This dissertation aims to develop an understanding of metal-organic interfaces which are crucial for determining electronic and spintronic device characteristics. Model systems investigated involve a well-known organic semiconductor tris (8-hydroxyquinolinate) aluminum (Alq3) adsorbed on several metal substrates (Cu(110), Au(111), Cr(001)) which have distinct surface properties and reactivities. The electronic and magnetic properties at Alq3/metal interfaces have been studied in detail with scanning tunneling microscopy (STM) and spectroscopy (STS). The observations can provide insights for interpreting the performance of organic devices and provide guidance for future organic electronic and spintronic applications.

Molecular resolved STM imaging of Alq3 on both Cu(110) and Cr(001) surfaces reveals strong structural disorder in the sub-monolayer thickness region which suggests strong metal-molecule interactions at the interface. While the film exhibits an amorphous structure, the molecules at sub-monolayer coverages tend to form random quasi-linear structures. This linear tendency is driven by anisotropic intermolecular interactions. The strong interfacial structural disorder does not lead to remarkably strong electronic disorder at the interface. The local density of states measurement by constant-current STS shows the spatial variation of lowest unoccupied molecular orbitals (LUMO)-derived levels for both Alq3/Cu(110) and Alq3/Cr(001) systems. The observed electronic disorder is significantly less than the strong electronic disorder inferred from device measurements. The weak distribution in energies of electronic states is attributed to several closely spaced unoccupied
states known for the isolated molecule. The discrepancy between our observation and device characteristics suggests that electronic disorder in devices has a significant contribution from polycrystalline electrodes.

Spin-polarized scanning tunneling microscopy (SP-STM) was developed to study spin dependent properties of the Alq3 molecule at metal surfaces. We observed a strong spin depolarization effect of Alq3 molecules on Cr(001) in a low bias region. Furthermore, we observed spin polarized electronic structure effects near the LUMO-derived states. Near the LUMO energies, spin up molecules always coexist with spin down molecules. The phenomenon reveals that Alq3 can have surface induced spin-polarization near LUMO-derived states. We argue that the directions of local magnetic moments are controlled by molecule chirality. This observation highlights the importance of metal-organic interfaces in determining the characteristics of spintronic devices. It shows that molecular geometric shape can alter magnetic properties indirectly by controlling metal-molecule interactions.

Lastly, by comparing iron phthalocyanine (FePc) growth on Au(111) and Cr(001), we observe that FePc molecules completely dissociate on Cr(001) surfaces. By creating a less reactive iron buffer layer on the chromium surface, it is possible reduce the likelihood of decomposition. The high likelihood of chemical reactions occurring at 3d metal-organic interfaces should be taken into serious consideration in manufacturing real electronic or spintronic devices.
Scanning Tunneling Microscopy and Spectroscopy of Metal-Organic Interfaces for Electronics and Spintronic Applications

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Physics

Raleigh, North Carolina

2012

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DEDICATION

To my parents
Zhaolian Wang
Yiyu Sun
You grant me what I get today.

To my wife
Haizhen Meng
We will walk together with two or three healthy children.

To my future son/daughter
I hope you can have a happy life.
Zhengang Wang was born in Lanzhou in Gansu Province, P. R. China on January 18th, 1983. He enrolled in the Department of Condensed Matter Physics at University of Science and Technology of China from September 2001, later enrolled in the Department of Computer Science as co-major. In June 2005, Zhengang graduated as one of outstanding students and received both Bachelor of Science and Bachelor of Engineering degrees. From August 2006, Zhengang enrolled in Department of Physics at North Carolina State University as a Ph.D student. In August 2008, he joined Dougherty research group at NC State University, focus on characterization of surface and interface phenomenon of organic semiconductors. Along with scientific study, he enrolled in Department of Electrical and Computer Engineering at NC State University for studying computer hardware design. He received Master of Science degree in Electrical Engineering in December 2010.
ACKNOWLEDGMENTS

First and foremost, I must acknowledge and thank my advisor, Prof. Dan Dougherty. Your guidance, direction, and patience were, without a doubt, imperative to the realization of this dissertation. In the past few years, you taught me a lot of things about how to become a successful researcher, including how to effectively conduct experiment, how to prepare oral presentations, and how to write research papers. Not only have I learned a lot professional knowledge from you, but also you impress me with your great enthusiasm for scientific research. No matter which area I choose for my future career, your attitude towards work will be a paradigm to me. Thank you very much.

I would also like to thank Prof Jack Rowe. Thank you for introducing me into lab environments. The initial support and encouragement from you are crucial for me to keep doing research. You are such a kind elder that make me feel pleasant to work with you. Thank you.

I am also graceful of the important feedback and advice from my advisory committee members, Dr. Jacqueline Krim, Dr. Marco Buongiorno-Nardelli and Dr. David Shultz. I especially appreciate Dr. Krim’s suggestions for my preliminary exam.

Thank you to all of my colleagues, members in Dougherty research group. Thank you Alex Pronschinske, we have had a lot of discussion from which I got plenty of information or inspirations. It is a nice experience to work with you to build and maintain our STM systems. Thank you Andreas Sadin, help me accommodate to lab environments. I would also like to appreciate Jiuyang Wang, your help saved me a lot of time.
Lastly, I would like to offer my inmost thank to my family, first to my wife. You gave me substantial supports both in spirit and in action. You encouraged me when I was down; you made me happy in my daily life; you cooked delicious food for me. Without you, I cannot imagine I can get this work done. Then I would like to thank my parents, Zhaolian Wang and Yiyu Sun. You gave me all you have. You raised me, supported me for my study and my life. Thank your genuine love. I want to dedicate this dissertation to my family.
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CHAPTER 1

Metal-Organic Interfaces for Electronics and Spintronics

1.1 Background of organic electronics and spintronics

As most of us have experienced, electronics has deeply changed our world. Computing hardware is now in every aspect of our daily work, study, and entertainment. Silicon-based electronics, which has been observed to follow Moore’s law, developed rapidly in past decade. Basically, the electronics industry has been able to “double of the maximum number of transistors on a chip every 18 months”. This trend described by Moore’s law will continue to guide Si-based electronics until 2015-2020. The trend is going to saturate as Si-based electronics encounters insurmountable barriers: huge power dissipation and rising non-recurring engineering cost. Consequently, finding new growth opportunities beyond Si-based devices for the electronics industry is becoming more and more urgent. Organic electronics is one of the important candidates for future niche growth of the semiconductor industry. It is a branch of electronics in which the functional parts of the devices consist of conductive polymers, plastics, or small molecules that are carbon-based. So organic electronics is also known as polymer electronics or plastic electronics. Organics offer the electronics industry new opportunities as a result of their application to flexible devices, large area efficiency in lighting and solar energy, and cost effectiveness.

The history of organic electronics can be traced backward to as far as the nineteenth century. In 1862, Henry Letheby, by anodic oxidation of aniline in sulphuric acid, obtained a partly conductive material, which was probably polyaniline. About one century later, in the
1950s, the discovery of polycyclic aromatic compounds that form semi-conducting charge-transfer complex salts with halogens\(^3\) indicated that organic compounds indeed could transport current. In 1974, an actual organic-polymer electronic device, a melanin voltage-controlled switch, was made at University of Texas Cancer Center\(^4\). Later, conductive polymers (also called synthetic metals) which possesses the electrical properties of a metal while retaining the mechanical properties of a conventional polymer, were discovered and developed in 1977 by Alan J. Heeger, Alan G. MacDiamid, and Hideki Shirakawa. This significant work was awarded with the Noble Prize in Chemistry in 2000\(^5\). In addition, Norbert Karl did great work on the study of anthracene single crystals which is an important organic species in developing subsequent organic molecules\(^6\). In 1987, Tang and VanSlyke from Kodak found specific organic thin films could emit light. They built a novel electroluminescent diode using organic thin films as its active layers. This device could achieve high luminous efficiency and brightness at low driving voltage\(^7\) and opened the door to important applications of organic compounds in electronics, namely Organic Light Emitting Diode (OLED) and Organic Photovoltaic (OPV).

In the past 30 years, the development of organic electronics has accelerated at a rapid rate. Now organic electronics has already been used in manufacturing of consumer electronics\(^8\). Organic semiconductors not only can substitute traditional semiconductors (e.g. silicon) by providing similar performance\(^9\) with much cheaper components, but also they also create the possibility of new applications that would be impossible with traditional materials. One distinct characteristic of organic devices is its compatibility with flexible substrates\(^10\), this makes the organic electronic devices bendable and lightweight. This feature along with
its ultra-low manufacturing cost\textsuperscript{11} provide the main reasons for interest in organic electronics as a technology. By conventional techniques, e.g. ink-jet printing, it is possible to create a large yield of large area, low cost devices that could become ubiquitous in consumer products and household applications\textsuperscript{12}. One day soon, we may use radio frequency identification tags made from interconnected organic field-effect transistors (OFETs), or install large-area photovoltaic cell (PVs) painted on building roofs that can be economically replaced every other year to match color preferences of homeowners\textsuperscript{11}. Bright, high-resolution flat-screen displays made from organic light-emitting diodes (OLEDs) have already been successful in commercial applications as displays for televisions, computer monitors, mobile phone screens, etc. Other potential uses of organic electronics include electronic paper, chemical sensors, and pressure-sensitive skin for robots.

Though electronic devices made by conductive molecules or polymers can have advantages as stated above, generally organic conductive compounds have a higher resistance and therefore conduct electricity poorly and inefficiently as compared to inorganic conductors. One of the major topics in the research of organic semiconductors is to improve the conductivity of organic thin films and to synthesize new molecules/polymers with higher conductivity. Researchers are also currently exploring ways of “doping” organic semiconductors with relatively small amounts of conductive metals to boost conductivity\textsuperscript{13}.

Another new and promising application of organic materials is in organic spintronics. The basic idea is to utilize organic compounds to transport or control spin-polarized current signals. Hence organic spintronics combines organic electronics with spintronics. The spintronics term is a combination meaning “spin transport electronics”. It is an emerging
technology that exploits both the intrinsic spin of the electron and its associated magnetic moment in addition to its fundamental electronic charge in solid-state devices\textsuperscript{14}. In classical electronics, charges are moved by electric fields to transmit information and are stored in a capacitor. In magnetic recording, magnetic fields have been used to read or write the information in magnetic bits which involves the manipulation/measurement of the local orientations of spins in ferromagnets\textsuperscript{15}. Now, spintronics offers us a way to combine these three operations: logic, communication and storage in same technology\textsuperscript{16}. The essence of spintronics is to effectively control the charge transport through magnetization; hence we are starting to see a new paradigm where magnetization dynamics and charge currents act on each other in nanostructured artificial materials\textsuperscript{15}. Compared to charge-based switching device, spintronic devices would greatly improve two parameters that are most concerned in semiconductor industry: switching speed and power consumption.

In charge-based switching device, digital ‘0’ and ‘1’ signals are usually represented by the locations of charges (electrons and holes). Hence to maintain/alter the locations of charges a barrier should be present between the two states and can be adjusted by applying voltage. It is reported that until 2018 the projected gate-switching energy for low-standby-power 10 nm gate width CMOS could be decreased to as low as 15eV. However this is still much larger than 23meV($kT\ln2$) that is the theoretical minimum switching energy\textsuperscript{17}. In contrast, information represented by electron spin orientation would not demand such large switching energies. Spin states (spin up, spin down) as the intrinsic properties of a spin polarized electron can maintain their presence for a long time (>10ns) at room temperature\textsuperscript{16} and so spintronic devices do not require an electrostatic barrier to control the states as
charge-based devices do. The switching can be manipulated by applying a small magnetic field which would pull up or pull down spin orientation coherently by rotating it 180°. Because this process can exclude charge motion, the minimum switching energy of charge-based devices mentioned above does not even apply to spintronic devices. Even with an electrical gate manufactured to control the spin, the switching energy of spintronic device still can be much smaller than a charge-based device\textsuperscript{18}.

Spintronics offers fast switching speed from GHZ to THZ that is determined by precession frequency of electron spins. The switching speed of charge-base devices is limited by charging/discharging of intrinsic and load capacitance.

Spintronics emerged from discoveries in the 1980s concerning spin-dependent electron transport phenomena in solid-state devices. This includes the observation of spin-polarized electron injection from a ferromagnetic metal to a normal metal by Johnson and Silsbee\textsuperscript{19}, and the discovery of giant magneto-resistance independently by Albert Fert et al.\textsuperscript{20} and Peter Grünberg et al.\textsuperscript{21}, which won them 2007 Nobel Prize in Physics. The origins of spintronics can be traced back even further to the ferromagnet/superconductor tunneling experiments pioneered by Meservey and Tedrow, and initial experiments on magnetic tunnel junctions by Julliere in the 1970s\textsuperscript{22}. The use of semiconductors for spintronics can be traced back at least as far as the theoretical proposal of a spin field-effect-transistor by Datta and Das in 1990\textsuperscript{23}. Now we use spintronic devices in every daily life, as the recent expansion of hard-disk recording owes too much to the development of the GMR spin valve sensor\textsuperscript{24}.

Modern spintronic devices mainly fall into the two categories of Giant Magneto-Resistance (GMR) and Tunneling Magneto-Resistance (TMR) devices\textsuperscript{14-16, 25}. To understand
how the GMR devices work, we can build a simple model that consists of magnetic multilayers with the thickness of individual magnetic layer comparable to the mean free paths determined by spin-dependent scattering probability (Figure 1.1). In Figure 1.1a, it shows simplest case of a triple-layer film of two ferromagnetic layers F1 and F2 sandwiching a non-magnetic metal spacer layer NM. When the magnetized directions of the two magnetic layers are parallel, the spin-up electrons can travel through this sandwich nearly unscattered while the spin-down electrons are almost all scattered. On the contrary, in the antiparallel case, both spin-up and spin-down electrons undergo collisions in one ferromagnetic layer or the other. In the scenario, the conductivity of this model at parallel magnetic field would apparently larger than antiparallel case. The relative magneto-resistance:

$$\frac{\Delta R}{R} = (R_{AP} - R_P)/R_P$$  \hspace{1cm} (1.1)

can reach 100% or more, and was named Giant Magneto-Resistance\textsuperscript{20, 21}. Two variants of GMR have been applied in devices:

1. Current-in-plane (CIP), where the electric current flows parallel to the layers.
2. Current-perpendicular-to-plane (CPP), where the electric current flows in a direction perpendicular to the layers.

Similar to GMR, Tunneling Magneto-Resistance (TMR) is another fundamental spintronic effect. In Figure 1.1a, if we replace the non-magnetic metallic spacer M of the spin valve by a thin (~1-2 nm) non-magnetic insulating layer, such as Al\textsubscript{2}O\textsubscript{3}, a magnetic tunnel junction (MTJ)\textsuperscript{26} is created as showing in Figure 1.1b. In this configuration the electrons can travel from the ferromagnetic electrode to the other by tunneling effect. The tunneling conductance is determined by the product of density of states of like spin bands. When
electron states on each side of the barrier are spin-polarized, then electrons will more easily find free states to tunnel to when the magnetization are parallel than when they are antiparallel. Usually the magneto-resistance of TMR effect is smaller than that of GMR, however, in certain conditions much higher magneto-resistance ($\frac{\Delta R}{R} = 1010\%$) has been achieved\textsuperscript{27}.

Because of the promising future applications of spintronic devices, people are motivated to seek various materials with different spin properties, which can be used in spintronic devices for different applications. Three categories of materials have been proposed:

- Dilute magnetic semiconductors. (e.g. GaMnAs\textsuperscript{28}, GeMn\textsuperscript{29}, ZnMnO\textsuperscript{30})
- Complex oxides. (Multi-Ferroics\textsuperscript{31}, such as YMO, BBO, etc)
- Organic polymers and discrete molecules. (e.g. Alq\textsuperscript{32}, metal phthalocyanine\textsuperscript{33, 34}, pentacene\textsuperscript{34}, C\textsubscript{60}\textsuperscript{35})

For the third category, organic compounds can be utilized in spintronic devices as in organic electronics. Organic spintronics not only has all of the advantages of organic electronics and spintronics as stated previously, but also organic materials are recognized as valuable in spintronics due to potentially very long spin relaxation time\textsuperscript{36}. This is usually attributed to the reduced spin-orbit and hyperfine scattering due to low atomic number elements of organic molecules. It is reported that the spin relaxation times of organic compounds are in the range 100-10000ns at room temperature\textsuperscript{37}. As aforementioned, this long spin relaxation time offers innate superiority of organic materials to store logic states, and reduce power consumption. In addition, various organic materials can be synthesized by
organometallic chemistry in order to tune spin properties\textsuperscript{38}. This means it may be possible to precisely control magnetic properties of organic spintronic device as needed to make application specific devices. Hence, studying spin dependent properties of potential organic materials is becoming urgent and attracting more and more attention in both academic and industrial research.

In such a context, a number of organic molecules have been proposed to have spin dependent charge transportation characteristics. Among them, Tris (8-hydroxyquinolinato) aluminum, abbreviated Alq3, is one of the very promising candidates for future spintronic devices. Alq3 is an molecule with the formula Al(C\textsubscript{9}H\textsubscript{6}NO)\textsubscript{3}, and its molecular structure is shown as Figure 1.2. It is a coordinate complex wherein aluminum is bonded in bidentate manner to the conjugate base of three 8-hydroxyquinoline ligands. This molecule previously has been primarily used in OLED’s as an electron transport and emissive layers due to its high luminous efficiency, high quantum efficiency and high brightness\textsuperscript{7}.

Surprisingly, in 2004, Xiong et al. reported that Alq3 exhibits a “GMR” effect in a spin valve structure, yielding a low-temperature MR as large as 40 percent\textsuperscript{32}. After this significant discovery, much research effort has been devoted to studying the Alq3 molecule’s spin related properties, including attempts to reproduce Alq3 GMR effects by independent groups. The results are controversial. Some groups reproduced similar observations compared to Xiong’s work\textsuperscript{39}, while some did not. For example, Jiang et al. did not observe any MR effect in their Alq3 spin valve\textsuperscript{40}. Carefully comparison of different experiments shows differences in the ferromagnetic electrodes used in the spin valve structures. In Xiong’s experiment, one electrode was made from the half-metallic oxide La\textsubscript{0.67}Sr\textsubscript{0.33}MnO\textsubscript{3}.
(LSMO) while in Jiang’s experiment they instead used an Iron thin film. In fact, the use of LSMO as an electrode seems to be very important for the observation of GMR effects in Alq3 films. This fact suggests that metal-organic interaction at the electrode interface may play an important role in determining the details of the Alq3 GMR effect. This possibility is the major scientific issue to be addressed in this thesis. The present work focuses on a detailed study of several Alq3-metal interfaces and focuses on answering four questions:

1. How does Alq3 adsorb on metal surfaces (Chapter 3)?
2. What is the electronic structure at the metal-Alq3 interface (Chapter 4)?
3. What is the spin dependence of the electronic structure at metal-Alq3 interfaces (Chapter 5)?
4. What surface physics and chemistry issues arise for other organic materials for spintronics (Chapter 6)?

The answers to each of these questions will provide insights into the spintronic functionality of molecular materials and are crucial to the ongoing development of the general field of organic spintronics.

1.2 Basic physics at metal organic interface

In either organic electronics or organic spintronics, the basic structure of devices consists of one or more layers of the active organic materials sandwiched or half sandwiched among the electrodes as shown in Figure 1.3. Though for various devices the different layers are optimized for different functions, such as for transporting electrons/holes, for generating photovoltaic charge carriers, or for emitting light, the metal-organic (MO) interfaces play an important role. Either injecting charges from an electrode to an organic
active layer or detecting charges from an organic active layer are necessary processes for normal operations of these devices. The efficiency of charge transfer across the metal-organic interface is one of the critical physical parameters for the performance of devices. It is determined by the size of the energy barrier to be overcome as the charge carrier crosses the interface. Hence understanding and predicting energy level alignment at metal-organic interface is crucial for both science and engineering. In organic spintronic devices, it is likely that interfacial energy level alignment will be spin-dependent and it is important to understand this and learn to optimize it for efficient spin injection.

