

**INTRINSIC CHARGE TRANSPORT AT INTERFACES BETWEEN  
ORGANIC SEMICONDUCTOR AND HIGH-K DIELECTRICS**

By

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## ABSTRACT OF THE THESIS

Intrinsic charge transport at interfaces between organic semiconductor and high-k dielectrics

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Rubrene single crystals have the highest field effect mobility ( $\sim 20 \text{ cm}^2/\text{Vs}$ ) among other organic single crystals for now. However, the charge transport mechanisms are still unsure. Some people think it is band-like transporting while others think it's small polarons hopping. Understanding the transporting mechanisms can help us optimize the device performance. It has been found that high-k materials will reduce the mobility of organic semiconductors due to the formation of Fröhlich polarons. And the field effect mobility is reversely proportional to the dielectric constants of dielectric layers. Until now, people have been fabricating devices with different methods to grow high-k dielectric layers on top of different piece of rubrene single crystals. In this way, it will create a large error instead of accurately study the relations between dielectric constants and mobility. In this thesis, we introduce a novel method called "vacuum lamination" in order to study the system more carefully. Through this method, a single piece of rubrene crystal with pre-painted contacts can be examined repeatedly with removable dielectric layers laminate on top of it. And we used atomic layer deposition (ALD) system to deposit high-k dielectric material

(Al<sub>2</sub>O<sub>3</sub>) on top of polyimide substrates which can be easily removed later without harming the surface of rubrene crystal. Different thicknesses of dielectric layers have been studied. In this study, we found the mobility reduced significantly after rubrene in contact with high-k material, and the mobility recovered after removing it.

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## Chapter 1 Introduction

Organic Field effect transistors (OFETs) as a promising application in the future have been studied frequently in the past few years. Although solution -processed OTFTs have benefits of cheap cost, large area application, flexibility, and easy to fabricate, the mobility is hard to enhance due to the defects and impurities create through fabrication process. Pristine single crystal FETs with flat and shin surfaces which has little defects and impurities, the mobility can achieve an order of magnitude lager than OTFTs.<sup>1</sup>

Rubrene single crystal, model of organic single crystals, has lots of advantages. One of them is the high mobility ( $\sim 20\text{cm}^2/\text{Vs}$ )<sup>2</sup> among other organic semiconductors which is highly reproducible. Second, it is stable even preserve under ambient environment in dark for years. And the device fabrication is cheap and easy compare to inorganic FETs. Although rubrene has been studied for decades, many mechanisms are still unknown and the understandings are only a little. For example, there are many theories about the charge transporting mechanisms in rubrene, from band-like transporting to small polarons hopping.<sup>3</sup> Understanding the transporting mechanisms can help us optimize the device performance. And the mechanism is complicate, different scattering mechanisms such as phonon scattering, roughness scattering, impurity scattering, and polaron scattering are all need to be considered. Mobility is not just the intrinsic property of organic semiconductors, but the intrinsic property of semiconductor-dielectric layer interface.

Different from inorganic materials which has a trend of using high-k materials as gate dielectric layer for lower operational voltage and reduced leakage currents due

to the shrinking size of devices, it has been found that high-k materials will reduce the mobility of organic semiconductors. According to Morpurgo et al<sup>4</sup>, they believe the field effect mobility is inversely proportional to the dielectric constant of dielectric layer ( $\mu \propto 1/\epsilon$ ) due to the forming of Fröhlich polarons. In their work, rubrene crystals are made into different devices with different dielectric layers through different fabrication methods which may create some errors. In order to study this system more carefully, a novel device fabrication method will be introduced later.

The method introduced here called “vacuum lamination”<sup>5</sup>. The idea is borrowed from a vacuum package, by placing a commercial bought polymer thin film (Mylar or Kapton) on top of a rubrene crystal with pre-fabricated source-drain contacts, the polymer thin film can be easily collapsed on top of rubrene crystal through the vacuum system connected beneath (a pressure of 710 torr is already enough for it). Here, the polymer thin film behaves as the gate dielectric layer. After lamination, we can just simply drop a silver paint on top of channel as gate. Through this method, a single piece of crystal can be measured repeatedly without degrading the surface of the crystal, hence different dielectric layers can be measured with exactly the same crystal.

The technique we choose to prepare different dielectric layer with different  $\epsilon$  is atomic layer deposition (ALD) due to the following reasons. First, ALD will grow the surface layer by layer in the atomic order and we expect to get comparatively smooth surface which is important in device fabrication. As we mention above, the mobility of device is the intrinsic property of semiconductor-dielectric interface. Second, the chemical reaction in ALD chamber is highly reactive and fast, in which we expect to get a pin-hole free, homogeneous surface. Finally, this technique



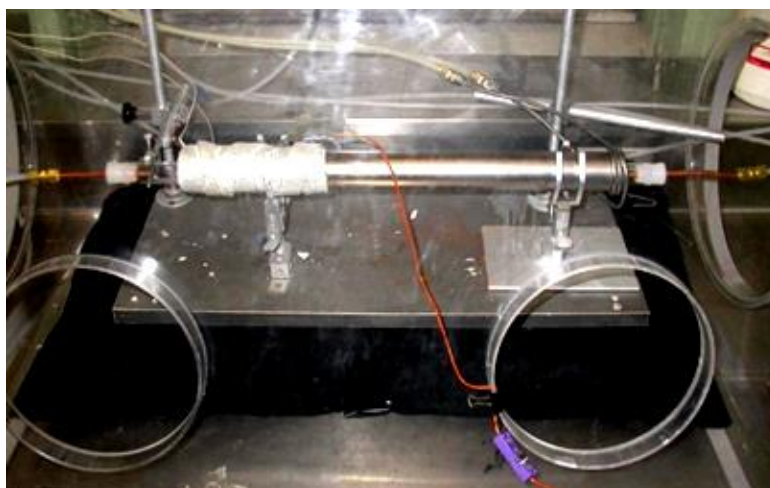
allows us to grow different dielectric layers through the same method, which is benefit for us to study the relationship between mobility and dielectric constant systematically.

