Instrumentation Development for Interfacial Studies and Analysis of Substrate-Supported Molecular Thin Films by Reflection High-Energy Electron Diffraction

A Thesis Presented to

the Faculty of the Department of Chemistry

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

By

Karjini Rajagopal

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Instrumentation Development for Interfacial Studies and Analysis of Substrate-Supported Molecular Thin Films by Reflection High-Energy Electron Diffraction

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ABSTRACT

Chemical and physical properties at interfaces play key roles in understanding a number of diverse phenomena. A better molecular-level understanding of the interfacial interactions is needed to utilize them in the potential applications. Different surfaceanalysis techniques have their own distinct level of surface sensitivity and probe different surface characteristics of the system of interest. Our interest is to directly visualize the structure of atoms and molecules at interfaces of the substrate-supported molecular thin films using reflective high-energy electron diffraction (RHEED). The shorter wavelength of an electron compared to typical bond lengths and its larger scattering cross section make it ideal for surface and interfacial probing.

Interfacial behaviors in structure, interactions, phase transition, and thermal evolution of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[EMIM][Tf_2N]$) vapor deposited ionic liquid (IL) thin films on substrate surfaces such as highly oriented pyrolytic graphite (HOPG), Hydrogen terminated Si(111), mica, Cu(111) and Ni(111) were studied. By comparing the ordered structural behavior of 3 nm thick [EMIM][Tf₂N] film on HOPG with other surfaces, it is found that the terrace surface morphology of HOPG plays a role as a template for vertical stacking of IL ion pairs. The phase transition of [EMIM][Tf₂N] on HOPG happened at 256 K, which matches with the melting point of bulk [EMIM][Tf₂N] IL. The desorption of 3 nm [EMIM][Tf₂N] IL from substrate happened starting from 340 - 360 K to ~ 375 K.

As a second system, the interfacial structural ordering of water molecules on cadmium telluride (CdTe(111)A) surface and oxidized CdTe(111)A surface was investigated. A molecular beam doser system was developed to deposit the water molecules in a controlled and quantitative way. On CdTe(111)A surface, the deposited water molecules became ordered ice crystallites by adopting the geometry of the underlying substrate as evidenced by the Bragg diffraction spots. On oxidized CdTe(111)A surface upon deposition, initially formed amorphous water layer turned into Debye–Scherrer diffraction rings indicating the randomly oriented ice crystallites of cubic ice form. From the studies of both systems, the main role of the supported substrate in the ordering of molecules at the interface is found.

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Chapter 1

Introduction

Surfaces and interfaces are the platforms for most of the chemical reactions that occur in our planet starting from nature to man-made technological devices. In comparison to the bulk material, the molecular environments at surfaces and interfaces are unique. The molecules in the bulk are surrounded by other neighboring molecules and experience an isotropic force field. In contrast, the molecules at interfaces that are in contact with gases, liquids or solid surface are subjected to unbalanced forces which lead them to arrange and interact differently than the bulk phase.¹ To gain a better molecular-level understanding of their interfacial interactions and utilize them in potential applications, we have to gather information such as the physical topography, the chemical composition, the structural arrangements, the electronic state, the description of bonding and reactivity of molecules at the interface. A detailed understanding of surface phenomenon needs several surface techniques since each technique has its own distinct level of surface sensitivity and probes different surface characteristics of the system of interest.²

Our interest is to directly visualize the structure of atoms and molecules at interfaces that is invisible to our naked eye. Those are much smaller in size, from nanometer to angstroms level. For the direct visualization of the interfacial structure, we need to reach the spatial resolution down to that level using an appropriate probe. This importance of atomic level probing was shown very clearly when 2014 was declared as the International Year of Crystallography (IYCr2014) by United Nations and celebrated as a successful 100th year of crystallography in remembrance of the first Nobel prize for crystallography awarded to Max von Laue in 1914 for discovering how crystals can

diffract X-rays. Then the second Nobel Prize in crystallography was shared in 1915 by Lawrence Bragg and his father William Bragg, who introduced the famous Bragg's law in X- ray diffraction studies. These remarkable discoveries founded the atomic-level visual science of crystallography to influence in all areas of chemistry, biology and physics even after a century of time.³ In addition to x-ray diffraction method, electron and neutron diffractions are also used in the structural analysis of natural and synthetic crystals, other condensed state of matters ranging from simple to high-tech materials and complex biological structures.

Our choice for the visualization of interfacial structures at atomic or molecular level is by reflective high energy electron diffraction (RHEED) using 30 keV electrons that have wavelength (~ 0.07 Å) shorter than typical bond lengths. Larger electron scattering cross section makes it ideal for surface and interface probing and RHEED is mostly used to monitor the film growth process due to its grazing incidence geometry.⁴ This thesis focuses on the interfacial studies of substrate-supported molecular thin films under ultrahigh vacuum conditions (UHV) by RHEED technique and the related instrumentation development.

In Chapter 2, important fundamentals of electron diffraction are discussed. Chapter 3 provides a description about the UHV apparatus used and developed for the current interfacial analysis. Chapters 4 and 5 present the interfacial studies on substratesupported molecular thin films. In Chapter 4, for the first time we introduce RHEED as a UHV based technique useful in directly visualizing the interfacial behaviors in structure, interactions, phase transition, and thermal evolution of the 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) ionic liquid on different kind of substrates such as highly oriented pyrolytic graphite (HOPG), H/Si(111), mica, Cu(111) and Ni(111). We found that substrate plays a main role in the ordering of the ion pairs. Due to the terrace morphology HOPG substrate, vertically stacked ordered crystal structure of [EMIM][Tf₂N] is facilitated to grow in the surface normal direction.

Lastly in Chapter 5, analysis of interfacial water assembly on solid substrates is presented. We developed a molecular beam doser system to deposit molecules from vapor phase to prepare solvent thin films. As an initial system, the interfacial structural ordering of water molecules on cadmium telluride (CdTe(111)A) surface and oxidized CdTe(111)A surface were investigated by RHEED technique under ultrahigh vacuum (UHV) environment. Upon annealing the deposited water film, ordered water layers were formed as evidenced by the Bragg diffraction spots. On the other hand, water film on oxidized CdTe(111)A surface showed Debye–Scherrer diffraction rings indicating the randomly oriented ice crystallites. Hence a lattice effect of CdTe(111)A assists the ordered ice formation which is absent when the surface is oxidized. Chapter 2

Fundamentals of Electron Diffraction

2.1 Electron Crystallography

The electron was discovered by J. J. Thompson as a negatively charged particle in 1897. In 1924, wave-particle dualism for electrons was postulated by De Broglie by considering Einstein's theory about the wave–particle duality of light. Later in 1927, this nature of electron was proved by Davisson and Germer with low energy range and by Thomson and Reid in high energy range electron diffraction experiments.^{5,6}

Geometrical theory of electron diffraction of electrons is similar as X-rays, but electrons have smaller wavelengths, 10⁵ times larger electron scattering cross-section, and show different radiation-matter interactions compared to X-rays. X-ray being an electromagnetic wave they interact with the electron cloud surrounding the atoms, whereas electrons are charged particles that get scattered by the positively charged nuclei and the surrounding electrons in the atom. For our analysis, kinematic theory which considers the elastic scattering and neglects the multiple scattering produced by the incident electron beam, is used to calculate the geometry of the reflection high energy electron diffraction (RHEED) pattern.^{7,8}

Due to the behavior of electron beams as particle waves, they possess characteristic wavelengths and wave vectors and involve in one or more of phenomena such as refraction, reflection, diffraction, and absorption. Electron wavelength λ is given by the de Broglie relation as,

$$\lambda = \frac{h}{p} \tag{2.1}$$

Where p is the electron momentum and h is Planck's constant. The relation between electron momentum and kinetic energy in classical mechanics is given as,

$$\lambda = \sqrt{\frac{h^2}{2mE}}$$
(2.2)

When λ is in Å and E in eV, the above equation can be written as (h = 6.626 x 10⁻³⁴ J s, m = 9.1 × 10⁻³¹ kg),

$$\lambda (in \text{ Å}) = \sqrt{\frac{150.4}{E (in \, eV)}}$$
(2.3)

In our case, we use 30 keV electron energy. Hence λ is 0.07 Å. For highly accelerated electrons with energies > 50 keV, relativistic effects cannot be neglected. Using Dirac's equation,

$$(E + m_o c^2)^2 = m_o^2 c^4 + p^2 c^2$$
(2.4)

Where $m_o = \text{rest}$ mass of electron. The relativistic wavelength is given by,

$$\lambda = \sqrt{\frac{h^2}{2m_o E (1 + E/E_o)}}$$
(2.5)

Where $E_o = 2m_o c^2$.



Figure 2.1: Bragg reflection from lattice planes. (AB = BC= d $sin(\theta/2)$, path difference is $2dsin(\theta/2)$)

Bragg formulation applies to electron as well. As shown in Figure 2.1, we can consider the crystals made of planes of atoms separated by distance, d. Strong diffraction peaks will be produced if the angle of incidence (ϑ) satisfies the following Bragg condition. Where n is the order of diffraction.

$$n\lambda = 2d \, \sin\left(\frac{\vartheta}{2}\right) \tag{2.6}$$



Figure 2.2: Elastic scattering process.