Normally, to determine the energy barrier at an interface we consider the electronic structure of the isolated materials. In the case of two dissimilar metals with different work functions, this energy barrier is the so-called built-in potential $V_{bi}$, which is the difference of their work functions ($W_s-W_m$) (Figure 1.4a).

When a metal and a semiconductor make contact, the energy alignment often obeys the Schottky-Mott rule. The electrons from the material with higher Fermi level (i.e. chemical potential) will flow to the other material, making one side positive charged the other negative charged. This charging effect will further change the materials’ potentials, making all electronic energy levels change correspondingly. As a result, the two Fermi levels would align at equilibrium. The built-in potential $V_{bi}$ would all drop in the depletion region created by ionizing donor or acceptor dopants, and this is said to cause energy “band bending” at the metal-semiconductor interfaces.

However, at metal-organic interfaces, the energy level alignment most often fails to obey the Schottky-Mott limit due to the possibility of charge transfer, Pauli repulsion, and /or
the presence of interface states\textsuperscript{44,45} These systems may not even reach equilibrium (i.e. Fermi levels would not be aligned) in part due to low carrier densities. Instead of band bending, a more common description of the MO interface involves the formation of an interfacial “dipole layer”. Here, the entire contact potential difference $V_{bi}$ is accommodated by the formation of an interfacial dipole layer, so no band bending occurs (Figure 1.4b). Regarding the origins of the interface dipole, it can be the result of mutual actions of several physical mechanisms including:

1. The rearrangement of charge at the interface. Even somewhat weak interactions involve the redistribution of electron density within the molecule and within the nearby region of the metal\textsuperscript{46}.

2. “Pauli repulsion”-induced compression of the metal electron tails at the interface\textsuperscript{47,48}. The surface of a clean metal has an intrinsic dipole layer due to the “spill out” of electrons beyond the last plane of surface positive nuclei. The presence of an organic overlayer can interact with the electron density that extends beyond the top plane of nuclei. In general, because of Pauli exclusion, the spill-out is expected to be reduced, creating a positive change in the surface dipole moment and lowering the energy required to remove an electron from the metal (i.e. lowering the work function).

3. Permanent molecular dipoles\textsuperscript{49,50}. The permanent dipole of molecule can change the intrinsic dipole spill-out layer of the metal electrode.

4. Chemical reaction between metal and organic molecules\textsuperscript{51-53}. This includes the formation of a covalent bond with one or more surface atom causing partial charge transfer from metal to organic as well as ionization of the molecule leaving the
counter charge on the metal or replacement of atoms of metal surface to create a new organometallic complex.

To determine the injection barrier for charges, we must understand the electronic states available at the MO interface. The states for electron and hole injection are often colloquially called the LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular orbital) states respectively. However, this language refers to the ground state “frontier orbitals” of the molecule. For charge injection, the relevant states are charged excitations that are more accurately called electron and hole “quasi-particles”. The computational problem is to calculate the transport gap of organic molecules $E_g$, which involves the total energy difference of molecules in different charged states. Specifically, the transport gap is the difference between the ionization $I$ (lose one electron) and affinity $A$ (acquire one electron) energies\(^{46}\):

$$E_g = I - A$$

(1.2)

$$I = E(N) - E(N - 1)$$

(1.3)

$$A = E(N + 1) - E(N)$$

(1.4)

where $E(N_i)$ is the energy of the system with $N_i$ electrons. This quasi-particle excitation energy gap causes the so called “organic energy gap problem” of conventional Density Theory Function (DFT) calculations, and is absolutely analogous to the corresponding gap problem for inorganic semiconductors\(^{54}\). For organic molecules in the gas phase, the energy gaps are usually underestimated by conventional DFT\(^{55-57}\), this is primarily related to the fact
that only N-electrons are involved in Kohn-Sham DFT gap calculation while excited states of molecules determine their energy gap. Hence, appropriate corrections on the conventional DFT need to be performed to model organic energy gap correctly. These corrections can be computationally costly. It is crucial to directly measure charge transport states at the metal-organic interface as described in this thesis to provide input for the development of theoretical approaches to this difficult problem.

An example of recent theoretical developments can be found in the work of Flores et al\textsuperscript{46} who have suggested a simple approach of adding charged state corrections to the DFT calculated electronic spectrum of a neutral organic molecule. They approximate the contributions of electrons to the total energy in the charged state (N+1/N-1 electrons) by using the wavefunctions of the uncharged (N-electrons) state, and calculate the effect on the total energy of adding an electron or removing an electron from a certain molecular orbital. This approximation neglects charge rearrangement upon addition of a carrier. However, it can obtain an approximation to the organic energy gap from charged states. In this simple approach, the transport energy gap of the isolated molecule is given as:

\[ E_g = E_{KS} + E_{SI} \]  \hspace{1cm} (1.5)

In equation 1.5, the first term is the energy gap calculated by conventional Kahn-Sham DFT. The second term is the correction induced by charged states, which can be viewed as a kind of self-interaction energy of the isolated molecule. Therefore equation 1.5 clearly demonstrates that the self-interactions of organic molecules would increase their transport gap.
Besides the self-interactions experienced in organic solids, once organic molecules are brought closely to metal surface as in devices, another important effect takes place and should be seriously considered in determining the transport gap. This is the image potential effect due to image charges$^{46,51}$. As stated in classical electrostatics, when a charge is brought close to a metal surface, the charge would induce a redistribution of surface charges of the metal. The resulting electric field can be quantitatively analyzed by imposing an image charge in the metal, which replicates the boundary conditions of the problem$^{58}$. In practice, the image potential effects usually increase (decrease) the ionization (affinity) levels by a mount of $V_{im}^{59,60}$. This would directly lower the organic energy gap. In addition, the image potential has a correlation effect on the self-interaction energy that would indirectly lower the organic energy gap as well$^{61,62}$. The further corrections to the organic energy gap model taking image potential into account are given as$^{46}$:

$$E_g = E_{KS} + \gamma E_{SI} - V_{im}$$  \hspace{1cm} (1.6)

notice the $\gamma$ factor multiplying the self-interaction energy. This factor ($0<\gamma<1$) induced by metal-molecule interactions decreases the self-interaction energy. The molecule-metal interaction would delocalized the molecular states over the metal at MO interfaces, and this delocalization would reduce intra-molecular exchange-hole$^{46}$. Hence, the image potential effect at MO interface tends to cancel the self-interaction energy corrections, to make the organic energy gap close to the results of conventional DFT calculations.

Once the energy levels at MO interface is determined, the electron injection barrier is the difference between the metal Fermi level $\phi_M$ and organic’s affinity level (charge state related to the LUMO). Similarly the hole injection barrier is the difference between the metal
Fermi level $\phi_M$ and the first ionization level (charge state related to the HOMO). However, unlike the corresponding conduction and valence bands of their inorganic counterparts, the transport states of organic molecules are highly localized on individual molecules or on relatively short (1-2 nm) conjugated segments. Organic materials are classic examples of “molecular” solids for which weak intermolecular interactions do not strongly perturb localized molecular states. In the language of a tight binding model from solid state physics, the overlap integral between sites is small leading to small bandwidths. This leads to a tendency for localized transport states (again with narrow bandwidths) even in perfect (disorder-free) organic single crystals. For example, recent angle-resolved laser-assisted photoemission has shown relatively narrow bands in single crystals of rubrene$^{63, 64}$. In addition, two other concepts favor localization in organic solids: Anderson localization$^{65}$ due to structural disorder and polaron formation due to interaction between molecular vibrations and injected charges$^{66}$.

Anderson localization occurs when the electron bandwidth is less than the energetic disorder among the different molecular sites. This kind of localization is the usual case for organic semiconductors because one of their strong tendency to exhibit structural disorder in thin films. This leads to a spatially inhomogeneous distribution of electron energies among the molecular sites due to the interaction of the charge with all of the dipoles in the surrounding medium$^{67}$. Even if the single molecule has no net dipole moment, each heteroatomic bond can have a significant dipole moment, so even subtle changes in molecular arrangement can lead to large fluctuations of local dipole field$^{68}$. Alternately, the polarizability of molecules can lead to the induced dipoles upon charge injection$^{69}$.
If Anderson localization is not the case for specific organic molecule that is highly crystalline with good $\pi-\pi$ overlap (i.e. large bandwidth), the formation of a polaron quasiparticle would still drive the electron states to be strongly localized on molecules. Polaron formation, which is driven by the electron-phonon interaction, is particular effective in organic solids which have both strongly coupled intra-molecular phonons (vibrational modes) and many low energy intermolecular modes (librons). At low temperature, polaron formation by the interaction between electrons and phonons will lead an increase of their effective mass. As the temperature increases, the interaction will narrow the bandwidth of transport states. Ultimately this causes the formation of a “small polaron” that is localized on a single molecule due to nuclear distortions upon charge addition. Several works have reported that electron localization by the transition from large to small polarons occurs well below room temperature even in crystalline compounds with favorable molecular arrangements.

Therefore, the primary charge injection event at MO interface can be described as two steps process: First, charges are excited from an extended band-like state in the metal electrode into a localized states in the molecular layer. This new charge polarizes the electrons in the molecule on an almost instantaneous time scale ($\sim$fs) and on much slower time scales ($\sim$ps) can also polarize the nuclei leading to small polaron formation. Second, these injected quasi-particles hop from the localized state at the interface into the bulk of organic film.

The interfacial dipole not only accommodates the potential drop across the MO interface, changing injection barrier correspondingly, but also in theory it has been shown
that energetic disorder at the interface can enhance charge injection by lowering the effective injection barrier\textsuperscript{76-78}. The density of states (DOS) of molecules in the interfacial disorder layer often follows a Gaussian distribution. Due to this broadened distribution, the charges can tunnel into or hop among lower energy states in the tail of distribution instead of going to a higher narrower band. In another word, this phenomenon can be viewed as adding lower permissible energy states below/above organic LUMO/HOMO. That means the injection barrier is lowered, so the injection current can be enhanced in this manner. However, this unique characteristic of metal-organic interface has not been fully understood and utilized partially due to its inhomogeneity at different metal-organic interfaces, hence it needs further characterization in both theory and experiment.

1.3 Review of important surface science contributions to metal-organic interfaces

Due to the important role of MO interfaces in determining device characteristics, they have attracted particular attention in academic surface science research. This part of thesis will be dedicated to review some of the important contributions of traditional surface science to the study of metal-organic interfaces.

As discussed in the last section, energy level alignment at MO interfaces is the key factor in determining carrier injection barriers. Studying energy level alignment at MO interfaces starts with characterizing organic transport gaps. Ultraviolet photoelectron spectroscopy (UPS) is a common method for studying ionization energy I, which is the binding energies of HOMO-derived states and vacuum level positions. A. Kahn and his group characterized different organic molecules (CBP, PTCDA, \(\alpha\)-NPD, Alq3, BCP, CuPc, \ldots).
PTCBI) and the interfaces of these organics with Si:Cr:Au substrates by UPS. Their results show that there are strong interfacial dipoles that create vacuum level offsets at all of the MO interfaces. Even for organic semiconductors with undefined Fermi levels, their study still shows strong dipole formation at MO interfaces, suggesting that this interfacial dipole layer is not driven by populating or emptying Fermi level-pining gap states. H. Ishii and K. Seki and their colleagues also made great contributions to the study of energy level alignment at MO interfaces by photoemission spectroscopy. With UPS, they studied energy alignments of complex organic-metal systems (e.g. Al/Alq3/TPD/ITO) as well as binary MO interfaces. In their study, they also observed vacuum levels shift at MO interfaces and attribute this to the formation of interfacial dipoles. Besides organic growth on metals, the interfaces formed by metal deposited onto organics are also important from a device perspective. In many cases, the deposited metal atoms can diffuse into organic molecular layers. W. R. Salaneck and his colleagues specifically studied metal deposited conjugated polymers and their obligomers by UPS along with XPS. The results show complex chemical reactions and metal diffusion can happen at these MO interfaces.

X-ray photoemission spectroscopy (XPS), which has been widely used in studying MO interfaces, is closely related technique of UPS. XPS, also known as electron spectroscopy for chemical analysis (ESCA), is mainly used for measuring the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. Hence XPS has the ability to detect possible chemical changes that occur at MO interfaces, and determine band-bending effects. Y. Gao and his group are among the world leaders in combining XPS with UPS for studying MO and OO interfaces. They found
that for reactive metal surfaces there may be both charge transfer and chemical reactions at MO interfaces\textsuperscript{82}. For example, they characterized a system consists of Ca on Alq3. It is found that a staged interface formation happened at the interface, which starts with charge transfer across the interface. Subsequently, one of the three quinolates of Alq3 accepts the electron donated by Ca resulting in structural deformation of Alq3 molecules that can accelerate chemical reactions between the molecule and Ca. Similarly, strong interactions were observed for the case of Mg on Alq3, which showed a higher binding energy of Alq3 and an extra peak above the HOMO of Alq3. This extra peak, which can effectively lower hole injection barriers, suggests chemical reaction or charge transfer to the Alq3 LUMO.

While ionization energy (I) can be measured experimentally by UPS, affinity energy (A) of organics is more difficult to determine since there are no electrons to be photo emitted. The main technique in use is inverse photoemission electron spectroscopy (IPES), which directs a well-collimated beam of electrons of a well-defined energy (<20eV) to the sample. These electrons couple to high-lying unoccupied electronic states and decay to low-lying unoccupied states with photon emitted, the emitted photons then are detected and an energy spectrum, photon counts vs. incident electron energy, can be generated. Due to the low energy of the incident electrons, their penetration depth is only the length of a few atomic layers, making IPES a particular surface sensitive technique. By IPES, A. Kahn’s group finely plotted energy gaps of many organic molecules (e.g. PTCDA, α-NPD, Alq3, ZnPc, CuPc)\textsuperscript{83} on metal surfaces. They compared their experimental results with corresponding DOS calculated by the semi-empirical Hartree-Fock intermediate neglect of differential overlap (INDO) method. The great similarity between experimental and theoretical results
suggests a potential theoretical approach for describing energy levels of these molecules\(^{84}\). Besides Kahn’s group, N. Sato and his coworkers also measured unoccupied electronic states of PTCDA, and further examined the electron injection behaviors due to alkali metal doping to these molecules. They created a model directly relating electron injection ability to the dopant concentration\(^{85}\). In addition, they also did unoccupied electronic structure studies of 3d-metal phthalocyanines (MPc: \(M=\text{Mn, Fe, Co, Ni, Cu and Zn}\)) and metal-free phthalocyanine (H\(_2\)Pc) by IPES. As the result, they claim the positions of unoccupied molecular orbitals of MPc are directly related to the central metal atoms of MPc\(^{86}\).

Two photon photoelectron spectroscopy (2PPE) can also be used in probing empty states in organic semiconductors. 2PPE is ideally suited for the investigation of heterogeneous electron transfer, and is particularly good for strong electronic interaction between molecules solid surfaces. In practice, X. Y. Zhu and his group use 2PPE technique to study heterogeneous electron transfer of C\(_6\)F\(_6\) on Cu(111)\(^{87}\). By analyzing experimental results, they attributed the photon induced electron transfer to the molecular \(\sigma^*\) LUMO level which is lowered at the MO interface due to the previously mentioned image charge effect. For comparison, they also studied the interfacial electronic structure of self-assembled monolayers (SAMs) of pentafluorothiophenolate (C\(_6\)F\(_5\)SH) on Cu(111) by 2PPE\(^{88}\). They found molecule’s HOMO-LUMO gap further reduced at this MO interface due to strong electronic coupling between metal and molecular orbitals that in turn is caused by –S– bonding formed between surface Copper atoms and C\(_6\)F\(_5\)SH molecules.

C. B. Harris’s group also studied interfacial band structure of SAMs by 2PPE. They characterized the interfacial energy alignment of the methanethiolate on Ag(111), extracted
molecular occupied and unoccupied state energies as a function of SAM coverage, and deduced effective mass of the adsorbate bands. In addition, they have characterized the dynamics of two-dimensional small polaron formation at MO interfaces (alkane/Ag(111)) by femtosecond time- and angle-resolved 2PPE. The time frame of quasi-free electrons trapping as polarons and their decay back to metal were determined to be a few hundred femtoseconds and less than picoseconds respectively. They also modeled the energy dependence of the self-trapping rate. This work made a great contributions to better understand carrier dynamics at MO interfaces.

In addition, there is a technique that has made great contribution to the study of MO interfaces, namely scanning probe microscopy (SPM). SPM can probe the positions of HOMO and LUMO levels of molecules relative to the Fermi level of the underlying metal substrate. Specifically, scanning tunneling spectroscopy (STS) implemented by STM can directly measure energy gap of organic molecules on metal surface. Besides, due to distinctive local nature of SPM, the morphology of organic films and molecular assemblies on metal surfaces can be probed simultaneously with their electronic structure.

K. W. Hipps and his group made early great contributions on characterizing organic semiconductor on metal surface by SPM techniques. For example, this group studied cobalt phthalocyanine (CoPc), Cobalt Tetraphenylporphyrin (CoTPP) and a co-adsorbed mixture of the two on Au (111) by STM and Orbital-Mediated Tunneling Spectroscopy (OMTS). They focus their experiments in the submonolayer region of CoPc and CoTPP films. STM images of CoPc/CoTPP mixtures showed two closed-packed surface structures, with different compositional percentages and some disorder. CoPc was also observed exclusively in one-
dimensional chains and as single, isolated molecules below 220K. They reported occupied 
and unoccupied energy levels measured by different spectroscopy techniques. Nearly 
identical constant-current contours are observed over the central Co$^{2+}$ ions of CoTPP and 
CoPc, indicating that the attenuation of the $d_{z^2}$ orbital-mediated tunneling current induced by 
the structure of TPP relative to Pc is at most a factor of about 10. However, the orbital-
mediated tunneling spectra of CoTPP and CoPc are distinctly different and allow these 
structurally similar species to be distinguished.

Beside K.W. Hipps’s group, M. F. Crommie and his group also did great work on 
MO interfaces by STM. They especially focus attention on fullerenes on metal surfaces. $C_{60}$ 
as a fundamental component can be made into a variety of new carbon nanostructure, such as 
endohedral fullerenes, peapod nanotubes$^{92}$, $C_{60}$ dimers$^{93}$, and single molecule transistors$^{94}$. 
Among their contributions, they have used Scanning Tunneling Spectroscopy (STS) to 
spatially map the energy-resolved local density of states (LDOS) of individual $C_{60}$ molecules 
on the Ag(100) surface, including HOMO, LUMO and LUMO+1$^{95}$. They observed that 
LDOS is strongly spatial inhomogeneous, this inhomogeneity reflects the structure and 
symmetry of $C_{60}$ molecular orbitals at different energies. In addition, they observed enhanced 
splitting of the $C_{60}$ LUMO states in the vicinity of the metal Fermi energy and are able to 
map out the spatial structure of molecular states near metal Fermi level. This exemplifies the 
great advantage of studying the MO interface with a combination of STM/STS: single 
molecule spatial resolution is routine and can be used to identify trends in the relationship 
between local structure at the interface and electronic properties at the interface.
Subsequently, D. B. Dougherty et al. observed direct evidence of the local environment in determining electronic properties of organic molecular films at nanometer length scales. They specifically studied C\textsubscript{60} molecules adsorbed on an anisotropic pentacene bilayer template that is grown on Ag(111)\textsuperscript{96}. In sub-monolayer region, it is found that C\textsubscript{60} formed chain like linear structures by filling into spaces between parallel rows of pentacene molecules. By using STS to measure the local transport gap locally on the linear C\textsubscript{60} chains, they found the transport gap is apparently higher than that of bulk C\textsubscript{60}. They attribute this increase of transport gap to the reduced coordination of the linear configuration that lowers the overall polarization energy upon addition or removal of electrons by the STM tip.

