calibrated using an *in situ* non-contact infrared-to-analog converter module (Omega, OSM101). After the deposition of each layer, growth is paused to collect diffraction patterns at various azimuthal rotations and to allow for shutter switching. In-plane lattice constants of the organic layers were measured from the RHEED patterns with the initial KBr pattern as a reference. The out-of-plane lattice structure was confirmed by X-ray diffraction (XRD) in the Bragg-Brentano configuration using a Cu K α source (Rigaku Miniflex II). Atomic force microscopy (AFM) was performed in contact mode to study the film morphology and early stage nucleation. A silicon tip coated in Ti/Ir was used for the AFM measurements (Asylum Research). Isolated surface energies of different planes were calculated with Materials Studio *v*7.0 (Morphology) using the equilibrium method with the universal force field, validated against standard systems discussed elsewhere⁷⁰.

To understand the predicted equilibrium alignment of the organic-inorganic and organicorganic lattices, full surface potentials between substrate-adlayers were calculated in Matlab by summing the non-bonding interactions (van der Waals) between every atom-atom combination in respective layers.⁷⁰ The film lattice constants used in the calculations were obtained directly from RHEED measurements. The equilibrium separation is first determined for a fixed adlayer lattice (e.g. 5×5) over an excess of substrate lattices (50×50). The full system energy is then calculated as a function of translation across an entire unit cell at every rotation angle, θ . Thus, a plot of the minimum energy at every rotation can identify the overall equilibrium orientation registry. For reference, the rotation angle is defined as the angle between one of the two real lattice vectors of the adlayer (b_1^A) and substrate (b_1^S) (inset in **Figure 5.5b**). Calculations were repeated for surface mesh sizes of 5×5 and 9×9 adlayer meshes over 50×50 substrate meshes, respectively, to avoid edge effects. This method has been used previously to successfully identify nearly all known quasiepitaxial lattice registries.^{70, 141, 165}

5.2 NTCDA and DIP

NTCDA is a wide bandgap semiconductor, which we have already demonstrated to grow quasiepitaxially on KBr crystals with excellent ordering and registry at room temperature⁷⁰. The archetypal perylene derivation, DIP, was paired with NTCDA due to its 1) promising electron and hole mobilities in thin-film transistors >1cm²V⁻¹s⁻¹; ¹⁷⁶ 2) good crystallization behavior, stability against decomposition and oxidation at high temperature, and moderate photoluminescence efficiency;¹⁷⁶⁻¹⁷⁸ and 3) close surface energy matching of LES to that of NTCDA. A number of studies have investigated DIP growth on inorganic surfaces like SiO₂¹⁷⁹⁻¹⁸³ showing an upright crystalline orientation with little in-plane ordering. The 3D growth of upright DIP has also been observed on organic layers including F₁₆CoPc and F₁₆CuPc¹⁸⁴⁻¹⁸⁵ with in-plane disorder. Bulk structures for NTCDA and DIP are shown in **Figure 5.1**.



Figure 5.1. Crystal structures of NTCDA, α -DIP and β -DIP. (a)The bulk structure for NTCDA is monoclinic (a = 0.788nm, b = 0.532nm, c = 1.260nm, $\alpha = \gamma = 90^{\circ}$, $\beta = 107.26^{\circ}$). DIP crystal has two common polymorphs, (a) a triclinic phase referred to as α -DIP (a = 1.166nm, b = 1.301nm, c = 1.470 nm, $\alpha = 98.44^{\circ}$, $\beta = 98.02^{\circ}$, $\gamma = 114.55^{\circ}$) and (b) a monoclinic phase referred to as β -DIP (a = 0.717nm, b = 0.855nm, c = 1.680nm, $\alpha = \gamma = 90^{\circ}$, $\beta = 92.42^{\circ}$).¹⁷⁴⁻¹⁷⁵

5.3 Ordered Alternating Crystalline Growth

A typical series of reflection high-energy electron diffraction (RHEED) patterns for the growth of NTCDA/DIP alternating layer structures grown at room temperature are shown in **Figure 5.2**. Although there is no lattice matching between layers, RHEED patterns reveal that each layer is highly crystalline with its own well-defined surface lattice and registry. Schematic



Figure 5.2. *In situ* **RHEED patterns of ordered NTCDA/DIP alternating growth.** *In situ* RHEED patterns for the (a) the bare KBr substrate, (b,c) first, (d,e) second and (f,g) third pair. (h,i) AFM images of the first two layers. Note that as the number of layers increases, the streaked patterns for the NTCDA start to become less streak-like indicating an accumulating surface roughness. Crystal structure of the KBr substrate and molecular structures of NTCDA and DIP are shown (C: gray; O: red; K: purple; Br: maroon and H: white).

structural models of the NTCDA and DIP multilayer heterostructure are shown in **Figure 5.3**, along with the schematic of the individual layer orientations for growth directly on glass.

When NTCDA is grown on the KBr substrate, the RHEED patterns show continuous streak features (similar to the starting substrate), indicative of a crystalline flat surface that is consistent



Figure 5.3. XRD characterization and structure models. X-ray diffraction characterization of (a) NTCDA(20nm) on glass. (b) NTCDA powder. (c) DIP(20nm) on glass. (d) DIP powder. Growth on glass substrates exhibits the LES for NTCDA(100) and β -DIP(001). (e) DIP(30nm) on NTCDA(20nm) on KBr. (f) NTCDA(10nm) on KBr. (g) DIP(30nm) on KBr. (h) the bare KBr substrate. The peaks at 2θ =11.80° belongs to NTCDA(100). The peak at 2θ =20.68° is the β -DIP(020) peak and the other peaks between 22.5-25° are satellite peaks from the KBr(200) peak at 27.00°. Structural models of (i) NTCDA growth on glass. (j) DIP growth on glass. (k) NTCDA/DIP alternating growth on single crystal KBr. (N is for NTCDA and D is for DIP).

with measurements with atomic force microscopy (AFM). The diffraction streak spacings vary with different azimuthal angles indicating the ordered single-crystalline-like growth. XRD patterns show that the LES of NTCDA, the (100) plane, is formed parallel to the KBr and glass substrates (**Figure 5.3a, f**). The bulk lattice of NTCDA with this orientation has a rectangular unit mesh with lattice constants b_1 =0.531nm and b_2 =1.257nm, while the measured lattice from RHEED is b_1 =0.534(±0.001)nm and b_2 =1.319(±0.002)nm, indicating a slight distortion as seen previously.

With the subsequent growth of the DIP layer at room temperature, long unbroken NTCDA diffraction streaks are eventually replaced by spotty diffraction patterns of DIP which indicates a roughening of the crystalline surface. Nonetheless, clear azimuthal registry is still observed and the single-crystal-like rotational dependence of the RHEED patterns indicates that the DIP continues to remain aligned in-plane on top of the NTCDA layer. Despite the fact that β -DIP(001) is the LES and has a close energy matching with NTCDA(100), the β -DIP(020) plane is formed on the NTCDA surface, which is confirmed by both RHEED and XRD data. From the RHEED patterns of the first DIP layer, we measure out-of-plane spacings of $d_{(020)}=0.868(\pm 0.007)$ nm, which is close to the spacing of $d_{(020)} = 0.855$ nm for the bulk lattice. The (010) peak, which is not typically an allowed peak, is in fact observed under the dynamical conditions with electron diffraction from multiple scattering events in RHEED.¹⁸⁶ In contrast, the (020) series of peaks are observed in the pattern where dynamical scattering is not appreciable, and the measured XRD $d_{(020)}=0.859(\pm 0.003)$ nm from XRD is in good agreement within the error of the RHEED data. DIP is also grown directly on glass as a comparison showing the LES orientation (upright DIP molecules) with $d_{(001)}=1.684$ nm, which is in stark contrast to the growth on NTCDA. While typical DIP powder is a mixture of both α and β phases (Figure 5.3d), only the phase β is observed in the growth and the LES β -DIP(001) is formed on glass (Figure 5.3c). From the RHEED patterns of the first DIP layer, measured unit mesh dimensions are $b_1=0.712(\pm 0.001)$ nm, $b_2=1.734(\pm 0.002)$ nm and $\beta=94.1(\pm 0.3)^\circ$, which shows only a very slight distortion compared to the bulk surface structure of $b_1 = 0.717$ nm, $b_2=1.680$ nm and $\beta=92.42^\circ$.

5.4 Reversed Order Growth

To further understand this multilayer ordering, growths were performed with a reverse layer sequence, starting with the DIP layer. Interestingly, the RHEED patterns in **Figure 5.4b** no longer align orthogonally to the substrate surface and the stacking of β -DIP(120) plane is instead observed,



Figure 5.4. Reverse order growth. *In situ* RHEED patterns of (a) the bare KBr substrate, (b,d) the DIP layer (10nm) on KBr and (c,e) subsequent growth of NTCDA (10nm) on DIP. Note that the diffraction pattern of (b) for DIP on KBr is distinct to the pattern for DIP grown first on NTCDA (**Figure 5.2c**) indicating a significantly altered molecular stacking orientation, β -DIP (120), that subsequently leads to a 3D disordered powder with NTCDA deposited on top.

which is an entirely distinct growth orientation. AFM shows the formation of long nanowire features which is also distinct from the growth on NTCDA (**Figure 5.4d**). Subsequent growth of NTCDA on DIP/KBr results in ring diffraction patterns (**Figure 5.4c**) which indicates the evolution of three-dimensional crystalline disorder (i.e. crystalline powder) after just the first layer pair (**Figure 5.4e**).

5.5 In-plane Registry Modelling

The measured azimuthal registry of NTCDA films with the underlying KBr substrate is consistent with both full-structure potential energy and geometric model of exposing the LES parallel to the substrate on weakly interacting surfaces.⁷⁰ Indeed, when NTCDA and DIP are deposited individually on glass (SiO₂) substrates (**Figure 5.3a,c**), a weakly interacting surface, they both grow with the LES parallel to the substrate; these surfaces are NTCDA(100)(12.1 kcal mol⁻¹ nm⁻²) and β -DIP(001)(10.1 kcal mol⁻¹ nm⁻²), respectively. Consistent with this picture, we have found that many common organic molecules (**Section 4.2**), grow with their LES on both glass and this highly ordered NTCDA layer without a preferential nucleation at edges. In the case of DIP, however, we observe the stacking of β -DIP (020) on NTCDA (100), which is an unexpected

and non-LES orientation. In this growth orientation, DIP molecules lay flat on NTCDA, leading to the potential for higher transport in the normal direction and one of the in-plane directions, which could be ideal for solar cell or anisotropic transistor applications. The results of the fullstructure potential energy calculations predict an equilibrium registry between (020) DIP and (100)



Figure 5.5. Surface potential modeling of the DIP/NTCDA quasiepitaxial registry. (a) Measured real (b_1, b_2) , and reciprocal (b_1^*, b_2^*) lattice vector alignments for NTCDA and DIP layers. (b) Van der Waals potential energy as a function of adlayer-substrate azimuthal angle (θ) for DIP 5×5 (9×9) unit cells over an NTCDA 50×50 mesh. The azimuthal angle (θ) was defined as the angle between b_1 of the DIP adlayer (b_1^A) and NTCDA substrate (b_1^S) . The minimum in the potential energy gives an equilibrium rotation angle (registry) of 65.9° compared to the measured angle of 0±5° (red arrows). Model of (c) the measured and (d) predicted real-space overlayer alignment for DIP on NTCDA.



Figure 5.6. Calculated dependence of the normalized geometric potential, V/V_{θ} , as a function of the azimuthal angle θ for (020) DIP on (100) NTCDA. This geometric model has successfully predicted registry for a number of overlayer-substrate systems.^{70, 141} The film lattice constants used in the calculations are obtained directly from RHEED measurements. The results for 5×5, 9×9 DIP on 50×50 NTCDA give the same optimum quasiepitaxy at 138.6°, which also fails to predict the measured registry between DIP and NTCDA of 0±5° (shown in red arrows) from RHEED.

NTCDA at a rotation angle of 65.9°, independent of the number of DIP cells (**Figure 5.5b**). However, the measured orientation of DIP on NTCDA was determined to be $0\pm5^{\circ}$ from the RHEED data, which is in stark disagreement to the predicted registry. **Figure 5.5c,d** show the schematics of the measured and predicted alignments. In contrast to NTCDA on KBr, both the full-structure potential energy (**Figure 5.5b**) and geometric (**Figure 5.6**) models fail to correctly predict the registry of (020) DIP grown on NTCDA or KBr, even though full potential modeling¹⁴¹ has successfully predicted the registry of hundreds of organic-inorganic quasiepitaxial systems including the registry of NTCDA on KBr in this work.^{69-70, 140-141, 165, 187-190} This failure, and the emergence of a non-lowest energy surface suggest that there are other aspects that are dominating the ordered crystalline multilayer growth.