Via the method we mentioned above, research of organic semiconductor with different dielectric layers is in progress. Not only the tunable mobility with different dielectric constant, but also the changing mobility dependent on changing thickness of dielectric layer we want to study at the first time.

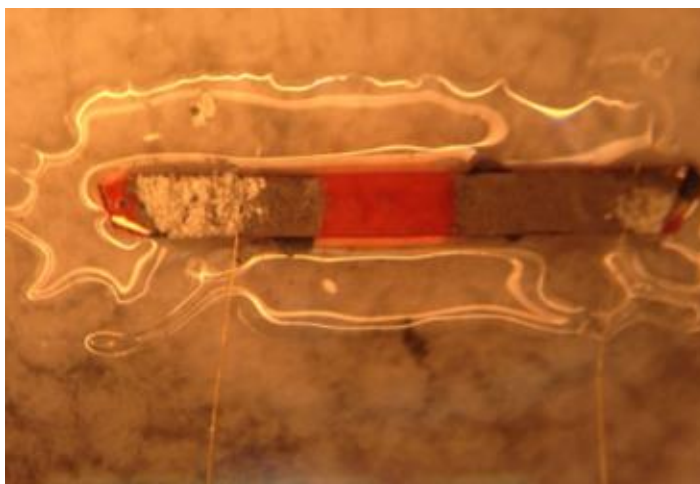
## Chapter 2 Experimental Results and Discussion

### 1. Preparation of Rubrene Crystal

High quality rubrene single crystals are grown in a stream of ultrahigh purity helium (flow rate~0.1L/min) with physical vapor transport (PVT) method. A PVT furnace consists of a quartz tube and an external heater unevenly wrapped on the metal tube outside the quartz tube which can create a stable temperature gradient along the quartz tube. The rubrene raw material is bought from Sigma-Aldrich and put into an inner quartz tube to start the growth. Figure 1 shows the PVT system we use. After we get the appropriate crystal with shinny surface, source-drain contacts are drawn onto it with graphite paste and then gold wires are attached on it. Figure 2 shows the finished rubrene crystal that is ready to measurement.