For elastic scattering, amplitude of incident $(\overline{k_i})$ and scattered (\overline{k}) wave vectors are same.

$$|k| = |k_i| = \frac{2\pi}{\lambda} \tag{2.7}$$

Scattering vector s is given by,

$$s = k - k_i \tag{2.8}$$

$$|s| = \left(\frac{4\pi}{\lambda}\right) \sin^{\vartheta}/2 \tag{2.7}$$

The diffraction patterns observed in this geometry are a direct reflection of the structural features in reciprocal space which is a Fourier transform of real space lattice. From the real lattice vectors (\vec{a} , \vec{b} , and \vec{c}), reciprocal lattice vectors (\vec{a}^* , \vec{b}^* , \vec{c}^*) can be written as,

$$\vec{a} \cdot \vec{a}^* = \vec{b} \cdot \vec{b}^* = \vec{c} \cdot \vec{c}^* = 2 \pi$$
$$\vec{a} \cdot \vec{b}^* = \vec{b} \cdot \vec{c}^* = \vec{c} \cdot \vec{a}^* = \vec{b} \cdot \vec{a}^* = \vec{c} \cdot \vec{b}^* = \vec{a} \cdot \vec{c}^* = 0$$
(2.8)

$$\vec{a}^* = 2\pi \frac{\vec{b} \times \vec{c}}{\vec{a} \cdot (\vec{b} \times \vec{c})}, \ \vec{b}^* = 2\pi \frac{\vec{c} \times \vec{a}}{\vec{b} \cdot (\vec{c} \times \vec{a})}, \ \vec{c}^* = 2\pi \frac{\vec{a} \times \vec{b}}{\vec{c} \cdot (\vec{a} \times \vec{b})}$$
(2.8)

The Laue condition is satisfied when $\exp(i \vec{s} \cdot \vec{R}) = 1$, where $\vec{R} = \text{set}$ of vectors connecting atoms of the Bravais lattice in real space. For any reciprocal lattice vector (\vec{G}) , it can be written as,

$$\vec{G}_{hkl} = h \, \vec{a}^* + k \, \vec{b}^* + l \, \vec{c}^* \tag{2.9}$$

Where *h*, *k*, and *l* are integers called Miller indices.

Hence, $\exp(i \vec{G} \cdot \vec{R}) = 1$. The Laue condition of constructive interference is satisfied if and only if $\vec{s} = \vec{G}_{hkl}$, for certain *h*, *k* and *l*.

The Ewald sphere construction is a graphical method by which the conditions of constructive interference and single elastic scattering are combined to find the directions of diffracted intensity maxima (Figure 2.3). The reciprocal lattice rods extend normal to the sample's surface and that the RHEED pattern is a picture of these rods.



Figure 2.3: Ewald sphere construction for RHEED geometry.⁹

RHEED patterns have relationship with the surface topography. An amorphous surface gives diffusive pattern with fuzzy rings, polycrystalline materials give a series of defined concentric rings, flat and clean crystalline surfaces produces sharp spots, clean, wavy or two dimensional surface gives streaks, surface with protrusions shows transmission like pattern.¹⁰ Due to the glancing incident geometry of RHEED technique, these structural information we get are sensitive to surface rather than bulk. Considering the elastic scattering with 30 keV energy, the elastic mean free path (Λ_{el}) of electrons for carbon containing thin films is 55 nm ($\Lambda_{el} = 1/N \sigma_{el}$, where N = number of atoms per unit volume and σ_{el} = total elastic cross-section).¹¹ Using this, for 1° glancing incident angle, these electrons can probe 4.8 Å depth of the surface. For a surface containing Cu atoms ($\Lambda_{el} = 7.8$ nm), depth of 0.68 Å can be probed using same conditions as above. These numbers provide a figure of merit estimate for the probed depth from which the diffraction patterns are generated. Therefore for the thin films having lighter atoms, the probed region is on the order of one to few nanometers. For the thin films with heavier atoms, essentially the top layers are being probed. These parameters are useful in the surface sensitive analysis mentioned in Chapter 4.

Chapter 3

The UHV Apparatus for Interfacial Analysis

3.1 Introduction

This chapter provides an introduction to the reader about the ultrahigh vacuum (UHV) apparatus used in this thesis. Surface analysis at molecular level needs surface cleanliness and the interactions of probes with the surrounding gaseous molecules has to be fully eliminated. Hence the usage of ultra-high vacuum (UHV) conditions are essential. The general setup of the chamber is briefly explained with its facilities for interfacial studies.

3.2 UHV Chamber System

The UHV chamber system is custom made with flanges or ports available for the attachment of instruments for analysis (Figure 3.1). It has a main chamber for diffraction studies and a preparation (load lock) chamber for sample preparation. A gate valve is installed in between these two chambers to isolate them. The isolated main diffraction chamber with the ion pump for evacuation, can reach 10^{-10} Torr pressure level. An electron gun, phosphor screen, a charged-couple device (CCD) camera, 5-axis goniometer (manipulator), molecular dosing system, are Residual gas analyzer assembled at the main diffraction chamber. The isolated preparation chamber is pumped with a turbo molecular pump that is connected to a scroll pump (Figure 3.2). A sample transfer arm, sample storage and heating assembly, ion sputtering gun, effusion cell, and residual gas analyzer are assembled at the preparation chamber. The pressure readings at the chambers are measured by convection vacuum gauges (1 x 10^{-9} to 5 x 10^{-2} Torr).



Figure 3.1: Schematic of the UHV apparatus for RHEED studies.



Figure 3.2: Vacuum pumps at preparation chamber (a) Scroll pump, (b) Turbo molecular pump.

3.2.1 Five-Axis Goniometer

Inside the main diffraction chamber, the sample is movement controlled using a high precision goniometer (from McAllister Technical Services, ID, USA) with 3 degrees of freedom in translation (x-, y-, and z- directions) and 2 axes (Φ , and ϑ) of rotation (Figure 3.3 (b)). The sample holder on the goniometer is coupled to a Model ST-400 UHV Supertran continuous flow cryostat system (Janis Research Company, MA, USA), which allows for both liquid nitrogen and liquid helium cooling. A needle valve is incorporated in the transfer line, and is used to regulate the flow of cryogens to the sample mount. For experiments requiring higher temperature, the sample holder can be heated using the electrical wires installed underneath the goniometer up to approximately 500K. (Our temperature dependent experiments in Chapter 4 and Chapter 5 utilize this system)



Figure 3.3: Diagram of 5-axis goniometer. (a) Full view from top, (b) Five degrees of freedom of high-precision goniometer, (c) A photo showing the mounted sample inside the diffraction chamber.

3.2.2 Electron Gun and CCD Camera

Our electron gun (from The Kimball Physics, NH, USA) uses a lanthanum hexaboride (LaB_6) cathode to provide a small electron spot, down to 10 µm with 30 keV beam energy (Figure 3.4 (a)). The electron gun has a blanker element which diverts the electron beam into an in-line Faraday cup and provides a means of cutting off the beam while the gun is running. During our RHEED analysis in Chapter 4, beam blanking was used to eliminate the beam damage to the sample. Our CCD camera, an Aspen® model (from Apogee Imaging Systems, CA, USA), that has a 36 x 23.9 mm imaging area with 7.4 x 7.4 microns pixel size. It is coupled to the phosphor screen attached to the diffraction chamber (Figure 3.4 (b)). The image saving is controlled by the Labview program.



Figure 3.4: Diagram of electron gun and electron probing. Schematic diagrams of (a) electron gun, (b) the set up for electron diffraction.

3.2.3 Ion Sputter Gun

Our Ion sputter gun is a Model NGI3000 ion gun (from LK Technologies, Inc., IN, USA) designed for cleaning surfaces in UHV by noble gas ion sputtering. We leak ultrapure Ar gas through a leak valve to produce Ar^+ ions by electron impact ionization using this ion gun. The Ar^+ ion beam (energy from 0.2 to 3 kV) is then accelerated out of the ionization chamber (canister) to the target.



Figure 3.5: Photo showing the Ion Sputter Gun.

3.2.4 Quartz Crystal Microbalance

We have a customized design of quartz crystal microbalance (from Nor-Cal, CA) as shown in Figure 3.6. It has a 14 mm diameter quartz crystal with 6 MHz resonant frequency with gold electrode material as a sensor material. It is attached in a sensor head placed in the direct view of the evaporation source. The quartz crystal utilizes its piezoelectric property that accumulates charge and oscillates upon the mass change sensed during the thin film deposition process. A 2.75" CF flanged feed through connects to the sensor head using 55° bent water cooling lines and connects a vacuum coaxial cable to transfer the quartz crystal's piezo-electric vibrations to the oscillator. Oscillator then conditions the signals and transfers to the deposition monitor connected to a computer, from where we can get the thickness readings. A schematic diagram of QCM sensor is given in Appendix A.1.

With the increase in the mass deposition Δm_q , decreases the oscillation frequency shift of the crystal Δf . This is given by the Sauerbrey equation,¹²

$$\Delta f = -\frac{2f_o^2}{\rho_q v_q} \frac{\Delta m_q}{A_q} \tag{3.1}$$

Where, f_o = the resonant frequency of the crystal, ρ_q = the density of the quartz, v_q = the speed of the propagating acoustic wave and A_q = the effective area of the quartz crystal.



Figure 3.6: Quartz Crystal microbalance (QCM) sensor. (a) Image of QCM sensor indicating sensor head, in-vacuum signal transfer cable, water cooling lines, and the BNC connector at feedthrough, (b) Top view with attached Quartz crystal.

3.2.5 Single Filament Effusion cell

Our effusion cell is a commercially available low-temperature cell with operating temperature from 0 - 600 °C (from SVT Associates, MN) and customized to fit our length requirements. It is installed on the top port at the preparation chamber and out gassed prior to operation. The material to be evaporated is loaded in to the 10 cm³ crucible made of high purity graphite which is welded inside the housing made of Inconel alloy via the exit hole shown in Figure 3.7 (c) and 3.7 (d). The heating temperature is controlled by the Eurotherm 2216e controller unit. The needed temperature for the evaporation is obtained by the current level set at the controller and the crucible temperature is read using a type K thermocouple. The evaporation flux is controlled by an attached movable shutter under the crucible exit hole (Figure 3.8 (b)).