5.6 Edge-driven Mechanism

Considering the elemental simplicity of these organic systems, this suggests that the DIP adlayer interacts with and nucleates from the step edges of the NTCDA. The absence of such edge nucleation in other acene molecules (which predominately show intra-terrace nucleation) points to a key distinguishing interaction between the NTCDA and DIP directly. Indeed, the DIP has a perylene core capable of near covalent-like bonding to other aromatic rings, metals,¹⁹¹⁻¹⁹³ and can support hydrogen bonding interactions,¹⁹⁴ which has been previously seen in PTCDA and



Figure 5.7. AFM image of early-stage nucleation and structural model of the step edge growth. (a) AFM image of a sub-monolayer film of DIP (< 1nm) deposited on NTCDA (10nm). The DIP nuclei are marked with white arrows. (b) Schematic of DIP molecules lying cofacially with the NTCDA molecules at terraces showing edge nucleation. Interactions between molecular cores are highlighted in blue.

exploited for molecular templating.¹⁹⁵⁻¹⁹⁷ This can create stronger interactions between the DIP molecule and the flat facing edge of the NTCDA step (**Figure 5.7b**). From the RHEED patterns of the multilayer growth, the LES (001) of the DIP is indeed growing from either the (002) or (102) plane of NTCDA and DIP(110) from the NTCDA(011), which orients the DIP cofacially with the NTCDA edges. The initial monolayer growth of DIP is shown in AFM images for DIP on NTCDA (**Figure 5.7a**), where, indeed, we observe a clear evidence of DIP nucleating from the step edges of NTCDA and subsequently filling individual NTCDA terraces. Despite a coverage nominally approaching 1 ML (and a uniform deposition flux/coverage observed concurrently for DIP on SiO₂

here and as in ref. ¹⁹⁸) we do not find DIP islands uniformly distributed on every NTCDA terrace, and find particularly few DIP islands on the largest terraces. This indicates that there is both a small Ehrlich–Schwöebel barrier ^{133, 199} for DIP molecules to reach different terraces and there is high diffusivity for DIP on NTCDA at room temperature. This high diffusivity also likely plays a role in the ability to observe this growth mode, similarly to the role that diffusivity plays in the transition between layer-by-layer and step flow growth in inorganic systems.

The fact there is a layer sequence dependence (whether DIP or NTCDA is grown first) for the first layer, but not subsequent layers, further confirms the role of NTCDA edge-nucleation in guiding this quasiepitaxial growth – NTCDA plays an important role in initiating a growth orientation capable of supporting multilayer quasiepitaxy. This highlights the impact that the nucleation environment can play as a dominant mechanism in the structural evolution for a range of organic molecules designed to interact more strongly with molecular moieties. It is likely that by targeting these properties, such as hydrogen bonding or aromatic interactions between molecules at step edges, other systems can be tailored to show a similar growth mode.

5.7 Conclusion

In this chapter, we demonstrate the ordered hetero-quasiepitaxial superlattice growth of two distinct organic crystalline films on single-crystal substrates via deposition from the bottom up, reminiscent of molecular beam epitaxy of inorganic quantum wells and quantum dots. The crystalline alignment, monitored with *in situ* RHEED, can be maintained for many pairs, where DIP grows on NTCDA exposing its non-lowest energy β -DIP (020) plane. This surprising growth configuration is shown to derive from edge-nucleation driven quasiepitaxial dynamics confirmed by *in situ* diffraction, equilibrium energetic predictions, growth order reversal, and early growth studies. The understanding of this non-equilibrium quasiepitaxial growth of crystalline organic

multilayers could provide new routes to controlling molecular orientation in ordered organic superlattices via control over nucleation dynamics through the design of step-edge molecule interactions. Therefore, these results could enable entirely new opportunities for enhancing unique excitonic tunability and could also be used as a platform to study organic exciton confinement and strong coupling.

Chapter 6 – Homoepitaxial Growth of Alkali Halide Crystals

In this chapter, we investigate the homoepitaxial growth of NaCl on NaCl (001) investigated with *in situ* reflection high-energy electron diffraction (RHEED) and *ex situ* atomic force microscopy (AFM). Epitaxial growth is explored as a function of temperature and growth rate which provides the first detailed report of RHEED oscillations for alkali halide growth that uncovers previously unrecognized growth modes. This chapter provides the foundation for the epitaxial growth of halide perovskites on metal halide substrates described in the subsequent chapters.

6.1 Introduction

Alkali halide crystals are widely used in many optical and optoelectronic applications. NaCl crystals are used as one of the most common infrared transmission windows for spectrophotometers and useful for energy detection in x-ray monochromators.²⁰⁰⁻²⁰¹ Doped NaCl bulk crystals have been used for single crystal emitters and scintillation detectors²⁰²⁻²⁰⁴ and thin film NaCl can be used as buffer layers for OLEDs.²⁰⁵⁻²⁰⁶ NaCl crystal surfaces have been used for studying epitaxial growth of organic and inorganic thin films.²⁰⁷⁻²¹¹ The large range of lattice constants of alkali halide crystals could also enable growth of epitaxial metal-halide perovskites. Thus, understanding fundamental aspects of homoepitaxial metal halide growth could have a significant impact.

RHEED intensity oscillations have been routinely used during epitaxial growth of metals and semiconductors to monitor the growth rate,^{136, 212} understand crystal growth mechanisms and surface reconstructions,²¹³⁻²¹⁶ estimate surface diffusion,^{152, 217-218} and measure dopant incorporation.²¹⁹⁻²²⁰ A better understanding of the characteristics of the oscillations would provide insight into the microscopic processes during epitaxial growth. Although significant progress has been made in studying RHEED oscillations in epitaxial growth on metals²²¹⁻²²⁴ and semiconductors,²²⁵⁻²²⁸ there are no reports on halide insulators. Hetero- and homoepitaxial growths of alkali halides using molecular beam epitaxy (MBE) have been studied by both electron and He atom scattering, however with a limited growth parameter range in ultrahigh vacuum.²²⁹⁻²³⁵ In the case of the studies with RHEED in MBE, electron beams had to be removed within seconds to avoid charging, therefore limiting the ability to monitor oscillations and to obtain real time growth mode information. In the case of the studies with He scattering very little variation was found as a function of growth conditions. In this work, NaCl homoepitaxial growth on NaCl (001) surfaces is performed by thermal evaporation and studied using both *in situ* ultra-low current RHEED and ex situ atomic force microscopy (AFM), which reveal strong variations in the growth modes as a function of growth conditions. Layer-by-layer growth is observed at room temperature accompanied by clear RHEED oscillations while the growth mode transitions to an island (3D) mode at low temperature. At higher temperatures (>100°C), RHEED oscillations and AFM data indicate a transition to a step-flow growth mode. To show the importance of such metal halide growth, green organic light-emitting diodes (OLEDs) are demonstrated using a doped NaCl film with a phosphorescent emitter as the emissive layer. This study demonstrates the ability to perform in situ and non-destructive RHEED monitoring even on insulating substrates that could enable doped single crystals and crystalline substrates for a range of optoelectronic applications.

6.2 Experimental

Vapor deposition of NaCl was performed in the multisource thermal evaporator (Angstrom Engineering) equipped with real-time and *in situ* RHEED system (STAIB Instruments) operated with an ultra-low (< 10 nA) current and beam energy of 30.0keV. By using ultra-low current, the damage and charging of the film is negligible over the growth times investigated enabling the use

of this technique on organic and insulating surfaces.²³⁶ RHEED oscillations are monitored with substrates fixed at various in-plane orientations (KSA400). Rotation dependent patterns were collected after growth was halted.

The NaCl single crystal substrates were freshly cleaved in a glovebox prior to deposition with the (001) surface exposed and attached to the substrate holder using conductive tape. Deposition rates were measured *in situ* with a quartz crystal microbalance and calibrated *ex situ* by cross-sectional scanning electron microscopy (SEM) using single crystal potassium bromide as a substrate for layer contrast. The heating/cooling stage inside the chamber was used to preheat/cool the NaCl single crystal substrates to the required temperature before deposition. Substrate temperature was monitored and controlled (Watlow EZ-Zone) with a thermocouple integrated into the substrate heating/cooling plate that was calibrated to the surface temperature using an *in situ* non-contact infrared-to-analog converter module (Omega OSM101). Atomic force microscopy (AFM) was performed in contact mode for *ex situ* film morphology characterization. A silicon tip coated in Ti/Ir was used for the AFM measurements (Asylum Research). Electrical characterization was performed using a digital source meter (Keithley 2420) and a picoammeter (Keithley 6487). Luminescence current was measured using a large area Si photodetector (Hamamatsu) and electroluminescence (EL) spectra were measured using a calibrated spectrometer (Ocean Optics USB 4000).

6.3 Growth Modes of NaCl Homoepitaxy

Experiments were performed to study homoepitaxial growth of NaCl on NaCl (001) surfaces as a function of growth rate and temperature. For NaCl, the monolayer (ML) and bilayer (BL) thicknesses are defined as a/2 (2.8Å) and a (5.6 Å), respectively, consistent with other BCC and FCC crystals.²³⁷ In the first set, growths were performed at room temperature (25°C) with different rates to confirm RHEED oscillation interpretation: 0.1 BL/s, 0.3BL/s and 0.6BL/s. In the second set, low (-120°C) and high temperature (120°C) growths were performed at a growth rate of 0.1 BL/s as comparison to the room temperature growth to study the effect of temperature on the growth mode. RHEED patterns of NaCl homoepitaxial growth of 200Å at different temperatures are compared in Figure 6.1. A typical RHEED pattern of the NaCl single crystal is shown in Figure 6.1a. At growth temperatures of 25°C and 120°C, the sharp and continuous streak



Figure 6.1. Temperature dependent *in situ* **RHEED patterns of NaCl homoepitaxy.** Diffraction patterns for (a) bare single crystal NaCl cleaved along the (001) plane; homoepitaxial growth of 200Å NaCl at (b) -120°C, (c) 25°C and (d) 120°C. Note that the Kikuchi lines and continuous streaky patterns of the NaCl persist after growth at 25°C and 120°C, while at -120°C Kikuchi lines disappear, and streaky pattern becomes discontinuous after growth.



Figure 6.2. RHEED oscillations of NaCl homoepitaxial growth vs. growth rate and temperature. Room temperature growths as a function of growth rate: (a) $0.1 (\pm 0.02)$ BL/s, (b) $0.3(\pm 0.05)$ BL/s and (c) $0.6(\pm 0.1)$ BL/s; fixed rate growths of 0.1BL/s as a function of growth temperature (d) -120° C, (e) 25° C and (f) 120° C. RHEED oscillations intensities were recorded from the specular spot and correspond to one unit cell (or BL) per oscillation. Note that (a) and (e) are the same data.

features of the patterns are still present after the growth with a clear single-crystal rotation dependence and Kikuchi patterns still observable. For growth at -120°C, broken streak patterns are observed with a corresponding disappearance of Kikuchi patterns. Specular RHEED intensities are shown in **Figure 6.2** for each growth. Depositions performed at 25°C at each rate all show clear RHEED oscillations with a sudden specular intensity drop when the growth is initiated. The period of the RHEED oscillations is consistent with the deposition rate within the error of the deposition rate recorded by the quartz crystal microbalance (± 0.1 Å /s), where each period corresponds to a complete unit cell (or BL) similar to the oscillations observed for stoichiometric FeAl on AlAs.²³⁸ As the growth proceeds there is an overall damping of the specular intensity

shown in **Figure 6.2a-c**. At a growth temperature of 120°C, continuous RHEED oscillation are observed for > 25 BLs, along with a recovery in the specular intensity during longer deposition times as shown in **Figure 6.2d**. In contrast, the oscillations observed at low temperature growth at -120°C persist for only a few BLs as shown in **Figure 6.2f**. **Figure 6.3** shows the contact mode AFM morphology of 200 Å of homoepitaxial NaCl growth for each growth temperature. The average step heights in these AFM images correspond to either ML (~2.8Å) or BL (~5.6 Å) steps where BL steps are only observed at low temperature (line scans shown in **Figure 6.4**). At room temperature, intra-terrace nucleation is clearly evident by the emergence of isolated ML-thick circular islands speckled within terraces. When the growth temperature is reduced to -120°C, rougher terraces with greater terrace heights (closer to a BL) are found to form during growth



Figure 6.3. NaCl temperature dependent homoepitaxial growth mode and 3D morphology. AFM images for (a) bare single crystal NaCl and as a function of growth temperature for homoepitaxial growth of 200Å NaCl at (b) -120° C, (c) 25° C, (d) 120° C. (e) Crystal structure of NaCl. Line scans showing step height are included in the Supplementary Information. Two average step heights are observed: 2.5 Å (corresponding to the ML) and 5.0 Å (corresponding to the BL), with the ML steps observed most frequently.