**Figure 1** PVT furnace system.



**Figure 2** Rubrene crystal with contacts.

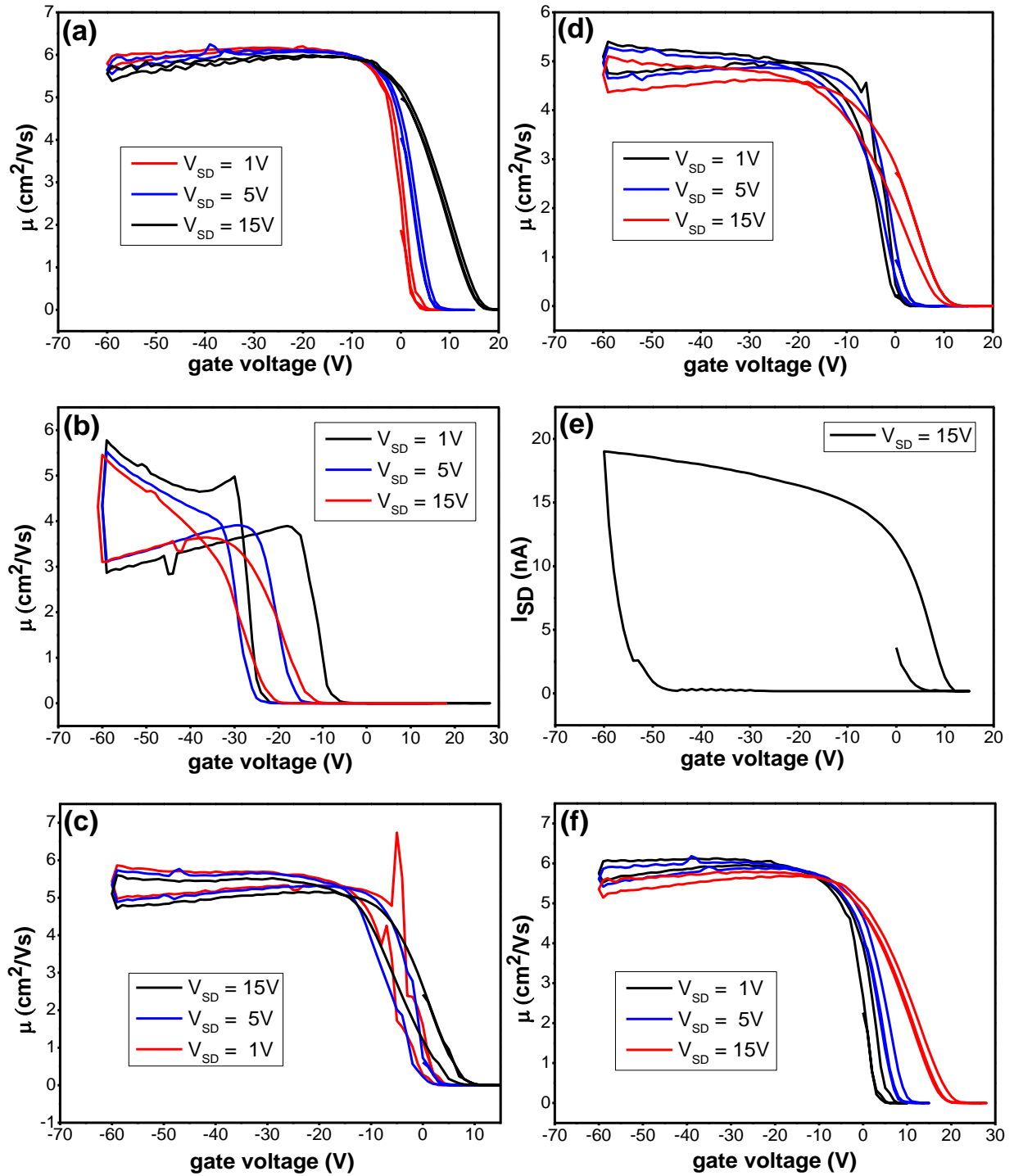
## 2. Device Measurement

The measurements is done by two K2400 source meters provide gate voltage ( $V_g$ ) and source-drain voltage ( $V_{sd}$ ) separately, and a K6517 electrometer measures source-drain current ( $I_{sd}$ ). The dielectric material we choose to try first is  $\text{Al}_2\text{O}_3$  ( $\epsilon \sim 9.4$ ). Use  $7.5\mu\text{m}$  Kapton ( $\epsilon \sim 3.4$ ) as substrate to grown  $\text{Al}_2\text{O}_3$  on it. The film is grown under  $250^\circ\text{C}$  and the melting point of Kapton is  $400^\circ\text{C}$ , so we don't need to worry the polymer will melt and contaminate the ALD chamber. The capacitance per unit area ( $C_i$ ) of Kapton is measured before growth, and the value is  $0.4\text{nF}/\text{cm}^2$ . We use this value as the total capacitance of  $\text{Al}_2\text{O}_3/\text{Kapton}$  film ( $\text{Al}_2\text{O}_3$ , Kapton is electrically connected in series), as the thickness of ALD grown  $\text{Al}_2\text{O}_3$  is about  $30\sim 130\text{nm}$ . Compare to the thickness of Kapton ( $7.5\mu\text{m}$ ), it is really small and thus in the parallel capacitor its contribution is irrelevant ( $1/C_{\text{total}} = 1/C_{\text{kapton}} + 1/C_{\text{alumina}}$ , where  $C = \epsilon_0\epsilon_r/d$ ,  $d$ = thickness). In the following measurement, the mobility of linear and saturation regime is calculated through the following equations:

$$\mu_{lin} = -\frac{L}{W} \frac{1}{C_i} \left( \frac{\partial I_{sd}}{\partial V_g} \right) \frac{1}{V_{sd}} \quad (1)$$

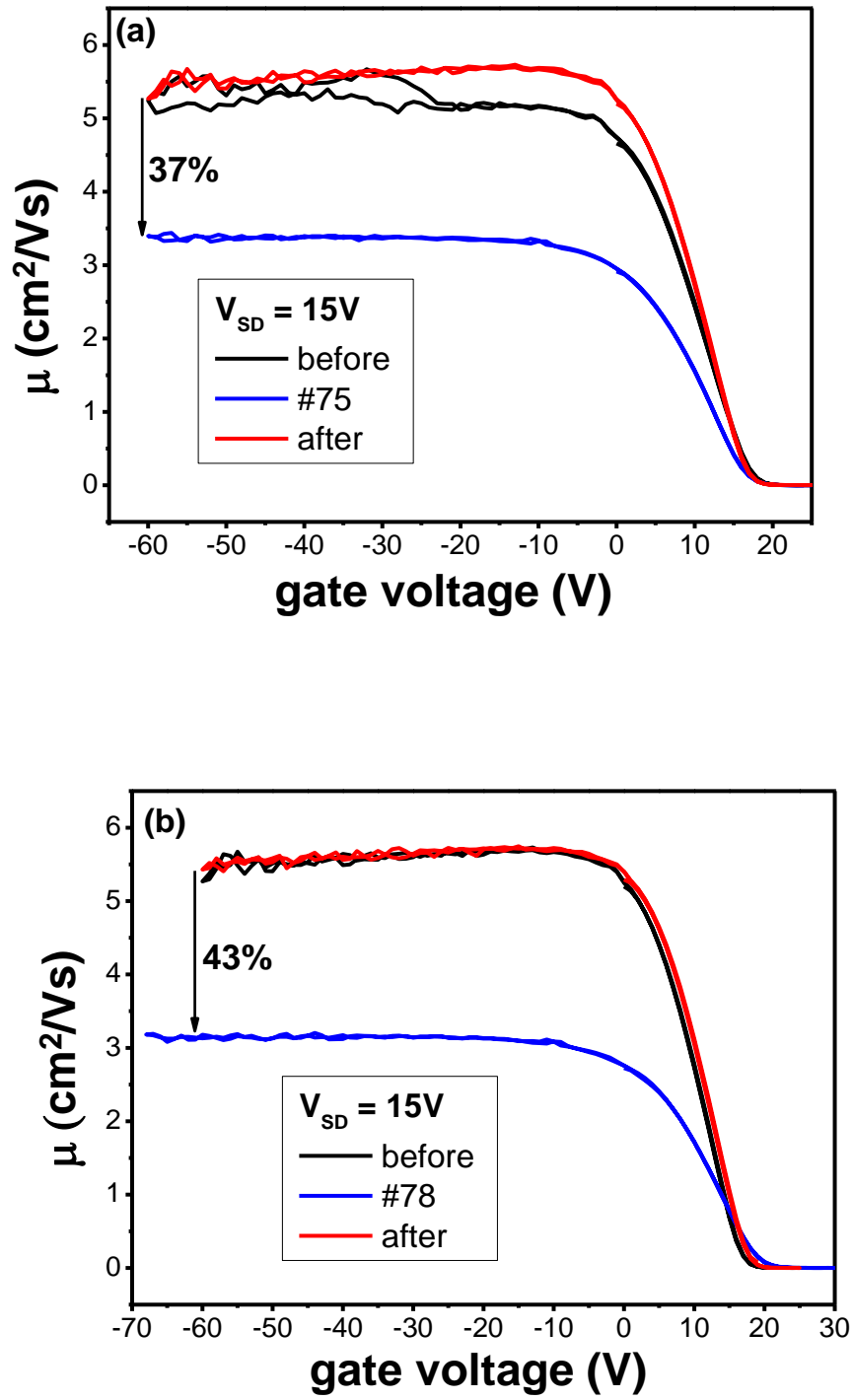
$$\mu_{sat} = \frac{2L}{W} \frac{1}{C_i} \left( \frac{d\sqrt{I_{sd}}}{dV_g} \right)^2 \quad (2)$$

, where  $L$ =channel length;  $W$  = channel width.