Figure 3.7: Effusion cell and its parts (a) Assembly of effusion cell on preparation chamber, (b) effusion cell with its furnace and shutter, (c) Crucible or Ionic Liquid Reservoir, (d) bottom view of crucible with the exit hole for IL, (e) View after insertion of crucible into the heating furnace, (f) Side view of the heating jacket.

b)

3.2.6 Molecular Beam Dosers

In the surface science research, the quantitative exposure of gas molecules on a substrate is used as an experimental technique to study the interaction of gas phase adsorbates with the surface of a substrate.¹² The molecular beam doser has become a tool to probe these interactions with the surface of interest in a controlled environment.¹⁴ There are many applications at present still using the simple valve control techniques which results in a high chamber pressure to expose the sample. This method can deteriorate the base pressure of chamber and introduce uncontrolled gas influx due to outgassing from the other parts of the chamber such as walls, manipulator parts, and hot filaments. To overcome this situation and enhance the gas flux on surface of the sample over the background gas, directional dosing systems have been explored.¹³

The three common designs of directional doser types available are single capillary doser, pinhole doser, and multichannel capillary array doser. The first type of single capillary (or "needle") doser having small aspect ratio (diameter/length), emits a highly directional and excellent enhancement of adsorbate flux over the diffuse background when the length of the capillary is comparable to the distance to the sample. In most situations the flux distribution is considered to be uneven and it is a sharply peaked function of solid angle. In the second type of doser design, pinhole doser ("cosine emitter") is considered to provide the adsorbate flux through an orifice of a thin metal foil. Compared to the earlier type, its larger aspect ratio provides flux distribution which gradually decays as the cosine of the angle measured from its centerline, more uniform flux with lower enhancement. The third type uses a multichannel capillary array made out of dense grids of parallel capillaries. An excellent uniform total flux is obtained due to the superposition of flux distribution when the capillary array has comparable size with the sample and good flux enhancement can be obtained by positioning the doser at a very small distance to the sample.¹⁵

3.2.6.2 Design of Molecular Beam Doser and Gas Handling System

For the controlled and quantitative exposure of surface to gas molecules, a molecular beam dosing system is designed and built consisting a gas-handling system with a microchannel capillary array beam doser as shown in Figure 3.1. The dosing system is installed on the top port of the main chamber using a 6" customized zero-length reducer flange such that the tip of the doser is centered at the substrate on the sample holder. This zero-length reducer flange has two ports, one 2.75" CF port for dosing assembly and a 1.33" CF port for the entry of optical pump pulse. The need of these two ports, makes the 2.75" CF port of the doser to offset by 0.83" from center of the flange. Due to this space constraints as shown in Figure 3.2 (a), the UHV side of the doser line has a 45° bend before the head of the doser.

The gas handling system (GHS) is constructed using 0.5" outer diameter (OD) stainless steel tubing (from Kurt J. Lesker Company, OH) with Swagelok® VCR fittings at the vacuum side and Swagelok fittings at the high pressure side (from Swagelok Company, Solon, OH). The VCR vacuum fittings provides leak-tight metal to metal seal by compressing the stainless steel metal gasket in between the male-female nuts. This system is equipped with convection pressure gauges for pressure monitoring, scroll pump for rough pumping and turbo molecular pump for fine pumping to evacuate the gas vapors.



Figure 3.8: Schematic of Gas Handling System with Micro Capillary Array Beam Doser.



Figure 3.9: Shematic diagram of doser body (a) Doser body with 45° connector, (b) Doser head with the order of insertion of baffle, Microchannel plate and its cap, (c) Crossectional view of doser head.



Figure 3.10: Real view of doser head (a) Top view of doser head, (b) doser head with attached baffle, (c) side view of doser head, (d) After complete assembly of MCP.

Single-Ended Miniature Sample Cylinders of 50 ml volume with VCR fittings are used as gas bottles (from Swagelok Company, Solon, OH). The gas delivery lines from the gas bottle are connected to blowdown needle valves with Swagelok fittings (from Swagelok Company, Solon, OH). After performing freeze pump thaw cycles (described in section 3.2.6.3) to degas the solvent in the gas bottles, the pure solvent vapor is allowed to fill the gas delivery line and directed to a precision leak valve (from Kurt J. Lesker Company, OH), which provides a fine leak of low pressure gas molecules to enter into the doser. This GHS is attached to the 9.2" long feedthrough with 2.75" CF flange (custom-made from Nor-Cal, CA), which is mounted on a manual Z-shift translator (from McAllister Technical Services, ID). This provides the flexibility to move the doser system in order to adjust the doser to sample distance and retract the doser housing up when it is not in use.

The leaked gas flux from leak valve enters through the orifice (from Lenox Laser, MD) with a 2 μ m diameter made out of stainless steel mounted inside the VCR fitting as a deformable gasket controls the effusion rate of gas molecules and acts as a flow restrictor inside the doser head. The motion of gas flux from this pinhole aperture is randomized before striking the micro capillary array plate using a baffle made of oxygen free copper material as the shape shown in Figure (3.9 (b)). The baffle is attached to the doser head using two stainless steel socket head cap screws and is lifted at two sides by inserting 2 mm height Cu tube spacers. This design of baffle plate allows the gas molecules to randomize into the doser head to reach the tip of the doser where a micro channel plate is held in place by a doser cap. Our micro channel plate (from PHOTONIS USA, MA) has 10 mm outer diameter, 1.00 mm thickness, 5 μ m pore size, and zero bias

angle where millions of glass capillary tubes are fused together perpendicularly to the input surface to provide uniformly arranged mechanically rigid structure. It also has NiChrome coating at its surfaces to avoid charge accumulation. When the randomized gas molecules from baffle enters this micro channel plate, it serves as a collimator to gain uniformity of gas flux across the surface of the substrate. This plate is seated in the tip of the doser head (Figure 3.10 (b)) inside a groove of 0.0375" depth and held by a 0.63" thick doser cap as shown in Figure (3.9 (b)). (A detailed drawing of the design is given in Appendix A.6) using four socket head cap screws.

3.2.6.3 Operation of Doser

The solvent to be used as a source of gas vapor molecules is added to the gas bottle and degassed initially by ultrasonication using an ultrasonicator. After assembling the gas bottle to GHS, solvent is subjected to freeze-pump-thaw cycle. Using this technique, solvent is frozen using liquid nitrogen. When the solvent is frozen, open the blowdown needle valve (Figure 3.1) and pump off the unfrozen vapor and other gases left in the space using the scroll pump for 10 - 30 min. Then valve is closed and the solvent is allowed to thaw using a room temperature water bath to produce pure vapor. Again the solvent is frozen using liquid nitrogen and this cycle is repeated for three times.

Once the pure solvent vapor produced and introduced in the line, the leak valve is opened to the desired pressure to allow the gas to enter into the doser to deposit on the sample at low temperature. After the desired time of dosing, the leak valve is closed and the gas vapor is dumped by opening the bellow sealed valve to the roughing line connected to the mechanical pump. For the fine evacuation of the line, valve to mechanical pump is closed and the valve to the turbo molecular pump is opened (Figure

3.1). In the above steps, convection pressure gauges are used for pressure monitoring.

3.2.6.4 Calculations

The gas flow can be categorized into viscous, molecular and translational. In viscous flow, intermolecular collisions of gases occur more frequently than collisions with the walls of the container. Molecular flow happens when the gas molecules collide dominantly with the walls of the container and both types of collisions occur in the translational flow. When we consider a fine leak with small dimensions of leak channel, the gas flow through it can be assumed as in the molecular flow regime.¹⁷



Figure 3.11: Schematic arrangement of doser components: gas reservoir, flow restriction, effusion source, emitter, sample chamber and pumping direction.

As Shown in the above figure, a molecular dosing system can be considered with three parts namely reservoir, effusion source and chamber to get a quantitative understanding of the gas flow through it. For a long tube of uniform cross-section, the molecular conductance (C) is given as,¹⁶

$$C = \frac{1}{4} A_r \nu_a \tag{3.2}$$
Where, A_r = the cross-sectional area in cm², v_a = the average velocity in cm/sec,

$$v_a = \sqrt{\frac{8RT}{\pi M}} \tag{3.3}$$

Where, R = gas constant, T = absolute temperature, M = mass of one molecule.

By substituting for v_a and A in equation (3.2),

$$C = \frac{1}{4} \left(\pi \ \frac{D^2}{4} \right) \sqrt{\frac{8RT}{\pi M}}$$
(3.4)

The equation (3.4) can be simplified as,

$$C = \frac{D^2}{4} \sqrt{\frac{\pi RT}{2M}}$$
(3.5)

By applying Dushman's vacuum conductance correction factor K' to the equation (3.5), it can be written as,¹⁷

$$C = \frac{D^2}{4} \sqrt{\frac{\pi RT}{2M}} \times K' \tag{3.6}$$

Where D = diameter of the orifice and *K*' is,

$$K' = \frac{1}{1 + \frac{3l}{4D}}$$

Equation (3.6) can be re written as,

$$C = \frac{D^2}{4} \sqrt{\frac{\pi RT}{2M}} \frac{1}{1 + \frac{3l}{4D}}$$
(3.7)

Substitution of our system parameters ($D = 2 \ \mu m$, $l = 127 \ \mu m$, $T = 300 \ K$, $M = 28.0134 \ g/mol$) in equation (3.7), conductance of the orifice is calculated as 7.691 x 10⁻⁹ 1 s⁻¹. Conductance of the emitter can also be calculated by the same equation.