Figure 6.4. NaCl temperature dependent homoepitaxial growth mode and 2D line scan. AFM images for (a) bare single crystal NaCl and as a function of growth temperature for homoepitaxial growth of 200Å NaCl at (b) -120° C, (c) 25° C, (d) 120° C. (e-g) Corresponding line scans showing step height. (h) Crystal structures for one NaCl unit cell (BL, 5.6 Å) and half unit cell (ML, 2.8Å).

along with a large density of "voids". At 120°C, smooth terraces are formed with smaller width and no observable intra-terrace nucleation.

At room temperature, layer-by-layer (2D) growth of NaCl is observed for both low and high rate deposition indicated by strong intensity oscillations. From the rate-dependence, it is clear that highly quality epitaxial growth can be maintained even for the highest rates measured here (0.6 BL/s), which allows the growth of 1 micron thick film in 50 min.

In general, RHEED oscillations stem from interference of the periodic formation and coalescence of 2D nuclei during the deposition of each layer.¹⁵¹ This mechanism is briefly described: when the deposition is initiated there is a formation of 2D nuclei that creates a disruption in the crystal potential and causes part of the diffraction beam to become out-of-phase. The coalescence of multiple islands into a smooth surface returns the layer to a uniform potential and restores coherence and specular intensity.²³⁹ In the case of NaCl with FCC symmetry, the full period of the RHEED oscillation corresponds to a full unit cell (or BL). This means that the bottom of the oscillation corresponds to a completed half unit cell (or ML) and each ML forms a complete layer prior to the next. This picture is consistent with the top-layer interference model described above where a completed half unit cell has greater destructive interference analogous to the phase mechanism that forbids the (001) and allows (002) diffraction peaks. This also explains the observation of half unit cell (or ML) step heights in AFM images. In the case of perfect layer-bylayer (2D) growth on singular surfaces, each layer is completed before nuclei are formed on the next layer – the resulting oscillations would then persist ideally with the same amplitude (undamped) indefinitely. However, in many cases adsorbates begin to nucleate on the previous layer before it is fully completed, resulting in either an accumulating degree of roughness or a lack of oscillation coherence that dampens the overall intensity of the specular spot. For the latter, this specular decay is also typically seen for layer-by-layer growth on vicinal surfaces such as with GaAs homoepitaxy where growth on a singular surface (miscut < 1 mrad) results in a nearly constant oscillation amplitude while vicinal surfaces (miscut ~ 7 mrad) results in an intensity decay²¹⁸. Given the vicinal nature of the cleaved NaCl (001) shown in Figure 6.4a, this is the most likely behavior at 25°C.

When the growth temperature is increased to 120°C the RHEED oscillations persist (with a smaller amplitude) for over 25 BLs and there is an overall recovery of the specular intensity (instead of a decay). This specular recovery is a hallmark of step-flow driven growth.¹⁸⁶ That is, as the temperature and the surface diffusivities of adsorbates increase, eventually only growth from the step edge is favorable and intra-terrace nucleation is suppressed. When the diffusion length of adsorbates becomes large enough to allow adsorbates move freely between the boundaries of the terraces, a roughly constant step density is maintained that flows uniformly across the substrate and results in a RHEED intensity that recovers to a nearly constant value. This growth mode and specular recovery is consistent with the morphology in Figure 6.3d where only terraces are observed (no ML islands). The continued observation of weak oscillations suggests that we are close to the transition between layer-by-layer (2D) and step-flow growth at 120°C. Indeed, it is likely that we are observing a mixed-mode growth where growth is initiated at step edges but grows radially across the terrace from these nucleation points. This can be clearly seen in the AFM as apparent triple junctions at the end of steps. Thus, it would be expected to see a superposition of both weak oscillations and an overall intensity recovery.

For the low temperature growth at -120°C, the Kikuchi features of the base NaCl substrate disappear within a coverage of 200Å, which suggests the formation of an increasing number of grain boundaries and dislocation density. In this case, the fast drop of oscillation intensity within the growth of less than 5 BLs indicates a transition from layer-by-layer (2D) to island (3D) growth. The AFM image in **Figure 6.3b** shows non-uniform coverage at the terraces, larger terrace step height, and a rougher surface morphology. Interestingly, it was predicted that for alkali halide epitaxy, diffusivities would be large enough to see RHEED oscillations at growth temperatures above $0.1xT_M$ (absolute melting temperature),²³² which translates to -166°C and which is

surprisingly consistent with our observations (weak but still present oscillations at -120°C). This would then place the diffusivity in the 10^{-7} - 10^{-8} cm²/s range at low temperature (-100°C to -150°C) and 10^{-4} to 10^{-5} cm²/s at room temperature.²³²

6.4 NaCl Based OLEDs

To further demonstrate the potential of NaCl in electronic devices, we show the incorporation of vapor deposited NaCl as the host in a green phosphorescent OLEDs structure. OLEDs utilizing NaCl as the host were fabricated on degreased substrates coated with indium tin oxide(ITO) using the following structure: ITO/ MoO₃ (150 Å) / NaCl:Ir(ppy)₃ (6 vol.%, 200 Å)/ LiQ(8 Å)/ Al (800 Å) where Ir(ppy)₃ is *fac* tris(2-phenylpyridine)iridium and LiQ is 8-hydroxyquinoline lithium. The control device used the same structure without any emitter in the NaCl. The reference conventional device structure is: ITO/ α -NPD (400 Å) / CBP: Ir(ppy)₃ (6 vol.%, 200 Å)/ LiF(8 Å)/ Al (800 Å), where α -NPD is 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl, CBP is 4,4'-N,N'-dicarbazole-biphenyl and Alq₃ is tris-(8-hydroxyquinolinato) aluminum. **Figure 6.5a** shows a comparison of current density (*J*) and luminescence current density (*L*) vs. voltage (*V*) of the NaCl:Ir(ppy)₃ device and the control device



Figure 6.5. NaCl based OLEDs. (a) Current density (*J*) and luminescence current density (*L*) vs. voltage (*V*) of the NaCl, NaCl:Ir(ppy)₃ and CBP:Ir(ppy)₃ devices. (b) Electroluminescence (EL) spectrum of the conventional CBP:Ir(ppy)₃ and NaCl:Ir(ppy)₃ devices. (Inset) Photograph of the NaCl:Ir(ppy)₃ device showing green electroluminescence.

with only NaCl as the emissive layer. The absence of electroluminescence from the control devices confirms that the emission in the NaCl:Ir(ppy)₃ device originates from Ir(ppy)₃. **Figure 7.5b** shows the EL spectrum of the device, which is consistent with the EL for the conventional host architecture.²⁴⁰ While the peak external quantum efficiency (EQE) for the NaCl:Ir(ppy)₃ device is low at 0.005%, the performance could be improved substantially with additional thickness optimization, layer optimization (e.g. exciton blocking layers), or host codoping. Considering NaCl can be doped to become conductive (at least at high temperatures)²⁴¹ or epitaxially coupled with highly conductive halide perovskites, these demonstrations suggest new potential pathways to integrate epitaxial NaCl layer into optoelectronics.

6.5 Conclusion

In this chapter, *in situ* and real time RHEED monitoring of homoepitaxial growth of NaCl on NaCl (001) is demonstrated. RHEED oscillations and AFM morphologies are observed and discussed to show the impact of growth rate and temperature on changes in growth mode which were previously unrecognized. This study demonstrates the capability of performing RHEED monitoring of epitaxial growth on insulating halide crystals in thermal evaporators. This understanding could be used to enable the mixed growth of alkali halides with tunable lattice constants and enable epitaxial halide perovskite growth for photovoltaic and optoelectronic applications discussed in **Chapter 7 and 8**. We have also demonstrated NaCl as a potentially interesting component for OLEDs, further suggesting new opportunities for metal-halide and metal-halide-perovskite based single-crystal epitaxial optoelectronics.

Chapter 7 – Single-Domain Epitaxy of Cesium Tin Bromide (CsSnBr₃)

In this chapter, we focus on the crystalline growth of CsSnBr₃, which has been shown to be a promising and air-stable candidate in optoelectronics with a bandgap of 1.8 eV. We demonstrate single-domain epitaxy enabled by room-temperature reactive vapor phase deposition onto single crystal metal halide substrates with congruent ionic interactions and find this approach to be generally applicable across the halide (X) series. The lattice constant of cubic CsSnBr₃ (5.80 Å) is most closely lattice matched from all the MX alkali halide salts with NaCl (cubic lattice constant of 5.64 Å). While the compressive misfit between CsSnBr₃ and NaCl is -2.8%, this provides one of the smallest misfits readily available. For this archetypical halide perovskite, we uncover two epitaxial phases, a cubic phase and tetragonal phase, which emerge via stoichiometry control that are both stabilized with vastly differing lattice constants and accommodated via epitaxial rotation. We exploit this epitaxial growth to demonstrate multilayer 2D quantum wells of a halideperovskite system. This work ultimately unlocks new routes to push halide perovskites to their full potential.

7.1 Experimental

Reactive vapor deposition of halide perovskites was performed in a multisource custom thermal evaporator. The two precursors, CsBr and SnBr₂, were co-evaporated from separate tungsten boats to form the perovskite layer. Prior to growth, pre-polished NaCl (100) single crystal substrates were prepared through cleaving in a glovebox or used as polished. RHEED oscillations were monitored with substrates fixed at various in-plane orientations (KSA400). Rotation dependent RHEED patterns were collected after each deposition was halted via source and substrate shutters. Quantum well multilayers were fabricated under similar growth conditions, where epitaxial NaCl was vapor deposited from a NaCl powder source with a rate of 0.02 Å/s and a thickness of 1.5 nm. Cross-section transmission electron microscope (TEM) samples were prepared by focused ion beam (FIB), attached to a FEI Nova 200 Nanolab SEM/FIB, and then investigated by a JEOL 3100R05 Double Cs Corrected TEM/STEM. A carbon top-layer was deposited on the cutting area to protect the epitaxial film. Scanning electron microscopy (SEM, Carl Zeiss Auriga Dual Column FIB SEM) was performed for ex situ film thickness calibration and morphology characterization. Photoluminescence spectra were measured using a PTI Quanta Master 40 spectroflurometer under nitrogen atmosphere and various excitation wavelengths. Dielectric long-pass filters were used during the PL measurement to prevent both wavelength doubling and light bleeding. UV-VIS transmission spectra were taken using Perkin Elmer UV-VIS Spectrometer (Lambda 900). X-ray diffraction was characterized by using a Bruker D2 Phaser XRD instrument with a Cu Ka source at 30 kV and 10 mA and a Ni filter in the Bragg-Brentano configuration. X-ray photoelectron spectroscopy was performed in a separate chamber with a Kratos Axis Ultra XPS using a monochromated AlKa (1.486 keV) as the X-ray source. Before collecting XPS data, the films were etched by Argon ions for 1.5 min to prevent the interference of surface contamination.

Epitaxial lift off device fabrication was performed by immersing the epitaxial film grown on the substrate into liquid nitrogen for about 30 s to fully cool the sample. The film and substrate were then quickly immersed into diethyl ether. After warming to room temperature, the film and substrate were removed from the solvent and copper tape was pressed onto the halide perovskite film (with a pre-deposited gold layer of ~300 Å on top). The tape was slowly peeled to separate the halide perovskite epitaxial film from the substrate. C_{60} (M. E. R. Corporation 99.9%), bathocuproine (BCP, Lumtec >99%), silver (Kurt Lesker, 99.99%), and tris-(8hydroxyquinolinato) aluminum (Alq₃, Lumtec, >99.5%) were then deposited onto the surface of halide perovskite film in sequence followed by Ag(4nm)/Alq₃(60nm) as the transparent cathode for top illumination. Photoconductive-atomic force microscope (AFM) measurements were carried out on an MFP-3D-AFM from Asylum Research in a nitrogen filled cell. The illumination condition was established by a light fiber shining from the top of the sample. Pt/Ir coated tip with the spring constant of 0.2 N/m was used in the pc-AFM measurements, while 20 nN force was applied between tip and sample. As the tip moved across the surface, the topology was measured. In the point *I-V* measurements, the AFM tip was fixed at different locations. While a bias connected to the bottom electrode was varied, the current between the AFM tip and bottom electrode was recorded.

Electronic band structures and densities of states (DOS) of CsSnBr₃ and CsSn₂Br₅ were calculated using density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP). The exchange-correlation functional utilized were the Perdew-Burke-Ernzerhof (PBE) functional²⁴², which belongs to the generalized gradient approximations (GGA) class, and the screened Heyd-Scuseria-Ernzerhof (HSE06)²⁴³ hybrid functional. Additional computational details can be found in the Supporting Information. Crystal structures were drawn using VESTA and selected area electron diffraction (SAED) patterns were calculated with CrystalMaker.