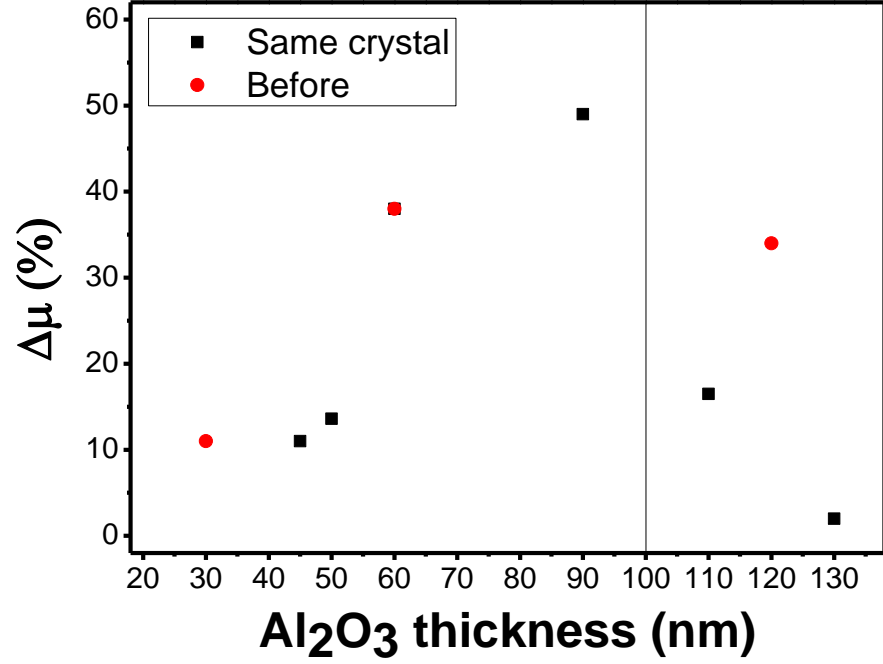


**Figure 3** (a)measure with pure Kapton film before any ALD film lamination (b)30nm Al<sub>2</sub>O<sub>3</sub>/Kapton film (c)30nm Al<sub>2</sub>O<sub>3</sub>/Kapton film after annealing at 200°C for 1.5hr (d)film from (c) put preserve in a desiccator for 5 days (e) 60nm Al<sub>2</sub>O<sub>3</sub>/Kapton film with 1.5hr annealing (f) pure Kapton measurement after 30nm Al<sub>2</sub>O<sub>3</sub>/Kapton film lamination

Every time before and after the measurement of an ALD grown film, we will measure the pure Kapton film as reference. Although the measurement of pure Kapton film is quite stable, we met some problem when measuring the  $\text{Al}_2\text{O}_3/\text{Kapton}$  film at first. Figure 3(a) shows the measurement of a pure Kapton film right before the vacuum lamination of a 30nm  $\text{Al}_2\text{O}_3/\text{Kapton}$  film, the mobility is really high ( $\sim 5.8\text{cm}^2/\text{Vs}$ ) and without hysteresis. After lamination of 30nm ALD film, we can see large hysteresis appears in figure 3(b). Base on the process of ALD which has cycles of  $\text{H}_2\text{O}$  released into the chamber, we doubt there may be water or hydroxyl group trap in the film or stay on the surface which can seriously influence the mobility and cause the big hysteresis. To prove the point, we try in-situ annealing the ALD film gently at  $200^\circ\text{C}$  for 1.5hr after growth of 30nm film. From Fig. 3(c), one can find the hysteresis decrease. And we kept the film in a desiccator for another five days and re-measured again (Fig. 3(d)), the situation got even better. As for another 60nm  $\text{Al}_2\text{O}_3/\text{Kapton}$  film, even if we annealed it for 1.5hr after growth, it still shows very large hysteresis which informs us the thicker the film the longer annealing process we need. After we did proper annealing for different thickness's ALD film, the problem of hysteresis never appear again. Figure 3(f) shows the measurement of pure Kapton again after the ALD film had been removed. We can see the high reproducibility and reversibility of it compare to Figure 3(a).



**Figure 4** (a) mobility decrease of 60nm  $\text{Al}_2\text{O}_3/\text{Kapton}$  film (b) mobility decrease of 90nm  $\text{Al}_2\text{O}_3/\text{Kapton}$  film.



**Figure 5** Comparison of decreasing ratio of mobility with different thickness.

We have measured many ALD films with different thickness including 30nm, 45nm, 50nm, 60nm, 90nm, 110nm, 120nm, and 130nm. Some of them show relatively large decrease of mobility while some of them not (we will discuss it later). In Figure 4, both 60nm and 90nm Al<sub>2</sub>O<sub>3</sub>/Kapton film have obviously decreased mobility and the device is reversible after remove the film. And there is no threshold voltage shift in this case showing that there is no charging or doping effect. For 60nm case, 37% decrease of mobility is calculated from linear regime appear in Fig. 4. Value calculate from saturation regime is 38%. For 90nm case, 43% decrease from linear regime and 49% decrease from saturation regime. This ratio is calculated from  $(\mu_{Kapton} - \mu_{Al2O3}) / \mu_{Kapton}$ .