In the real system conditions, the flux of molecules striking the sample from doser (i.e., the number of gas molecules emitted from the doser in unit time) is affected by the factors such as the doser-to-sample distance, temperature of the sample, sticking coefficient (i.e., the ratio of molecules stick to the surface to the total number of molecules impinge on the surface during a time period), and pumping speed of the chamber. Let F = the flux of molecules from doser, N_{tot} = total number of molecules emitted by the doser in molecular flow regime, f = measure of the efficiency of a particular doser configuration and A = area of the sample.

$$F = f \frac{N_{tot}}{A} \tag{3.8}$$

Where N_{tot} can be written as,

$$N_{tot} = A_r P_r \sqrt{\left(\frac{N_A}{2\pi M k_b T}\right)}$$
(3.9)

Where A_r = area of the orifice, P_r = pressure of gas at orifice, k_b = Boltzmann's constant, and N_A = Avogadro's number.

The pressure on the sample results from this flux (F), P_{doser} can be written as,

$$P_{doser} = \sqrt{\left(\frac{2\pi M k_b T}{N_A}\right)} f N_{tot} / A \cong f\left(\frac{A_r}{A}\right) P_r$$
(3.10)

From the total number of molecules emitted by the doser (N_{tot}), if fN_{tot} molecules strike the sample, (1- fN_{tot}) molecules will contribute to the background pressure as they are missed by the sample. All the molecules that strike the sample may not stick. By considering the sticking coefficient (s), sfN_{tot} molecules will stick and $(1-s)fN_{tot}$ will reflect from sample. Hence, the total amount of molecules (*N*) responsible for the background pressure in the chamber can be written as,

$$N = (1 - sf)N_{tot} (3.11)$$

Since the number of molecules entering the chamber is equal to the number of molecules being pumped out of the chamber at equilibrium, *N* can be written as,

$$N = \frac{PS}{k_b T} = (1 - sf)N_{tot}$$
(3.12)

Where, S = pumping speed (240 l s⁻¹), and P = background pressure. Therefore P is,

$$P = (1 - sf)(\frac{k_b T}{S})N_{tot}$$
(3.13)

The effective pressure (P_{eff}) and the corresponding flux (F_{tot}) are,

$$P_{eff} = P_{doser} + P = \sqrt{\left(\frac{2\pi M k_b T}{N_A}\right)} f N_{tot} / A + (1 - sf)(\frac{k_b T}{S}) N_{tot}$$
(3.14)
$$F_{tot} = \sqrt{\left(\frac{N_A}{2\pi M k_b T}\right)} P_{eff}$$
(3.15)

We can rewrite equations (3.13) and (3.14) as,

$$P \cong \frac{(1-sf)C_r P_r}{S} \tag{3.16}$$

$$P_{eff} \cong f\left(\frac{A_r}{A}\right)P_r + \frac{(1-sf)C_rP_r}{S}$$
(3.17)

From the above equations using the 2 μ m flow restriction aperture, for H₂O vapor with 10 Torr pressure, conductance can be calculated as 9.59 x 10⁻⁹ l/s with the molecular

flux of $3.0 \ge 10^{+14}$ molecules/cm²/s. Deposition of water molecules for 30 min will result in ~ 170 nm thick film of cubic ice form on top of a substrate held at low temperature. Usage of this doser is mentioned in Chapter 5. Chapter 4

Analysis of Solid-Supported Ionic Liquid Thin Films

4.1 Introduction

4.1.1 Ionic Liquid

Room-temperature ionic liquids (RTILs) are novel class of chemical solvents, which have attracted the scientific interest over the past decade for numerous applications. RTILs are composed solely of cations and anions; where in general, these cations are organic compounds with low symmetry and anions are weak basic organic or inorganic compounds. Due to the ionic nature, RTILs might be expected to be crystalline solid at room temperature, but they stay as liquid having melting point below 100° C. The reason for the low melting point is the lattice packing of sterically mismatched cation and anions with low charge densities leading to weak intermolecular interactions.¹⁸⁻¹⁹ A few common cations and anions are shown in Figures (4.1), and (4.2). The resulting combination of these positive and negative ionic pairs can form large structural diversity

1-alkyl-3-methylimidazolium

1-alkyl-pyridinium

Dialkylpyrrolidinium





Tetraalkylphosphonium

Trialkylsulfonium

 $R_{1,2,3,4}$ = alkyl chains (ethyl, butyl, hexyl, octyl, decyl)

Figure 4.1: Common cations in ionic liquid preparation.



Figure 4.2: Common anions in Ionic liquid preparation.

in RTILs with unique physico-chemical properties. Apart from the low melting point, RTILs show other remarkable properties such as extremely low volatility, non-flammability, wide electrochemical window, very large liquid range, electro-conductivity, high thermal stability, unusual solvation and miscibility characteristics.¹⁸ These properties make them suitable for many chemical applications including solvent for chemical reactions and separation process,²⁰⁻²¹ organometallic catalysis,²² lubrication,²³ electrochemistry,²⁴ and photovoltaic power generation.²⁵ Most of these applications involve in reactions at RTIL – solid interfaces. For the advancement of these applications, a better molecular level understanding of the interfacial interactions, molecular arrangements and topography of solid supported ionic liquid thin films is needed to be investigated.

In most situations, surface analysis at molecular level needs surface cleanliness and the interactions of probes with the surrounding gaseous molecules has to be fully eliminated. Hence the usage of ultra-high vacuum (UHV) conditions are very essential. At earlier surface studies, UHV compatibility of RTILs were not known.²⁶ The surfacesensitive techniques such as sum frequency generation (SFG),²⁷ X-ray and neutron reflectometry,²⁸⁻²⁹ surface tension measurements,³⁰ grazing incidence X-ray diffraction,³¹ and molecular dynamic simulations that need not require UHV environment have been employed.³² Later on, it was realized that the property of negligible vapor pressure of RTILs can be utilized for the studies inside UHV without the contamination of the system. Therefore UHV-based surface analysis techniques such as X-ray photoelectron spectroscopy (XPS),³³ UV photoelectron spectroscopy (UPS),³⁴ inverse photoelectron spectroscopy (IPES),³⁵ near-edge X-ray absorption spectroscopy (NEXAFS),³⁵ metastable ion spectroscopy (MIES),³⁶ direct recoil spectroscopy (DRS),³⁷ high resolution electron energy loss spectroscopy (HREELS),³⁸ low energy ion scattering (LEIS),³⁹ time-of-flight secondary mass spectroscopy (TOF-SIMS),⁴⁰ soft X-ray emission spectroscopy (SXES),⁴¹ Rutherford backscattering (RBS),⁴² Infrared reflection absorption spectroscopy (IRAS),⁴³ and helium atom scattering technique are being applied to obtain the atomic level accuracy in the analysis.⁴⁴ These surface techniques have distinct level of surface sensitivity and probe different surface characteristics of the system of interest. Hence a single technique may not provide all the needed interfacial information. Therefore combinations of these techniques are needed for the complete analysis of RTIL-solid interfaces.45-46

Success of the probing technique greatly depends on the preparation of the sample for analysis. Here our main focus is towards the thin-film samples on a solid substrate. Techniques such as spin-coating,⁴⁶ dip-coating,⁴⁷ continuous wave infrared (CW-IR) laser deposition,⁴⁸ physical vapor deposition,⁴⁹ electrospray ionization deposition are being used in thin film preparation of RTILs during the past years.⁵⁰ A variety of substrates such as glass, ³³ alumina, ⁴³ highly oriented pyrolytic graphite (HOPG),⁴⁶ Au(111),^{44,50} Ni(111),⁵¹ mica,⁵² and silica are used as a solid support for the deposition of RTIL thin films.⁴⁷



Figure 4.3: Possible arrangements of cations and anions on a substrate. (a) and (b) Bilayer or sandwich arrangement, (c) Alternating cations and anions in a checkerboard arrangement and h indicates 1 monolayer (ML) coverage on surface. (not drawn to scale), (d) Formation of drop-on-layer for thicker films.

As shown in Figure 4.3, relating to previous studies, initial RTIL growth on solid substrate is found to be arranged in sandwich (or bilayer) arrangement with either anions or cations in direct contact with the surface or in checkerboard arrangements with alternating cations and anions that are in direct contact with the surface. The layering occurs two dimensionally (2D) by wetting process or three dimensionally (3D) by dewetting process depending on the chemical nature of the IL and substrate.⁵¹ If the RTIL film is ultrathin, it can form solid like layering and with thick films, less attraction between solid – RTIL and increase in cation-anion cohesion that can lead to the formation of droplets or sponge-like structures (Figure 4.3 (d)).⁴⁷ A rough estimate for the height (*h*) of 1 monolayer (ML) can be estimated from the bulk molecular volume (V_m) using equation (4.1).⁴³

$$h = \sqrt[3]{V_m} = \sqrt[3]{\frac{M/_{N_A}}{\rho}}$$
(4.1)

Where M = molar mass of IL, $\rho =$ mass density of IL, $N_A =$ Avogadro's constant. For example if we consider the RTIL as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]), M = 391.31 g/mol , $\rho =$ 1.52 g/cm³ , $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$, the approximated h value is calculated as 7.53 Å.

We selected 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][Tf₂N]) RTIL for our initial interfacial studies by RHEED (details of IL are given in Table 4.1). The alkyl substituted imidazolium cations are widely studied and several factors such as thermal stability having higher decomposition temperature ($[Tf_2N]^-$ > halides), low H- bonding ability with atmospheric water ($[Tf_2N]^- < [ClO_4]^- < [NO_3]^- < [CF_3CO_2]^-$), matching size of the packing anion ($[Tf_2N]^- = 7.89527$ Å) and

cation ($[EMIM]^+ = 7.52821$ Å) compared to other alkyl substituents on cation (Figure 4.4), low viscosity compared to larger alkyl group substitution in the imidazolium cation, and the available crystallographic data for $[EMIM][Tf_2N]$) were considered in selecting the RTIL for our study.⁵³⁻⁵⁴

Table 4.1:	Details	of IL	<i>investi</i>	gated	in	this	study
				0			

Name and	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide							
Abbreviation	$[C_2C_1Im][Tf_2N]$] or [EMIM]	$[Tf_2N]$					
Chemical	C	Cation			Anion			
structure								
	3 N							
Physical	Molecular	Melting	Decon	nposition	Density	Viscosity		
state	weight	point	temperature					
Colorless liquid	391.31 g mol ⁻¹	256 K	52	23 K	1.52 gcm ⁻³	39.4 mPa s		



Figure 4.4: Sketch of the ion pairs (a) $[Tf_2N]^-$ anion and (b - e) 1-alkyl-3-methyl imidazolium cations; (alkyl group = methyl, ethyl, propyl, and butyl).