Even for ordered organic molecular film growth on the metal, the electronic states of molecules have strong correlation with local site specificity due to intrinsic asymmetry of molecular structure and local environments. Soubatch et al. reported site-specific molecular affinity levels of a highly ordered tetracene films on Ag(111)\textsuperscript{97}. The energy level shifts from molecule to molecule were up to \(~1.0\text{eV}\). They traced these apparent energy shifts to the site-specific polarizations screening of organic molecules with complex unit cells. They accounted for this site specificity due to a combination of molecular environments, the anisotropic molecular polarizability, and the influence of the substrate. This discovery can have a profound impact on characterization of organic devices which may be considered as being made of electronically distinct species even for a single organic material.

In another example of this spatial inhomogeneity, M.-C. Blüm et al. studied the self-assembly of rubrene on Au(111) and Ag(111)\textsuperscript{98}. They reported that the molecules are adsorbed on the metal surface in different 3D conformations, and that this difference directly
determines the ionization energy (HOMO) shift from molecule to molecule measured by STS. They also observed the same electronic structure of adsorbed rubrene on a metal as that of rubrene in the gas phase. This implies that the adsorption of the molecules leaves the HOMO and LUMO essentially unperturbed despite the proximity of the underlying metal surface. They attributed this decoupling to the non-planar conformations of rubrene molecules adsorbed on the surface. Hence the 3-D structures of organic molecules may play an important role in determining their interface electronic states.

H. Petek and his coworker studied C_{60} adsorbed on Cu(111) by both experiments (STM/STS) and theory (DFT)\textsuperscript{99}. They have extracted the relation between C_{60} spherical structure and unoccupied electronic states. The novel discovery in their work is the superatom molecular orbitals (SAMO’s) which are bound states of electrons to the core of the hollow C_{60} cage. The hybridization of SAMOs between adjacent C_{60} adsorbates is believed to be the key driving force of the formation of dimers, one-dimensional chains and two-dimensional quantum wells observed by their STM study.

Recently, three important papers have been published on magnetic related properties at MO interfaces by spin-polarized STM (SP-STM). R. Wiesendanger and his coworkers studied spin- and energy-dependent tunneling through a single CoPc molecule adsorbed on Fe thin film\textsuperscript{100} and also the inversion of the spin polarization at organic sites on surfaces.\textsuperscript{101} Iacovita et al. studied spin transport across CoPc adsorbed on magnetic nanoleads at low temperature\textsuperscript{102}. These leading researches on SP-STM studying MO interfaces will be discussed further in later chapters.
Figures

Figure 1.1 Schematic representations of spin valve based on (a) GMR effect. When the magnetization directions in ferromagnetic electrodes F1 and F2 are parallel, electrons with one spin state (i.e. spin-up) can travel through nearly scattered while electrons with the other spin state (i.e. spin-down) are almost scattered. When the magnetization directions in F1 and F2 are antiparallel, both electron species would experience considerable scattering. (b) TMR effect. Tunneling conductance is determined by the product of densities of states of like spin bands. It reaches maximum in parallel geometry.
Figure 1.2 Tris(8-hydroxyquinolinate) aluminium (Alq3) (a) chemical compound (b) three dimensional view of molecular structure.
Figure 1.3 Typical arrangement of organic semiconductor devices. (a) organic photoconductor (OPC) (b) organic light emitting diode (OLED), organic photovoltaic cell (OPV), organic crosspoint memory (ORAM) (c) organic field effect transistor (OFET).
Figure 1.4 Band alignment at (a) metal-inorganic semiconductor interface. Vacuum level aligns at the interface and the potential difference $V_{bi}$ is accommodated on the charge depletion region in semiconductor side. (b) metal-organic semiconductor interface. Vacuum level shift, the potential difference $V_{bi}$ is accommodated by the formation of an interfacial dipole layer.
References

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CHAPTER 2

Scanning Tunneling Microscopy and Spectroscopy

2.1 Introduction to Scanning Tunneling Microscope

The Scanning Tunneling Microscope (STM) is a scientific instrument for imaging surfaces at the atomic level. It was invented by Gerd Bining and Heinrich Rohrer (at IBM Zürich) and implemented by Bining, Rohrer, Gerber, and Weibel in 1981. This great invention for nano-technology earned its inventors the Nobel Prize in Physics in 1986. Compared to the other surface sensitive analytic methods (e.g. UPS, XPS, IPES) which probe average and usually macroscopic electronic and/or chemical information at the surfaces, STM is a local surface science technique. The resolution of STM is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms or molecules within materials are routinely imaged and even manipulated. The STM has wide applicability: it can be used not only in ultra high vacuum (UHV) but also in air, water, and various other liquid or gas environments. It can also be used over a wide temperature range from 100mK up to a ~ 1000 K.

A typical STM apparatus can be described as follows (Figure 2.1): a probe tip, usually made of tungsten or platinum-iridium alloy, is attached to a piezo-driver which consists of three mutually perpendicular piezoelectric transducers to control tip moving in three dimensions (x and y parallel to the plane of the surface and z perpendicular to the surface). Upon applying a voltage, a piezoelectric transducer expands or contracts, which in turn controls the tip position relative to the sample. Using the coarse positioner and the z
piezo, the tip can be brought to within a tunneling distance (1-15Å) to the sample. The electron wave functions in the tip overlap electron wave functions in the sample surface. By applying a bias voltage between the tip and the sample, a tunneling current is generated (1pA-10nA). The tip is rastered across the surface while maintaining a constant current by means of an electronic feedback loop; hence the scanning image is a measure of the changes in the tip height in response to the topography of the sample. Due to the issues surrounding wavefunction overlap, the tip response also incorporates the local electronic structure of the sample as described in more detail later in this chapter.

In many instruments, the STM tip is at virtual ground due to its direct connection to the input of an op-amp based current-to-voltage converter. The bias voltage $V$ is the sample voltage. If $V>0$, the electrons are tunneling from the occupied states of the tip into the empty states of the sample, thereby the unoccupied electronic states of the sample are probed (Figure 2.2a). If $V<0$, the electrons are tunneling from the occupied states of the sample into the empty states of the tip, correspondingly measuring the occupied electronic states of the sample (Figure 2.2b). The current feedback mechanism is implemented by converting the tunneling current to a voltage by the current amplifier, which is then compared with a reference value; the difference is amplified to drive the $z$ piezo: if the absolute value of the tunneling current is larger than the reference value, then the voltage applied to the $z$ piezo tends to withdraw the tip from the sample surface, and vice versa.
2.2 Background theory for Scanning Tunneling Microscope/Scanning Tunneling Spectroscopy

2.2.1 STM Theory

As its name suggests, the operation of STM relies on quantum tunneling effect, which is one of the fundamental features of quantum mechanics that distinguishes it from classical mechanics. In classical mechanics, the particle would be deflected if it tries to cross an energy barrier whose energy is larger than its energy (e.g. a soccer ball hitting the goal bar would bounce back), however, in quantum mechanics the particle has a non-zero probability of tunneling through the potential barrier. The wave-like nature of electron allows it to tunnel through a high potential barrier. It has a non-zero, exponentially decaying probability of penetrating through the barrier that has a finite thickness. The quantum tunneling has played a vital role in many branches of modern physics. In the last half of the 20th century, four Nobel Prizes in physics were awarded to discoveries and inventions related to tunneling: the tunneling junction experiment of Giaever, the discovery of the Josephson effect, the invention of tunnel diode by Esaki, and of course, as mentioned above, STM.

Here, we start the approach to the theory of STM with the case of STM operation under vacuum. A vacuum barrier separates the tip and the sample. As aforementioned, when the tip approaches the sample, the wavefunctions in the sample and tip overlap, and an applied bias would generate a net tunneling current. For quantifying the tunneling current, the most widely applied theory is Bardeen’s first-order perturbation theory. The conceptual picture used in this approach is to imagine scattering of an electron from the tip to the sample...
and to calculate scattering rates with time dependent perturbation theory. For simplicity consider a one-dimensional case when the tip and the sample are far apart. The electron wavefunctions of tip and sample satisfy separate Schrödinger equations:

\[
i\hbar \frac{\partial \psi}{\partial t} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_t \right] \psi
\] (2.1)

\[
i\hbar \frac{\partial \psi}{\partial t} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_s \right] \psi
\] (2.2)

where \(U_t\) and \(U_s\) are the potential function of tip and sample respectively, the solutions to the time-evolved Schrödinger equations are the time-independent wavefunctions multiplied by time evolution operator, namely:

\[
\psi = \psi e^{-iEt/\hbar}
\] (2.3)

where the time-independent wavefunctions \(\psi\) and energy eigenvalues \(E\) satisfying

\[
\left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_{s/t} \right] \psi = E \psi
\] (2.4)

By bringing the sample and tip closely, the Schrödinger equation of the combined system is

\[
i\hbar \frac{\partial \psi}{\partial t} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + U_t + U_s \right] \psi
\] (2.5)

the potential function of the combined system is \(U_t + U_s\). The wavefunctions for this system can be written in the usual time dependent perturbation theory form as the sum of wavefunctions of sub-systems:

\[
\]
\[ \Psi = \psi_u e^{-iE_u t / \hbar} + \sum_{v=1}^{\infty} c_v(t) \chi_v e^{-iE_v t / \hbar} \]  

(2.6)

where \( \psi_u \) and \( \chi_v \) stand for the spatial wavefunctions of tip and sample respectively, the coefficient \( c_v(t) \) is related to the probability of finding the electrons of the sample in the tip side, basically the tunneling probability. For solving \( c_v(t) \), Bardeen’s tunneling theory makes an assumption of that the two sets of wavefunctions are approximately orthogonal:

\[ \int \psi_u^* \psi_v d^3r \equiv 0 \]  

(2.7)

Inserting time-dependent wavefunctions (equation 2.6) to the system Schrödinger equation (equation 2.5), and solving for \( c_v(t) \), yields:

\[ c_v(t) = M_{uv} \frac{e^{-i(E_u - E_v)t / \hbar} - 1}{E_u - E_v} \]  

(2.8)

where \( M_{uv} \) is the tunneling matrix element, defined as:

\[ M_{uv} = \int_{x > z_0}^{\infty} \psi_u U_z \chi_v^* d^3r \]  

(2.9)

Hence starting with the \( u \)-th state of the tip, the probability of having the \( v \)-th state of the sample at time \( t \) is

\[ p_{uv}(t) \equiv |c_v(t)|^2 = |M_{uv}|^2 \frac{4 \sin^2[(E_u - E_v)t / 2\hbar]}{(E_u - E_v)^2} \]  

(2.10)

the tunneling probability reaches its maximum at \( E_u = E_v \), and approaches zero rapidly for \( E_u \neq E_v \). Hence, the tunneling current depends on how many states of the sample near the energy of a state of the tip are available to tunnel into. If the density of states of both sample and tip does not vary appreciably in the vicinity of Fermi energy, the tunneling current can be written as:

\[ \frac{dI}{dt} = \sum_{uv} |M_{uv}|^2 \frac{\sin^2[(E_u - E_v)t / 2\hbar]}{(E_u - E_v)^2} \]  

(2.11)
where $\rho_s(E_F)$ and $\rho_t(E_F)$ are the density of states at Fermi level of sample and tip respectively, V is a applied bias. $M_{uv}$ is tunneling matrix:

Because usually STM tip is made of metal\textsuperscript{12,13}, for which the density of states near the Fermi level is small and featureless equation 2.11 shows that the tunneling current is a direct measure of the density of states of the sample. In simple words, STM images are a convolution of topographic and electronic properties of the sample surface. In real STM operation, due to often large applied voltages V, the actual tunneling current is sum of tunneling currents of a range of states. Since at the finite temperature, the electron distributions in both tip and sample follow the Fermi distribution and the Fermi distribution function can be approximate to a step function, hence the tunneling current is the integral\textsuperscript{4}:

$$I = \frac{2\pi e^2}{h} |M_{uv}|^2 \rho_s(E_F)\rho_t(E_F)V$$

(2.11)

Since $|M_{uv}|^2$ in equation 2.12 determines tunneling probability between tip and sample, we define tunneling transmission coefficient $T = |M_{uv}|^2$, which can be calculated by the WKB approximation to be:

$$T = \exp \left( -2 \frac{m}{\hbar} \int_0^d \sqrt{E_F + \epsilon - eV(x)} \, dx \right)$$

(2.13)
2.2.2 STS Theory

Though the STM images are convolution of surface topographic and electronic structures, the electronic structure of the sample surface can be solely probed by STM via scanning tunneling spectroscopy (STS)\textsuperscript{14-17}. With STS, the differential conductance ($dI/dV$) or tip-sample separation ($z$) is recorded as a function of sample bias at fixed position of sample. This allows extraction of the local electronic properties of the surface for fixed topographic contribution. STS can be carried out with single molecule/atom precision\textsuperscript{18}, providing a distinct advantage over surface averaged techniques (e.g. UPS, XPS) for examining the exact local electronic structure of surfaces and interfaces.

Conventional STS is carried out in constant-height mode, namely with constant current feedback loop off, by measuring tunneling current versus applied bias. It is expected to extract electronic structures of the sample by normalized $dI/dV$ curves. The theory for this mode is straightforward. Recall the tunneling current in equation 2.12, and assume the tip density of states is approximately constant:

\[
I \propto \int_{0}^{eV} \rho_{s}(E_{F} + \epsilon)T(E_{F} + \epsilon - eV, E_{F} + \epsilon)d\epsilon \tag{2.14}
\]

where $\rho_{s}$ is the density of states of the sample. T is the transmission probability, V is applied bias, eV is the “probe” energy. Thus the differential conductance ($dI/dV$) is:

\[
\frac{dI}{dV} \propto eT(E_{F}, E_{F} + eV)\rho_{s}(E_{F} + eV) \tag{2.15}
\]

\[
+ \int_{0}^{eV} \rho_{s}(E_{F} + \epsilon) \frac{dT(E_{F} + \epsilon - eV, E_{F} + \epsilon)}{dV}d\epsilon
\]
From equation 2.15, it shows \( \frac{dI}{dV} \) is directly associated with the density of states of sample superimposed on the exponential dependence of applied voltage \( V \) and sample-tip separation \( d \). If we normalize the differential conductance with \( I/V \) the result is:

\[
\frac{dI}{dV} \cdot \frac{V}{I} \propto \rho_s(E_F + eV) + \int_0^{eV} \frac{\rho_s(E_F + e) \cdot dT(E_F + e - eV, E_F + e)}{dT(E_F + eV, E_F + e)} \, d\epsilon 
\]

(2.16)

in the above expression, because transmission probability \( T \) appears in both numerators and denominators as ratios, their exponential dependences on \( V \) and \( d \) tend to be cancelled for small voltages leaving:

\[
\frac{dI}{dV} \cdot \frac{V}{I} \propto \rho_s(E_F + eV) 
\]

(2.17)

this normalized differential conductance is the conventional approach to extracting sample density of states from STS measurements.

In this thesis, another less commonly-used STS mode is mainly used for probing organic semiconductor molecules on surfaces, namely constant-current STS or "\( z(V) \) spectroscopy". The operation of this mode STS involves keeping the constant current feedback loop on, and then varying the voltage across the tunnel junction. In response to the changing voltage, the tip must move vertically to maintain the constant current. It retracts away from the surface as voltage increases and advances toward the surface as voltage decreases. Intuitively, the rate of tip motion is proportional to the tunneling probability, so it is expected that a bias regime with an enhanced LDOS will result in an increase in the rate of vertical motion.

A differential equation for tip position \( z \) as a function of voltage \( V \) has been deduced\(^{19} \).
\[ \alpha \sqrt{\phi} I \frac{dz}{dV} + \frac{\alpha eI}{4\sqrt{\phi}} Z - eB \rho_T \rho_S(eV) T(z, V, E = eV) = 0 \quad (2.18) \]

Where \( \alpha = \frac{2\sqrt{m}}{\hbar} \), \( B = 1/2*\pi \hbar^3 m^{-2} A \) with \( A \) being the effective tunneling junction area and \( m \) the mass of the tunneling electron, \( \phi \) is the apparent barrier height of the tunneling junction, \( \rho_T \rho_S \) is the density of states of the tip and the sample. The function \( T \) is the tunneling transmission probability. Equation 2.18 clearly demonstrates the relationship between \( dz/dV \) spectra and the local electronic states of surface. In addition, Pronschinske et al. did numerical studies for different potential barriers and to a good approximation they found that:

\[ \rho_s(E_F + eV) \propto \frac{dz}{dV} \cdot \frac{V}{Z} \quad (2.19) \]

Equation 2.19 is the precise analog to the traditional normalization of \( dI/dV \) spectra, which has been commonly used for probing surface electronic structures. Hence constant-current STS can be a valid alternative to constant-height STS.

The major advantage of constant-current STS is to minimize perturbation of the surface by the tunneling process. Constant-height measurements often result in a high current, which has a strong probability to perturb small structures on the surface by injecting too many electrons from the STM tip. Instead, constant-current measurement can maintain a small tunneling current to minimize the perturbation brought by tip, and hence allow STS measurements routinely at higher biases than constant height mode. This is a very significant advantage for the study of molecular adsorbates, which may have important electronic states at high energies and are susceptible to tip-induced chemical reactions, diffusion, or desorption.
2.3 Background Theory for Spin-Polarize Scanning Tunneling Microscope

As one of the most important specialized application of STM, Spin-Polarized STM (SP-STM) can provide detailed information of magnetic phenomena on the single-atom scale in addition to the intrinsic atomic resolution imaging structure possible with STM. SP-STM opened a novel approach to study static and dynamic magnetic processes by precise investigations of domain walls in ferromagnetic and antiferromagnetic systems, and thermal and current-induced switching of nano-magnetic particles\textsuperscript{20,21,22}.

The electron is a well-known fermion which has two eigenstates, often denoted as spin-up and spin-down states. For ferromagnets, near the Fermi level, the density of states of electrons depends on the state of spin\textsuperscript{23}:

\[
\rho_{\uparrow}(E_F) \neq \rho_{\downarrow}(E_F) \quad (2.20)
\]

in implementation of SP-STM, the STM tip is usually coated with a ferromagnetic material, e.g. Fe, or Gd, to make the tip density of states spin-polarized\textsuperscript{20,21}. In other words, the spin-up tip DOS and the spin-down tip DOS are different, making the local magnetic properties of the sample accessible to atomic resolution imaging as illustrated below.