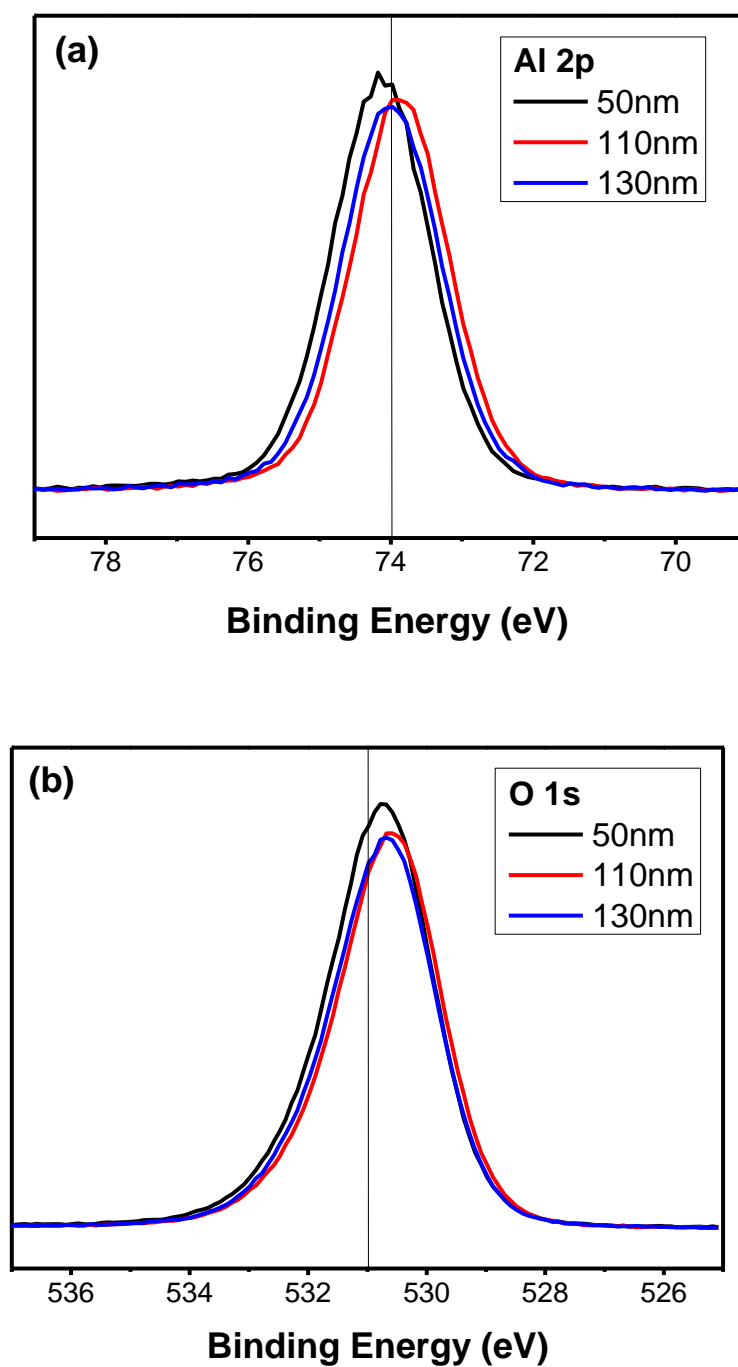
As we mentioned above, not all the  $\text{Al}_2\text{O}_3/\text{Kapton}$  films we measured have this obvious decreasing mobility. In Figure 5, films with thickness smaller than 100nm seems to have a trend that mobility decrease with increasing  $\text{Al}_2\text{O}_3$  thickness while the films over 100nm seems to not agree with it. Notice that the black dots in Figure 5 were measured with the same rubrene crystal, and the mobility of pure Kapton layer before and after each  $\text{Al}_2\text{O}_3/\text{Kapton}$  film measurement is reproducible (60nm, 90nm in black dots are the same in Fig. 4). Red dots are the result measured with different crystal. Until now, we can't adjudge which part is artifact and which one is true until we get more evidence and the reproducible result. So we don't make an explanation of the increasing mobility difference with increasing thickness until we make sure the trend. Although we can't make sure the trend, we can examine our films or measurement to find out what maybe went wrong. In the next part, we pick three films with different thickness (50nm, 110nm, 130nm) which made on different days to do surface analysis.

### 3. Surface Characterization of $\text{Al}_2\text{O}_3$

#### 3.1 X-ray Photoemission Spectroscopy (XPS)

First we need to make sure the dielectric layer we grew onto Kapton is really  $\text{Al}_2\text{O}_3$  and the atomic ratio is correct. X-ray photoemission spectroscopy (XPS) is done with k-alpha in NPL. A survey scan is done for each film first, and more than one point is examined. All of them show peaks of Al, O, and C. The brief atomic ratio for 50nm film is Al : O : C = 37.7 : 53.43 : 8.87 (Al : O~2 : 2.83); for 110nm film is 38.9 : 53.4 : 7.7 (Al : O~2 : 2.75); for 130nm film is 38.14 : 52.18 : 9.68 (Al : O~2 : 2.74). In three films the ratio of oxygen is approximate but a little less than 2:3. Then we scan the range of Al and O for further details. Figure 6(a) shows Al 2p binding energy. The peak positions are 74.18eV, 73.88eV, 73.98eV for 50, 110, 130nm films respectively. Although they all in the range of binding energy according to NIST's database (73.62~75.9eV), there exist small shift between themselves. This may due to the different carbon ratios on the films where the carbon comes from TMA precursor used in the last cycle in ALD process. Figure 6(b) shows O 1s peaks as 530.83eV, 530.69eV, and 530.78eV for 50, 110, 130nm films respectively. It's still in the range but also with slightly shift.