The fitting method of the Bohr radius (a_B) is explained below. The emission energy of a quantum well is described by the Brus equation as²⁴⁴⁻²⁴⁵

$$E_{g}^{well}(L_{z}) = E_{g}^{0} + \Delta E(L_{z}) = E_{g}^{0} + \frac{\hbar^{2}\pi^{2}}{2m^{*}L_{z}} - \frac{1.8q^{2}}{4\pi\varepsilon_{r}\varepsilon_{o}L_{z}},$$
(7.1)

where E_g^0 is the bulk band gap, ΔE is the confinement energy of both electrons and holes, \hbar is reduced Planck constant, L_z is the thickness of the quantum well, and m^* is the reduced mass that can be obtained from the effective masses of the electron (m_e^*) and the hole (m_h^*) as $\frac{1}{m^*} = \frac{1}{m_e^*} +$ $\frac{1}{m_h^*}$, *q* is the charge of electron, ε_r is the relative permittivity, and ε_0 is the vacuum permittivity. Since the exciton binding energy of CsSnBr₃ has been reported to be less than 1 meV²⁴⁶ the size dependence of the quantum well bandgap can be expressed as²⁴⁷

$$E_{total} = E_g^0 + \Delta E = E_g^0 + \frac{\hbar^2 \pi^2}{2m^* L_z^2},$$
(7.2)

The value of m^* obtained by fitting the PL data of quantum well PL data can be extracted and then used for calculation of Bohr radius of this material by using²⁴⁸

$$a_{B} = \frac{4\pi\hbar^{2}\varepsilon\varepsilon_{o}}{e^{2}} \left(\frac{1}{m_{e}^{*}} + \frac{1}{m_{h}^{*}}\right),$$
(7.3)

where a_B is the Bohr radius, e is the electron charge, ε_o is the vacuum permittivity, and ε is the dielectric constant of the semiconductor which has been reported for CsSnBr₃ to be 32.4.²⁴⁶

7.2 Phase Study via Stoichiometry Control

RHEED patterns captured during the epitaxial growth of the perovskite at room temperature are shown in **Figure 7.1**. The first row of **Figure 7.1** shows the initial RHEED patterns of the NaCl(100) crystal with the electron beam directed along the NaCl[110]. The impact of the precursor ratio on the crystal structure of epitaxial film is investigated with CsBr:SnBr₂ molar ratios ranging from 0.25:1 to 1.5:1. We confirm that the epitaxially deposited halide perovskite films form single-domain epitaxial layers from the rotation dependent RHEED (**Figure 7.2a-d**).



Figure 7.1. In situ RHEED patterns of the epitaxial growth of CsSnBr₃ on NaCl. The epitaxial halide perovskite film is grown on single crystalline NaCl(100) substrates with various ratios of precursors, CsBr to SnBr₂, where two distinct phases are observed depending on stoichiometry: cubic (1:1) and tetragonal (0.25:1 and 0.5:1). The epitaxial growth of stoichiometric CsSnBr₃ (cubic) is highlighted in the box. The uncertainty of film thickness is 1-1.5 MLs.

When depositing CsSnBr₃ using a molar ratio of 1:1 (CsBr:SnBr₂), the RHEED patterns remain streaky, indicating the formation of a smooth crystalline layer. After the deposition of the first monolayer, the underlying substrate Kikuchi lines disappear as expected due to the shift in elemental composition and lattice type (face-centered to primitive). The geometry and spacing of these reciprocal lattice points obtained along the [110] and [100] direction indicate that the crystal structure of the perovskite is cubic with a calculated lattice constant of 5.8±0.1 Å. The lattice



Rotate from [200] to [020] of NaCl

Figure 7.2. Rotation dependent RHEED patterns of CsSnBr3 and CsSn2Br5 epitaxial film on NaCl. Streaky RHEED patterns of (a-d) cubic phase CsSnBr3 taken from different rotation angles showing that single-domain epitaxial layer is formed on the substrates. RHEED patterns of roughened (e-h) tetragonal phase CsSn2Br5 taken from different rotation angles.

constant is further confirmed with *ex situ* X-ray diffraction (XRD) to obtain an out-of-plane lattice constant of 5.80±0.01 Å (discussed below). Several other bulk phases have been reported for CsSnBr₃, including tetragonal and monoclinic phases; however, only the cubic phase is stable at room temperature²⁴⁹⁻²⁵⁰. The high symmetry shown in all of the diffraction data clearly indicate the presence of the cubic phase (**Figure 7.2a-d**). Thus, we find the films are not pseudomorphic past the first monolayer, which is not surprising considering the level of compressive misfit. This implies there is a critical thickness and that there will be a considerable dislocation density to



Figure 7.3. RHEED oscillations of CsSnBr₃ growth on NaCl. Specular RHEED intensity recorded during CsSnBr₃ epitaxial growth at 1:1 stoichiometry on NaCl at (a) 0.28 Å/s and (b) 0.14 Å/s. The oscillation period is 5 s and 10 s for (A) and (B), respectively, and corresponds to thickness of a half monolayer. (C) Cross-section SEM image used for calibration of the growth rate.

accommodate this misfit. However, because it is compressive misfit, this is less likely to lead to film cracking than if it were tensile misfit,²⁵¹ and no cracking was observed for thicknesses > 2000 Å. During the 1:1 growth, we also observed clear RHEED oscillations that vary with deposition rate. Such oscillations are a hallmark of layer-by-layer growth (**Figure 7.3**), where the oscillation period typically corresponds to the growth of a monolayer or bilayer,²⁵² but can also show complex bimodal periods.²⁵³ Here, we find the oscillation period corresponds to half a monolayer (two periods per monolayer), which suggests a more complex underlying reactive growth mechanism or an associated reconstruction during the reaction. This is also similar to RHEED oscillation



Figure 7.4. Ordering of the halide perovskite at the halide salt interface. (a) Enlarged crosssection TEM image (viewed along the [100] direction of NaCl) of sample prepared at 1:1 CsBr:SnBr₂ ratio with CsSnBr₃ film thickness of ~25 nm, where the black arrow shows the boundary between epitaxy and NaCl; (b) Enlarged image of the area marked by white frame; (c) cross-section SEM image showing the smooth surface of epitaxial film. (d) and (e) show the film color prepared at different ratios 0.25:1 and 1:1, respectively. Schematics of the epitaxial structures: (f) Top and (g) side view of cubic CsSnBr₃ on NaCl. (h) Top and (I) side view of tetragonal CsSn₂Br₅ on NaCl. Green spheres are Cs; gray spheres are Sn; red spheres are Br; yellow spheres are Na; and light green spheres are Cl.

beating seen in ZnSe migration-enhanced epitaxial growth on GaAs where the oscillation period corresponded to a half monolayer.²⁵⁴ Cross-section TEM images of the epitaxial CsSnBr₃ film are shown in **Figure 7.4**. Due to the inherent misfit, we do observe dislocations in the first several monolayers at the interface (**Figure 7.4b**) when no pseudomorphic layer is present. Nonetheless, the atomic arrangement of the two materials are nearly indistinguishable, which is consistent with the observation of the RHEED patterns. The cross-section SEM images shown in **Figure 7.4c** further confirms the smooth surface of films prepared with 1:1 ratio of CsBr and SnBr₂, indicating its suitability for the fabrication of thin-film optoelectronic devices.
0.5:1 (CsBr:SnBr₂)



Figure 7.5. *In situ* real-time RHEED monitoring of the phase transition. A phase transition from the cubic to tetragonal phase occurs when the deposition ratio of CsBr to SnBr₂ is 0.5:1 after 1-2 monolayers. Note that while the pattern for the tetragonal phase appears monoclinic, it is actually a rotated tetragonal phase and the diffraction spots are therefore not along primary axes.

In contrast to the growth with a 1:1 stoichiometry, growth with a 0.5:1 stoichiometry results in a phase transition from the cubic CsSnBr₃ to a stable tetragonal phase that takes place at the earliest stages of growth within the first two monolayers. Rotation dependent RHEED patterns for the tetragonal phase are shown in **Figure 7.2e-h**. While tetragonal distortions are common for large lattice misfits in pseudomorphic growth, this tetragonal phase is not a simple distortion, nor is it the low temperature tetragonal phase;²⁴⁹⁻²⁵⁰ it even appears to be a monoclinic phase when monitored along the NaCl [110] direction. This indicates that the growth with moderate Cs deficiency leads to a susceptibility to transitioning to CsSn₂Br₅. This phase transition process is further elucidated by the RHEED data in **Figure 7.5** where only the first ML is cubic and then the subsequent layers transform to the tetragonal phase. The transition was monitored under rough growth conditions with substrates fixed at NaCl [110] due to the symmetry and lattice matching of the *a-b* plane of the tetragonal phase. The RHEED intensity monitoring also allows the study of phase transitions from cubic to tetragonal because RHEED pattern changes can be monitored as a change of particular diffraction peak locations (**Figure 7.6**). At later stages of growth (>7 MLs) the spotty patterns of the tetragonal phase become streaked, which is indicative of the crystalline film changing from rough to smooth while maintaining the initial tetragonal crystal structure.

To further confirm the phases shown in the RHEED patterns, XRD was used to determine the out-of-plane lattice parameter for the epitaxial films. As the ratio of CsBr to SnBr₂ increases from 0.25:1 to 1:1, the peaks at 11.57° ($d = 7.64 \pm 0.01$ Å) and 23.46° are replaced by peaks at 15.31° ($d = 5.80 \pm 0.01$ Å) and 30.83° as shown in **Figure 7.7**. The observed peaks are consistent with the d-spacings along the c-axis calculated from RHEED patterns and correspond to the (001)/(002) and (002)/(004) peaks of the cubic CsSnBr₃ and tetragonal CsSn₂Br₅ phases respectively. Based on the RHEED and XRD data, the measured lattice constants and orientations of the two epitaxial



Figure 7.6. RHEED oscillations monitored during the phase transition. (a) RHEED pattern with the monitored intensity area highlighted with the red circle and the corresponding (b) RHEED intensity profile with time.

phases are summarized in **Table 7.1**. Surprisingly, we find that both the cubic $CsSnBr_3$ and tetragonal $CsSn_2Br_5$ can grow epitaxially, even though the lattice constant of $CsSn_2Br_5$ is much

larger and the mismatch between $CsSn_2Br_5$ and NaCl is 4.9 %. This larger lattice is accommodated via the rotation of $CsSn_2Br_5$ relative to the metal halide substrate. Schematics of the epitaxial growth of $CsSn_2Br_5$ and $CsSnBr_3$ on NaCl substrates are shown in **Figure 7.4f-i**.



Figure 7.7. Crystal structure characterization of the two epitaxial phases, CsSnBr3 and CsSn2Br5. XRD patterns of NaCl (blue) and samples grown at different ratios of CsBr:SnBr2: 0.25:1 (black) and 1:1 (red).

Bulk Crystal Structure		CsSnBr ₃	CsSn ₂ Br ₅
		Pm3m, <i>a</i> = <i>b</i> = <i>c</i> =5.80 Å	I4/mcm, $a=b=8.48$ Å,
			<i>c</i> =15.28 A
	0.25:1	-	Observed
Precursor Ratio of CsBr to SnBr ₂	0.5:1	Observed $< 2 \text{ ML}$	Observed $> 3 \text{ ML}$
	1:1	Observed	-
	1.5:1	Pm3m, $a=b=c=5.80$ Å $5:1$ - :1 Observed < 2 ML	-
	Along NaCl [110]	[110]	[210]
Orientation	Along NaCl [100]	[100]	[310]
	Along NaCl [001]	[001]	[002]
Misfit		-2.8 %	4.9 %

 Table 7.1. Lattice constants, film orientation and misfit of two phases, CsSnBr3 and CsSn2Br5.

Dressurger Datis of CoDr to SuDr	Real Ratio		
Precursor Ratio of CSBr to ShBr ₂	Cs	Sn	Br
0.25:1	1.0 ± 0.1	10.0 ± 1.0	13.3±1.3
0.5:1	$1.0 {\pm} 0.1$	3.0±0.3	$5.0 {\pm} 0.5$
1:1	1.0 ± 0.1	1.3±0.1	2.9±0.3

Table 7.2. Elemental ratio of as-deposited films with different precursor ratio of
CsBr:SnBr2 obtained from XPS data.

Epitaxial growths with both a greater CsBr deficiency (0.25:1) and CsBr excess (1.5:1) were also investigated as shown in **Figure 7.1**. At the CsBr deficient (0.25:1) ratio, the pure tetragonal phase is observed without first seeing the cubic structure. In contrast, the CsBr excess (1.5:1) ratio resulted in ring-like patterns, which indicates the film becomes a three-dimensional polycrystalline powder.