4.1.2 Physical Vapor Deposition

Vapor deposition process allows to prepare uniform, well-defined in situ thin film in the range of few nanometers to thousands of nanometers from thermally stable substrates. It is classified into physical vapor deposition (PVD) and chemical vapor deposition (CVD). PVD can be again categorized in to vacuum evaporation, ion plating, sputtering, and pulsed laser deposition. In a PVD method, the source material is energized using heat, plasma or laser to vaporize it and then thin film is deposited on the wanted substrate.⁵⁵ In our case, we used vacuum evaporation which is a PVD process by heating the thermally stable RTIL. In the preparation of IL thin films, this method is considered to be advantageous than other techniques involve with IL solutions in volatile solvents and evaporating the solvent to obtain the thin films because the introduction of impurities during the PVD process is lower.³³ We perform the PVD process at our lab using an effusion cell (Details are given in Chapter 2 –Apparatus – Single filament effusion cell).

Here in my current study, for the first time we introduce reflection high-energy electron diffraction (RHEED) as another UHV-based technique useful in directly visualizing the interfacial behaviors in structure, interactions, phase transitions, and thermal evolution of the RTIL on different kind of substrates such as HOPG, H/Si(111), mica, Cu(111) and Ni(111). We found that substrate plays a main role in the ordering of the ion pairs. Due to the terrace morphology HOPG substrate, vertically stacked ordered crystal structure of [EMIM][Tf₂N] is facilitated to grow in the surface-normal direction. Atomically flat H/Si(111) shows no template structure for guided growth of IL. Mica substrate's charging nature didn't allow to probe the structural changes and the surface

roughness of metallic single crystals of Cu(111) and Ni(111) also affects the structural growth of IL.

4.2 Materials and Experimental Section

4.2.1 Operation of Effusion Cell and Calibration Using QCM

Knudsen effusion cell and QCM (details are given in Chapter 3) are assembled to our preparation chamber having fixed orientation with 0.5" source to QCM sensor distance. The RTIL, [EMIM][Tf₂N] (Ultrapure, > 99.5 % purity, used as obtained from IoLiTec Inc., AL, USA) was loaded to the crucible and deposited on QCM from vapor phase from the evaporation source held at temperature ranging from 60 °C to 180 °C. The optimization of the deposition conditions was carried out at 1 x 10⁻⁷ Torr. Initially effusion cell current was set to 0.7A to reach 50 °C (1 hour), then current levels 1.8 A, 1.9 A, and 2.0 A were tried. It took longer time (>3 hours) to get the desired rate (~ 1 Å/s) for deposition, which was monitored from the thickness controller. Then higher currents (e.g. 1 A, and 2 A) were applied at the beginning. During the evaporation process, the partial pressure readings from residual gas analyzer for the mass fragments of [EMIM][Tf₂N] were also reordered. The protocol to obtain a reasonable rate was finally found by applying 2 A current at the beginning, and continue heating for 2 hours until it reaches 158 – 160 °C while monitoring the mass peak-111 from [EMIM]⁺ cation.

Infrared spectrums of the IL inside crucible, IL deposited on quartz crystal and shutter were obtained using IR spectrometer in transmission mode. Samples were prepared by placing a drop of IL sample and sandwiching in between two CaF_2 (transmission range from 896 – 79500 cm⁻¹) disks.

4.2.2 Sample Preparation of Different Substrates

The substrates, HOPG, Si(111), mica, Cu(111) and Ni(111) used in this study were purchased from MTI Corporation, CA. Different methods were used to obtain the freshly cleaned surfaces for each substrates. Highly Oriented Pyrolytic Graphite - HOPG of 10 mm x 10 mm x 1.0 mm was cleaved using a scotch tape and immediately mounted on the sample holder using a Cu tape and transferred to the vacuum chamber immediately.

An atomically flat hydrogen-terminated H/Si(111) sample was prepared from a Si(111) wafer (p –type, B doped, 0.5 mm thick, resistivity: 1-10 ohm-cm). A piece of Si(111) wafer was first etched using HF for 20 seconds followed by rinsing in miliQ water and drying using He gas. It was then mounted on a sample holder using Cu tape and transferred to the preparation chamber.

Highest grade mica disk of 9.9 mm diameter was cleaved using scotch tape to obtain the fresh flat surface. Then it was mounted on a sample holder using Cu tape and transferred to the preparation chamber quickly to minimize the exposure to air.

The metal samples, Cu(111) single crystal (10 x 10 x 1.0 mm in size, 1 side polished) and Ni(111) single crystal (5 x 5 x 0.5 mm, 1 side polished) were mounted on the sample plates as received and transferred to the preparation chamber. After checking the surface condition by reflective high-energy electron diffraction (RHEED) at main chamber, they were sputtered with 1.5 keV Ar⁺ ions to remove the surface contaminants such as oxides and hydrocarbons. Sputtering times were 1 min, and 1.5 min for Cu(111) and Ni(111) samples respectively.

4.2.3 Deposition of [EMIM][Tf₂N] IL on Different Substrates

[EMIM][Tf₂N] thin films were prepared by the physical vapor deposition from the low temperature effusion cell (details are given in Chapter 3 - UHV Apparatus - low temperature effusion cell). For the evaporation, a cleaned crucible was filled with 3.5 ml of $[EMIM][Tf_2N]$ IL and attached to the effusion cell assembled on the preparation chamber. To avoid bubbling of IL, the chamber was slowly pumped by the turbo molecular pump to reach UHV pressure level overnight. Based on the thickness calibration data from QCM, effusion cell was given 2 A current and kept for 130 minutes prior to evaporation on the substrate. At this condition, the effusion cell temperature is 158 - 160 °C and the rate of deposition is ~ 0.5 Å/s. During the deposition, the substrate is kept at room temperature at the middle of the chamber using the transfer arm to match the exit hole of the crucible. Several IL thin films with several thickness were obtained (1.2nm, 3 nm, 20 nm films for HOPG, 3 nm on mica, Si(111), Cu(111) and Ni(111) substrates). After deposition, the IL – substrate sample is transferred to goniometer at the main chamber (held at ~ 10 $^{-10}$ Torr) for the RHEED studies. For the phase transition studies, goniometer was cooled by liquid nitrogen to reach ~ 88 K then heated to anneal the sample to room temperature. For the desorption studies, the sample stage was heated to reach ~ 420 K. During each temperature-dependent study, 30 keV electron beam was blanked for every 0.5 K change to minimize the beam damage to the IL thin film. [The following temperatures of the sample held in goniometer (during cooling, annealing and desorption studies) are reported using the temperature reading measured at the bottom of the sample mounting Cu head. An independent and direct measurement of substrate's

surface temperature shows that during higher temperatures ~ 200 - 300 K, the uncertainty of the temperature reported in the following could be ~ 5 °C].

In order to find the wettability of the IL on substrates (Cu(111), mica, HOPG, H/Si(111), rock salt (NaCl), Sapphire (Al₂O₃)), contact angle measurements of 5 μ l IL droplet on substrate surface were examined by a contact angle goniometer (from Ramè-hart, Inc, NJ, USA).

4.3 Results and Discussion

4.3.1 Calibration of Film Thickness by QCM

The optimized protocol from this calibration was found as to apply 2 A current to the effusion cell to heat the crucible to reach 158 -160 °C temperature in 2 hours duration. A relationship between the rate and the partial pressure of cation mass peak - 111 (from residual gas analyzer partial pressure readings for mass peak - 111) was found as shown in Figure 4.5. From the graph, the rate of IL deposition at the particular time can be found. From that, the thickness of the deposited IL film can be estimated.



Figure 4.5: Variation of Partial pressure of cation mass peak -111 (in blue) and Rate of deposition (in green) with time.

In addition to 111- cation peak from partial pressure vs mass spectrum of RGA, mass peak at 64 due to SO₂ from $[Tf_2N]$ ⁻ breakage and mass peak at 82 due to 1methylimidazole from $[EMIM]^+$ breakage were observed when the vaporized $[EMIM][Tf_2N]$ hit the hot filament of RGA.⁵⁶ To confirm that the deposited ion pairs remain intact after thermal evaporation after the long hours of calibration process, the IL sample deposited on the quartz crystal, shutter and the remained IL from crucible were subjected to IR spectroscopic analysis. The obtained IR spectrums were compared with the original ionic liquid from the bottle. By the comparison of IR spectrum in Figure 4.6, the original [EMIM][Tf₂N] as received from bottle (in blue) and [EMIM][Tf₂N] from crucible after several evaporations during calibration (in red) shows the coinciding peaks except 3567 – 3650 cm⁻¹ region due to the absorption of moisture after few hours exposure of crucible in the laboratory atmosphere. Peak assignments of IL stretching/bending modes are given in Table 4.2 given below.⁵⁷



Figure 4.6: Comparison of IR spectrums of original $[EMIM][Tf_2N]$ as received from bottle (in blue) and $[EMIM][Tf_2N]$ from crucible after several evaporations during calibration (in red).