To theoretically study spin-polarized tunneling, Bardeen’s tunneling theory should be extended to include spin\textsuperscript{4}. Instead of using a single-component wavefunction, two components are necessary to describe a state of an electron with spin. In general, a sample state can be represented by s spinor:

\[
\psi = \begin{pmatrix} \psi_{\uparrow}(r) \\ \psi_{\downarrow}(r) \end{pmatrix} e^{-iE_{\text{uf}}/\hbar} \quad (2.21)
\]
Thus the derivation of tunneling current involves a spinor transformation from the spin coordinate system of one electrode to the spin coordinate system of the other electrode. The result of tunneling conductance is given as:

\[
G = 2\pi^2 G_0 \left( \rho_{t\uparrow}\rho_{s\uparrow}|M_{\uparrow\uparrow}|^2 + \rho_{t\uparrow}\rho_{s\downarrow}|M_{\uparrow\downarrow}|^2 + \rho_{t\downarrow}\rho_{s\uparrow}|M_{\downarrow\uparrow}|^2 + \rho_{t\downarrow}\rho_{s\downarrow}|M_{\downarrow\downarrow}|^2 \right) \tag{2.22}
\]

The tunneling matrix in the coordination system of magnet A is

\[
\begin{pmatrix}
M_{\uparrow\uparrow} & M_{\uparrow\downarrow} \\
M_{\downarrow\uparrow} & M_{\downarrow\downarrow}
\end{pmatrix}
= M_0 \begin{pmatrix}
e^{i(\phi+\psi)/2} \cos(\theta/2) & e^{i(\phi-\psi)/2} \sin(\theta/2) \\
e^{-i(\phi+\psi)/2} \sin(\theta/2) & e^{-i(\phi-\psi)/2} \cos(\theta/2)
\end{pmatrix}
\tag{2.23}
\]

Where

\[
M_0 = \frac{\hbar^2}{2m} \int_\Sigma \left( \psi \nabla^* \chi - \chi^* \nabla \psi \right) \cdot dS \tag{2.24}
\]

By defining the spin-averaged density of states

\[
\rho_t = \rho_{t\uparrow} + \rho_{t\downarrow} \quad \rho_s = \rho_{s\uparrow} + \rho_{s\downarrow} \tag{2.25}
\]

And the spin-polarized density of states

\[
m_t = \rho_{t\uparrow} - \rho_{t\downarrow} \quad m_s = \rho_{s\uparrow} - \rho_{s\downarrow} \tag{2.26}
\]

Equation 2.22 can be written in:

\[
G = 2\pi^2 G_0 |M_0|^2 (\rho_t \rho_s + m_t m_s \cos \theta) \tag{2.27}
\]

Introducing \( G_{sa} = 2\pi^2 G_0 |M_0|^2 \rho_t \rho_s \), the spin-averaged tunneling conductance; and \( G_{sp} = 2\pi^2 G_0 |M_0|^2 m_t m_s \), the spin-polarized tunneling conductance, Equation 2.27 be written as:

\[
G = G_{sa} + G_{sp} \cos \theta \tag{2.28}
\]
It is clear that if one of the electrodes, either sample or tip, is not spin-polarized, namely $m=0$, equation 2.27 will reduce to conventional STM case as derived in the last section. From the above relationship, the tunneling conductance in the magnetic case is expected to depend on the spin-resolved local density of states at the Fermi energy for both tip and sample, and it is associated with the angle between the magnetization directions of the tip and sample. The tunneling conductance is maximum when the magnetic directions of two electrodes are parallel ($\theta = 0^\circ$); the tunneling conductance is minimum when the magnetic directions are anti-parallel ($\theta = 180^\circ$). This is a so-called spin valve effect that is the fundamental working principle of Spin-Polarized STM.
2.4 General instrumentation description

All of the experiments discussed in this thesis were carried out in an ultra-high vacuum (UHV) system (Figure 2.3), which consists of three parts: STM, preparation chamber, and fast entry lock (FEL).

- **STM**: its function is for characterizing the features of the samples prepared in-situ or ex-situ.
- **Preparation Chamber**: a multi-function chamber which is mainly for transporting and cleaning samples and tips. It also can do UHV level sample preparation, STM tip cleaning and coating etc.
- **Fast Entry Lock**: mainly services for loading/unloading samples in the system. At the same time, it serves as an organic deposition system.

The whole UHV system is built on four equally distributed NEWPORT air legs whose job is for isolating vibrations. On top of them, a frame built by uni-strut specifically designed for bracing the components of the system. The STM chamber and preparation chamber are connected without isolation while they connect to FEL through a gate valve (see schematic drawing of the system in Figure 2.4). So the system can also be treated as two interconnected chambers. We call the STM chamber and the preparation chamber together the “main chamber”.

To achieve UHV, three level pumps pump the main chamber: a roughing pump ($\sim 10^{-1}$torr), a VARIAN TV81-M turbo pump ($\sim 10^{-6} - 10^{-7}$torr), and a GAMMA Vacuum ion pump ($<1 \times 10^{-10}$torr). A VARIAN UHV-24 ionization gauge monitors the pressure. The gas composition in the chamber can be checked by a residual gas analyzer (RGA) mass
spectrometer. The pressure of this chamber can reach lower than $7 \times 10^{-11}$ torr by carefully baking. The prep chamber itself is home designed with 10 ports, and all the ports points to the center of the chamber in order for the easy integration of different peripheral vacuum instruments. A manipulator (Figure 2.3 & Figure 2.4), which is free of movement in three dimensions, fulfills the transportation of sample between intermediated chamber and STM. Meanwhile, it also can heat/anneal sample by an integrated PBN heater. Temperature is monitored by a K-type thermocouple attached near the sample.

The other modules attached to intermediated chamber include (Figure 2.4):

- **ISE 5 Ion Source**: it is a compact and versatile ion sputtering source which features high target currents and a wide range of energies. It is mainly used for sputtering samples for cleaning purpose. Due to its nature, to differentiate it with another sputtering source of the chamber, we call it ‘cold sputter gun’.

- **High Voltage Sputter Source**: another sputter gun served for the system. Since it requires currents running through a filament to emit electrons while working, it is called the ‘hot sputter gun’. This sputter gun is mainly for long time sputtering (several hours, e.g. cleaning Cr) because the high risk of carbon accumulation restricts the use of previous ‘cold sputter gun’. Further descriptions on these sputter source will be discussed later.

- **Argon Gas Leak Value**: leaking in high purity Argon gas for Ar$^+$ sputtering.

- **MDC E-Vap 100 Precision Evaporation Source**: this evaporator is this evaporator is used in our system as Fe-evaporator, which coats multi-layers of iron on STM tip for implementing SP-STM.
• STM Tip Heater: this homemade electron bombardment heater is designed for cleaning STM tip quickly and thoroughly under UHV, this process is critical requirement for implementing SP-STM.

The part interconnected with the main chamber is the fast entry lock (FEL) (Figure 2.3 and Figure 2.4). A PFEIFFER economy pumping station, which consists of a roughing pump and a turbo pump, is responsible for pumping and maintaining the pressure in high vacuum (base pressure ~ $1 \times 10^{-8}$ torr). A long transfer arm is attached to FEL as showing in Figure 2.3 & Figure 2.4. It serves for transferring samples and tips between FEL and intermediated chamber. The FEL usually has two homemade molecular source evaporators attached for molecular beam epitaxy (MBE) growth of organic semiconductors on single crystal metal surfaces. Two quartz crystal monitors (QCM) are also attached to monitor the molecular flux coming from each molecular evaporator.

The STM control and data collecting is fulfilled by MATRIX software bundle, which collects the current information coming from STM preamplifier, and then it makes necessary transformation for displaying. It has a user-friendly interface for controlling tip movement, adjusting scanning parameters, and measuring constant-height or constant-current STS. The stored data are often further processing and analyzed by specialized software: Scanning Probe Image Processor (SPIP) software package is the primary one while WSxM is occasionally used as a secondary processor.
2.5 Specific description of instruments used in the thesis

2.5.1 VT-STM

The whole UHV system is designed and implemented for operating STM in vacuum. As the most crucial part of the system, it needs a particular description here. Our STM system is a commercial OMICRON VT-STM-XA. In the name, VT stands for variable temperature since the STM has the ability to heat/cool samples in-situ. To implement cooling, a bath cryostat is fixed to the STM base flange. Liquid nitrogen is poured into this cryostat, which is thermally connected to STM mounting sample stage by highly flexible copper braid in the vacuum. In this manner, the sample can be cooled to ~130K. To minimize the vibration input through the copper braid, it is mechanically decoupled at the copper braid decoupling stage. For heating a direct PBN heater element is embedded in STM sample stage. For our system, the temperature can be increased to as high as 650K, and is monitored by a K-type thermocouple.

For successful high-resolution STM a high quality vibration decoupling system is essential. The VT STM XA base plate is suspended by four soft springs which are protected by surrounding columns. The resonance frequency of the spring suspension system is about 2 Hz. Vibrations of the suspension system are intercepted using nearly non-periodic eddy current damping mechanism. For this purpose a ring of copper plates that comes down between permanent magnets surrounds the base plate. In order to allow tip or sample exchange, adjustments etc., a push-pull motion feedthrough is used for locking the spring suspension system.
The VT STM utilizes a single tube scanner to achieve a scan range (xyz) of 12µm × 12µm × 1.5µm. The tips are exchangeable in-situ. The first I/V conversion stage is located in-situ, close to the scanner in order to achieve the best signal-to-noise ratio and optimal performance. The scanner is mounted on an independent, orthogonal, and guided three-dimensional coarse positioning device with 10mm × 10mm × 10mm travels in xyz direction. The basic principle and workflow of STM have been introduced in the beginning of this chapter. Besides those essential parts, e.g. piezo electrodes, preamplifier, feedback amplifier, our STM chamber equips several complementary gadgets or tools:

- 12 Slot Carousel: Store samples and tips in UHV.
- Wobblestick: Transfer sample between STM stage and manipulator, or sample carousel.
- CCD Camera: Directly point to STM stage to assist with coarse z-direction movement of tip.

The STM tips used in our system are primarily electrochemically etched tungsten tips. By using OMICRON Tip Etching Kit, atomically sharp W tips can be routinely prepared by DC etching in KOH. Then the tip is mounted on a tip holder (Figure 2.5) with proper electrical contact and insulation. The tip with its holder is loaded into UHV system by utilizing a tip carrier that can be mounted on scanner or stored in the carousel.

Our STM system uses standard OMICRON sample plates (Figure 2.6), on which the actual sample cannot exceed the red area (Figure 2.6b) of size 11nm × 11nm and sample thickness must less than 3mm. The philosophy of this XA series is to provide maximum
compatibility with many different surface science techniques, like MBE, RHEED, and different kinds of electron spectroscopy.

2.5.2 Iron Evaporator (MDC E-Vap 100 Precision Evaporation Source)

The iron evaporator in our system is responsible for coating Fe on STM tip for SP-STM or depositing Fe films on sample surface. Its schematic is drawn in Figure 2.7. The evaporation source (Fe here) is placed with a line of the substrate. The electron beam produced by a tungsten filament is focused onto the evaporant material which is in the shape of a rod. The electron beam’s kinetic energy is converted to thermal energy at the beam’s impact point (evaporant surface) causing the evaporant to be elevated in temperature. The electron beam’s current (emission current) is monitored and regulated to allow control of the amount of energy dissipated into the evaporant material. Above certain temperature, the evaporant material starts to evaporate; the evaporated material is emitted from the source according to a distribution whose shape is dependent upon the portion of the evaporant tip providing the emitted vapor flux. The shield aperture collimates the atomic beam to improve the uniformity of the vapor flux.

The evaporator equips a linear motion drive to control the position of evaporant source within the evaporator head because this position has a significant influence upon the operating characteristics of the source. There is found to be an optimum position at which the space charge limited current is incident upon the tip of the evaporant to produce the maximum vapor flux at the substrate. This maximum evaporation rate will correspond to the tip of the evaporant being near the top of the focusing tube opening. Typically, we use the
motion drive to adjust Fe rod position to its nearly maximum flux position. The position must be continuously adjusted during experiments to compensate for the consumption of the rod.

2.5.3 STM Tip Heater

Similar to the Fe evaporator, our homemade tip heater (Figures 2.8) use an electron bombardment mechanism to clean the tip. Basically, we use two of barrel connecters to grasp a tungsten filament. These barrel connecters then are connected to electrical feedthrough outside the vacuum by copper wire, the connection is insulated from the chamber and tip stage by using ceramic beads and fiberglass wrapper. As Figure 2.8 shown, the tip with its carrier is held by a stage that is electrically isolated from the rest of the chamber. By applying a high voltage, usually 1kV, the tip end would have a positive high voltage. Once we apply applicable current to filament, electrons emitted from the filament are expected be accelerated to bombard to the tip. The temperature at the tip end is expected to elevate quickly (3-5 second) to burn the dirt off, and even possibly make the tip more blunt in order to further coat Fe. Due to the electrostatic focusing of electrons at the sharp tip end the magnets at the bottom of the tip holder which used for mounting tip on the scanner can be kept cool enough during these short flashes to maintain their magnetization.

2.5.4 Molecular Evaporator

As the source of our molecule deposition (Figure 2.9), we built the evaporator by using a degassed quartz crucible wrapped tightly by Tantalum filament coil. The molecular source material, usually powdered, is held in the quartz crucible. The Tantalum filament is connected to electrical feedthroughs outside the vacuum. Hence the crucible and its
molecules are heated by direct current filament heating. A stainless sheet is wrapped around the crucible to provide radiation shielding.

2.5.5 Cold Cathode Sputtering Source and Hot Sputtering Source

Ar⁺ sputtering is our main technique to clean single crystal metal samples in the UHV system. There are two sputter units in our UHV system. One is OMICRON ISE 5 ion source. The schematic of it is shown in Figure 2.10. It decomposes Ar to create Ar⁺ and electrons in the gas cell, and then Ar⁺ travels through a flight tube to finally reach the sample. Another sputtering source in our system is a PHI Model 04-161 2kV Sputter Ion Gun. We differentiate it with the previous one by calling it hot sputter gun. As its name suggests, it has filaments which emit electrons by thermionic emission. Then the electrons would ionize Ar to Ar⁺ plasma, the Ar⁺ ions are accelerated by high voltage to reach the sample. The resulting argon ion beam has a cleaning effect on the sample surface by removing a surface layer. The surface layer removal proceeds as surface atoms and molecules which are struck by argon ions are ejected from the sample into the vacuum due to momentum transfer from the ions.
Figure 2.1 Schematic diagram of scanning tunneling microscope imaging the local sample surface.
Figure 2.2 Energy level alignments at metal tunneling junctions (a) electrons tunneling from tip to sample (b) electrons tunneling from sample to tip.
Figure 2.3 Photos of the ultra high vacuum scanning tunneling microscope system in Dougherty research laboratory with main components marked (a) top view (b) side view.
Figure 2.4 Schematic diagrams of the ultra high vacuum scanning tunneling microscope system in Dougherty research laboratory with main components marked (a) top view of overall system (b) side view of intermediated chamber (c) side view of fast entry lock (FEL).
Figure 2.5 Omicron VT-STM-XA series tip utensil, tungsten or other metals tip are mounted in the center cylindrical tube, the tip holder provides electrical contact for tip with STM scanner stage.
Figure 2.6 Omicron VT-STM-XA Sample plate (a) photo (b) schematic drawing, red part limits actual sample range.
Figure 2.7 Schematic diagram shows working principles of MDC E-Vap 100 Precision Evaporation Source. An iron source is loaded in the center, heated by electron bombardments which are generated by a hot filament and accelerated by an external field.
Figure 2.8 Schematic diagram of home-built STM tip heater. Tip is applied 1kV positive voltage. A filament is insulated from tip carrier stage. Hot electrons emitted from filament accelerate in high filed to bombard tip for cleaning purpose.
Figure 2.9 Schematic diagram of organic evaporator located in fast entry lock. A fully degassed crucible is wrapped tightly with tantalum wire, organic compounds placed in the crucible can be heated to evaporate by controlled filament currents. A stainless shield is added for centralizing evaporation flux.
Figure 2.10 Schematic diagrams of two argon sputtering units (a) OMICRON ISE 5 Ion Source (b) PHI Model 04-161 2kV Sputter Ion Gun.
References


CHAPTER 3

STM Studies of the Structure of Alq3-Metal Interfaces

3.1 Introduction

The demonstration of an organic light emitting diode (OLED) in 1987 by Tang and van Slyke\textsuperscript{1} was a major driving force in creating the intense modern interest in organic materials for electronics and optoelectronic applications. Organic device materials have already made a commercial impact in displays and show significant promise to expand into large area lighting and photovoltaic applications\textsuperscript{2}. The emissive materials used in Tang’s and van Slyke’s original OLED was tris (8-hydroxyquinoline) aluminum (Alq3). In the past 20 years, its basic interfacial properties have been characterized extensively\textsuperscript{3,4} and it remains a very common emissive layer in state-of-the-art OLED’s\textsuperscript{5}.

Single crystals of Alq3 can be grown by vapor transport methods and show a number of polymorphic structures all driven to a large extent by van der Waals interactions between the \( \pi \) electrons on hydroxyquinolato ligands on adjacent molecules\textsuperscript{6}. In contrast, thin films relevant to layered OLED’s are structurally disordered and often referred to as “amorphous”. For example, an X-ray diffraction study by Brinkmann et al. showed no sign of order in vapor deposited films\textsuperscript{6}. This disorder is crucial to properly modeling thin film device operation\textsuperscript{7}. It impacts the voltage and temperature dependence of carrier mobility in space charge limited transport\textsuperscript{7} and can modify injection-limited current as describe below\textsuperscript{8-10}. Strong disorder is likely to be a common feature of organic molecular films in which molecules (such as Alq3) have non-planar 3D structures. For example, a recent scanning
tunneling microscopy (STM) study of rubrene on Au(111)\textsuperscript{11} reported disorder due to coexisting 3D conformations of this important molecule.

Electrical transport in thin films of Alq3 contacted by electrodes with high to moderate work functions have often been found to be injection limited\textsuperscript{8,12,13} due to the large energy difference between electrode Fermi levels and molecular orbital-derived transport levels. Disorder has been demonstrated to quantitatively modify the current voltage ($I/V$) characteristics of injection limited devices. Burin and Ratner derived a simple analytical model for the impact of disorder on charge injection that illustrated how the usual Richardson-Schottky formula for injection-limited current could be altered\textsuperscript{9,10}. A clear consequence of this model is that the injection limited current in a device increased as the width of the Gaussian distribution of transport levels increase. A broader distribution has a greater number of energetically accessible states in its tails that enhance injection.

For Alq3 thin films sandwiched between Mg:Ag and either Al or Mg:Ag electrodes, Baldo and Forrest\textsuperscript{8} observed very unique temperature and thickness dependent $I/V$ characteristics that required implementation of a new model of injection into a disordered solid\textsuperscript{8}. In the Baldo and Forrest model, it was hypothesized that disorder was enhanced near the metal-organic interface in such a way that the limiting charge injection process was not direct injection from the metal electrode into the disordered Alq3 film but rather injection from a highly disordered interfacial molecular layer into the somewhat less disordered bulk film. A possible physical origin of the interfacial disorder was suggested to be random variations in orientations of Alq3 molecules that result in strongly varying local interfacial dipoles\textsuperscript{14} in the plane of the metal-organic interface.
Only a few scanned probe experiments directed at visualizing Alq3 film structure at the molecular level have been attempted. Alvarado and his co-workers found that Alq3 diffused too rapidly on the surface to image by STM at room temperature on Au(111)\textsuperscript{15}. However, they were able to estimate the transport gap for Alq3/Au(111) using tip distance-versus-voltage spectroscopy\textsuperscript{15,16}. More recently, linear Alq3 nanostructures were observed on ultrathin KBr films, but intermolecular distances were not reported\textsuperscript{17}. Numerous studies have used atomic force microscopy (AFM) to image the nanometer scale morphology of thick Alq3 films\textsuperscript{18-20}.

In my work, we studied the first layer of Alq3 on a Cu(110) surface by scanning tunneling microscopy observations that achieve single molecule resolutions. These experiments show a poorly ordered interface that results from growth on a room temperature substrate and that persists after annealing up to about 590K. While no long-range order is observed in this first monolayer, intermolecular interactions are revealed by the formation of randomly oriented chain-like aggregates of Alq3 molecules. We describe the origin of these disordered chain structures from anisotropic intermolecular interactions using model density functional theory (DFT) calculations.

3.2 Experimental methods

Experiments were carried out in an STM ultrahigh vacuum system with two interconnected chambers as described in Chapter 2. The main chamber (base pressure $<7\times10^{-11}$ torr) houses facilities for substrate cleaning and STM characterization. Fast entry lock (FEL) (base pressure $\sim1\times10^{-8}$ torr) is separated from the first by a gate valve and houses home-built organic evaporators and a quartz oscillator for flux monitoring.
The substrate was a Cu(110) single crystal (Princeton) cleaned by repeated cycles of 1keV Ar\(^+\) sputtering following by annealing for 20 minutes at \(\sim 700\) K. During deposition, the Cu(110) crystal was held at room temperature. Powdered tris-(8-hydroxyquinoline) – Aluminum (“Alq3”, Sigma-Aldrich – 99.995%) was loaded as received into an organic evaporator which consists of a degassed quartz crucible that could be heated by a tightly wrapped Tantalum filament coil. The Alq3 was outgassed for several hours in the deposition chamber prior to film growth. The stability of Alq3 flux was monitored with a quartz oscillator before and after deposition. Absolute flux calibration was carried out by direct STM imaging with molecular resolution.