Epitaxial films were also characterized by X-ray photoelectron spectroscopy (XPS) to measure the elemental ratios in the films deposited using various ratios. By fitting the XPS peak, the elemental ratio of Cs to Sn can be extracted, and the results are summarized in **Table 7.2**. The epitaxial film deposited with 1:1 ratio of CsBr to SnBr₂ is indeed stoichiometric CsSnBr₃ (1:1:3 for Cs:Sn:Br). The other two ratios of 0.25:1 and 0.5:1 both lead to films deficient in Cs. The combination of RHEED, XRD and XPS analysis indicates that the growth of CsSnBr₃ is more



Figure 7.8. Epitaxial growth of CsSnBr3 on pseudomorphic interlayers of NaCl-NaBr. (ae) RHEED patterns of growth of pseudomorphic interlayers of NaCl-NaBr on NaCl substrates. The ratio of NaBr: NaCl is gradually increased to reduce the misfit between substrates and interlayers. Note that when the ratio of NaBr: NaCl reaches 1:1, the lattice constant of interlayers is 5.81 Å perfectly matching that of CsSnBr3 (5.80 Å). During the growth, the lattice constant calculated from RHEED patterns shows gradual increase along with increasing the ratio of NaBr: NaCl. (f-i) RHEED patterns of growth of CsSnBr3 on pseudomorphic interlayers of NaCl-NaBr.

favorable when Cs is stoichiometric or in slight excess, while CsSn₂Br₅ dominates when there is a

Cs deficiency.

Both selective elemental vacancies and lattice misfit can ultimately play a role in initiating strain-driven phase transitions in these systems. While the elemental vacancies can be controlled by stoichiometry, the lattice misfit can be tuned through compositional alloying of the metal halide substrate, either in the bulk or as thin pseudomorphic interlayers. NaBr has larger lattice constant



Figure 7.9. XRD patterns of alloyed NaCl-NaBr pseudomorphic interlayers and CsSnBr3. (a) Comparison of NaCl substrate alone and alloyed NaCl-NaBr layers. (b) Enlarged view of (a) shows a shoulder peak arises in the sample of alloyed NaCl-NaBr pseudomorphic interlayers on NaCl substrates. (c) Enlarged view shows the peak splitting that reflects the change of lattice constant from NaCl substrate, alloyed NaCl-NaBr, and CsSnBr3.

(5.98 Å) than cubic CsSnBr₃. Therefore, alloying NaBr and NaCl can provide near perfect lattice matching for epitaxial growth of cubic CsSnBr₃(**Figure 7.8 and 7.9**), representing a general strategy for tuning the lattice misfit and dislocation density.

7.3 Epitaxial Lift-off

The epitaxially deposited halide perovskite films are strongly bonded to the metal halide crystals (see **Figure 7.10a-c**). The strong bond formed at the interface of the halide perovskite and metal halide substrates is very likely due to the similar ionic characteristic between halide perovskite and metal halide salt. This is confirmed by the attempted growth of halide perovskite



Figure 7.10. Film adhesion of the epitaxial growth of CsSnBr₃ on NaCl and epitaxy lift-off/regrowth. (a) Epitaxial CsSnBr₃ sample before application of Scotch tape; (b) after attachment on the film surface; and (c) after peeling off. (d) Epitaxial lift-off procedure: the epitaxial CsSnBr₃ grown on NaCl with a gold layer (~300 Å) on the top is rapidly immersed into liquid nitrogen and then rapidly transferred into diethyl ether; Cu tape is then pressed onto the surface and then slowly peeled which results in separation of the epitaxial film from the substrate; (e-f) RHEED patterns for the epitaxial re-growth of CsSnBr₃ after epitaxial lift-off.

on Ge and InP substrates, which have similar degree of lattice misfit but are more covalent in their bonding character. According to the RHEED pattern shown in **Figure 7.11**, neither Ge nor InP provides readily suitable surfaces for epitaxial growth of halide perovskite, which leads to the formation of polycrystalline films.

With the successful growth of single-domain epitaxial films we further demonstrate an epitaxial lift-off (ELO) process to allow the separation of these epitaxial layers from single crystalline substrates and enable substrate regrowth (**Figure 7.10d-g**). ELO has been shown to be an important processing method for making, for example, single-domain GaAs more economically viable for solar cells.²⁵⁵⁻²⁵⁸ In our work this is achieved by flash cooling/heating with liquid



Figure 7.11. RHEED patterns of growth of CsSnBr₃ on Ge and InP. (a) Ge single crystalline substrate along the [100]; (b) CsSnBr₃ grown on Ge; (c) Ge single crystalline substrate along the [100] pre-treated with HCl acid etching for 10 min; (d) CsSnBr₃ grown on Ge from (c); (e) InP single crystalline substrate along the [100]; (f) CsSnBr₃ grown on InP.



Figure 7.12. Absorption spectra of CsSnBr₃, CsSn₂Br₅ and NaCl substrate. (a) CsSnBr₃ of varying well thickness and (b) CsSn₂Br₅ (black curve) and NaCl (blue curve). The spectra are converted from (1-Transmission) and shifted for clarity.

nitrogen immersion followed by rapid immersion in diethyl ether to initiate cracking at the interface of the substrate and epitaxial film by differences in the thermal expansion coefficients.



Figure 7.13. Electronic band structures of $CsSnBr_3$ and $CsSn_2Br_5$. PBE band structure, density of states (DOS) and projected density of states (PDOS) of (a) $CsSnBr_3$ and (b) $CsSn_2Br_5$. HSE06 band structure, density of states (DOS) and projected density of states (PDOS) of (c) $CsSnBr_3$ and (d) $CsSn_2Br_5$.

Subsequently, epitaxial films are peeled with conductive copper tape. Moreover, the substrates can be reused for further epitaxial growth (**Figure 7.10d-g**).

7.4 Discussion

Experimental and theoretical studies are performed on the CsSn₂Br₅ and CsSnBr₃ phases to understand the properties for each. Absorption spectra of as-prepared epitaxial films are shown in

Figure 7.12a and confirm that the band-gap of epitaxial CsSnBr₃ is 1.83±0.02 eV, which is

Materials	PBE band gaps (eV)	HSE06 band gaps (eV)	Experimental value (eV)
CsSnBr ₃	0.40	0.84	1.83±0.02
CsSn ₂ Br ₅	2.33	3.12	3.34±0.04

Table 7.3. Calculated band gaps of CsSnBr3 and CsSn2Br5 using the DFT-PBE and
DFT-HSE06 methods.



Figure 7.14. Solar cell device from epitaxial lift-off of CsSnBr3. AFM image of (a) singledomain epitaxial lift-off film, and (b) amorphous film. (c) Device architecture of the photovoltaic cells. (d) *I-V* curve of devices fabricated with the single domain epitaxy film and amorphous film, respectively, showing nearly an order of magnitude more photocurrent and double the voltage for single domain films versus the amorphous film.

consistent with both theoretical²⁴⁶ and experimental²⁴⁹ results reported previously. For $CsSn_2Br_5$, we measure a bandgap of 3.34 ± 0.04 eV, which is clearly distinguishable from the NaCl bandgap

of ~9 eV (Figure 7.13b). The calculated band structures, density of states (DOS) and projected

density of states (PDOS) of CsSnBr3 and CsSn2Br5 using the DFT with the HSE06 functional

Figure 7.13c-d. A summary of the calculated band gap values can be found in **Table 7.3**. The resulting HSE06 band gaps for CsSnBr₃ and CsSn₂Br₅ are 0.84 eV and 3.12eV, respectively. Note that DFT methods underestimate the gap of most semiconductors. These values are in reasonable agreement with the observed properties of CsSnBr₃ and CsSn₂Br₅. Had the perovskite been pseudomorphic on pure NaCl, we predict that the bandgap would decrease by around 0.5 eV, which is clearly not observed experimentally. For comparison, the PBE band structures, DOS and PDOS of CsSnBr₃ and CsSn₂Br₅ are shown in **Figure 7.13a-b**. These calculations further confirm that the tetragonal phase is CsSn₂Br₅ with a large bandgap.

Given the suitable bandgap of CsSnBr₃ for solar cell applications we fabricated photovoltaic devices to compare the optoelectronic properties of single-domain epitaxial films and amorphous films of CsSnBr₃. AFM images show that the surface of epitaxial films is much smoother than that of amorphous films (**Figure 7.14a-b**). Current-voltage (*I-V*) curves measured by conducting probe AFM show that the devices fabricated with the single-domain epitaxial film as the absorber layers have both higher I_{sc} and V_{oc} than the control devices fabricated with amorphous films by a factor of 10 and 2 respectively (**Figure 7.14c-d**). This clearly indicates that the high defect concentration present in amorphous and polycrystalline CsSnBr₃ is



Figure 7.15. Epitaxial CsSnBr₃ based 2D Quantum well fabrication. RHEED patterns of (a) NaCl along the [110] direction, (b) NaCl/CsSnBr₃(~40 nm), and (c) NaCl/CsSnBr₃(~40 nm)/NaCl (1.5 nm). (d) Schematic illustration of NaCl/CsSnBr₃ quantum well structure, green spheres are Cs; gray spheres are Sn; red spheres are Br; yellow spheres are Na; and light green spheres are Cl; (e) PL spectra of quantum well samples with various well width: 5 nm (black curve), 10 nm (red curve), 20 nm (blue curve), 40 nm (magenta curve), 80 nm (orange curve), and 100 nm (violet curve). (f) Emission energy of quantum wells with varying well width. The fitting is described in the Supporting Information. The inset shows the photograph of samples illuminated under UV light. Samples from left to right are bare single crystal, quantum well of NaCl/CsSnBr₃(40 nm), and quantum well of NaCl/CsSnBr₃(~100 nm).(g) PL spectra of quantum well samples CsSnBr₃/CsSn₂Br₅ with various well widths: 20 nm (black curve), 40 nm (red curve), 80 nm (blue curve), 100 nm (green curve). PL of quantum well samples CsSnBr₃/NaCl as a comparison: 80 nm with NaCl (orange curve), and 100 nm with NaCl (olive curve).

indeed a key limitation for enhancing device performance⁹⁶ that can be overcome with epitaxial layers.

Based on the control afforded by this epitaxial halide growth, we further fabricate quantum wells with varying well thicknesses for CsSnBr3 paired with both vapor-deposited NaCl and CsSn₂Br₅ as the well barrier. Quantum wells are important in a range of optoelectronic devices and provide critical insight into the physical properties of quantum confined charge carriers, twodimensional electron gas,²⁵⁹ and tunable luminescence. The growth process was investigated by RHEED to confirm the formation of epitaxial multilayers as shown in Figure 7.15a-c where NaCl was grown under similar conditions to homoepitaxial growth demonstrated previously.¹²⁵ The data in shows that no obvious change occurs after depositing the epitaxial barrier layer on the halide perovskite or after depositing multiple quantum well layers. That is, the NaCl epitaxial layers are pseudomorphic with the perovskite film. The PL spectrum of CsSnBr₃/NaCl quantum wells were studied by adjusting the well thickness shown schematically in Figure 7.15d. When the well thickness is reduced from 100 nm to 5 nm, the emission peak redshifts (Figure 7.15e) to a similar degree as seen with colloidal nanocrystals.²⁶⁰ From fitting the size dependence of the bandgap, we can estimate an effective reduced mass of $m^* = 0.30$ m_e, where m_e is the rest mass of the electron, and the Bohr radius of CsSnBr₃ of \sim 5.6 nm). This is similar in magnitude to CdSe (5.6 nm)²⁶¹ and Si (~5nm)²⁶², smaller than PbS (20 nm)²⁶³ and larger than ZnS (2.5 nm).²⁶⁴ In moving from the weak to strong confinement regime, we expect that the bandgap of CsSnBr₃ to reach up to 3.0 eV with the smallest well thickness around 1 nm. We note that quantum wells with CsSn₂Br₅ barrier layers were also feasible through switching of the stoichiometry. As shown in Figure 7.15g, the PL spectra of CsSnBr₃/CsSn₂Br₅ quantum wells show consistent changes with those of CsSnBr₃/NaCl quantum wells when varying well thickness. A summary of the emission energy of

Quantum Well Width (nm)	Emission Peak (nm)	Emission Energy (eV)
5	654	1.896
10	664	1.867
20	669	1.854
40	673	1.842
80	684	1.813
100	685	1.810

Table 7.4. Emission energy of quantum well CsSnBr₃/NaCl with various well width.

 Table 7.5. Emission energy of quantum well CsSnBr₃/CsSn₂Br₅ with various well width.

Quantum Well	Emission Peak	Emission Energy
Width (nm)	(nm)	(eV)
20	665	1.865
40	672	1.845
80	673	1.842
100	677	1.832
100 (NaCl)	681	1.821

CsSnBr₃/NaCl and CsSnBr₃/CsSn₂Br₅ quantum well with various well width are shown in **Table 7.4 and 7.5**. This provides a route to better index-match the two layers in multiple quantum wells with enhanced potential for electrical injection.