Comparison of the IR spectrums of original $[EMIM][Tf_2N]$ as received from bottle (in blue) and $[EMIM][Tf_2N]$ from shutter after several evaporations during calibration process (in green) is given in Figure 4.7. This also indicates us the coinciding IR peaks of both samples.

Frequency, v / (cm ⁻¹)	Vibrational peak assignments		
	Ring in-plane antisymmetric stretch, C-C stretch,NCH ₃ twist,		
1060	SNS antisymmetric stretch		
1139	SO ₂ symmetric stretch		
1202	CF ₃ antisymmetric stretch		
1353	SO ₂ antisymmetric stretch		
1/32	Ring in-plane antisymmetric stretch, $CH_3(N)$ CN stretch, $CH_4(N)$ HCH symmetric bend		
1432			
1.455	CCH HCH antisymmetric bend, CH ₃ (N)HCH symmetric bend,		
1457	terminal CH ₃ HCH antisymmetric bend		
1472	Ring in-plane antisymmetric stretch, CH ₃ (N) stretch		
1576	ring in-plane symmetric / antisymmetric stretch, CH ₃ (N) stretch, CH ₂ (N) CN stretch		
2951	Terminal CH ₃ HCH antisymmetric stretch		
2993	CH ₃ (N)HCH antisymmetric stretch		
3125	Ring NC(H)NCH stretch		
	Ring HCCH antisymmetric stretch, ring in-plane symmetric		
3161	stretch		
3567 3650	Additional peaks due to the presence of moisture upon exposing		
5507, 5050	the IL to laboratory atmosphere.		

Table 4.2 Assignment of the obtained IR bands of [EMIM][Tf₂N]

The amount of sample deposited on quartz crystal is very low for the sample preparation for IR spectroscopy. IL on quartz crystal was dissolved in acetone to obtain the spectrum. As shown in Figure 4.8, apart from the acetone peaks (in blue), we can obtain the matching IR peaks for the deposited IL and the original IL. Based on the results from IR spectroscopy, we can make sure that both ions, $[EMIM]^+$ and $[Tf_2N]^-$ were deposited as ion pairs without any decomposition due to the thermal conditions used in our current study.



Figure 4.7: Comparison of IR spectrums of original $[EMIM][Tf_2N]$ as received from bottle (in blue) and $[EMIM][Tf_2N]$ from shutter after several evaporations during calibration (in green).



Figure 4.8: IR spectrum from quartz crystal. (a) snapshot of the quartz crystal using optical microscope showing the deposited IL droplets, (b) Comparison of IR spectrums of original [EMIM][Tf₂N] as received from bottle (in green), [EMIM][Tf₂N] from quartz crystal after several evaporations during calibration (in red) and solvent (acetone) spectrum (in blue).

4.3.2 [EMIM][Tf₂N] Thin Film on HOPG

4.3.2.1 Analysis of 3 nm Film

After the deposition of [EMIM][Tf₂N] ionic liquid, the HOPG diffraction pattern becomes weaker and the deposited IL gives diffuse scattering due to its mobile liquid nature. The HOPG pattern is still faintly present and it indicates the very thin IL film in few nanometer thickness. As we began to cool the substrate (Figure 4.9 (c)), at around 220 K the [EMIM][Tf₂N] IL started to crystallize showing the formation of Bragg spots, which were different from the diffraction of HOPG. The sample was continued to cool till it reaches 88 K (Figure 4.9 (d)). The fully crystallized IL at 88 K showed very fascinating distinct Bragg spots in the vertical direction. In close observation, we can observe weak spot pattern in the horizontal direction as well.







Figure 4.9 : RHEED pattern of 3nm [EMIM][Tf₂N] on HOPG (a) HOPG bare substrate, 3nm [EMIM][Tf₂N] film on HOPG at 290 K (b), at 220 K during cooling (c), (d) Fully crystallized [EMIM][Tf₂N] thin film on HOPG at 88 K.

As shown in Figure 4.10, the spacing between the spots were calculated by the vertical and horizontal line profiles of Bragg spots. The vertical spacing was calculated as 9.46 Å (by measuring the pixels of the image in CCD camera and converting it in the real space using camera length = 140 mm, de Broglie wavelength of electron = 0.07 Å) and the spots are regularly arranged in similar distance. The horizontal spacing was calculated as 8.49 Å.



Figure 4.10: Estimation of the separation of Bragg spots. (a) RHEED pattern of IL at low temperature, (b)Vertical line profile of IL Bragg spots along Y-Y', (c) Horizontal line profile of IL Bragg spots X-X'.

The reported crystalline [EMIM][Tf₂N] has a orthorhombic crystal structure (space group $Pca2_1$), with lattice constants a = 18.499 Å, b = 8.626 Å, and c = 19.255 Å (Figure 4.11 (a)). ³⁸ Our calculated vertical spacing is similar to the half of the lattice constant c and horizontal spacing is similar to the lattice constant b. The observed vertical ordered structure is possible due to the terrace morphology of HOPG with interlayer

distance of 3.35 Å between the parallel graphene planes of its structure (Figure 4.11 (b)). Three of the graphene planes with 3.35 Å in HOPG can accommodate half of the unit cell of [EMIM][Tf₂N] crystal in c direction along the cleavage shown in Figure 4.11 (b) within 4% mismatch [((19.225/2)/(3.35*3))*100 = 4.2 %]. Hence we can confirm that, this well-defined intense nature of the vertical Bragg spots represents the vertically stacked IL layers which is facilitated by the surface morphology of the HOPG substrate. The lateral ordering seems to be weak by looking at the intensity of the horizontal Bragg spots. It tells us that it is not fully random but affected by several configurations along that direction. An azimuthal (φ) rotation was carried out for the substrate with IL at 88 K. No other diffraction spots appeared during the rotation. It tells us the absence of other horizontal orientation of the IL on HOPG. RHEED patterns for each 30° rotation is given in Figure 4.12.





Figure 4.12: Diffraction patterns during the rotation of phi (ϕ) angle. (a) initial probing position, (b) rotated by 30° angle, (c) rotated by 60° angle.



Figure 4.13: RHEED patterns for 3 nm IL film showing (a) annealing of IL film on HOPG at 250 K (b) annealing of IL film on HOPG at 270 K, and (c) Observation of the diffraction intensity of IL Bragg spot with temperature of the indicated spot on left panel during annealing.

During the annealing process to room temperature by heating (Figure 4.13), the Bragg spots of [EMIM][Tf₂N] started to get weak around 240 K and the diffraction intensity of the indicated IL spot started to drop. Diffraction intensity decreased faster during 245 K to 254 K. After 255 K, it shows the disappearance of the ordered IL Bragg spots. This is related to the phase transition from ordered crystal phase to disordered liquid phase, which matches with the melting point (256 K) of the bulk [EMIM][Tf₂N] IL.



Figure 4.14: Desorption of 3 nm IL thin film on HOPG, (a) before desorption at 296 K, (b) during desorption at 355 K, (c) desorption at 375 K (d) Indication of the HOPG streak chosen for the analysis during desorption, (e) Plot showing intensity variation of the HOPG spot with increase of temperature during desorption

The desorption behavior of the [EMIM][Tf₂N] on HOPG substrate was analyzed by the RHEED intensity variation of the indicated HOPG spot shown in Figure 4.14. During desorption, it can be seen that the diffraction intensity of the indicated HOPG spot starts to rise at 340 K, and considerable IL ions pairs desorb during 340 K to 375 K. The sharp peaks or sudden intensity variations from the graph is due to the movement zdirection of manipulator to check the desorption behavior at other positions on HOPG surface. This intensity change at different positions is also a clear evidence of the presence of HOPG steps. After 375 K, HOPG diffraction pattern is very clear indicating the full desorption of IL from substrate. The obtained residual gas analyzer (RGA) partial pressure readings for the cation mass peak -111 are shown in Figure 4.14 (f), this indicates a slight increase in the partial pressure of 111- peak. But the sensitiveness of the RGA is low due the chamber volume and its located position from sample.

To compare this observation of ordered Bragg spots formation due to the substrate assisted crystallization of 3 nm IL film thickness, a thinner film (1.2 nm) and a thicker film (20 nm) of IL on HOPG were studied as shown in the following section.

4.3.2.2 Analysis of 1.2 nm and 20 nm Thin Films

Thin films of $[EMIM][Tf_2N]$ having 1.2 nm and 20 nm thickness on HOPG were prepared and treated with the similar cooling, annealing, and desorption processes described above. After the deposition of thinner (Figure 4.15) and thicker (Figure 4.17) IL films on HOPG, both the RHEED pattern show diffuse scattering. Upon cooling to 100 K and annealing to 290 K, no noticeable changes occurred to indicate the crystallization of the IL. The thinner film has thickness of 12 Å, which is smaller than the lattice constant (c) of 19.255 Å. Absence of crystallization is due to the insufficient thickness to form a full unit cell of $[EMIM][Tf_2N]$. The thicker IL film is 200 Å in thickness, which is about the height of 10 unit cells of $[EMIM][Tf_2N]$ crystal. The absence of ordered structure is due to the decay of strong interfacial substrate assisted ordering when it reaches a bulk like thick IL film.

Desorption behavior of thin and thick film happens as expected. The RHEED intensity of the appearance for HOPG pattern during the desorption of 1.2 nm IL film (Figure 4.16) shows that desorption slightly starts at 360 K. After 360 K, intensity of HOPG Bragg spot rises and becomes stable around 380 K, which shows a full desorption of IL. For the thick film (Figure 4.18), it took longer time to desorb fully at higher temperature around 410 K. In both cases partial pressure variation also show the same trend in desorption temperatures.



Figure 4.15: RHEED patterns for 1.2 nm IL film analysis (a) bare HOPG substrate, (b) After deposition of ~ 1.2 nm IL thin film,(c) Decrease T to 95 K. (d) At room T after annealing at 290 K, (e) During desorption at 360 K, (f) After full desorption at 380 K.