STM imaging was carried out at room temperature with the commercial STM described in last chapter operated in constant current mode with electrochemically-etched tungsten tips. Annealing experiments after Alq3 deposition were performed by heating the sample in the main chamber manipulator with an integrated PBN heater. Temperature was monitored by a K-type thermocouple attached near the sample and corrected by adding 120 K to estimate the real sample temperature. This correction is based on infrared pyrometry at temperatures greater than 820 K and is expected to be accurate only to about \(\pm 30\) K.

### 3.3 Results

In Figure 3.1a, an STM image of the large scale morphology of the Cu(110) substrate surface is shown. Relatively flat terraces separately by single-atom high steps can be seen. After a very short deposition of Alq3, it is possible to see a number of uniformly sized approximately circular protrusions on the terraces that are single Alq3 molecules (Figure 3.1b).
Upon further deposition, Alq3 molecules begin to aggregate, displaying a strong tendency to form pairs as shown in Figure 3.2a. These pairs are spaced typically just under 1 nm apart (center to center), which is a distance consistent with near-neighbor spacing in bulk Alq3 crystals. We note that the pairing direction does not show any strong preference with respect to crystallographic directions in the plane of the Cu(110) surface. At these low coverages, there is apparently a significant mobility of some surface species as evidenced by the streaky noise surrounding bright molecular protrusions in STM images.

As the coverage of Alq3 increases in the first monolayer, a tendency to form chain-like aggregates is observed building from the paired molecules in Figure 3.2a. This is shown in Figure 3.2b-d where randomly-oriented chains of 3-7 Alq3 molecules can be seen. The spacing (0.8-1.0 nm) between near neighbor molecules in chains is similar to the spacing in pairs. The lack of long-ranged order and the tendency toward chain formation persist upon annealing up to 590 K as shown in Figure 3.3. Figure 3.3a shows an STM image of a Alq3 film deposited at room temperature and Figure 3.3b shows the result of annealing the same film to 590 K. This observation indicates that the amorphous monolayer created by deposition of Alq3 on Cu(110) is relatively stable structure. Despite significant open space on the surface, it was never observed to convert to an ordered molecular layer.

3.4 Discussion

3.4.1 Interfacial Disorder

The most significant observation reported above is that the first monolayer of Alq3 is highly disordered when deposited onto a room temperature Cu(110) surface. Many other
organic semiconductors exhibit ordered monolayers on this surface, templated by strong substrate-molecule interactions. For example, pentacene forms an ordered first layer with intermolecular spacings that have been argued to be determined by substrate-mediated interactions\textsuperscript{21}. In addition, PTCDA has been shown to form ordered monolayers\textsuperscript{22} (accompanying substrate surface reconstruction) followed by beautifully crystalline 3D islands\textsuperscript{23, 24}.

The fact that disorder in the first Alq3 layer is not easily removed by annealing suggests that it is the dominant structural motif on Cu(110) and that the well-known amorphous structure of Alq3 films can begin in the first layer. As mentioned in the introduction, Baldo and Forrest suggested an Alq3 diode device model that included strong electronic disorder in the first few layers near the metal-organic interface\textsuperscript{8}. Our observations are consistent with such a picture, since the observed structural disorder should translate into significant disorder in electronic density of states. This could result from random local electronic polarization environments due to variable local coordination number\textsuperscript{25-27}. Alternatively, it could result from random local interface dipoles due to disorder in either molecular orientations or site location\textsuperscript{28}.

3.4.2 Alq3 Chain Formation

The single molecule resolution afforded by STM measurements allows an elaboration of the subtle details of disorder at the Alq3/Cu(110) interface. The prominence of linear structures in the disordered first monolayer of Alq3 on Cu(110) shows that intermolecular interactions are important enough to establish significant local molecular correlations at the metal-molecule interface. Such local ordering has been argued to be important in determining
optoelectronic properties of thick organic films\textsuperscript{29}. In addition, aggregation on the scale of a few molecules has been shown to influence exciton dynamics\textsuperscript{30}.

In this section, we address the origin of the chain-like Alq3 structures using density functional theory (DFT) calculations of intermolecular interactions designed to capture some important aspects of the direct intermolecular interactions that are likely to be operative on a metal surface. In order to explain the observed tendency to form chain-like aggregates, it is necessary that intermolecular interactions are anisotropic to some degree. Such anisotropy is intuitively plausible for Alq3 since the molecule has a relatively low symmetry (C\textsubscript{1} point group for the most stable “meridional” isomer) and a large (\~5D) intrinsic dipole moment\textsuperscript{31}.

Previously, the adsorption configuration of Alq3 on aluminum surfaces has been studied using density functional theory by Yanagisawa et al\textsuperscript{31,32}. These calculations illustrate that the intrinsic dipole moment of the molecule is only slightly reduced when adsorbed on a Al(111) surface\textsuperscript{31}. We hypothesize that adsorbed Alq3 molecules are not completely free to rotate out of the plane of the surface (i.e. they cannot change the orientation of their intrinsic dipole moment with respect to the surface normal). In this case, the crucial direct intermolecular interactions on a surface occur between Alq3 molecules each with a fixed orientation with respect to the surface plane. This orientation may vary from molecule to molecule on the surface but cannot change to optimize intermolecular interactions to achieve a bulk-like crystal structure\textsuperscript{6}.

Density functional theory calculations were carried out using the Gaussian 09 software package. We optimized the geometry of an isolated meridional Alq3 molecule using Hartree-Fock calculations with a 3-21G basis set. This method was chosen based on reports
that Hartree-Fock most accurately produces the experimentally-determined molecular geometry and dipole moment. After single molecule optimization, we calculated single point energies (i.e. with no further optimization permitted) for pairs of molecules in different configurations as described below. These calculations were carried out using density functional theory (DFT) with a 3-21G basis set and the hybrid B3LYP functional in order to capture some aspects of non-covalent intermolecular interactions. This methodology is not ideal for highly accurate calculations of most non-covalently bound systems and the binding energies that we report are likely to be underestimated. The goal of the calculations is to understand the anisotropy of intermolecular interactions for molecules that are geometrically constrained to mimic some effects of a substrate surface even though metal substrate atoms are not explicit included in the DFT calculation.

Substrate-defined molecular orientation is implemented in our model DFT calculation (which does not include the substrate atoms) by maintaining the dipole moment vectors of adjacent molecules rigidly fixed in direction with respect to an imaginary plane (Figure 3.4a). We then rotated one molecule about the other as indicated schematically in Figure 3.4b to determine whether there is an anisotropic intermolecular interaction given this orientation constraint. At each angular position, we calculated binding energy as a function of separation between molecules. The separation is reported here as the distance between central Al atoms on different molecules and the binding energy is calculated as the difference between the calculated total energy of a pair at each (r,θ) position and twice the energy of the single molecule (each calculated with 3-21G, B3LYP).
Two different relative orientations of adjacent molecules were considered to explore the favorable adsorption geometries (either dipole “up” or dipole “down”) in the DFT studies of Yanagisawa et al.\textsuperscript{31}. The first is shown in Figure 3.4a and corresponds to adjacent dipole moment vectors both pointed in the same direction. This configuration mimics adsorption geometries in which adjacent molecules are either both “dipole up” or both “dipole down”. The binding energy curves for different angles for this configuration are shown in Figure 3.4c and exhibit an energy minimum at an angle near 70°. The intermolecular distance at the binding energy minimum in Figure 3.4c is about 0.8 nm, consistent with intermolecular spacing observed in our STM studies. Due to the symmetry of this relative arrangement of two Alq3 molecules, only angles between 0° and 180° were calculated since angles from 180°-360° would be repeat configurations with the roles of the two molecules reversed.

The second configuration considered is shown in Figure 3.5a and corresponds to one molecule with an “up” dipole moment and the other with a “down” dipole moment (or \textit{vice versa}). As shown in the calculated binding energies in Figure 3.5b, the most significant favorable interaction occurs at an angle of 60° and in the range of about 200°-240°. Intermolecular spacings of just under 0.7-1.0 nm at the binding energy minima are again consistent with STM experiments. In this case, the lower symmetry of the pair requires direct calculation for all angles between 0° and 360° since configurations do not repeat.

The anisotropic intermolecular interactions in these calculations are evident by reference to the polar plots in Figure 3.6. Points in this figure correspond to the energy at the minimum in the binding energy curve along the radial coordinate (e.g. extracted from Figure 3.4c and 3.5c) as a function of the angular displacement of the rotating molecule. In Figure
3.6a, there is a clear set of angles within ±20° about 0° where the interactions are least favorable or possibly repulsive. For most other angles there is a weak binding energy with a maximum at 70° and 250°. Figure 3.6b shows a slightly different and weaker anisotropy for configurations with oppositely-oriented dipoles. In this case, there are favored orientations at 60°, 200°, and 240°. Weaker favorable interactions occur for other angles.

The anisotropy seen in Figure 3.6 can explain the propensity for disordered chain formation observed in our STM studies. For the two adsorption configurations considered, there is a range of angles for which intermolecular interactions are least favorable. In addition, the range of angles where favorable interactions can occur is relatively broad. This would be expected to lead to anisotropic aggregation where the direction of linear aggregation is somewhat random due to the large angular range of favorable interactions. Our model calculations suggest that this mechanism for chain formation does not demand strict orientational order of Alq3 with respect to the substrate. Molecules could have several random orientations “frozen in” upon arrival at the surface and the general anisotropy inherent in intermolecular interactions would still favor quasi-linear aggregation as opposed to purely random adsorption.

From a more microscopic perspective, it is plausible that the anisotropic interactions partially originate from direct electrostatic dipole interactions between adjacent Alq3 molecules. The range of angles with favorable binding energies in the model DFT calculations in Figure 3.4 suggests nearly head-to-tail dipolar interactions. In fact, the angular pattern of binding energies is reminiscent of the general shape of an electrostatic dipole potential. However, it is important to recognize that the molecular geometry is strongly
anisotropic and would lead to chain like aggregation even in the absence of intrinsic molecular dipole moments. In particular, steric effects due to the propeller shape of the molecule will lead to anisotropic interactions even in the absence of a permanent dipole moment.

Direct electrostatic multipole interactions between molecules in the first monolayer on a metal surface have only been reported to drive structure formation in a few cases\textsuperscript{35,36}. In general, such interactions would be expected to be strongly screened by the metallic substrate. This can be viewed as an interaction with induced “image dipoles” in the metal surface. However, in the case of Alq3, the charge separation within the molecule is associated with the chemical bonds between the ligands and the central Al atom. These bonds may be sufficiently separated from the metal surface that electrostatic screening does not significantly reduce electrostatic dipole interactions. We have checked that a simple model of screening does not qualitatively change the conclusions about anisotropy drawn from Figure 3.6 by calculating the binding energy of a system that includes mirror image molecules to represent image dipoles at selected angles (not shown here). The image dipoles have the effects of making all binding energies more positive, but do not significantly change the range of angles where favorable interactions occur.

A complete microscopic understanding of the mechanism of intermolecular interactions would require further calculations that explicitly include the substrate. Of particular importance in such calculations would be the consideration of substrate–mediated intermolecular interactions that could result from the formation of hybrid metal-molecule interface states\textsuperscript{37,38}. Furthermore, if there is charge transfer between the metal and the
molecule, the resulting change in interface dipole could strongly modify intermolecular interactions. Strong charge transfer has recently been found to be a crucial consideration in determining intermolecular interactions at metal molecule interfaces\textsuperscript{39}.

3.5 Summary and Conclusions

In summary, the growth of the first layer of Alq3 on a Cu(110) surface has been directly visualized with scanning tunneling microscopy. Strong disorder is observed in the first layer with no tendency toward long range ordering even for films annealed up to 590K. However, a clear tendency for aggregation of molecules into dimers at low coverage and randomly wandering chains at high coverage is observed. The formation of chain-like aggregates is attributed to the strong anisotropy of intermolecular interactions that is illustrated by model DFT calculations. Anisotropic interactions may have an electrostatic dipole contribution as well as contributions from intrinsic molecular shape anisotropy.

These observations are significant to ongoing consideration of the most accurate modeling approach for Alq3 device operation. In particular, the observation of strong disorder at the metal-organic interface is in accord with the suggestion of its crucial role in explaining macroscopic device current-voltage characteristics. However, the film structure we observe is not completely random. Our STM measurements show chain-like aggregates that suggest the possibility of correlated disorder at the metal-Alq3 interface. Long range spatial correlations in electronic states in disordered organic films have been shown to be a crucial consideration for device modeling\textsuperscript{40, 41} and should be considered for injection limited transport in Alq3 films.
Figure 3.1 (a) STM image (100 nm x 95 nm, -0.8 V, 30 pA) of the clean Cu(110) substrate; (b) STM image (25 nm x 25 nm, -1.0 V, 2 pA) after deposition of a small quantity (90s deposition time) of Alq3. Single molecules are imaged as bright protrusions.
Figure 3.2 Coverage-dependent STM images (all 25 nm x 25 nm) during the growth of the first monolayer of Alq3 on Cu(110); (a) 0.16 nm$^2$ (-1.3 V, 1 pA); (b) 0.33 nm$^2$ (-1.2 V, 5 pA); (c) 0.49 nm$^2$ (-1.4 V, 3 pA); (d) 0.63 nm$^2$ (-0.6 V, 1 pA).
Figure 3.3 (a) STM image (25 nm x 24 nm, -1.3 V, 10 pA) of an as-deposited Alq3 film with coverage of 0.25±0.02 nm²; (b) STM image (25 nm x 24 nm, -1.2 V, 20 pA) of the same film as in (a) after annealing to 590 K. The coverage is 0.24±0.02 nm².
Figure 3.4 (a) Schematic of relative orientation of dipoles for identically oriented molecules with respect to an imaginary surface plane; (b) Schematic depiction of model DFT calculations of the interaction between two Alq3 molecules with dipole oriented as indicated in part (a); (c) Binding energy as a function of intermolecular distance for different angular displacement of one molecule with respect to the other.
Figure 3.5 (a) Schematic of the relative orientation of dipole moments of adjacent molecules differently-oriented with respect to an imaginary surface plane; (b) Schematic depiction of model DFT calculations of the interaction between two Alq3 molecules with differently-oriented dipoles as indicated in part (a); (c) Binding energy as a function of intermolecular distance for different angular displacement of one molecule with respect to the other.
Figure 3.6 (a) Polar plot of the depth of the energy of the minimum in each curve from Figure 3.4c as a function of angular displacement; (b) Similar polar plot of the minima from Figure 3.5c along with other angles.
References


CHAPTER 4

Scanning Tunneling Spectroscopy of Alq3-Metal Interfaces

4.1 Introduction

Tris (8-hydroxyquinolinato) Aluminum (Alq3), since its first use in OLED’s by Tang and van Slyke\(^1\), has been a prototype organic electronic material that has helped advance the field to the point of bringing commercial displays to market. Among the basic facts illuminated by the study of Alq3 is the importance of the metal-organic interface. In all organic devices, a metal layer is needed to provide electrical contacts or connections\(^2\). The properties of organic molecules at metal interfaces, which generally differ from those in the bulk\(^2,3\), play an important role in determining device characteristics. In particular, large energetic barriers to charge injection across the metal-organic interface can limit the current through a device. Thin film devices made from Alq3 are often found to be in this injection-limited regime as described below.

While single crystals of Alq3 show good ordering due to the van der Waals interaction of the \(\pi\) electrons of ligands on adjacent molecules, Alq3 thin films are structurally disordered\(^4,5\). When amorphous Alq3 films are contacted by metal electrodes with high to moderate work function, the current is usually found be to injection limited\(^6-8\), which makes the molecular orbital-derived transport levels at the interface key quantities in determining device current. Theoretically, it has been demonstrated that the disordered nature of organic film can enhance the injection current by providing a broad statistical distribution of energetically accessible transport levels\(^9,10\).
It has been suggested that the electronic disorder of Alq3 films at the metal-organic interface is significantly greater than in the bulk of the film, and that the rate limiting charge injection process occurs when moving carriers between the interfacial molecular layer and the bulk. Due to very strong disorder, charges might easily move into the low energy tails of the statistical distribution of interfacial molecular states, and then more slowly hop to the narrower distribution of states in the rest of the film. However, while a large amount of work has been done to determine the average molecular transport levels of Alq3 molecules on metal surfaces by photoemission spectroscopy, the local interfacial electronic states of Alq3 film in sub-monolayer region have not been directly characterized. Intuitively, disorder in the interfacial energy levels needs to be probed by spatially resolved tunneling spectroscopy which can directly map electronic inhomogeneity with single molecule resolution.

In this work, we study the molecular orbital-derived transport levels of the first layer of Alq3 on Cu(110) and Cr(001) by scanning tunneling spectroscopy which has single molecule resolution. Hence we are able to characterize the local transport properties at Alq3-metal interfaces. We report the positions of energy levels induced by the lowest unoccupied molecular orbitals (LUMO) at Alq3-metal interfaces, the observed variations of energetic position induced by the lowest unoccupied states are less significant than that observed in devices. We attribute this observation owning to the closely spaced lowest unoccupied levels which are inherent for Alq3 molecules. The result suggests weak intrinsic electronic disorder at Alq3-single crystalline metal interfaces. This suggests that the interactions with poly-
crystalline electrodes are a major reason for the strong interfacial electronic disorder observed in devices.

4.2 Experimental Methods

Experiments were carried out in an ultrahigh vacuum system which is designed for STM-based surface science studies. The structure of the system has been described in detail in chapter 2. It consists of two interconnected chambers. The main chamber (base pressure $<7 \times 10^{-11}$ torr) houses facilities for substrate cleaning and STM characterization. A fast entry lock (FEL) (base pressure $\sim 1 \times 10^{-8}$ torr) is separated from the first chamber by a gate valve and houses home-built organic evaporators and a quartz oscillator for flux monitoring. Cu(110) and Cr(110) were chosen as substrates. Copper is chosen as an example of a relatively moderately reactive surface that is nevertheless easy to clean. Chromium is chosen as a model magnetic surface as discussed in detail in the following chapter. In our experiments, Cu(110) was cleaned by repeated cycles of 1keV Ar$^+$ sputtering following by annealing for 20 minutes at $\sim 700$K. The Cr(001) surface is much harder to clean than Cu(110) due to segregation of bulk carbon, nitrogen, and oxygen contaminants$^{19}$. The recipe we choose is to Ar$^+$ sputter Cr(001) at $\sim 1000$K at which temperature both carbon and oxygen segregation are sufficient to separate them from the Cr bulk. This hot sputtering process takes several hours and is then followed by 15-20 minutes sputtering with the heater off. After this “cool-down sputter” 7-8 minutes of annealing at $\sim 1000$K was performed to heal the ion beam damage.

After the substrates were cleaned, Alq3 molecules were deposited onto them while they were held at room temperature. Powdered Alq3 from Sigma-Aldrich (99.995%) was
loaded as received into an organic evaporator which consists of a degassed quartz crucible that could be heated by a tightly wrapped Tantalum filament coil. The Alq3 was outgassed for several hours in the deposition chamber prior to film growth. The stability of Alq3 flux was monitored with a quartz oscillator before and after deposition. Direct Scanning Tunneling Microscope (STM) imaging with molecular resolution was carried out for absolute flux calibration.