7.5 Conclusion

In summary, we demonstrate a route to the room-temperature epitaxial growth of inorganic halide perovskites using low cost metal halide crystals and show the emergence of two epitaxial phases of cesium tin bromide (CsSnBr₃ and CsSn₂Br₅) with vastly differing lattice constants and bandgaps based on stoichiometry control. The larger lattice of CsSn₂Br₅ is accommodated via the rotation of crystal planes relative to the metal halide substrates. The phase transitions between the

cubic CsSnBr₃ and tetragonal CsSn₂Br₅ phases were manipulated and observed in real-time. The lattice misfit between the ionic epitaxial film and the substrate is precisely tuned by applying a pseudomorphic buffer layer of alloyed alkali metal halide salts and an epitaxial lift-off method has been demonstrated for further device fabrication. The dominant performance of devices fabricated with the epitaxial film confirms that the high crystallinity and low defect intensity are beneficial for halide perovskite optoelectronic applications. We further exploit the epitaxial growth of CsSnBr₃ to demonstrate multilayer epitaxial quantum wells of a halide perovskite and extract the Bohr radius for CsSnBr₃ of 5.6 nm, which provides a guide for manipulating quantum confinement in this class of materials. These demonstrations are likely to spark the exploration of a full range of epitaxial halide perovskites and help enable their ultimate potential in many emerging applications.

Chapter 8 – Epitaxial Stabilization of Tetragonal Cesium Tin Iodide (CsSnI₃)

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In this chapter, we demonstrate the single-domain epitaxial growth of cesium tin iodide (CsSnI₃) on closely lattice matched single crystal potassium chloride (KCl) substrates. One of the critical challenges for improving the optoelectronic performance of CsSnX₃-based (X = Cl, Br, and I) devices is controlling the phase during film growth. For cesium tin iodide (CsSnI₃), four different phases can form depending on the temperature including cubic (B- α), tetragonal (B- β), orthorhombic (black, B- γ) and orthorhombic (yellow, Y) phases where only the orthorhombic (black) and orthorhombic (yellow) phases are stable at room temperature.^{164, 265} These phases have different optical and electronic properties which impact carrier transport. To date, most research on CsSnI₃ focuses on the orthorhombic (black, B- γ) phase as the absorber layer.²⁶⁶ However, there has been little work on the cubic and tetragonal phases since they are both unstable at room temperature.

In the previous chapter, the epitaxial growth of the cubic and tetragonal phases of CsSnBr₃ are achieved on NaCl substrates via stoichiometry control. Using similar growth techniques, we demonstrate the room-temperature epitaxial growth of CsSnI₃ on single crystalline alkali halide salt substrate KCl. The substrate was chosen to closely match the high-temperature cubic phase lattice constants and maintain similar ionic bonding character of the film. However, we find that the epitaxial growths lead to a new stable tetragonal phase at room temperature that has a lattice constant similar to the high temperature cubic phase. This "epitaxial stabilization" method provides a route to the stabilization of a metastable phase. The impact of strain is explored by

tuning substrate lattice constants via alloyed interlayer deposition. Exploiting the precise growth enabled by vapor phase epitaxy, we also explore the quantum confinement effect in this material and determine a surprisingly small effective Bohr radius. Finally, epitaxial films of CsSnI₃ are integrated into a lateral photodetector application with good photoresponse. This work provides new insight into the stabilization of halide perovskite crystal phases and expands the selection of epitaxial halide perovskites.

8.1 Experimental

The epitaxial growth of CsSnI₃ was carried out by using a customized multisource thermal evaporator (Angstrom Engineering) equipped with a reflection high energy electron diffraction (RHEED) system (STAIB Instruments). The perovskite layer was formed by co-evaporating the precursors, CsI and SnI₂, from separate tantalum boats. Prior to growth, KCl single crystal substrates were cleaved to expose the fresh (100) surfaces in a glovebox. The base pressure during epitaxial growth was controlled to be less than 3×10^{-6} torr and the deposition rates were measured in situ with separate quartz crystal microbalances for each source. The crystal structure was monitored in real-time and in situ using RHEED (30.0 keV) optimized with an ultra-low current (< 10 nA) to eliminate damage and charging of the film over the growth times investigated. The capability of performing low-current RHEED on insulating halide crystals has been demonstrated in our previous studies.²⁶⁷ RHEED oscillations were monitored with substrates fixed at various inplane orientations (KSA400). Rotation dependent RHEED patterns were collected after the deposition was halted via substrate shutters. Quantum well multilayers were fabricated under similar growth conditions. Epitaxial KCl (barrier layer) was vapor deposited from a KCl powder source with a rate of 0.002 nm/s and a barrier thickness of 1.5 nm.

Cross-section TEM samples were prepared by focused ion beam (FIB), attached to a FEI Nova 200 Nanolab SEM/FIB, and then investigated by a JEOL 3100R05 Double Cs Corrected TEM/STEM operated in TEM mode. A carbon top-layer was deposited on the cutting area to protect the epitaxial film. Scanning electron microscopy (SEM, Carl Zeiss Auriga Dual Column FIB-SEM) was performed for *ex situ* film thickness calibration and morphology characterization. PL spectra were measured using a PTI Quanta Master 40 spectrofluorometer under nitrogen atmosphere and various excitation wavelengths. Dielectric long-pass filters were used during the PL measurement to prevent both wavelength doubling and light bleeding. UV-Vis transmission spectra were taken using a Perkin Elmer UV-Vis Spectrometer (Lambda 900). Nitrogen gas was purged during both PL and UV-Vis measurements to protect the sample during the scan.

Out-of-plane XRD and pole figure were characterized by using a Rigaku SmartLab XRD instrument with a Cu K α source at 40 kV and 44 mA and using a Ni filter in the Bragg-Brentano configuration. The sample was placed in a nitrogen sealed dome to protect from oxygen and moisture during the scan. Note that the intensity of the film peaks is reduced due to the presence of the dome. Accelerated synchrotron XRD data were collected at 100 K at the NE-CAT beamline 24-ID-C, Advanced Photon Source (APS) (wavelength: 0.0619870 nm). The sample was prepared by carefully cleaving the single crystalline epitaxial film from the substrate and mounting/folding the film onto a copper holder stored at liquid nitrogen during transferring. The data were processed with XDS as implemented in RAPD (https://github.com/RAPD/RAPD). XPS was performed in a separate chamber with a Kratos Axis Ultra XPS using a monochromated AlK α (1.486 keV) as the X-ray source. Before collecting XPS data, the films were etched by Argon ions for 1 min to prevent the interference of surface contamination.

Lateral photodetectors were fabricated by depositing a thin layer (70 nm) of Au film onto the epitaxial $CsSnI_3$ single crystalline film by e-beam deposition. The channel between the two Au electrode was fabricated by placing an Au wire (diameter 50 µm, Alfa Aesar) or a Cu wire (diameter 250 µm, Alfa Aesar) over the $CsSnI_3$ film as the mask to form the channel region. Silver paste (Ted Pella) was used to fix a gold wire onto each Au electrode for better electrical connection. The gold wires of both electrodes were connected to a customized photocurrent set-up with a Keithley 2420 source meter. Simulated AM1.5 G solar illumination (xenon arc lamp) was used as the light source, with NREL-calibrated Si reference cell with KG5 filter.



Figure 8.1. Schematic of the epitaxial growth. (A) The epitaxial halide perovskite film is grown on a single crystalline KCl (100) substrate with two precursors, CsI and SnI₂ (1:1). *In situ* RHEED is used to monitor the growth in real time. (B) A schematic of the epitaxial structure of the CsSnI₃ film on KCl (100) (Cs: orange; Sn: grey; I: purple: K: blue; Cl: light green).

8.2 Epitaxial Phase Stabilization

Thin film CsSnI₃ was grown epitaxially on KCl single crystalline substrates via reactive thermal deposition of CsI and SnI₂ with a molar ratio of 1:1, which was monitored *in situ* and realtime using reflection high-energy electron diffraction (RHEED). A schematic of the epitaxial growth is shown in **Figure 8.1b**. The freshly cleaved KCl substrate exhibits sharp streaked peaks along the [100] direction along with Kikuchi lines indicative of the single crystalline (single domain) and thick nature of the KCl substrates. After growing one monolayer of CsSnI₃, the



Figure 8.2. *In situ* **RHEED patterns of the epitaxial growth of CsSnI₃.** (a) RHEED pattern of the bare KCl substrate and 20nm of CsSnI₃. (b) Rotation dependent RHEED patterns of the smooth CsSnI₃ epitaxial film. (c) RHEED oscillations monitored by capturing the peak intensity change of the central streak of the pattern as a function of time. The observation of 0.5ML/period is consistent with the epitaxial growth of CsSnI₃. (Note the growth rate 0.02nm/s is for the reacted

pattern changes and the KCl Kikuchi patterns disappear. A new set of streaked lines emerge overlapping with the (20) streaks of KCl, along with (10) streaks between the (20) streaks (**Figure 8.2a**). These additional streaks are expected as the structure changes from a face-centered cubic (FCC) lattice of the substrate to the primitive cell of the halide perovskite. These patterns are observed without any substrate rotation, indicating good lattice matching and alignment between the film and the substrate. The streaked RHEED patterns remain essentially unchanged up to and beyond thicknesses of ~20 nm. The streaked pattern is an indication of a smooth crystalline layer which is consistent with the morphology shown in the scanning electron microscope (SEM) (**Figure 8.6c-d**). To further understand the crystal structure of the epitaxial film, rotation dependent RHEED patterns were collected (**Figure 8.2b**). The patterns collected from different azimuthal angles vary as expected for a single crystal, indicating single-domain growth is achieved



Figure 8.3. RHEED pattern of the bare KCl substrate and surface reconstruction of CsSnI_{3.} Half-order streaks are occasionally observed at high growth rate indicating a surface reconstruction of the perovskite monolayer.

across the KCl substrate. From the *d*-spacing obtained at various azimuthal angles, we obtained the lattice constant of the epitaxial film: $a = b = 0.622 \pm 0.007$ nm.

During the epitaxial growth, low source deposition rates (<0.02 nm/s) are found to aid in the formation of smoother films and more streaked patterns. If the sources are deposited with a much higher growth rate, spotty patterns quickly replace the streaked patterns from the KCl substrate, indicating that a rough crystalline film is formed. The growth mode was also studied by monitoring the intensity of the RHEED patterns (**Figure 8.2c**). When using low source deposition rates, RHEED oscillations are observed indicating Frank-van der Merwe (layer-by-layer) growth mode. Two full cycles of the oscillation are found to correspond to the growth of one monolayer (half of a complete unit cell) of the CsSnI₃ film as confirmed from *ex situ* thickness measurements (**Figure 8.2c**). This is similar to the observation for epitaxial CsSnBr₃ growth on KBr discussed in **Chapter 7**.²⁶⁸ Under certain growth conditions (e.g. high rate growth), half-order RHEED streaks sometimes appear as seen in **Figure 8.3**. This indicates the formation of a surface reconstruction. In these cases, the half-order streaks fade as the film growth proceeded to higher thickness. Because these streaks are only observed under high growth rates, it is unlikely to be indicative of the underlying growth front mechanism. That is, the growth front does not typically proceed via a surface reconstruction.



Figure 8.4. XRD and synchrotron XRD scans of epitaxial CsSnI³ (a) Out-of-plane XRD scan of 40nm of CsSnI₃ on KCl substrate and photograph of the film on a 1cm *x* 1cm substrate. The KCl (200) peak is at 28.35° (CuK_{β} and WL_{α} peaks are seen at 25.50° and 27.42°) and the CsSnI₃ (001) and (002) peaks are at 14.46° and 29.16°. (b) Synchrotron X-ray diffraction (XRD) patterns of 20nm of CsSnI3 removed from the substrate and formed into a folded (textured pseudo-powder) film. An obvious peak split is seen at 11.28° and 11.39° (inset), which corresponds to the (200) and (002) planes of the epi-tetragonal phase respectively.



Figure 8.5. Pole figure scans of CsSnI₃ on KCl. (a) The (111) pole figure scan of KCl substrate. (b-d) The (112) (021) (112) pole figure scan of 40nm of CsSnI₃ on KCl substrate. α and β are tilt and rotation angles around the sample surface normal direction. (e-f) Simulated stereographic projections of KCl and epi-tetragonal CsSnI₃, which are in good agreement with the experimental scans. Note that a couple of the (211) peaks are missing due to the slight tilt of the crystal. (The (112) (021) (112) poles for epi-tetragonal CsSnI₃ are clearly distinguishable from the KCl substrate.