Figure 4.16: Intensity variation of 1.2 nm film during desorption. (a) Plot showing intensity variation of the HOPG spot with increase of temperature during desorption, (b) Plot of partial pressure of peak 111 vs desorption temperature.

After observing the substrate assisted ordering in HOPG, we wanted to try the deposition of IL on other types of substrates with different surface properties. In the following sections, [EMIM][Tf₂N] IL thin film analysis on substrates such as Si(111); an atomically flat surface, mica; a charged surface, Cu(111) and Ni(111); single crystal metal surfaces are given. Their behaviors during cooling, annealing and desorption are discussed.



Figure 4.17: RHEED patterns of 20 nm IL film on HOPG, (a) – (c) cooling of IL film on HOPG, (d) – (f) annealing of IL film on HOPG, (g) – (i) desorption of IL film on HOPG.



Figure 4.18: Desorption of 20 nm IL film from HOPG (a) Plot showing intensity variation of the HOPG spot with increase of temperature during desorption, (b) Plot of partial pressure of peak 111 vs desorption temperature.

4.3.3 [EMIM][Tf₂N] Thin Film on H/Si(111)

Hydrogen terminated Si(111) is an atomically flat hydrophobic surface. Deposition of IL 3 nm IL thin film gave diffusive diffraction pattern denoting the randomly oriented IL ions pairs on the surface (Figure 4.19 (b)). RHEED patterns during the cooling and annealing of the substrate covered with IL thin film remained same as the one obtained after deposition (Figure 4.19). This observation tells us the atomically flat H/Si(111) surface provides no template structure for the substrate guided growth of ionic liquid along a certain direction. Desorption of ionic pairs happened around 350 - 360 K (Figure 4.19 (g), 4.19 (h)).



Figure 4.19: RHEED patterns of IL – H/Si(111). (a) bare H/Si(111), (b) after IL deposition, (c) After cooling to 97 K, (d)-(f) desorption of IL from Si(111), (g) Plot showing intensity variation of the Si(111) spot with increase of temperature during desorption, (h) Plot of partial pressure of peak 111 vs desorption temperature.

4.3.4 [EMIM][Tf₂N] Thin Film on Mica

Muscovite is a mica with atomic composition of $KAl_2Si_3AlO_{10}(OH)_2$. Due to its layered nature it can be freshly cleaved using a scotch tape and the resulting is a negatively charged transparent surface. Around 3 nm thick [EMIM][Tf₂N] film was deposited on the freshly cleaved mica substrate. Mica is an insulator, hence shows charging effect when the electron beam is incident on its surface. To overcome this problem, we reduced the source voltage of electron gun to 1.4 - 1.3 V, which reduced intensity of the image. This gave difficulty in identifying the diffraction intensity changes.

The sample was cooled to 120 K, annealed to room temperature and then heated to desorb the IL film. As shown in Figure 4.20, the cooled sample at 120 K and then during annealing, no apparent signs of crystallization was observed with the probing conditions used. Desorption of ion pairs started near 400 K and completed at 420 K (Figures 4.20 (g), 4.20 (h)).

In a previous study using atomic force microscope (AFM) for the same [EMIM]⁺ cation, an observation of fewer, not well defined layers of IL were observed compared to the ammonium cation used in their analysis. The reason can be due to the low electrostatic interactions between the surface and the sterically hindered charge of [EMIM]⁺.⁵⁸ In our case, fewer ion pair layering on mica was insensitive in RHEED patterns may be due to the charging effect of the substrate. This issue can be eliminated by using the pulsed electrons in future studies of mica substrate.



Figure 4.20: RHEED patterns of [EMIM][Tf₂N] film on mica. (a) Freshly cleaved bare substrate, (b) After deposition, (c) During annealing at 123 K, (d) Spots starts to appear at 413 K, (e) Clear spots at 417 K, (f) Fully appeared spots at 420 K, (g) Plot showing intensity variation of the mica spot with increase of temperature during desorption, (h) Plot of partial pressure of peak 111 vs desorption temperature.

4.3.5 [EMIM][Tf₂N] Thin Film on Single Crystalline Metal Surfaces

Single crystalline Ni(111) and Cu(111) metal surfaces were chosen as substrates to deposit 3 nm [EMIM][Tf₂N] thin film. As received substrates had roughness in the order of 3 nm (Figure 4.21 (a)). Sputtering using Ar⁺ ions was performed to reduce the surface roughness and to eliminate the contaminants such as native oxides and hydrocarbons. The sputtering improved the surface and made it flat as shown by the streak patterns from RHEED (Figure 4.21 (b)). On both metal surfaces, the RHEED patterns show diffusive scattering from the very-randomly oriented ion pairs (Figure 4.22 and 4.23). On Cu(111), along with the diffusive pattern, the underlying diffraction from the metal surface is also visible (Figure 4.22). During the cooling and annealing of the IL film on metal surfaces, structural changes due to crystallization or phase transition were not observed in RHEED patterns. This may be due to the surface roughness which affected the layering of ions pairs.

Desorption behavior on Ni(111) was monitored using RHEED patterns and the RGA partial pressure peaks of mass peak - 111. The appearance of the Ni(111) substrate peak started ~ 360 K and desorption of IL ion pairs from substrate happened until 430 K (Figure 4.23). After 430 K, very bright substrate diffraction pattern showed up. In an earlier study by X-ray photoelectron spectroscopy (XPS) analysis of 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ([C₁C₁Im][Tf₂N]) on Ni(111) and NiO, they showed a delayed desorption (500 – 700 K) on NiO due to [C₁C₂IM][OH] formation at elevated temperatures.⁵¹ In our study, we can confirm that our Ni(111) surface is mostly free from NiO after sputtering that is confirmed by the observation of

clear Ni(111) substrate RHEED pattern indicating the early desorption of [EMIM][Tf₂N] at around 430 K.



Figure 4.21: RHEED patterns of $[EMIM][Tf_2N]$ on Ni(111). (a) As received Ni(111), (b) Ni(111) after sputtering, (c) after the deposition of 3 nm $[EMIM][Tf_2N]$ thin film on Ni(111), (d) cooling the sample at 170 K, (e) cooling the sample at 119 K, (f) annealing the sample at 256 K.



Figure 4.22: RHEED patterns of $[EMIM][Tf_2N]$ on Cu(111).(a) Cu(111) after sputtering (b) after the deposition of 3 nm $[EMIM][Tf_2N]$ film on (c) cooled sample at 99 K, (d) annealing the sample at 156 K, (e) annealing at 250 K, (f) annealing at 278 K.



Figure 4.23: Desorption of $[EMIM][Tf_2N]$ IL film from Ni(111). (a) desorption at 357 K, (b) desorption at 400 K, (c) fully desorbed at 429 K, (d) Plot showing intensity variation of the Ni(111) substrate spot with increase of temperature during desorption, (e) Plot of partial pressure of peak 111 vs desorption temperature.

In order to check the wettability of the IL on different surfaces, the static contact angle measurements were done (Table 4.3). All the obtained angle values are below 90°. Lower the contact angle, higher the wettability of $[EMIM][Tf_2N]$ drop with the

substrates, indicates better adhesiveness. This gives us an idea in selecting the substrates for thin film deposition.

Substrates	Contact angle (9)/ (degrees) $\pm 1^{\circ}$	Contact angle measurement
Cu(111)	35	
Mica	43	•
HOPG	48	9
H/Si(111)	52	Liquid
SiO ₂	54	Solid
Rock salt (NaCl)	56	
Sapphire (Al ₂ O ₃)	64	

Table 4.3: Contact angle measurements of [EMIM][Tf₂N] IL on other substrates

4.4 Conclusion and Outlook

From the analysis of vapor deposited [EMIM][Tf₂N] IL thin films on different substrates by RHEED technique in UHV environment, we are able to understand the interfacial structures, phase transition, and desorption behaviors. By comparing the ordered structural behavior of [EMIM][Tf₂N] ion pairs on HOPG with other different surfaces, we can conclude that the terrace surface morphology of HOPG plays a role as a template for vertical stacking of IL ion pairs. For thicker [EMIM][Tf₂N] thin film, strong interfacial substrate assisted ordering decays with distance and the ordering of ion pairs is not facilitated. The phase transition of [EMIM][Tf₂N] on HOPG happened at 256 K from ordered crystal phase to disordered liquid phase, which matches with the melting point of bulk [EMIM][Tf₂N] IL. The desorption behavior of 3 nm [EMIM][Tf₂N] IL on other substrates with similar 3 nm thickness showed a common trend as starting from 340 - 360 K and full desorption at ~ 375 K.
In order to expand our knowledge on IL/Solid substrate interfaces, in addition to the static RHEED structural analysis mentioned in this research, dynamic structural changes can be studied by time-resolved ultrafast electron diffraction analysis using femtosecond pump-probe technique. To analyze the obtained electron diffraction patterns, theoretical simulation related studies are also required. In the sample preparation of the substrate, for example to get a perfect single crystalline metallic surfaces (Cu(111) or Ni(111)), along with the currently performed Ar⁺ sputtering, high temperature annealing of the substrate is needed to obtain contaminant free well defined ordered metallic surface. Chapter 5

Analysis of Interfacial Water Assembly on Solid Substrates

5.1 Introduction

Water, being a simple molecule, plays a crucial role in many scientific fields starting from biology, environmental and atmospheric sciences to technological investigations. With intermolecular hydrogen bonding interactions, numerous crystalline and amorphous forms were found in solid water. From twelve crystalline modifications, only hexagonal (ice Ih) and cubic ice (ice Ic) can be obtained at ambient pressure or below.⁵⁹ More attention is paid towards the interfacial ice layers which is responsible for different phenomena in areas like electrochemistry, heterogeneous reactions and tribology.⁶⁰ In recent ultrafast electron diffraction studies, direct determination of the interfacial water structure and dynamics were reported on hydrophilic (chlorine terminated silicon) and hydrophobic (highly oriented pyrolytic graphite -HOPG) surfaces.⁶¹⁻⁶²



Figure 5.1: Diagrams for the structure of water. (a) Unit cell of cubic ice (only oxygen atoms are shown), (b) Cubic ice structure showing H- bonds. (only the oxygen atoms are shown, which are connected by H bonds), (c) Unit cell of hexagonal ice (only oxygen atoms are shown).