At room temperature, we carried out STM imaging by using a commercial instrument (Omicron VT-XA) operated in constant current mode with electrochemically-etched tungsten tips. Constant-current Scanning Tunneling Spectroscopy ($z(V)$) is used for probing electronic energy state of the molecules instead of constant-height STS. The main benefit of the $z(V)$ measurement is to minimize perturbation of molecules due to large currents injected by the STM tip in traditional constant height mode. The detailed of the relationship between sample density of states and $z(V)$ curves has been discussed in Chapter 2 and by Pronschinkse et al.\textsuperscript{20}. In brief, constant-current STS in distance-voltage mode uses the logarithmic derivative of relative tip distance with respect tip voltage ($V/z(dz/dV)$) as an accurate representation of the shape of the density of states of the sample.

4.3 Results

Alq3 molecules were deposited onto Cu(110) and Cr(001) from the sub-monolayer region to more or less one complete monolayer. As described in the last chapter, the Alq3 film on Cu(110) is amorphous except for some local quasi-linear aggregation\textsuperscript{5}. In fact, essentially identical growth in the first monolayer was also observed on Cr(001) as shown in Figure 4.1a and 4.1b. On both Cu(110) and Cr(001), chain-like aggregates of Alq3 molecules
are observed as shown in Figure 4.1b for Cr(001) suggesting anisotropic intermolecular interactions. This is ostensibly different than the very ordered dimerized chains observed for Alq3 on Cu(111)\(^1\) that are reminiscent of the p-p interactions that drive the bulk Alq3 crystal structure\(^4\). The comparison suggests that, on the more reactive surfaces considered in this chapter, molecule-substrate bonding is more important than the typical intermolecular interactions in bulk Alq3.

By performing constant current \(z(V)\) measurements, two possible unoccupied electronic states of the Alq3 molecules at the interface were identified. Figure 4.2a shows the average of large sets of \(z(V)\) curves (for \(~300\) different molecules) with its corresponding logarithmic derivative, \((V/z)dz/dV\), which is expected to be proportional to the sample density of states\(^2\) in Figure 4.2b. Figure 4.2c and 4.2d show similar co-averaged spectra for Alq3 on Cr(001). The spectra on both Cu(110) and Cr(100) clearly show a broad peak in the unoccupied density of states centered at \(~1.7-1.8\) eV. In addition, a sharper state exists at 3.4-3.5 eV above the Fermi level of the metal substrates.

The lowest unoccupied states showed significant variation for different molecules in the same local region of the monolayer film. As an example of this effect, an STM image of Alq3/Cu(110) is shown in Figure 4.3a. The substrate (darkest areas) of the Figure is Cu(110), the uniformly sized approximately circular protrusions on the terraces are single Alq3 molecules. Constant-current STS was measured on the different molecules as marked on Figure 4.3a (imaging distortion exists in this measurement due to interrupted scanning during STS sweeps). The corresponding \(z(V)\) curves are shown beside them in Figure 4.3b. The sigmoidal shaped retractions in the \(z(V)\) curves (peaks in the \(dz/dV\) curves) indicate the
presence of the lowest unoccupied electronic states already mentioned. It is clearly shown in Figure 4.3b that the LUMO states vary for the different individual molecules in the same local area.

To quantify the variability, in Figure 4.4a and 4.4b we plot a histogram of all measured positions of LUMO-derived peaks in (V/z)dz/dV spectra for Alq3 on Cu(110) and Cr(001) respectively. These histograms were each fit with a single Gaussian using weighted nonlinear least squares fitting implemented in MatLab. The fitting results are summarized in Figure 4.4 and discussed more fully in section 4.4b.

4.4 Discussion

4.4.1 Nature of the Unoccupied States for Alq3

The unoccupied electronic structure of Alq3/metal interfaces has been studied primarily by inverse photoemission for thick films on Au\textsuperscript{15,22}. There is general consensus that peaks in the unoccupied density of states exist around 2 eV and also at around 3.5 eV. Questions of the detailed quantitative identification of transport gaps from these data remain controversial, but to within the experimental resolution for IPES of 0.4-0.5 eV, different groups obtain identical IPES spectra\textsuperscript{15,22}.

The lowest energy unoccupied state observed in our constant current STS measurements at about 1.8 eV above the Fermi level for both Cu(110) and Cr(100) is similar to the energetic position of LUMO-derived electron polaron states measured for multilayer Alq3 on Au(111) by Alvarado et al. who observed a sharp tip retraction indicating a state at 1.8-2.0 eV above the Au Fermi level\textsuperscript{23}. These authors carried out STM-based z(V)
spectroscopy during which they allow the tip to penetrate into a thick organic or polymer film during the low voltage parts of the sweep. While this differs in detail from our $z(V)$ measurement approach, the correspondence suggests the possibility of assigning the state at 1.8 eV as a LUMO-derived transport level. In fact, the Alq3 molecule has a closely-spaced set of unoccupied orbitals (LUMO, LUMO+1, and LUMO+2) localized on \textit{different} hydroxyquinolate ligands. The LUMO is located on the ligand with the largest Al-O and Al-N bonds lengths. The LUMO+1 and LUMO+2 are located each on one of the other two ligands and are nearly degenerate with one another. This grouping of lowest unoccupied levels has been shown to persist when Alq3 is strongly adsorbed on Al(111)\textsuperscript{23}. We will refer to the lowest state near 1.8 eV in our measurements as the LUMO-derived state without commenting at this point about the distinction between the three closely spaced orbitals. The unoccupied electronic state at about 3.4 eV in our STS measurements closely corresponds to a similar state observed in IPES\textsuperscript{15}. Most likely this originates from the LUMO+3-derived state of the molecule which is known to be significantly separated in energy from the three lower energy unoccupied states.

It is likely that the LUMO-derived state on Cu(110) and Cr(001) is not purely molecular in character. In comparison with the IPES measurements of Hill et al.\textsuperscript{22} and Krause et al.\textsuperscript{15}, the lowest energy peak observed in our measurements is ~ 0.8 eV closer to the Fermi level. This difference is consistent with our measurement of the density of electronic states in the first monolayer compared to the multilayer films studied by IPES. At the least, it is known that electrostatic polarization effects are very different due to the metal substrate in
the first monolayer\textsuperscript{24}. In addition, there is the possibility of direct electronic hybridization between molecular orbital-derived states and continuum metal substrate bands\textsuperscript{25,26}.

The very broad appearance of the peak near 1.7-1.8 eV in our data (notably more broad than in the data of Alvarado et al.\textsuperscript{23}) suggests that indeed it significantly interacts with the band states of the metal substrate. This possibility is consistent with a comparative UPS study of Alq\textsubscript{3} films on Au and Co substrates where the Alq\textsubscript{3} valence band spectra suggest strong hybridization\textsuperscript{13}. Both the Cu(110) and Cr(001) surface studied here can be considered reactive when compared to Au based on the position of the d-band centroid (especially in the case of Cr(001) and based on the reduction in atomic packing density compared to Au(111)). Therefore, we consider metal-molecule electronic mixing to be highly likely and to enhance the width of the grouping of unoccupied states at \textasciitilde1.8 eV. Moreover, the interpretation of strong metal-molecule interactions is consistent with the different aggregation and molecular size and shape observed in our experiments compared to the low temperature STM experiments on the less reactive (more densely packed) Cu(111) surface\textsuperscript{21}. As already mentioned, Alq\textsubscript{3} on Cu(111) self-assembles\textsuperscript{21} in a manner reminiscent of the structure of bulk Alq\textsubscript{3} single crystals\textsuperscript{4}. This is not the case for either Cu(110) or Cr(001) indicating a more significant molecule-surface interaction.

Electronic hybridization at metal-molecule interfaces is important for determining band alignment since it is expected to influence the “charge neutrality level” for the organic\textsuperscript{3,25,27,28}. It has also been strongly implicated as necessary for the remarkable “Giant Tunneling Magnetoresistance” observed in nanometer-sized Alq\textsubscript{3} diodes employing ferromagnetic contacts\textsuperscript{29}. Most importantly for this work, metal-molecule hybridization must be considered
in assessing the origin of electronic disorder at the metal-Alq3 interface as discussed in the following sub-section.

To summarize, we assign the states observe in our STS measurements as orbital-derived affinity levels related to those observed in IPES and STM-based charge injection spectroscopy. However, the broad shape of the peaks (even for single molecules) and the different imaging appearance and molecular aggregation when compared to Alq3 on other surfaces suggests strong interaction with the continuum metal states.

4.4.2 Origin of Electronic Disorder at the Metal-Alq3 Interface

The most important question to understand about the unoccupied electronic structure of Alq3 at metal surfaces is: What causes the spatial variation of the electronic states for different molecules in the same local region that is illustrated in Figure 4.3? Disorder at the metal-Alq3 interface was modeled by Baldo and Forrest as a Gaussian of half-width approximately 0.36 eV compared to 0.13 eV only 4 layers separated from the interface. Here we attempt assess whether the spatial variation observed for Alq3 on Cu(110) and Cr(001) is consistent with their general picture. For the strong structural disorder that we observe in Alq3 monolayers on both surfaces, it is natural to suggest that random differences in local surroundings can give rise to the shifts in energetic position of the states. For example, the local coordination number of a given molecule can have a significant impact on electronic states due to the high polarizability of the surrounding molecules. As reported for C60 chains on top of a pentacene film and also for C60 monolayers, molecules with more near-neighbors will have a larger polarization stabilization of their first affinity level, pulling it closer toward the electrode Fermi level. While this hypothesis is plausible for the Alq3
monolayer considered here, we have not been able to identify any systematic trend relating the lowest unoccupied state energy to the number of other molecules in its vicinity. This is apparent already from the small subset of molecules visible in Figure 4.3 which do not show a connection between local environment and position of lowest energy state. In fact, the disordered linear Alq3 aggregates tend to result in most molecules having about 2 near-neighbors, so we conclude that electrostatic polarization energy variation due to different local environments does not significantly contribute to the observed electronic disorder.

Another alternate possibility for explaining the observed spatial variation in the electronic states between different Alq3 molecules could be different molecular orientation. Variation in molecular orientation across the surface could occur due to the predicted comparable binding energies of the “dipole up” and “dipole down” orientations described by Yanagisawa et al.\textsuperscript{32} and in the last chapter. Density Functional Theory studies have shown that the two orientations can have significantly different energies for their low energy unoccupied states by up to about 1 eV. Thus, based on the variation indicated by the histograms in Figure 4.4, it must be judged unlikely that such large changes in molecular orientation coexist on the surface.

The simplest explanation for the variation arises from the intrinsic electronic disorder of Alq3 molecule. Recall that Alq3 molecule has a set of unoccupied orbitals: LUMO, LUMO+1, LUMO+2 which are energetically closely spaced\textsuperscript{32, 33}. These three lowest energy levels primarily reside on three different hydroxyquinolate ligands\textsuperscript{32}. As Alq3 molecules deposited on the surface, the molecules are predicted to be adsorbed on the surface determined by strong interaction between the O atoms on the hydroxyquinolate ligands and
surface lattice. This strong molecule-metal interaction can lead in two favorable molecular orientations. In both of the favored molecular orientations, it is possible to probe the electronic states on all of the three ligands, thus it is possible to probe all of the three lowest unoccupied molecular orbitals induced states. In our measurement, the scanning tunneling spectroscopy technique has the resolution to study intra-molecule local density of states. Hence for different $z(V)$ measurements on Alq3 molecules, we actually measured one of three degenerated LUMO derived states as $z(V)$ lower energy peak. Because we cannot identify intra-molecular features in imaging, we probed the states randomly, with equal probability. This can account for why we observed local spatial variation in the electronic states between different Alq3 molecules which can not be related to the local coordination of surrounding molecules.

In the histogram in Figure 4.4, fits to a Gaussian distribution of LUMO-derived states give a half-width of $0.255\pm0.015$ eV for Alq3/Cu(110) and $0.25\pm0.05$ eV for Alq3/Cr(001). These widths must have some convolution with the experimental energy resolution and so represent an upper bound on the half width of the true density of states. On ordered molecular domains we have found the typical half width of the distribution of energies of a p*-derived state to be about $0.05$ eV. Assuming that the disorder-induced and instrumental widths add in quadrature, the best estimate of the half-width of the Gaussian due to disorder alone is $0.25$ eV for Alq3/Cu(110) and $0.24$ eV for Cr(001).

These measured values are systematically lower than the interfacial $0.36$ eV half-width inferred from device modeling. These smaller values are consistent with the explanation of probing at random LUMO-derived states which are closely spaced ($\sim0.3$eV).
Due to metal-molecule interactions, the states are further broadened, hence the measurements can be fit by a Gaussian distribution. This broadening effect has been often discussed in the context of molecular electronics and is consistent with the basic idea that disorder at the metal molecule interface can be enhanced compared to disorder in the bulk of a film. The weak electronic disorder we observe on single crystal surfaces can only explain part of the spread in electronic states reported for devices. Remaining contributions to interfacial electronic disorder in devices are likely to be related to use of polycrystalline electrodes which create different metal-molecule interactions.

4.5 Summary and Conclusions

In summary, we have carried out STS measurements of the unoccupied states of Alq3 adsorbed in the first monolayer on both Cu(110) and Cr(001). The following results have been obtained:

1). A broad unoccupied state occurs at about 1.8 eV above the Fermi level on both substrates that is assigned as derived from the LUMO orbital with contributions from closely-spaced LUMO+1 and LUMO+2 levels. A higher energy state near 3.5 eV is assigned as derived from the LUMO+3 level.

2). The unoccupied states are found to vary in energy for different molecules in the same local surface region. The statistical distribution of LUMO-derived energies can be fit by Gaussians with half-widths 0.25 for Alq3/Cu(110) and 0.24 eV for Cr(001).

3). The LUMO+3 unoccupied state can also shift in energy, but its shift is uncorrelated in magnitude with the lower energy state.
We infer from our STM and STS observations that the electronic disorder at Alq3 metal interfaces is weak compared to strong electronic disorder inferred from device characteristics. The discrepancy mainly rises from crystalline structure of metal electrodes. For single crystal electrode, we suggest that the origin of weak disorder at the metal-Alq3 interface can be traced to intrinsic closely spaced unoccupied states of Alq3 molecules and metal-molecule interactions at the interface. This means that the disorder does not arise from a simple rigid shift of band alignment due to electrostatic interface dipole effects.

Electronic disorder is a dominant factor in organic electronic devices and it is necessary to characterize it with high spatial resolution to reveal both its magnitude and qualitative origin. This is of paramount importance as organic electronic materials enter the market in display devices and loom on the horizon in solar to electric energy conversion. Moreover, recent work has suggested that disorder in organic films can have implications for emerging organic spintronics technologies where random hyperfine fields influence magnetoresistivity.
**Figures**

**Figure 4.1** STM images of Alq3 sub-monolayer growth on (a) Cu(110) (25nm x25nm, -0.8V, 1pA) ; (b) Cr(001) (50nm x50nm, 1.5V, 3pA).
Figure 4.2 Constant-current scanning tunneling spectroscopy (STS) of Alq3 on metals (a) $z(V)$ of Alq3/Cu(110); (b) logarithmic derivative of $z(V)$ of Alq3/Cu(110); (c) $z(V)$ of Alq3/Cr(001); (d) logarithmic derivative of $z(V)$ of Alq3/Cr(001).
Figure 4.3 Local variety of Alq3 lowest unoccupied molecular orbitals (LUMO) derived states. (a) Local region of Alq3/Cu(110) surface with spectroscopy collected spots marked by circles of different colors; (b) the corresponding constant-current STSs clearly presents LUMO energy shifts among the sites.
Figure 4.4 The histogram of the lowest unoccupied molecular orbitals derived states and weighted nonlinear least squares Gaussian fit for (a) Alq3/Cu(110) $\sigma=0.255\pm0.0152\text{eV}$; (b) Alq3/Cr(001) $\sigma=0.254\pm0.054\text{eV}$. 

$\sigma=0.254\pm0.054\text{eV}$
References

CHAPTER 5

Spin Polarized STM of Alq3/Cr(001)

5.1 Introduction

In order to continue to miniaturize and improve electronic and magnetic devices, a new concept has been raised which merges molecular electronics and spintronics. As discussed in the introductory chapter, the new spintronic devices utilize electronic spins to carry information. Functional molecules with synthetically designed magnetic properties could become active device components in such circuitry. This concept opens an exciting approach to building future nano-scale devices.

The spin valve, which is the prototype spintronic device, has been extensively studied for metallic systems and resulted in the Nobel Prize in Physics in 2007\textsuperscript{1}. In the layered spin valve structure, a nonmagnetic layer is used to decouple two magnetic electrodes. This nonmagnetic layer must allow spin polarized current to travel through it. Due to the low atomic number elements of organic molecules, spin transport properties are more likely to be preserved in organic nonmagnetic layers due to minimal effects of spin-orbit coupling. This enables well-chosen organic molecules to act as the functional layer of a spin valve.

Alq3 is one of the proposed candidates that have exhibited significant spin dependent transport properties, namely an inverse GMR effect in spin valve geometry\textsuperscript{2}. However, the GMR effects of Alq3 are controversial experimentally. Though the effect has been reproduced by several groups\textsuperscript{2-6}, it appears to occur most readily when a half-metallic lanthanum strontium maganite (LSMO) electrode is used. A study by Jiang et al. that
attempted to create a spin valve with Fe and Co electrodes found absolutely no magneto-
resistance through thick films of Alq3\textsuperscript{7}.

Theoretically, there is no consensus on the explanation of GMR effects in Alq3 spin
valves. The situation is made particularly difficult by the need to explain the observation of
both positive and negative MR in similarly-prepared devices\textsuperscript{8,9}. Bobbert et al. proposed that
the strong structural disorder in Alq3 films can lead to random hyperfine fields of the
Hydrogen nuclei that combine to create a random effective magnetic field applied to charge
carriers traversing the film\textsuperscript{10}. This model can produce up to 7\% inverse GMR and is
compatible with spin diffusion lengths reported in device\textsuperscript{2} and muon spin rotation
measurements\textsuperscript{11}. As such, it can only semi-quantitatively explain the full set of GMR
observations on Alq3 and does not address issues related to interface effects or the negative
results of Jiang et al\textsuperscript{7}.

Barraud et al. reported a very surprising 300\% "tunneling GMR" effect in nano-pores
filled with Alq3\textsuperscript{12}. They developed an interesting model based on well-known electronic
broadening effects due to interactions at the metal-organic interface that can explain this
effect and that can also generate both normal and inverse GMR when transport is by a
tunneling mechanism. However, the most interesting and controversial GMR effects in Alq3
occur for films too thick to allow significant tunneling current\textsuperscript{2,3}.

Generally, the situation surrounding Alq3 GMR effects demands new experiments
expressly designed to strip away the complexities of device fabrication and operation. In this
chapter, we present our study of Alq3 molecules on the antiferromagnetic Cr(001) surface in
the sub-monolayer region, utilizing spin-polarized scanning tunneling microscopy. This
model experiment provides the possibility to probe the local molecular spin-dependent electronic structure to help clarify unresolved issues associated with Alq3 spin valves in a well-defined and reproducible microscopic system.

We find that at the Alq3/Cr(001) interface there is a strong spin depolarization effect at low biases that is larger than the reported depolarization in Alq3-based TMR spin valves\textsuperscript{13}. In addition, we observe unique contrast variation as a function of sample bias near the Alq3 LUMO-derived orbital states that suggests the relevance of molecular chirality to determining spin dependent metal-molecule hybridization.