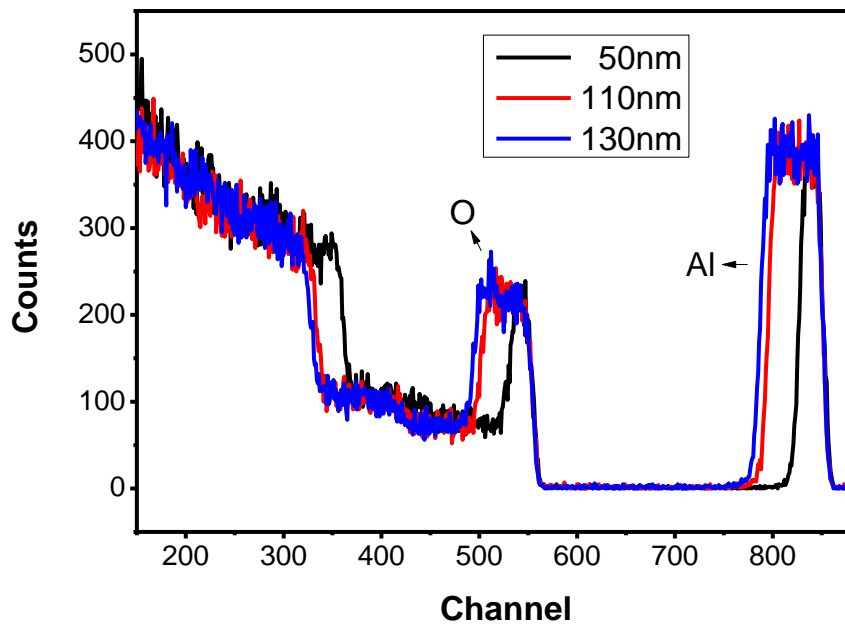
For the carbon present on the surface, it comes from the trimethylaluminum (TMA) precursor that didn't completely react due to the last run. But it's possible the reason of the smaller oxygen atomic ratio compare to aluminum, and the reason of small binding energy shift in Al 2p scans.



**Figure 6** (a) Al 2p and (b) O 1s XPS spectra of 50, 110, 130nm Al<sub>2</sub>O<sub>3</sub> films.

### 3.2 Rutherford Back Scattering (RBS)

From the above XPS result, we know the films indeed have aluminum oxide grown on it and the elemental ratio is correct except some carbon exists. But we can't make sure the thickness of films from XPS due to its photon energy can only transfer through tens of angstrom. Rutherford back scattering (RBS) is a good technique to tell the thickness here. It uses 2000keV He ion beam to hit the sample, through the energy loss of back scattered ions collected at the analyzer, we can know the thickness of our films. The thicker the film, the larger the peak width will be (Figure 7).



**Figure 7** RBS spectra of 50, 110, 130nm Al<sub>2</sub>O<sub>3</sub> films, peak widths represent the thickness of films.

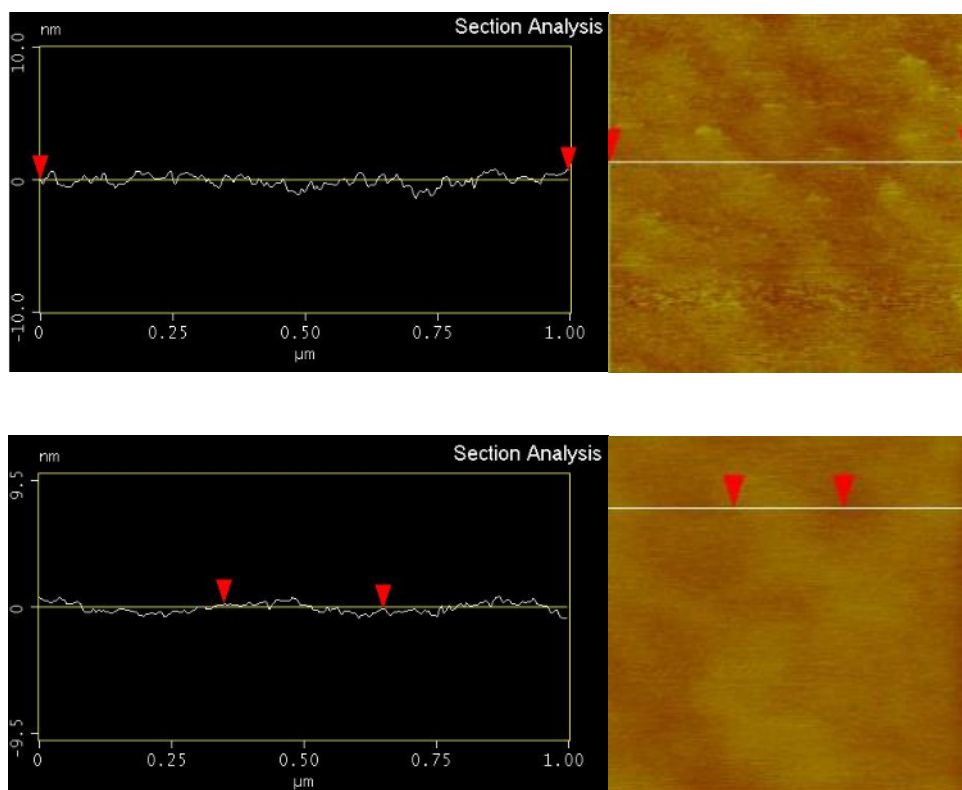
After the simulation, we get areal densities of  $478 \times 10^{15}$ ,  $1070 \times 10^{15}$ ,  $1215 \times 10^{15}$  (atoms/cm<sup>2</sup>) for 50, 110, 130nm respectively. The thickness calculated from it will be ~50.6nm, 113.2nm, and 128.6nm for three films (use  $d=3.2\text{g/cm}^3$  for ALD grown Al<sub>2</sub>O<sub>3</sub>) which fit the theoretical value quite well.