Out-of-plane X-ray diffraction (XRD) data was collected to confirm the crystal structure of the epitaxial film (**Figure 8.4**). The peaks observed at 14.46° and 29.16° are the (001) and (002) of the epitaxial phase respectively, which gives a lattice constant $c = 0.612\pm0.002$ nm. Combined with the RHEED data, we determine that this is an epitaxial tetragonal (referred to as "epi-tetragonal") phase ($a = b = 0.622\pm0.007$ nm, $c = 0.612\pm0.002$ nm) stabilized by lattice matching with the KCl



Figure 8.6. TEM and SEM image of CsSnI³ **on KCl.** (a) Cross-section HRTEM image at the interface. The film is shaded in red on the left side of the image. Note a substrate step can be observed just to the bottom right of the shading. (b) SAED pattern of the film clearly indicating the tetragonal nature of the film. (c) SEM and (d) cross-section SEM image of 40nm of CsSnI³ on KCl substrate.

substrate (a = 0.629nm) that has a significantly different structure and atomic arrangement from the bulk high-temperature tetragonal phase.¹⁶⁴ The *d* spacings are well matched with the substrate in the early growth stage (within error) and remain nearly unchanged as the growth proceeds to higher thickness indicating the growth is pseudomorphic. The (112), (021), and (211) pole figure

Precursor Ratio		Real Ratio	
	Cs	Sn	Ι
1:1	1.0	1.4	2.7

Table 8.1. Elemental ratio of as-deposited CsSnI₃ film obtained from XPS data.

scans of the film are shown in Figure 8.5. These were chosen as they are clearly distinguishable from any substrate peaks and not allowed for KCl. The fixed diffraction angles for each pole figure scan are calculated from the lattice constant of the epi-tetragonal phase. The (112) and (021) pole figure show the expected 4-fold symmetry while the (211) scan show the expected 8-fold symmetry. The a/c ratio obtained from the transmission electron microscopy (TEM) highresolution images of the epitaxial interface is 1.03, which clearly emphasizes the tetragonal nature of the structure and is close to the 1.02 value obtained from diffraction data (Figure 8.6). The TEM also clearly confirms the pseudomorphic nature of the film. To further verify the crystal structure, the film was removed from the substrate and folded to obtain a pseudo-powder (textured powder) for synchrotron X-ray characterization. This data confirms that the epitaxial film is a new tetragonal phase as shown in Figure 8.4b. An obvious peak split is seen at 11.28° and 11.39° that correspond to the (200) and (002) planes of the tetragonal phase respectively. From the synchrotron XRD data fitting, we obtain lattice constants of the epitaxial film: a = b = 0.6240 nm, c = 0.6178 nm, which are close to and consistent with the XRD and RHEED analysis. The slight difference is due to the temperature difference of the scan conditions. Extrapolating the lattice constant from room temperature to 100K for comparison to the synchrotron data, the lattice constant of the cubic KCl substrate would be 0.625±0.001nm, assuming a thermal expansion coefficient 3.2x10⁻⁵/K, ²⁶⁹ which is within error of the in-plane lattice constant measured with the synchrotron (a = b =

0.6240nm). This further confirms the pseudomorphic nature of the film and is consistent with the findings from TEM.

When determining the crystal structure and phases of these compounds, it is important to consider the oxidation states. For example, Sn^{2+} and Sn^{4+} oxidation states have been observed in this class of materials, which leads to other analogs such as Cs₂SnI₆ (cubic, $a = 1.165 \text{ nm}^{270}$). This phase is ruled out from the simulated diffraction patterns (**Figure 8.7**). Furthermore, we confirm the chemical state of Sn and the ratio of these three elements with X-ray photoelectron spectroscopy (XPS). The ratio matches with the stoichiometry of CsSnI₃ and the Sn is found to have a +2 valence state in the epitaxial film (**Table 8.1**). We note that we do obverse a phase transformation from CsSnI₃ to Cs₂SnI₆ when epitaxial films are exposed to air for more than 20hrs (**Figure 8.8**). This is consistent with other reports for the B- γ and Y phases of CsSnI₃.²⁷¹ However, we do not observe this transformation for films kept in a N₂ environment under dark conditions or under illumination (~1-Sun) (**Figure 8.8**).



Figure 8.7. Simulated Cs_2SnI_6 diffraction patterns. (a) Simulated SAED and (b) XRD patterns of Cs_2SnI_{6}



Figure 8.8. Lifetime test for the epitaxial CsSnI₃ on KCl. (a) XRD patterns and (b) color change of an epitaxial CsSnI₃ film (40nm) on KCl as a function of time in the dark and exposed to air. (c) XRD patterns and (d) color change of an epitaxial CsSnI₃ film (40nm) on KCl as a function of time under light soaking and in N₂. (e) Color change of an epitaxial CsSnI₃ film (40nm) on KCl as a function of time in dark and in N₂.

Both the tetragonal phase and the cubic phase are unstable at room temperature.²⁷² Epitaxy has been commonly deployed to grow meta-stable phases at lower temperature.²⁷³ The mechanism for stabilization can include pseudomorphism (strain accommodating lattice matching) or

superstructures, while relaxation past a critical thickness would result in a bulk structure. In our case, pseudomorphism is the dominant mechanism (seen directly in the high resolution TEM and synchrotron data) where lattice matching constraints result in a phase that looks similar to the high temperature cubic phase but exhibit tetragonal distortion to accommodate the tensile strain and perovskite octahedra.



Figure 8.9. Growth of CsSnI₃ on KBr. (a) RHEED and (b) XRD patterns of $CsSnI_3$ growth on KBr.

We subsequently utilized the growth on other halide crystal salts with much larger lattice misfit (> 10%) to emphasize the control over the resulting phase. When changing the substrate to KBr (a = 0.660nm),¹⁶⁴ growth of the orthorhombic phase was observed from RHEED and XRD (**Figure 8.9**). The RHEED pattern of the film grown on KBr substrate shows the formation of rotated microdomains. The increase in misfit strain to a value where the critical thickness is less than a monolayer results in unstrained incommensurate (quasiepitaxial) film growth that then exhibits the expected room temperature orthorhombic phase.

As we have shown previously, lattice engineering by alloying epitaxial metal halide interlayer films is an effective approach to reduce the misfit strain between the film and the substrate.²⁶⁸ For CsSnI₃ growth, a thin alloyed layer (6nm) of KCl and NaCl with a ratio of 6.7:1 is grown homoepitaxially on the KCl substrate to provide a near-ideal lattice match to the halide perovskite. Streaked RHEED patterns of the alloyed layer and the epitaxial CsSnI₃ layer are shown in **Figure 8.10**. By adding a tuned pseudomorphic interlayer of alloyed alkali halide salts, the misfit defect concentration is likely to be reduced even further.



Figure 8.10. Epitaxial growth of CsSnI³ **on pseudomorphic interlayers of KCI-NaCI.** RHEED pattern of the bare KCl substrate, the alloyed growth of 5nm of KCl and NaCl (6.7:1) and 5 nm of CsSnI₃.

8.3 Optical Properties and Quantum Well Fabrication

The optical properties of the CsSnI₃ epi-tetragonal phase on KCl were studied as shown in **Figure 8.11**. The band gap energies were extracted with a Tauc plot, giving a direct band gap of 1.85 eV (**Figure 8.11a** inset). This value is consistent with the photoluminescence (PL) peak emission and onset emission at 1.47eV and 1.60eV respectively. The bandgap simulation of all the relevant phases uses the B3LYP hybrid functional using the CASTEP module in Material Studio 7.0 with the B3LYP functional. (300 eV cutoff energy with the k-points set to $2 \times 2 \times 2$ for the Brillouin zone integration). The epi-tetragonal bandgap is calculated to be 2.07 eV. This overestimation from simulation is consistent with slight overestimation for the orthorhombic phase (1.40 eV from simulation and 1.31 eV from experiment²⁷⁴). This bandgap is notably distinct from the high-temperature tetragonal phase of 0.41eV. As discussed above, the epitaxial growth allows the stabilization of a new epi-tetragonal CsSnI₃ phase. Thus, the observation of a larger bandgap is not surprising.



Figure 8.11. Absorption of the epitaxial CsSnI₃ film and PL of the quantum wells. (a) Absorption spectrum of 40nm CsSnI₃ grown on KCl substrate. The absolute absorption from the film is plotted. The Tauc plot shows the extrapolation of a direct bandgap of 1.85eV (inset). (b) PL spectra of quantum wells with well width of 17nm, 34nm and 60nm showing peaks at 838nm, 836nm and 843nm, respectively.

Quantum wells were fabricated with the halide perovskite as the well and KCl was used as a barrier to study the quantum confinement effect. KCl was grown under similar conditions to the homoepitaxial growth demonstrated previously.²⁶⁷ RHEED was used during growth to confirm that each layer was crystalline and smooth as indicated by streaked patterns. PL spectra of the quantum wells show that by varying well width from 60 nm to 34 nm, the photoluminescence peak shifts modestly from 843 nm to 836 nm indicating that the Bohr radius of CsSnI₃ is relatively small (< 10nm). A similarly small quantum confinement effect has been reported for CsSnBr₃ nanocrystals and CsSnBr₃ quantum wells.^{268, 275}

Table 8.2. Crystal structures, lattice parameters, experimental and simulated bandgaps of the CsSnI₃ cubic, tetragonal, orthorhombic and the epi-tetragonal phase from this work. Crystal structures, lattice parameters, experimental and simulated bandgaps of the cubic, tetragonal, orthorhombic and the epi-tetragonal phase from this work.¹⁶⁴ Band structure and bandgap calculations were performing using the CASTEP module in Material Studio 7.0 with the B3LYP functional.

Phase	Cubic (High T)	Tetragonal (High T)	Orthorhombic (Room <i>T</i>)	Epi-tetragonal (Room <i>T</i> , this work)
Crystal Structure Cs Sn I				
Lattice Parameters(nm)	<i>a</i> =0.62057	<i>a=b=</i> 0.87182, <i>c=</i> 0.61908	<i>a</i> =0.86885, <i>b</i> =1.23775, <i>c</i> =0.86384	$a=b=0.622\pm0.007,$ $c=0.612\pm0.002$
Experimental Bandgap (eV)	-	-	1.31 ²⁷⁴	1.85
Simulated Bandgap (eV)	0.76	0.41	1.40	2.07

8.4 Epitaxial CsSnI₃ Thin Film Based Photodetector Fabrication

Single crystalline CsSnI₃ thin film-based photodetectors were fabricated with the architecture shown in **Figure 8.12**. The CsSnI₃ film serves as the photosensitive material to absorb light and Au electrodes were vapor deposited on the epitaxial CsSnI₃ layer to collect photogenerated charge carriers. The symmetrical and linear characteristics of the current-voltage (I-V) curve indicates the ohmic contact between the Au electrode and CsSnI₃. When the channel width between the two Au electrodes is 50 μ m, the photocurrent is over two magnitudes higher than the photocurrent obtained with 250 μ m wide channel. This indicates that the width of the depletion region is less than 250 μ m. In **Figure 8.12**, the photocurrent is shown to continuously increase with increasing illumination intensity. It is noted that the photocurrent increases significantly faster at the lower range of illumination intensity. The responsivity (*R*) is a key parameter commonly utilized to evaluate the performance of a photodetector. The responsivity is calculated as:

$$R = \frac{I_{light} - I_{dark}}{P_{incident} \times A},$$
(8.1)

where I_{light} and I_{dark} represent the current measured with or without light illumination respectively, $P_{incident}$ is the incident light power density, and A is the active area. R is typically reported as a function of wavelength but can also be reported for broadband light sources. For this proof-ofprinciple demonstration we utilize the average incident white light power since we were better able to characterize the incident power density of white light versus monochromatic light in this configuration. As shown in **Figure 8.12**, the responsivity exhibits different trends from the photocurrent. As the responsivity is closely correlated to



Figure 8.12. Epitaxial CsSnI₃ based photodetector fabrication and characterization. (a) Architecture of single crystalline CsSnI₃ thin film-based photodetector. Devices with 50 μ m and 250 μ m channel width are fabricated and tested using simulated AM1.5 G solar illumination. (b) I-V characteristics of the device with 50 μ m-wide channel width under different illuminations. The arrows indicate the increase in the current when increasing the light intensity. (c) I-V characteristics of the device with 250 μ m-wide channel width under different illuminations. (d) I-V characteristics of the device with 250 μ m-wide channel width under different testing voltages. (e) Photocurrent, photoresponsivity and specific detectivity of the device with 50 μ m-wide channel at 1V.

quantum efficiency, the quantum efficiency then decreases with increasing intensity. This reduction is likely due to an accumulation of space charge that creates additional carrier scattering and has been shown to turn off halide perovskite solar cells.²⁷⁶ Nonetheless, the photocurrent is significantly higher than the solution-processed lead-based hybrid halide perovskite CH₃NH₃PbI₃ incorporated in similar device configurations.²⁷⁷ For the photodetector with an applied bias, the specific detectivity (D^*) is limited by Shot noise as:

$$D^* = \frac{R}{\sqrt{2qJ_{dark}}},\tag{8.2}$$

where q is electron charge and J_{dark} is the dark current density.²⁷⁸ The average white-light detectivity gives a value of 1.32×10^{13} Jones (cm· Hz^{1/2}·W⁻¹).