5.2 Instruments

A Spin-Polarized STM was designed and implemented based on OMICRON commercial STM. The key to implementing SP-STM is making a magnetized scanning tip. Several ways have been proposed for making magnetic tips including electrochemically etched Cr tips\textsuperscript{14}. However, we choose the most common method of coating a tungsten tip with an Fe thin film\textsuperscript{15}. The W tips we used are electrochemically etched in a saturated solution of NaOH in distilled water (8g NaOH per 100ML H\textsubscript{2}O) from high purity 99.9999% polycrystalline W wire. The tip is treated in-situ in UHV using three steps to achieve magnetization: flashing, coating, annealing. A homemade tip heater was built for the purpose of flashing. It consists of a well-designed stage to hold the tip as well as to apply positive high voltage on the tip. An electrically isolated W filament is placed as closed as possible to the tip. It is expected that the hot electrons emitted from the W filament will be accelerated to bombard the end of the tip. The high-temperature flash can effectively remove oxides and other contaminants thereby enhancing the binding between the W surface and the magnetic
overlayer which will be introduced in the next step\textsuperscript{15}. It is also important for the tip to be heated to high temperature upon introduction into the UHV chamber to improve the tip stability; otherwise the magnetic coating material will be frequently lost during the coarse tip approach. The recipe used in our experiment for the tip flashing is to use 1keV electron energy and \(\approx 26\text{mA} \) emission current for 3 quick 15s flashes. During these flashes, the pressure in the chamber typically rises to \( \approx 1\times10^{-8} \text{ torr} \).

After flashing, we immediately coat tip with iron. The iron evaporation source we use is MDC E-Vap 100 Precision Evaporation Source loaded with a 2mm diameter Fe rod (Alfa-Aesar). To improve the efficiency of evaporation, the geometry of filament was altered compared to the manufacturer’s design to direct the electron beam more toward the Fe rod source. However, this alteration also brought a few problems. When the evaporator works under high voltage and high temperature, the shape of directly exposed filament sometimes distorts toward the Fe rod. Empirically, this happens above certain filament currents and so the filament current must be kept under control to avoid shorting the filament to the rod. Due to the restriction of emission current and tip angle relative to Fe source, the feasible flux is about 2-3ML per hour. Since it is reported that \(10^+\text{ML} \) of Fe are required to establish an in-plane component of the tip magnetization\textsuperscript{15}, we coat the tip for \( \approx 5\text{-}6 \) hours. After tip coating, we anneal the tip to \( \approx 600\text{K} \) for about 1 minute using the radiative heater in the sample manipulator.

5.3 Experimental Methods

Along with tip preparation, experiments were carried out in the STM UHV system, which has been described in detail in chapter 2.
Cr(001) were chosen as the magnetic substrate mainly because of its unique antiferromagnetic ordering in adjacent (001) planes. It provides a useful substrate for creating magnetic metal-organic interfaces and also gives us a good calibration substrate to confirm spin polarized tunneling. More discussion on the Cr(001) substrate will be presented in the next chapter. However, Cr(001) is a metal that is very hard to clean. Even in UHV, residual gas, carbon and oxygen can contaminate Cr(001) in hours. To clean them off requires many hours of high temperature Ar$^+$ sputtering. The recipe we choose is to sputter Cr(001) with Ar$^+$ ions at ~1000K substrate temperature where both carbon and oxygen segregation are sufficient to separate them from the Cr bulk$^{16}$. Empirically the hot sputtering process takes several hours, and then it is followed with 15-20 minutes sputtering with the substrate heater off. We call this process “cool down sputtering”. The reason for cool down sputtering is to clean off the residual segregated carbon and oxygen on the surface. After cool down sputtering, 7-8 minutes ~1000K annealing is used to heal sputter damage. Once the sample is cleaned and tip preparation is done preliminary experiments are required to verify if the tip is properly magnetized. In practice, we load the prepared tip onto STM scanner and scan the clean Cr(001) sample. The STM stage is cooled down 130K throughout the experiment by liquid nitrogen to improve the stability of tip magnetization and take advantage of a modest increase in Cr(001) surface magnetization at lower temperatures. As long as tip magnetization is verified by imaging the antiferromagnetic ordering on Cr(001), we quickly deposit Alq3 molecules on the room temperature sample as described in previous chapters.

After the growth, we quickly transfer the sample back to the cold STM. As long as tip magnetization is maintained during this retraction and the re-approach process, molecular
resolution of spin dependent properties of Alq3 can be acquired. Imaging is carried out with spin-polarized tips in constant current mode with a typical current set point of 1nA-1.5nA. We use a lock-in amplifier (SRS-830) to make dI/dV maps at the same time as topographic scanning. The tip bias is modulated at a frequency of 10.6 kHz with a RMS amplitude of 115 mV. We operate the STM with its current preamplifier in low gain (gain = 3x10^8V/A, bandwidth = 80kHz) mode in order to allow tolerable speed data acquisition. In principle, the conductance map acquired with a spin-polarized tip incorporates magnetic information about the sample surface.

5.4 Results

Sub-monolayer Alq3 molecules were deposited onto the Cr(001) substrate at room temperature. The sub-monolayer Alq3 film is amorphous: there is no trace of any ordering while molecules form dimers at extremely low coverage. As coverage increases, they start to form longer linear structures. This phenomenon has been fully discussed in the previous chapters. Figure 5.1 shows an STM image with single molecule resolution of Alq3 growth on Cr(001). The brighter tiny protrusions are single Alq3 molecules. In our SP-STM experiments, we studied Alq3 adsorbates film in the low coverage regime since we want the Cr(001) substrate still visible in order to confirm that the tip is magnetized. This shows the reason why we choose Cr(001) as magnetic substrate: the Cr(001) surface is a "topological antiferromagnet". It consists of a series of monatomic steps separating (001) planes. For each pair of adjacent terraces, the spin directions are opposite. In another words, the local magnetization directions of adjacent terraces are opposite. Hence if the tip is magnetized, and the STM operates in constant current mode at a bias corresponding to the energy position of a
spin polarized Cr(001) surface state\textsuperscript{18-20}, the tip sample distance is decreased if the magnetic directions of tip and sample are parallel but increased if the magnetic directions are anti-parallel\textsuperscript{21}. This can be intuitively understood as an application of the tunneling magnetoresistance (TMR) effect. In TMR, tunneling conductance between two magnetic electrodes depends on their relative magnetization due to fact that elastic tunneling preserves spin. Parallel magnetization results in higher tunneling current because of more efficient matching of the spin-split density of states of the two electrodes.

Hence on Cr(001), we can observe alternating step heights in Z topography, or even more clearly “spin contrast” in differential conductance maps as shown in Figure 5.2a and Figure 5.2b respectively. In Figure 5.2b, the brighter stripe is the Cr terrace with local spin direction parallel to the tip magnetization direction while the darker stripe is the terrace with local spin direction anti-parallel to the tip magnetization direction. Figure 5.2c shows the topography of Alq3 on Cr(001) by SP-STM while Figure 5.2d shows the differential conductance map acquired simultaneously at a bias of -0.7V where we often observe strong spin contrast on bare Cr(001). In both of figures, the brighter tiny protrusions are single Alq3 molecules. The appearance of molecules is more obvious in conductance map than in the topography. In our study, we stick to the very low coverage as shown in the Figures 5.2c and 5.2d which just have few molecules on the surface, so we can have a greater probability to obtain spin properties of the molecules and avoid the loss of tip magnetization during scanning. In Figure 5.2d, we can clearly see the expected “spin contrast” on the Cr(001) terraces, making us comfortable to extract spin dependent electronic properties of the molecules from these maps.
Observe in figure 5.2c and 5.2d that there are no clear differences between the appearance of molecules on the two adjacent terraces, i.e. the local conductance of the molecules on the “spin-up” terrace are identical to the local conductance of the molecules on the “spin-down” terrace. The apparent topographic heights of the molecules on the adjacent terraces are also indistinguishable. To quantitatively analyze the spin-dependent interfacial properties of Alq3 on Cr(001), we calculated the local spin asymmetry at the position of the Alq3 molecules using the definition\textsuperscript{22, 23}:

\[
A = \frac{G_{\uparrow\uparrow} - G_{\uparrow\downarrow}}{G_{\uparrow\uparrow} + G_{\uparrow\downarrow}}
\]  

We use the G values measured at the center of molecular protrusions taken from dI/dV maps. If the molecule is on a terrace that appears bright, it is assigned as $G_{\uparrow\uparrow}$ and if it is on a terrace that appears dark it is assigned as $G_{\uparrow\downarrow}$. We then compute an asymmetry as above for every pair of measured conductance on adjacent terraces and average them together. The results are shown in figure 5.3 for voltages from -1.0V to 1.0V. The spin asymmetries are less than 1% for almost all of the voltages we measured. At the same time, we also calculated the spin asymmetry of adjacent Cr(001) terraces for the same set of voltages. The results are shown in the same plot of figure 5.3. It is clear that around -0.7V energy region the Cr(001) adjacent domains separated by monatomic steps exhibit strong spin asymmetry: in the range of 4%-6%. However, when a molecule is inserted in the STM junction, the local spin asymmetries are significantly attenuated. In other words, the local spin state of Cr(001) terraces is depolarized by Alq3 adsorption.
We also measured SPSTM for Alq3 molecules near the LUMO-derived orbital position at ~1.8eV above the Fermi level that was described in the previous chapter. In this energy range, the spin polarization of the terraces cannot be observed, which we attribute to the lack of spin polarized surface states on the Cr substrate for these energies. However, we confirm the polarization of our tip after measuring in the LUMO energy region by returning to lower biases where spin contrast on the Cr(001) terraces can be seen.

A series of conductance maps were recorded in the broad LUMO energy region, from 1.4V-2.4V above the Cr Fermi level. While tip magnetism was maintained, we observed a subset of adsorbed “dark” Alq3 molecules that are lower in conductance than the surrounding terraces. In addition, we observed a subset of “bright” Alq3 molecules that were higher in conductance than the surrounding terraces. Interestingly, the dark molecules were observed to increase in local conductance as voltage was increased through the 1.4V to 2.4V regions. Simultaneously, the bright Alq3 molecules decreased in local conductance as applied bias increased (Figure 5.4). The total number of molecules that showed an increase in conductance (19) was approximately equal to the total number that showed a decrease (16).

When the same bias-dependent conductance mapping was carried out with a tungsten tip that had not been coated with Fe, the local conductance effects were observed to be dramatically different. As shown in Figure 5.5, all molecules have a local conductance that is identical and higher than the surrounding terraces. In addition, there is a only a decreasing trend in local tunneling conductance on top of the molecules as bias increases from 1.4 V to 2.2 V. However, the size of the decrease is small when compared to the subset of molecules that show decreasing conductance with a spin-polarized tip. In other words, using a spin-
averaged tunneling current there are not two clear populations showing opposite trends in conductance change. In Figure 5.6, we plot the average local tunneling conductance of the two populations of Alq3 molecules under spin polarized current conditions as a function of bias. In addition, a plot of the average conductance using spin-averaged current is shown in Figure 5.7. With spin polarization, there is a clear tendency for changes to saturate beyond 2eV. While our spin-averaged data do not extend over the same bias range, the dependence of local tunneling conductance on bias is clearly qualitatively and quantitatively different.

5.5 Discussion

5.5.1 Spin Depolarization Effects at Alq3/Cr(001) interfaces

As mentioned above, in our experiment the spin asymmetries (Equation 5.1) of adjacent Cr(001) antiferromagnetic terraces were examined in 4%-6% range near -0.7V (Figure 5.3). The strong spin asymmetries in this energy range indicate the magnetic surface state of Cr(001), since $d_{z^2}$-like surface state of Cr(001) is highly spin polarized and close to the Fermi level\textsuperscript{18,20,24}. In appearance, the dI/dV maps would exhibit high spin contrast near surface state of Cr(001) as shown in Figure 5.2b and 5.2d. However, with the adsorption of Alq3 molecules, the local spin asymmetries on the molecular sites are greatly attenuated near -0.7V (Figure 5.3). This significant decrease is unusual for Alq3 tunneling magnetoresistive devices. For example, the spin decay length of Alq3 molecules acting as an insulating barrier in a TMR device was recently reported as 4nm\textsuperscript{13}. Hence for a single Alq3 molecule with a diameter of around 0.8nm the spin asymmetry on the molecular sites should be only attenuated to 3%-5% according to:
\[ A' = A e^{-L/L_s} \]  

(5.2)

where \( L_s \) is the tunneling spin diffusion length\textsuperscript{25}. However, in our measurement, the local tunneling asymmetries at molecular sites are less than 1% and barely distinguishable from 0% in a wide range of energy from -1.0V to 1.0V.

There are two possible explanations for the small spin asymmetry. The Alq3 molecules could cause strong spin mixing effects that reduce spin polarization in the tunneling current. Alternately, the local magnetization at the position of the molecule could be primarily in the direction normal to the surface plane. For the later situation, our Fe-coated tungsten tips are not sensitive to out-of-plane magnetizations (see Chapter 2). However, we regard a completely out of plane magnetization for the molecule as an unlikely coincidence since it interacts with a completely in-plane surface magnetization on Cr(001). Thus, we infer from the measurements in Figure 5.3 that there are very strong spin depolarization effects at Alq3-Cr(001) interfaces. To quantitatively explain our observed asymmetries, we would need a spin decay length of less than the typical size a single Alq3 molecule. Thus, the molecules themselves cause spin depolarization at the Cr(001) interface.

Spin depolarization processes can help to explain the negative results of Jiang et al.\textsuperscript{7} as well as the apparently strong need to use a highly spin polarized half-metallic electrode (LSMO) in most successful Alq3-based GMR devices. In essence, strong coupling at the metal-molecule interface can result in spin mixing that eliminates the polarization from the Cr(001) substrate states. It is plausible that similar processes impact spin polarization in current injection into other Alq3 devices. We note that even in the recent measurements of TMR effects in Alq3 tunnel barriers, the most significant decrease in spin polarization was
reported in the thinnest films of thickness 2 nm\textsuperscript{13}. Thicker film barriers showed essentially constant spin polarization, indicating the major impact of spin depolarization at Alq3 interfaces that is consistent with the interpretation of Figure 5.3.

5.5.2 Spin Dependent Electronic Structure in Unoccupied States of Alq3

The behavior reported in Figure 5.4 and 5.6 near the LUMO region suggests the possibility of a random local spin polarization associated with this orbital-derived state. Molecules whose conductance increases upon increasing voltage above the LUMO state are assigned a local magnetization predominantly parallel to the tip magnetization while molecules with decreasing conductance are assigned a predominant antiparallel magnetization with respect to the tip. It is important to note that the behavior summarized in Figure 5.6 has no correlation with the local magnetization of the terrace on which a given Alq3 molecule is adsorbed. For example, a total of 35 molecules were tracked in the sequence of conductance measurements demonstrated in Figure 5.6, in which 19 turned dark and 16 turned bright. In this set of molecules, 13 molecules were on the “spin up” terrace (9 turning dark, 4 turning bright). The other 22 molecules were on the “spin down terrace” (10 turning dark, 12 turning bright). Similar observations have been reproduced in several other identical measurement sequences. They demonstrate that molecules are equally likely to show increasing or decreasing behavior on terraces that appear bright or dark in dI/dV maps at biases in the ±1V range.

To explain this behavior of conductance alteration near LUMO-derived orbital states, we must consider mechanisms for generating spin-dependent properties of Alq3. Tarafder et al. have proposed that nonmagnetic Alq3 molecules could be spontaneously spin-polarized
by electron injection\textsuperscript{26}. The injected charge fills nitrogen $p_z$-derived molecular orbitals in the molecule’s LUMO beginning with the one of lowest energy, which will allow a local magnetic moment to develop on the charged molecules. However, this explanation is not relevant to our observation because the Alq3 molecules in the first layer are only “charged” by the STM tip for a very short time and are completely discharged in between each tunneling event.

Instead, we can explain these unique observations by considering the combination of direct molecule-magnetic substrate hybridization and molecular chirality. Recent efforts by Wang et al. studying Co-doped Alq3 system point out the molecule can be spin-polarized in the unoccupied DOS by charge transfer from Cobalt to the molecule\textsuperscript{27}. Charge transfer takes place from Co atoms to primarily one hydroxyquinolate ligand of Alq3 molecules, leading to the formation of a local magnetic moment due to spin density separation. The induced magnetic moments primarily reside on the ligands near the magnetic ions. This mechanism can be very plausibly extended to the spin polarization of Alq3 by interaction with the Cr(001) substrate and explains the origin of interesting spin polarized conductance changes near the LUMO-derived states. However, it does not explain why there are two different populations of Alq3 molecules at every bias in the range.

To understand the origin of the two populations (bright and dark molecules) we note that Alq3 is a chiral molecule (it is nonsuperimposable with its mirror image, Figure 5.8) and that our deposited material is a racemic mixture. This means that there are 50% “left-handed” molecules and 50% “right-handed” molecules deposited on the surface. Simple molecular models suggest that if the spin density separation induced by interaction with the substrate is
similar to that reported for Co by Wang et al., then the induced magnetic moment of “left-handed” molecules points in the opposite direction compared to the “right-handed” molecules by the geometry. This situation is indicated in Figure 5.9. The combination of local metal-molecule hybridization together with molecular chirality can thus explain our observation of equally distributed aligned and anti-aligned local molecular magnetizations throughout the LUMO region.

As Alq3 molecules are evaporated onto Cr surface, instead of forming π stacking dimerized rows like they do in a bulk crystal\textsuperscript{28}, strong molecule-surface interactions cause the molecules to be adsorbed on the Cr surface in a fixed configuration, namely bonded by oxygen atoms with surface atoms\textsuperscript{29}. As charge transfer from the surface magnetic atoms magnetizes the nearby ligand of molecule, the metal-molecule interface acquires a local magnetic moment. Due to chirality, mirror image molecules adsorbed on the surface via the same local bonding will also establish a local magnetization in the opposite direction as shown in Figure 5.9. Surprisingly, the direction of local spin polarization is determined not primarily by the magnetization of the underlying substrate terrace, but by the chirality of molecules. This observation provides new insights into the kinds of spin dependent electronic phenomena that can occur at metal-Alq3 interfaces. More significantly, it shows an \textit{indirect} way in which the molecular chirality can play an important role in determining the performance of organic spintronic devices, by controlling metal-molecule interactions. This should be noted and utilized to engineer spintronic interfaces by molecular design.
5.6 Conclusions

In summary, we have used SPSTM to study a model magnetic system – Alq3/Cr(001). We acquired spin polarized conductance data with single molecule resolution. Two important results were obtained:

1) Strong spin depolarization effects in the bias range of ±1 V are revealed by small or vanishing spin polarized conductance asymmetries between differently magnetized domains.

2) Spin polarization can be induced by chirality-dependent metal-molecule hybridization in the LUMO-region of Alq3 on Cr(001).

These observations are relevant to understanding the diverse and sometimes controversial observations in the emerging field of organic semiconductor spintronics. Strong interfacial depolarization effects such as those reported here could be responsible for the absence of spin transport in Alq3 films prepared by Jiang et al.\textsuperscript{7} In addition, they can help to explain the abrupt decrease in spin polarization for thin Alq3 tunneling barriers reported by Szulczewski et al.\textsuperscript{13}.