### 3.3 Atomic Force Microscopy (AFM)

For the scan of atomic force microscopy (AFM), we use a bare Kapton film to compare with a 10nm Al<sub>2</sub>O<sub>3</sub>/Kapton film. Several spots in each film have been examined with tapping mode. From Figure 8 we can tell the roughness of Al<sub>2</sub>O<sub>3</sub> film is similar to the bare Kapton and it looks pretty homogeneous.

From the XPS, RBS, and AFM analysis above, at least we know the thickness, roughness and elemental composition is quite stable except a little amount of carbon exists on the film due to the TMA precursor. It's important to find out how it will influence our device measurement.

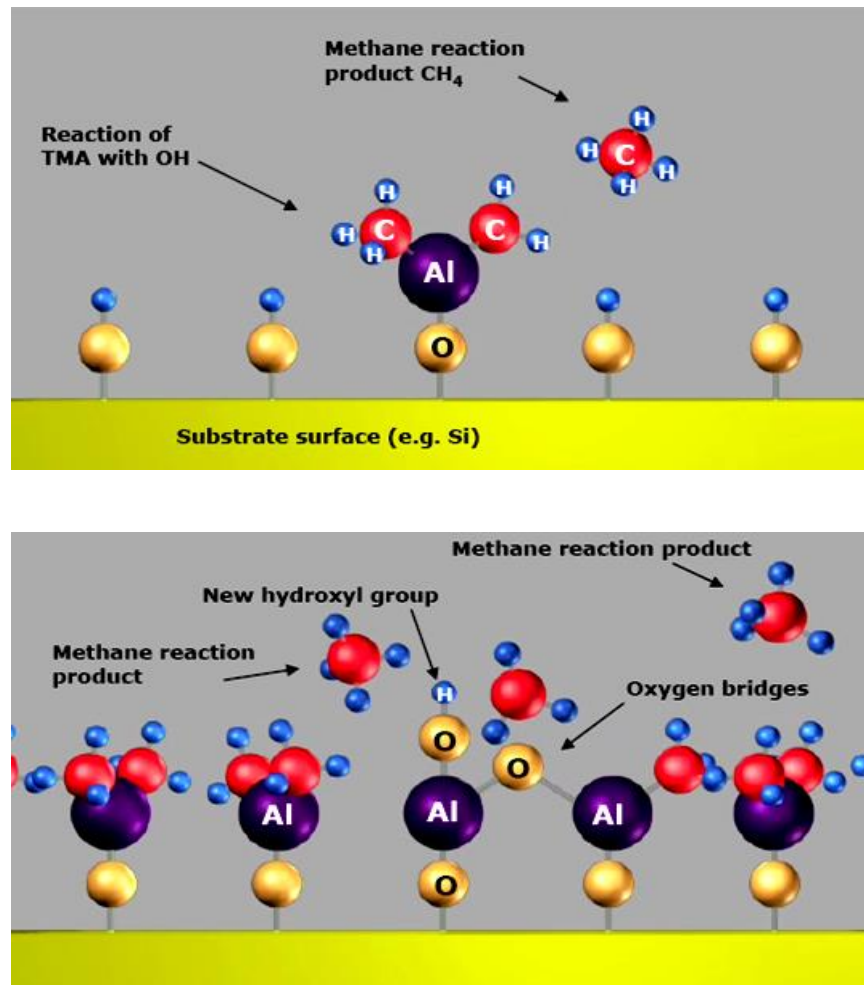
If the ALD grown Al<sub>2</sub>O<sub>3</sub> film is so stable and perfect, what are the factors that influence the reproducibility of our device performance? This is the problem we met now and I'll propose some methods to solve this problem in the next part.



**Figure 8** AFM images of (a) bare Kapton surface and (b) 10nm Al<sub>2</sub>O<sub>3</sub>/Kapton film.

#### 4. Possible Solutions and Extended Works

First, we know the carbon that exists on ALD grown films may due to the TMA precursor for it is the last run. Although we don't know how it can influence our device performance for now, only when the films have pure aluminum oxide (impurities free) on it we can believe in our data and see the pure polaron effect. As we know, by controlling the cycle of chemical reaction of ALD runs, we can leave the surface with Al-OH or Al-CH<sub>3</sub> terminal groups. If the last precursor put in is water, we'll get an Al-OH surface and vice versa (Fig. 9). In our ALD process, the last precursor put in is TMA which form Al-CH<sub>3</sub> terminate groups on Al<sub>2</sub>O<sub>3</sub>/Kapton surface. This surface may react with water in the ambient which depends on the humidity and weather right after we take it out from the ALD chamber. Although we carefully keep it in the desiccator, water vapor still have chance while we transferring the films or measuring. This can cause the films partially reacted into Al-OH groups and the ratio may base on the ambient condition that we can't control. The result is, films we measured did not maintain in a same condition, the surfaces are partially hydroxylated and partially methylated in an unknown ratio. This can also be seen from the XPS data above, the carbon ratio indeed have slightly different (if we consider a monolayer of carbon then 2% isn't a small different) and it possibly due to different degrees of hydroxylation. The reason above may cause the irreproducible data or some kind of artifacts. If the last cycle we put in the ALD chamber is water, then we can make sure the surface is homogeneously covered with -OH groups that can't further reacted with ambient water vapor. However, some people have mentioned the hydroxyl groups appear at the interface of gate dielectrics and channel will cause hysteresis and the -OH groups can trap the electrons and influence the



**Figure 9** Chemical reaction of ALD process (a) if end with precursor TMA, surface will have Al-CH<sub>3</sub> terminal groups (b) if end with water, surface will have Al-OH terminal groups.