Here in our study, we developed a molecular beam doser system (details are given in Chapter 3, Apparatus, Molecular beam doser) to deposit molecules from vapor phase to prepare solvent thin films in a controlled and quantitative way. As an initial system, the interfacial structural ordering of water molecules on Cadmium telluride (CdTe(111)A) surface was investigated by reflective high energy electron diffraction (RHEED) technique under ultrahigh vacuum (UHV) environment.

CdTe is known as a semiconducting material that has a unit cell with zinc blende structure (Figure 5.2 (a)). This CdTe crystal shows crystallographic polarity in which the structure and chemical properties of some pairs of opposing crystal planes are different. This difference is clearly seen in {111} faces of the structure which is terminated either with Cd or Te. By convention, the {111} surface is designated as A-terminated (Cd) and $\{\overline{1}\overline{1}\overline{1}\}$ as B-terminated (Te).⁶³ In this study, CdTe(111)A is used (Figure 5.2 (b), 5.2 (c)).



Figure 5.2 : CdTe structure with (111) plane. (a) Unit cell of CdTe indicating (111) plane, (b) CdTe structure with shaded (111) plane showing Cd rich surface, (c) Top view of CdTe(111)A plane showing the arrangement of atoms.

In this chapter, the direct interfacial structural determination of the vapor deposited water at ~ 85 K on sputter cleaned CdTe(111)A and oxidized CdTe(111)A surfaces was carried out under ultrahigh vacuum (UHV) condition is discussed. Upon annealing the deposited water film, ordered water layers were formed as evidenced by the Bragg diffraction spots. On the other hand, water film on oxidized CdTe(111)A surface

showed Debye–Scherrer diffraction rings indicating the randomly oriented ice crystallites. Hence a lattice effect of CdTe(111)A assists the ordered ice formation which is absent when the surface is oxidized.

5.2 Materials and Experimental Section

The substrate CdTe(111)A (undoped, P-type, surface roughness < 15 Å) was purchased from MTI Corporation, CA. The surface was prepared by sputtering with 1.5 keV Ar⁺ ions to remove the surface contaminants such as oxides and hydrocarbons. After the sputter cleaning, the substrate was transferred to the goniometer in UHV environment.

At the base temperature of 85 K, the CdTe (111)A surface was dosed by the degassed water (mili-Q® water, with resistivity ~ 18.2 M Ω . cm at 25 °C) using developed the molecular beam doser with saturated vapor pressure of ~10 torr at room temperature for 30 min. The water thin film preparation on oxidized CdTe(111)A surface also performed as above dosing procedure for 30 min. After the RHEED analysis at low temperature, temperature of the sample was increased for annealing to observe the structural changes. [The following temperatures of the sample held in goniometer (during annealing) are reported using the temperature reading measured at the bottom of the sample mounting Cu head. An independent and direct measurement of substrate's surface temperature shows that the uncertainty of the temperatures reported in the following could be ~ 5 to 10 °C].

5.3 Results and Discussion

The diffraction of the as-bought CdTe(111)A surface didn't show any RHEED pattern (Figure 5.3 (a)). This may be due to the surface roughness, and the coverage of native

oxide and other organic contaminants on the surface. The sputtering for 2 min, improved the surface condition and further 2 min sputtering gave bright elongated Bragg spots. This indicates the wavy nature of the substrate surface (Figure 5.3 (b) and 5.3 (c)).



Figure 5.3: Sputtering of CdTe(111)A. (a) As received surface, (b) After sputtering for 2 min, (c) After sputtering for 4 min.

After the deposition of water film at 85 K, the substrate's RHEED pattern became weaker and the covered water layer showed diffuse scattering due to the structural disorder in the arrangement of immobilized water molecules in the thin layer (Figure 5.4 (a)). Upon increasing the temperature by slow heating, new interesting features in the RHEED pattern starts to appear at 126 K and becomes more distinct at 137 K (Figure 5.4 (b), 5.4 (c)) and persists clearly until 142 K (Figure 5.4 (d)). Around 147 K the formed Bragg spots starts to disappear and water molecules leaves the substrate as shown by the RHEED pattern due to full sublimation from the surface at 149 K (Figure 5.4 (f)).

During the annealing process, at 137 K the amorphous water film to changes into a crystalline film with long range order. The additional symmetric Bragg spots (Figure 5.4 (c)) indicates a registered orientation on top of the CdTe(111)A surface. The cubic ice crystal has a lattice constant of a = 6.35 Å and the hexagonal ice has a = 4.501 Å and c = 7.348 Å. The substrate CdTe(111)A has a lattice constant of 6.4827 Å.⁶³⁻⁶⁴ The RHEED pattern of the crystallized ice obtained in this study may be due to the mixed stacking of both cubic and hexagonal ice forms that adopts the geometry of the underlying substrate. Further simulation studies needs to be carried out in order to confirm this observation.



Figure 5.4: RHEED patterns of water on CdTe(111)A surface (a) As deposited water film at 85 K, (b) Additional Bragg spots starts to appear at 126 K, (c) Ordered crystalline water film formation at 137 K, (d) Clearly formed ordered crystalline water film formation at 142 K, (e) Bragg spots from water film starts to disappear at 147 K, (f) After completion of water sublimation from surface.

This substrate effect on the ordering of water molecules is clearly confirmed from the results obtained from the oxidized surface of CdTe(111)A. The RHEED pattern of oxidized surface is given in Figure 5.5 (a). As deposited water film shows a broad ring pattern and upon heating the sample to 131 K, the sharp diffraction rings starts to appear. At around 134 K, the formed Debye–Scherrer diffraction rings are very distinct indicating the poly crystalline ice formation with randomly oriented small crystallites (Figure 5.6 (a)). The radially averaged diffraction intensity analysis for this ring pattern is shown in Figure 5.7. The experimental peak positions (Figure 5.7 (c)) are in good agreement with the previously reported (theoretically calculated) peak positions of cubic Ice (Ic) form.⁶¹

The water film starts to sublime around 146 K and the oxidized substrate is clearly visible at 152 K due to full sublimation. These diffraction rings on oxidied CdTe(111)A instead of the ordered Bragg spots, indicates that the oxide layer acts as a screen to prevent the water molecules to arrange in long range order with the surface of the CdTe(111)A substrate.



Figure 5.5: RHEED patterns of water on oxidized CdTe(111)A (a) Oxidized CdTe(111)A surface before deposition at 84 K, (b) After deposition of water film at 84 K, (c) Initial appearance of Debye–Scherrer diffraction rings at 131 K,



Figure 5.6: RHEED patterns of water on oxidized CdTe(111)A – anneal (a) After full crystallization of the water assembly into polycrystalline ice at 134 K, (b) Disappearance of ring feature at 146 K, (c) After completion of water sublimation from the oxidized surface.



Figure 5.7: Analysis of the diffraction ring. (a) Debye–Scherrer diffraction rings of polycrystalline ice on oxidized CdTe(111)A surface (b) Radially averaged image of the diffraction ring shown in (a), (c) Comparison of the experimentally obtained diffraction profile with the theoretically calculated diffraction patterns of cubic and hexagonal ice.⁶¹

5.4 Conclusion and Outlook

In this study, the direct visualization of the structural changes of the interfacial ice layer on CdTe(111)A and oxidized CdTe(111)A are investigated using reflective high energy electron diffraction (RHEED) technique. The immobilized water molecules at low temperature after deposition showed diffuse scattering and upon annealing ordered ice layers were formed as evidenced by the Bragg diffraction spots. On oxidized CdTe(111)A surface upon deposition, initially formed amorphous water layer turned into Debye–Scherrer diffraction rings indicating the randomly oriented ice crystallites of cubic ice form. From this we can conclude that CdTe(111)A surface assists for the water molecules to crystallize in a registered orientation with long range order on top of it. The RHEED patterns of the crystallized ice obtained in this study on CdTe(111)A may be due to the mixed stacking of both cubic and hexagonal ice forms that adopts the geometry of the underlying substrate.

In order to understand the forms of stacked ice on the CdTe(111)A interface, further simulation studies needs to be carried out. With the understanding of this static structural analysis, ultrafast electron crystallographic studies are needed to unveil the dynamics of interfacial water assembly on this surface. A thicker water film can also be deposited at high dosage from the molecular beam doser using a larger size of the flow restriction aperture. In addition to water, other solvents such as methanol and toluene can be tried as future candidates for the interfacial studies on different substrates using vapor deposition.

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Appendices

A.1 : Drawing of the Quartz microbalance sensor



**All units of the drawings given here are given in inches

A.2: Drawing of the effusion cell



A.3: Drawing for the flange for effusion cell



A.4 : Drawing of full nipple for effusion cell



ITEM NO.	PART NUMBER	DESCRIPTION	QTY.
1	R-SST-400	4" OD X .083W W304/304L POL OD/ID A270	A/R
2	600-400N	FLANGE, CF 6" X 4", NR, THRU HOLES	2

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A.5: Drawing for customized 6"- Zero length reducer flange for doser



A.6 : Drawing of doser head



A.7: Drawing of doser cap





A.8 : Drawing of customized feedthrough



A.9 : Drawing of 45° elbow used for doser



A.10 : Drawing doser to turbo-molecular pump connection