Despite large depolarization effects at some biases, our observations in the unoccupied states far from the metal Fermi level provide new evidence for significant spin-dependent electronic structure at Alq3-metal interfaces. The equally distributed local magnetization directions of Alq3 molecules at the LUMO-derived level are determined by molecular geometry and not electrode magnetization. This shows a possible mechanism for spin dependent transport of electrons in Alq3 thin films. Based on our observations, the observation of spin-dependent transport in Alq3 films (e.g. GMR) should be connected with a LUMO-transport level that is low enough in energy to allow efficient electron injection,
and can be connected with molecular chirality. More generally, these observations give a clear indication of the kind of novel phenomena that can arise in the emerging field of organic and molecular spintronics.
Figure 5.1 STM images of Alq3 growth on Cr(001) in sub-monolayer region. (a) 50nm x 50nm, sparsely molecules show quasi-linear structures as same as them on the Cu(110) surface. (b) 50nm x 50nm close to full monolayer coverage, the film shows amorphous nature.
Figure 5.2 Spin Polarized STM imaging of (a) Topography of Cr(001); (b) Differential conductance map of Cr(001), showing “spin contrast” on adjacent terraces; (c) Topography of Alq3/ Cr(001) with single molecule resolution; (d) Differential conductance map of Alq3/Cr(001), Alq3 molecules are resolved while “spin contrast” of Cr(001) substrate is maintained. The difference between the conductances of the molecules on the adjacent antiferromagnetic terraces is not distinguishable.
Figure 5.3 Comparison of spin asymmetry of Cr(001) adjacent domains with spin asymmetry of Alq3 molecules on the adjacent Cr(001) domains, the energy range span from -1.0 eV to 1.0 eV, showing significant depolarization by Alq3 molecules near the energies corresponding to surface Cr(001) spin density states.
Figure 5.4 Differential conductance mapping of Alq3/Cr(001) near LUMO-derived orbitals (1.2 eV – 2.2eV) by spin polarized tip. Blue circle indicates a molecule “turning bright” (conductance increase) while red circle indicates a molecule “turning dark” (conductance decrease). All images widths are 70nm, scale bar 14nm.
Figure 5.5 Differential conductance mapping of Alq3/Cr(001) near LUMO-derived orbitals (1.2 eV – 2.2eV) by spin averaging tip. All images are 60nm x 60nm.
Figure 5.6 The normalized local spin polarized conductance of Alq3/Cr(001) versus energy.

The conductances of some of the molecules decrease significantly while the others’ increase.

The ratio of two species is close to 1:1.
The conductance of molecules generally decreases; there is no significant species which has increasing conductance. Furthermore, the changes of the conductance are significantly lesser than that of scanning with spin-polarized tip; the attenuated conductance is possibly due to derivative effect of lock-in amplifier.

**Figure 5.7** The normalized local spin average conductance of Alq3/Cr(001) versus energy.
Figure 5.8 (a) Human hands represent the simplest example of chiral structures. Left and Right hands are mirror images of one another that are nonsuperposable upon translations or rotations. (b) Diagram depicting the chirality of Alq3 molecules. Two chiral isomers are structural same but mirror images of one another, hence have different geometric shapes.
Figure 5.9 Schematic depicting of the opposite directions of magnetic moments of Alq3/Cr(001) originated from molecule chirality and metal-molecule hybridization.
References


CHAPTER 6

Reactivity of Iron Phthalocyanine at Magnetic Surfaces

6.1 Introduction

As organic electronics and spintronics are emerging as important growth areas in the development of semiconductor-based materials and devices, a number of new materials and applications have been proposed. Most of these promising applications utilize the flexible properties of organics. The scientists and engineers hence can design and create unique macroscopic or microscopic features of organics by tuning their molecular structure and composition. In order to make real electronic or optical devices, these organics as the functional layers are usually deposited/coated on certain metal surfaces. Thus the many interesting physical or chemical phenomenon that can happen at the metal-organic interface can have significant impacts on device properties and efficiency.

Great efforts have been made in studying metal-organic interfaces, including the contributions in this thesis. An important question that must be answered in considering metal-organic interfaces in electronic and spintronic device is whether the active layer molecules can be strongly chemically altered by interaction with the surface. This has been studied using photoemission methods by Gao and co-workers for a number of organic semiconductors in contact with inert and reactive electrodes as discussed in Chapter 1\textsuperscript{1-3}. It has been a subject of significant concern in the development of organic spintronics especially given the sometimes-controversial magnetoresistance measurements\textsuperscript{4, 5}. This is particularly important given the known high reactivity of 3d transition metal surfaces that has been
argued to result from the high density of d-band states near the Fermi level\textsuperscript{6}. Photoemission experiments reveal a significant likelihood of chemical reaction at the metal–organic interface, especially due to top contact formation\textsuperscript{7}.

Metal phthalocyanines (MPcs) are important organic semiconductor compounds which have been widely considered for use as the functional layer in devices such as light-emitting diodes, photovoltaic, gas-sensing devices, fuel cells, and organic field effect transistors\textsuperscript{8-10}. A number of studies on MPc growth on metals have been carried out by different groups using a number of different techniques. Hill and co-workers utilized UPS, IPES, and XPS techniques to study the binding energies of the highest occupied molecular orbitals and the lowest unoccupied molecular orbitals and determined whether chemical reactions occurred at the metal-MPcs interface\textsuperscript{11-13}. Hipps and co-workers studied cobalt(II) phthalocyanine (CoPc) surface morphology by STM when deposited onto the Au(111) surface and determined LUMO and HOMO-derived electronic states of CoPc by STS\textsuperscript{14}. Gao and co-workers also utilized STM to study the epitaxial growth behavior of iron(II) phthalocyanine (FePc) molecules on Au(111), and rationalized the adsorption configuration and self-assembly behavior of this system\textsuperscript{15,16}.

Metal phthalocyanines (MPcs) have found particular use as donor materials in small molecule organic solar cells\textsuperscript{17,18}. More recently, they have been widely regarded as natural candidates for organic spintronic applications since their central metal atoms can be chosen to be open–shell paramagnetic species. This has already been shown to allow controlled magnetic coupling at MPc interfaces with magnetic electrodes\textsuperscript{19-21}. Furthermore, direct spin injection has been demonstrated using two photon photoemission spectroscopy of CuPc films.
on Co electrodes. All of the promising magnetic applications of MPc in spintronics involve the metal-organic interfaces with 3d transition metals that are known to be catalytically active due to the density of 3d electron bands at the Fermi level. However, what does high surface reactivity of 3d metals imply for the metal-organic interfaces relevant to spin injection? Can chemical reactions happen at the interface which can alter magnetic or spintronic properties uncontrollably? It is important to recognize that the few spin polarized STM studies related to metal phthalocyanines described here and in Chapter 1 all involve deposition onto cryogenically cooled magnetic substrates. This cooling inhibits both surface mobility and surface chemical reactivity and so may not be relevant for understanding MPC interface formation under practical conditions.

In this chapter, we report STM observations of significant dissociative adsorption of iron phthalocyanine (FePc) on the Cr(001) surface studied by scanning tunneling microscopy (STM). While FePc molecules maintain intact upon adsorbing on the Au(111) surface, they decompose on Cr(001) surface completely in the sub-monolayer region due to high surface reactivity of Cr(001). Even when Cr(001) is coated with a thin film of Fe(001) to acts as a less reactive buffer layer, there is still a high probability FePc decomposition. The observed phenomenon should be taken into consideration in determining the properties of the devices which consist of phthalocyanine molecules and high reactive metals.

6.2 Experimental Methods

In the experiment, the synthesis and characterization are carried out in the STM ultrahigh vacuum (UHV) system. The UHV system consists of two interconnected chambers as described in Chapter 2. The STM is assembled with a few facilities in a main chamber
whose base pressure is $7 \times 10^{-11}$ torr. Beside STM characterization, the facilities integrated into the main chamber are responsible for substrate cleaning and STM tip preparation. The organic evaporation sources are kept separate in another chamber which is interconnected with the main chamber, but can be separated by a gate valve. The Fast entry lock (FEL) whose base pressure can achieve $\sim 1 \times 10^{-9}$ torr after baking, is used for organic monolayer synthesis. Quartz oscillators are equipped in the FEL for flux monitoring.

The metal substrates we choose in these experiments are Au(111) and Cr(001) single crystals and also an epitaxial Fe(001) film grown on the Cr(001) surface. Both of Cr(001) and Au(111) were cleaned by repeated cycles of 1keV Ar$^+$ sputtering. The difference is Au(111) is fairly easy to clean due to its low surface reactivity. However contamination on the Cr(001) surface are rather difficult to clean off due to the segregation of bulk impurities. The Cr(001) surface cleaning procedure requires high temperature $\sim 1000$K for segregating contaminations (e.g. oxygen, carbon) from the crystal bulk to clean them off by sputtering. After sufficient sputtering, both of the crystals were annealed to heal sputter damage. Au(111) was annealed to $\sim 700$K, Cr(001) were annealed to $\sim 1000$K. For preparing the Cr(001) substrate with an epitaxial Fe(001) film, a MDC E-Vap 100 Precision evaporation source loaded with a 2mm diameter Fe rod was used. The feasible flux is about 2-3ML per hour. For absolute coverage calibration, we use direct STM imaging as the reference. After each Fe coating, the sample was annealed to $\sim 700$K to smooth out small Fe islands created during growth and make a more uniform film.

During deposition of molecules, both Au(111) and Cr(001) crystals were held at room temperature. Powdered iron phthalocyanine (Sigma-Aldrich, dye content ca 90%) was loaded
as received into a homemade organic evaporator which consists of a degassed quartz crucible that could be heated by a tightly wrapped Tantalum filament coil. The FePc molecules were fully outgassed for a few days in the FEL prior to the film growth. The criterion for outgassing is the background pressure in the FEL. The outgassing did not finish until the pressure recovered to close to base pressure of FEL. The stability of FePc flux was monitored with a quartz oscillator before and after deposition. The absolute flux calibration was carried out by direct STM imaging with molecular resolution. For preparing FePc/Au(111) system, the Au(111) surface was first overdosed with a multilayer FePc film that could not be easily imaged by STM. This was followed by annealing to ~550K to remove multilayer molecules in order to form a smooth and complete monolayer of FePc on Au(111). In the FePc/Cr(001) and FePc/Fe/Cr(001) experiments, sub-monolayer quantities of FePc molecules were deposited onto the surfaces to observe the initial growth of FePc molecules on the high reactivity metals.

STM imaging was carried out at room temperature with the commercial STM which has been fully described in the previous chapters. The STM was operated in constant current mode. The STM tip is electrochemically-etched tungsten. Beside the surface topography, the molecular orbitals derived electronic states of FePc were measured by constant current scanning tunneling spectroscopy (STS) and constant height STS on the Au(111) monolayer films. In the measurement of constant height STS, a lock-in amplifier was used to extract differential dI/dV signals in addition to I-V sweeps.
6.3 Results

For the sake of comparison, we first reproduce known results on monolayer films of FePc/Au(111)\textsuperscript{15}. A full monolayer of FePc molecules form ordered structures as shown in Figure 6.1. In Figure 6.1a, a large scale topography of FePc/Au(111) is shown. The topography shows a smooth FePc monolayer while the herringbone reconstruction of Au(111) surface is clearly visible. The two stacking patterns resulting from the surface reconstruction of the Au(111), fcc and hcp domains, are also marked in the figure. The Figure 6.1b is the zoom in picture of FePc ordered structures on Au(111). Each of cross shape protrusions is one FePc molecule. Besides reproducing the growth of FePc on Au(111), we also probed the molecular orbital derived electronic states of FePc molecules by STS. In Figure 6.2, we show both the unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) derived states as well as image potential-derived states of FePc molecules. In Figure 6.2a, constant-current STS normalized $dz/dV$ are plotted in positive energy region. Showing as a “peak” in $dz/dV$ curve, an unoccupied orbital is observed at 3.0eV and the higher energy state around 4.3eV is assigned as an image potential-derived state of FePc/Au(111). In Figure 6.2b, constant-height STS measurements of the HOMO-derived orbital are shown in the negative energy range. In the normalized $dI/dV$ curve of Figure 6.2b, the HOMO state of FePc is clearly shown at -1.3eV, in agreement with expectations based on UPS measurements of thicker FePc films on Au(001)\textsuperscript{23}. In addition, we examined the electronic states of FePc molecules which were on the different lattice structures, namely hcp and fcc of Au(111). Essentially, we found no difference in the electronic states. The efforts
have also been made to probe the local spectroscopies on center Fe atom and on surrounding ligands to make a comparison. The results show no significant difference either.

In Figure 6.3, we present the surface morphology after deposition of FePc onto Cr(001) surface. In Figure 6.3a, the large scale topography of FePc/Cr(001) in sub-monolayer region shows that molecules do not pack in an ordered structure like they do on the Au(111) surface at these low coverages. As seen in Figure 6.3b, while individual surface protrusions are clearly resolved, we cannot find “cross” shaped molecules on the surface which would be the simplest direct indication of FePc molecules. Even scanning in a wide range of biases, the topographies look similar without any “cross” shapes found. By measuring the sizes of individual protrusions on the surface, we found the their diameters are less than 1\text{nm}, i.e. significantly smaller than the diameter of an intact FePc molecule of \(~1.4\) nm. In addition, we notice that the sizes of protrusions on the Cr(001) surface are not uniform. The diameters of smaller protrusions are about 0.4 \text{nm} while the diameters of larger ones are 0.65 \text{nm}. The interesting fact is that the ratio of the number of larger to smaller species is close to 4:1 in a small local area, e.g. in Figure 6.3b. One reasonable explanation to all of the above observations would be the decomposition of FePc molecules. Upon adsorption on the Cr(001) surface, the molecules break their Fe-N bonds and C-N bonds of porphyrins, leading to one FePc molecule decomposing into one iron atom and four fragments derived from the phthalocyanine ligand macrocycle. A direct observation supporting the decomposition of FePc molecule is shown in inset of Figure 6.3b, the appearance of protrusions looks like a FePc molecule is “exploding” on the surface with four ligand fragments directed symmetrically around the center small Fe atom. Notice if we double the diameter of larger
protrusions, then plus the diameter of small protrusions $2 \times 0.65 + 0.4 = 1.7$nm, the number is quite consistent with the diameter of intact FePc molecules determined by STM measurement.

To test if the molecules are dissociated on the Cr(001) surface due to high surface reactivity, we grew an Fe(001) buffer layer on the Cr(001) surface. The thickness of Fe buffer layer can be precisely controlled, from sub-monolayer to several layers. Then FePc molecules are deposited onto the epitaxial Fe films on Cr(001) surfaces. Figure 6.4a shows sub-monolayer Fe growth on the Cr(001) surface, forming uniformly distributed Fe islands. In Figure 6.4b, FePc was deposited onto this surface. It shows similar features as the FePc/Cr(001) system. Not only are the molecules on the Cr surface decomposed as expected, but also the molecules on the Fe nano-islands. In Figure 6.4c, more Fe was coated onto the Cr surface at a thickness of $\sim 1$-2ML. Now the bright flat terraces are iron super-structures packed along (001) direction. Correspondingly, Figure 6.4d shows the surface topography after FePc deposition. It still exhibits similar features as the previous systems. No obvious intact FePc molecules can be found. We increased the thickness of the Fe buffer layer to $>3$ monolayers as shown in Figure 6.4e. After deposition of the FePc, while most of the molecules still decompose, some of them remain intact as marked in Figure 6.4f. These “cross”-shaped FePc molecules on the surface not only indicate that there are intact molecules on such thicker Fe Films system, but also directly prove that the other round protrusions are different from intact FePc molecules. Based on their small size, it is highly likely that they represent the result of decomposition.
6.4 Discussions

Chemical reactions happening upon gas or liquid contacting with metal/semiconductor surfaces are the primary concern for surface science for a long time. Diatomic gas molecules, such as hydrogen, oxygen, and nitrogen, have found to be chemically adsorbed on certain metals, such as Ag and Pt\textsuperscript{24,25}. The molecules break their bonds in favor of new bonds to the surface, the energy to overcome the activation potential usually come from the translation energy and vibrational energy\textsuperscript{24}. The similar dissociative chemisorption has also been observed on the semiconductor surface, e.g. hydrogenated GaN(0001) surface formed during the growth of gallium nitride using NH\textsubscript{3} nitrogen source\textsuperscript{26}. Since organic molecules primarily consist of bonds of lightweight atoms, such as carbon, nitrogen and hydrogen, similar dissociation and forming new bonds with surface atoms will be possible when the molecules are adsorbed on the substrate. For example, S. F. Bent reported dienes and amines chemically attached on the Si(100) – 2 × 1, Ge(100) and C(100) surfaces, forming new chemical species\textsuperscript{27}. Shin et al. observed oxidation and dissociative chemisorption of ethanol on the platinum surface\textsuperscript{28}, sb reported self-assembled monolayers (SAMs) are often formed by chemisorbing thiols (RS-H) onto gold surfaces forming Au-SR bonds\textsuperscript{29}.

In our experiment, when FePc molecules were deposited onto Cr(001) surface, the appearance of molecules is distinct from its expected cross shape. Furthermore, the fragments on the Cr(001) surface are apparently smaller than the size of intact FePc molecules. More importantly, the fragments can be distinguished as two species: one of which has larger size, the other one in smaller size. By examining a local area, the ratio of the two species is about
This fact suggests that FePc molecules are decomposed into one iron atom and four Pc ligands upon adsorption. The reasons that might cause this decomposition can be thought as high surface activity of Cr(001), for example, surface Cr atoms can interact with Fe atom in the center of FePc molecule. However, to determine the detailed mechanism of this dissociation requires the chemical identification of surface reaction products which has not been possible in our experiment.

The relative surface chemical reactivity of chromium and iron for FePc decomposition can be qualitatively understood by the energy shift of metal d-band centroid. Due to the lower energy of chromium d-band center of mass, we can expect it has larger local surface reactivity than iron. As the results shown in Figure 6.4, at small Fe coverage high surface reactivity still dissociates molecules completely. In submonolayer films this is obviously the result of the high reactivity of under-coordinated Fe island edges. For thin Fe films, reactivity may be increased due to deviations from the bulk Fe structure caused by the Cr substrate. As the thickness of the Fe film increases to >3ML, it should approach a bulk-like structure and exhibit reduced reactivity as observed in Figure 6.4f. In our observation, we find a few intact FePc “cross” shapes in Figure 6.4f as iron thickness ~3ML. The rarity of intact FePc molecules indicates that the surface of the Fe layer still exhibits significant local chemical reactivity which decomposes most of the FePc molecules. We note that evidence for partial decomposition of porphyrins on cobalt film surfaces has recently been reported that supports the idea that surface reactivity on 3d transition metal substrates must be a general concern.
6.5 Conclusions

In this chapter, we reported the decomposition of iron phthalocyanine on the Cr(001) surface and compared the observed decomposition of molecules with the ordered intact molecules on the noble Au(111) surface. We further proved the decomposition by creating a less reactive iron buffer layer on the Cr(001) surface. This results in a reduced probability of decomposition when the Fe buffer layer thickness is >3ML. As MPcs and the other organic molecules show promising applications in electronics and spintronics, the possible chemical reactions at metal-organic interface should be a very serious consideration in device design and characterization. This is especially critical when organics must contact high reactivity 3d transition metals as often required for spintronic devices. The possible decomposition can totally alter the physical properties of the molecules and interfaces.
Figures

**Figure 6.1** Iron phthalocyanine (FePc) adsorption on Au(111) surface. (a) 39nm x 39nm scale topography (1V, 80pA), FePc molecules form ordered pack while Au(111) herringbone reconstruction clearly visible, surface FCC and HCP domains are marked; (b) zoom-in 10nm x10nm topography (1V, 80pA), single FePc molecule diameter is measured ~1.4nm.
Figure 6.2 The molecular orbitals derived electronic states of FePc molecules measured by scanning tunneling spectroscopy (STS) (a) logarithmic derivative of constant-height STS in negative energy range, showing HOMO at -1.3eV; (b) logarithmic derivative of constant-current STS in positive energy range, showing LUMO at 3.0eV, image potential state at 4.2eV.
Figure 6.3 The decomposition of FePc on magnetic Cr(001) surface. (a) large scale topography (30nm x 30nm, 0.8V, 5pA) showing no “cross” shape intact FePc molecules. (b) Zoom in on a local area (20nm x 20nm, 0.8V, 5pA), the inset presents an example of molecule decomposing, the sizes of different remnant parts are marked.
Figure 6.4 The growth FePc on Fe/Cr(001) surface. (a) submonolayer Fe coverage; (b) FePc on submonolayer Fe/Cr(001), the molecules decomposed completely; (c) ~1ML Fe coverage. (d) FePc on 1ML Fe/Cr(001), still no FePc molecules founded; (e) ~3ML Fe coverage; (f) FePc on 3ML Fe/Cr(001), few intact FePc molecules founded and marked.
References