mobility of n-type OFETs.<sup>6</sup> We can't make sure the influence of it to p-type rubrene crystals. According to Lee et al.<sup>7</sup>, they studied the effects of different ratio's hydroxyl groups in polymer dielectrics on pentacene OTFTs (p-type). The higher the ratio of hydroxyl group exists in polymer dielectric layers, the higher the mobility but also the higher the hysteresis and gate leakage currents. It will be interesting to study the device performance using -OH and -CH<sub>3</sub> terminate Al<sub>2</sub>O<sub>3</sub>/Kapton films. After all,



they are two distinctive functional groups (hydroxyl group is electron-withdrawing and methyl group is electron-rejecting). Only when we measure these two kinds of films, we can make sure what kinds of influence it will make to our rubrene OFETs. The  $\text{-OH}$  and  $\text{-CH}_3$  terminate  $\text{Al}_2\text{O}_3/\text{Kapton}$  films in the same thickness will be prepared and measured. And it's better to compare with the case of pure  $\text{Al}_2\text{O}_3/\text{Kapton}$  film (control group). By method of thermal evaporation, we can release oxygen into the chamber occasionally and grow aluminum oxide on top of Kapton. XPS, FTIR can also help us to characterize the films we want to make sure the condition we want. Once we make sure of the influence of those functional end groups, we can keep study and confirm the original goal of this research — polaron effect in high-k materials that decrease the mobility of OFETs.

On the other hand, the unreacted TMA precursor during growth can also get trapped in the films that contribute to the carbon peak and behave as impurities that influence the device performance (Kapton film don't have hydroxyl surface as silicon wafer, the growth on Kapton may different from the growth on Kapton, that's why I doubt the possibility of leftover precursor trapped in the film). To eliminate this possibility, we can prolong the reaction time and purge time in each cycle to make sure the surface is completely reacted and the unreacted ones are pumped away.

After we make sure the homogeneity of the  $\text{Al}_2\text{O}_3/\text{Kapton}$  films (no partial  $\text{-OH}$  and  $\text{-CH}_3$  groups), we still need to make sure the “stretching issue” when it laminating on the rubrene crystal. The polymer films are stretched when pumping down and naturally collapsed onto the surface of rubrene. Pure Kapton film won't have the problem of cracks when stretching but  $\text{Al}_2\text{O}_3/\text{Kapton}$  film may have because aluminum oxide is not chemically bonded to the Kapton surface. If cracks formed

when measure, it is not a homogeneous, smooth high-k dielectric layer that we want to study. To make sure about this, samples with different stretching level made deliberately need to be prepared. Scans of AFM at several spots can tell us the existence of cracks. If the cracks exist, we can try to do UV-ozone treatment on Kapton to form hydrophilic surface and then thermal evaporate about 2nm aluminum on it as nucleation sites (it will directly become  $\text{Al}_2\text{O}_3$  after venting), finally put it into ALD chamber to grow thicker aluminum oxide.

The last thing we can do is try to measure each film with more than one spots and try to measure the films as many as possible to eliminate the odds.

Other high-k materials such as  $\text{HfO}_2$  ( $\epsilon \sim 15.6$ ),  $\text{ZrO}_2$  ( $\epsilon \sim 25$ ), and  $\text{TiO}_2$  ( $\epsilon \sim 83-100$ ) is going to be examined in this system. In each dielectric material, we will make different thickness's film to check whether it is thickness dependent. Finally, we expect to get the plot of mobility versus dielectric constant of dielectric layers and the plot of mobility versus thickness in each dielectric layers.

At the interface between high-k gate dielectric and rubrene channel, except the polarons effect, there may be other effect that also influence the mobility, such as scattering or traps that we don't know. In order to get rid of other effects and to focus on the influence of polarons, Hall measurement is necessary. By applying a vertical magnetic field, Hall measurement allows us to see only those charges in mobile due to the Lorentz force ( $F = q \mathbf{v} \times \mathbf{B}$ ,  $\mathbf{v}$  is velocity of electrons,  $\mathbf{B}$  = magnetic field). We can control the longitudinal voltage  $V_{sd}$  rather than the  $I_{sd}$ , in this way the intrinsic mobility that influenced by true polaron effect will be measured. The smaller the Hall voltage we measured, the smaller the mobility will be. Also, we can confirm the phenomena done by Morpurgo et al. through applying temperature while measure the

Hall voltage to see whether this intrinsic mobility is temperature dependent as the work done.

Combing the method of “vacuum lamination”, ALD, and Hall measurement, we expect to see the true polaron effect by laminating different high-k dielectric layers repeatedly on a single piece of rubrene crystal, which has higher accuracy.

## Chapter 3 Conclusions

In order to achieve applications such as bendable screen and wearable devices, the importance of organic field effect transistors (OFETs) has increased. Although the mobility of organic materials had improved a lot, it is still much smaller compare to inorganic semiconductors. In order to optimize the performance of OFETs, it is important that we understand the mechanism of carrier transportation in the channel area. In this study, we used the novel method “vacuum lamination” to study the relationship between dielectric constant of dielectric layer and mobility of rubrene single crystal. Also, we used atomic layer deposition (ALD) system to deposit high-k alumina on top of flexible polymer substrates (Kapton). By using these two methods, we successfully enhanced the accuracy of measurements. The mobility of rubrene crystal before and after lamination of alumina dielectric layer is consistent and reversible. Although there is big hysteresis exists at the beginning with those ALD films without post-annealing procedure, all hysteresis had been removed after optimization of ALD process.

We also in tempt to study the influence of thickness of dielectric layer on the rubrene mobility. However, the trend of decreasing mobility stopped when thickness

of alumina larger than 100nm. In order to make sure the quality of ALD-grown alumina films, a series of surface characterization had been done. XPS spectra of Al 2p and O 1s pointed that the elemental composition of alumina films are correct, and the RBS spectra also showed correct thickness information. AFM images told us the morphology of alumina films is smooth. These evidences shows the ALD-grown alumina films have good quality. Hence there is no certain relationship between dielectric layer thickness and rubrene crystal mobility in our case.

In conclusion, we have showed by applying high-k dielectric layer on top of organic materials, the field effect mobility decreased significantly and the mobility is reversible after removing the high-k layer.

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