8.5 Conclusion

In this chapter, we demonstrate a route to the room-temperature epitaxial growth of another lead-free inorganic perovskite CsSnI₃ on low-cost metal halide crystals via reactive thermal deposition characterized by *in situ* and *ex situ* diffraction techniques. This growth is investigated on KCl (100), KBr (100), and alloyed (NaCl/KCl) interlayers on KCl. The growth on KCl (100) reveals a new room temperature epitaxial tetragonal phase of CsSnI₃ that is closely lattice matched to the KCl. In contrast, the growth observed on KBr (with large misfit) results in quasiepitaxial films with the orthorhombic phase (common room temperature phase) and rotated microdomains. We further exploit the epitaxial growth of CsSnI₃ to demonstrate multilayer epitaxial quantum wells and lateral photodetectors. This work provides insight into the control over phase and ordering during halide perovskite epitaxial growth and expands the selection of photoactive materials for growing epitaxial halide perovskites that can be exploited in high performance electronic applications.

Chapter 9 – Conclusions and Future Outlook

In the first part of this work, organic crystalline is systematically studied. Homoepitaxy growth modes were mapped as a function of growth rate and temperature on high quality organic crystalline substrates. Organic-organic hetero-quasiepitaxy was studied showing energy mismatch (<20%) of lowest energy surfaces (LES) is ideal for achieving ordered alternating growth. A unique organic edge driven nucleation case was demonstrated providing new ideas for controlling molecular orientation. These growth studies on organic multilayer structures could motivate the exploration of organic exciton confinement phenomena and opens new opportunities for enhanced excitonic tunability. The control over the crystalline order and orientation demonstrated in this work are the key to managing energy transport for novel organic semiconductor devices.

In the second part of this work, we demonstrate a low-cost route to single domain halide perovskite thin film growth with excellent crystalline order that is lacking with solution processing. We utilize *in situ* RHEED on insulating alkali halide crystalline surfaces to investigate the homoepitaxial growth studies of alkali halide crystals. Phase studies including phase control by manipulating precursor ratio and phase stabilization were demonstrated. Photoluminescent tunability was observed for epitaxial perovskite layer-based quantum wells with different well width. These rsults could spark the exploration of a full range of epitaxial halide perovskites and lead to novel applications for metal-halide-perovskite based single-crystal epitaxial optoelectronics. Below, future work on organic-organic quasiepitaxy and perovskite epitaxy are discussed.

9.1 Molecular Dynamics (MD) Simulation of Organic Surface Diffusion

Understanding factors that govern molecular diffusion are key for gaining insight and control over epitaxial and organic quasiepitaxial growth modes. The balance between deposition
rate, grain nucleation, grain growth, equilibrium surface potential depth, and molecular diffusion are important for achieving highly ordered films. For hetero-quasiepitaxial systems, higher surface diffusion would help increase the ordering of each layer during the multilayer growth. Initial MD simulations were performed to study this effect that should be 1) expanded to organic-on-organic simulations and 2) experimentally verified.



Figure 9.1.The set-up of the admolecule-substrate system. The anthracene on KBr (100) is shown as an example.

Based on the initial exploration of organic surface diffusion using classical forcefieldbased molecular dynamics, we developed algorithms that we have applied to a large variety of admolecule/substrate systems for greater molecular combinations. The effect of molecular shape, molecular weight, and conjugation on surface diffusion behavior was studied with eight different organic admolecules. The molecules were selected by considering molecules that only have C-C and C-H bonds with varied shape, molecular weight, and aspect ratio. Simulations were performed on the same crystalline substrate, KBr (100) using Berendsen thermostat under COMPASS forcefield with the following procedure: 1) Start with a canonical isothermal ensemble (NVT) to set T, 2) Use a microcanonical constant energy ensemble (NVE) to run the experiment under more realistic fixed system energies, and 3) repeat the simulation for each



Figure 9.2. E_m and D_0 plots as a function of L/W and molecular weight (M). E_m plotted as a function of (a) L/W and (b) M for the eight molecules studied. Corresponding D_0 plotted as a function of (c) L/W and (d) M.

temperature with 30-40 runs for good statistical averaging. The example model for anthracene is shown in **Figure 9.1.** The diffusion process in these cases follows the Arrhenius behavior (**Equation 2.9**) The diffusivity (*D*) is extracted as the slope from the mean square displacement (*MSD*) as a function of time (*t*) according to (**Equation 2.10**). The diffusion barrier E_m can be obtained from the slope of a ln*D* vs. 1/*T* plot. Since D_0 is mechanistically composed of two contributions, the attempt frequency and the average hopping distance, we looked to separate the trend in the attempt frequency. Therefore, the trajectory is imported and analyzed in Matlab to extract the localized time (% $L_{ocalized}$) and fractional time of a molecule travel along [10]&[01] direction of the substrate (% $T_{<01>}$). The former should be inversely proportional to the attempt frequency. In general, we found a complex dependence of activation energy with length/width (L/W) aspect ratio. Close to an aspect ratio of 1, the activation barrier starts off very low and increases with increasing L/W, reaches a maximum, and then decreases with L/W. For highly symmetric molecules it is not surprising to observe both low E_m and D_0 . There is little driving force for the molecule to preferentially hop in a particular crystallographic direction resulting in little barrier for motion in any particular direction but also resulting in only short hops. In contrast, for highly anisotropic molecules there can be stronger barriers to find alignment along molecular axes of the substrate that can result in larger energetic barriers for hopping but larger hops when overcome. For D_0 we do not see a correlation to aspect ratio but rather see more straightforward trend of decreasing magnitude with increasing molecular weight (**Figure 9.2**). We find that larger L/W increases the localized time on the substrate, which is observed at both low T and high T conditions. Thus, we suggest that L/W > 1 can promote diffusion along crystallographic directions of the substrate indicated by longer fractional time along these trajectories (**Figure 9.3**), which is



Figure 9.3. (a) Fractional localized time ($\%T_{Localized}$) vs. *L/W*. (b) Fractional time of a molecule travel along <01> ($\%T_{<01>}$) vs. *L/W*.

more obvious at high *T*. This study suggests the activation energy and the attempt frequency are closely related to the anisotropy of the molecule.

Further studies are warranted on the simulation of admolecules on inorganic substrates

with other surface orientations such as KBr (111), (110), etc. and on organic substrates with different orientations (different surface energy). Step edges can also be introduced and could provide computational evidence to the organic edge driven mechanism discussed in **Chapter 5**.

9.2 Organic-organic Charge Transfer (CT) Complexes

In **Chapter 4 and 5**, we demonstrated the ability to grow ordered organic crystalline structures using bottom-up vapor-deposition routes. A key challenge moving forward is the ability to integrate conductive layers into organic quasiepitaxial multilayers to fabricate complete organic epitaxial devices. However, the growth of pure metals in these systems generally prevent the ability to maintain organic crystalline ordering grown from the bottom up. Organic CT complexes provide an enticing solution to this problem. We have demonstrated sustained alternating quasi-epitaxial layers of two organic semiconductors 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA), and dibenzotetrathiafulvalene-tetracyanoquinodimethane (DB-TCNQ) grown on single crystal substrates via vapor phase deposition. Both in-plane and out-of-plane ordering were



Figure 9.4. Preliminary results on alternating growth of charge transfer salts. (a) In situ RHEED patterns of alternating NTCDA/DBTTF-TCNQ growth on single crystal substrates. Ordering for over 2 pairs has been achieved with this combination, where there is a close surface energy matching of the LESs. (b-c) RHEED patterns of TTF-TCNQ and TCNQ growth. (d) RHEED patterns of alternating TCNQ/TTF growth.

preserved for each subsequent layer under optimized growth conditions despite the vastly differing lattice constants and lattice symmetries (**Figure 9.4a**). Other potential starting layers such as tetrathiafulvalene 7,7,8,8-tetracyanoquinodimethane (TTF-TCNQ) and TCNQ were preliminarily investigated using *in situ* diffraction (**Figure 9.4b-c**). Both materials show single crystalline like growth on KBr suggested by the rotation dependence of RHEED patterns. Paired growth of TCNQ/TTF have also been studied and show viable crystalline growth across the multilayer structure (**Figure 9.4d**). Based on these results, more growth pairings should be studied with greater growth optimization to identify and map quasi-epitaxial growth modes of select organic charge transfer single crystal thin films.

9.3 Expand Halide Perovskite Heteroepitaxial Growth Pairings

In **Chapter 7 and 8**, the heteroepitaxial growth of CsSnBr₃ and CsSnI₃ on metal halide single crystals are discussed. It is important to expand these growth studies to other lead-free perovskite compositions including CsSnCl₃ (to complete the CsSnX₃ series) and double perovskites such as Cs₂AgInCl₆, Cs₂AgBiX₆, Cs₂AuBiX₆, Cs₂CuBiX₆ (X=Cl, Br, and I), etc.²⁷⁹ as well as lead based compounds.

Such future studies can start with metal halide single crystals substrates that are most closely matched to each composition. Parameters such as growth temperature, pressure, stoichiometry and strain can be studied to clarify the specific accessible phase is at certain growth condition. Lattice engineering (described in **Chapter 7 and 8**) can be used to modify the surface lattice constant of the substrate by adding a pseudomorphic alloyed layer based on the Vegard's rule,

$$a_k = xa_i + (1 - x)a_j \tag{10.1}$$

where the alloyed lattice constant (a_k) is a linear function of the lattice constants from the two constituent materials with lattice constant as a_i and a_j . This method has been proved to help growing smooth crystalline growth based on the CsSnBr₃ growth on alloyed NaCl/NaBr and CsSnI₃ growth on alloyed KCl/NaCl that are discussed in **Chapter 7 and 8**.

9.4 Epitaxial Halide Perovskite Doping

To open up the possibilities for epitaxial perovskite film-based applications, controlled doping achieved by neat layer doping or modulation (delta) doping can be studied. ²⁸⁰ Neat layer doping is a method that can be achieved by co-evaporation of dopant and perovskite composition. The direct neat layer doping could affect the structural integrity of the quantum wells, thus modulation (delta) doping can be introduced. In modulation (delta) doping, the dopants are spatially separated from the well barrier layers so that the epitaxial layer is deposited on top of a doped single crystalline substrate.

9.5 Epitaxial Halide Perovskite Applications

After we understand the effect of doping methods and concentration on these epitaxial halide perovskites layers, it is possible to incorporate them into multilayer structures to build a range of interesting electronic devices including photodetectors, light emitting diodes (LED), and high mobility transistors. Since tunable optoelectronic properties were demonstrated with halide perovskite quantum well (QW) structures in **Chapter 7 and 8**, transport measurements should be performed o to explore interesting low temperature and quantum-based physics.

APPENDIX

List of publications and patent from this thesis

(1) Chen, P. and R.R. Lunt, Organic Step Edge Driven Heteroquasiepitaxial Growth of Organic Multilayer Films. *Adv. Mat. Interfaces*, 2016. **3**(17): p. 1600401.

(2) Chen, P., et al., Homoepitaxial Growth of Metal Halide Crystals Investigated by Reflection High-Energy Electron Diffraction. *Sci. Rep.*, 2017. 7: p. 40542.

(3) Wang, L., Chen, P., et al., Unlocking the Single-Domain Epitaxy of Halide Perovskites. *Adv. Mat. Interfaces*, 2017. **4**(22). (Co-first author)

(4) Wang, L., Chen, P., et al., Epitaxial Stabilization of Tetragonal Cesium Tin Iodide. ACS *Appl. Mater. Interfaces*, 2019. (https://doi.org/10.1021/acsami.9b05592, co-first author)

(5) Wang, L., Chen, P., Lunt, R. R. Method for Fabricating Epitaxial Halide Perovskite Films and Devices, filed as U.S. provisional patent application on June 13, 2017.

Additional publications

(1) Traverse, C. J.; Chen, P.; Lunt, R. R. Lifetime of Organic Salt Photovoltaics. *Adv. Energy. Mater.* 2018, 8 (21), 1703678.

(2) Liu, D.; Traverse, C. J.; Chen, P.; Elinski, M.; Yang, C.; Wang, L.; Young, M.; Lunt, R. R. Aqueous-Containing Precursor Solutions for Efficient Perovskite Solar Cells. *Adv. Sci.* 2018, 5 (1), 1700484.

(3) Liu, D., Yang, C., Chen, P., Bates, M., Han, S., Askeland, P.A. and Lunt, R.R. Lead Halide Ultraviolet-Harvesting Transparent Photovoltaics with an Efficiency Exceeding 1%. *ACS Appl. Energy Mater.* 2019

(4) Kuttipillai, P. S., Yang, C., Chen, P., Wang, L., Bates, M., Lunt, S. Y., & Lunt, R. R. Enhanced Electroluminescence Efficiency in Metal Halide Nanocluster Based Light Emitting Diodes through Apical Halide Exchange. *ACS Appl. Energy Mater.* 2018, 1(8), 3587-3592.

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Figure A.1. Cover Picture for Advanced Materials Interfaces Volume 3, Issue 17 (September 2016). Corresponding article: *Organic Step Edge Driven Heteroquasiepitaxial Growth of Organic Multilayer Films.*



Figure A.2. Cover Picture for Advanced Materials Interfaces Volume 4, Issue 22 (November 2017). Corresponding article: *Unlocking the Single-Domain Epitaxy of Halide Perovskites*

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