

Interfaces between Metal and Arylamine Molecular Films As Probed with the Anode Interfacial Engineering Approach in Single-Layer Organic Diodes

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The interfaces between metal and arylamine molecular films were studied by measurement of current–voltage characteristics in single-layer organic diodes with the aid of the anode interfacial engineering method. The diode turn-on voltage is shown to be very sensitive to the arylamine/metal interface and thus can serve as a means for characterizing such organic/metal interfaces. We show that the diode electrical performance depends on the arylamine substituent groups and chemical/electrical properties of the anode. The conduction mechanism of the diodes is shown to be injection limited, which can be well described with the Richardson–Schottky thermionic emission model. This work may provide some insight into the use of single-layer organic diodes and the interfacial engineering method to rapidly probe the organic/metal and even organic/organic interfaces.

Introduction

The field of organic electronics is developing at a rapid pace. So far, organic semiconductors have been used as active layers in various devices such as organic light emitting diodes, organic field effect transistors, and solar cells.^{1–5} It is recognized that organic/metal interfaces play a critical role in affecting the charge injection and device electrical performances.^{6–8} The usual choice to examine metal/organic interfaces is to use ultrahigh vacuum surface spectroscopies.^{9–11} While spectroscopic techniques have the advantage of high energy resolution, it is often difficult to study the organic/metal interface in a real device since the interface of interest is “buried”. It is desirable to find an easy way to probe the organic/metal interfacial electronic structure in simple but real device configurations. There have been great advances in studying single-layer organic diodes and anode interfacial engineering of light-emitting diodes,^{12–14} which may offer a new opportunity for investigating organic/metal interfaces.

Arylamine derivatives have been widely used as hole transporting materials due to the easy oxidation of the nitrogen centers and the ability to transport positive charges via the radical cation species.¹⁵ However, it is still not well understood how cyano (–CN) substituents affect the electrical properties of arylamine molecular films, arylamine/metal interfaces, and subsequent device performance. The cyano group is known to be a strong electron acceptor, therefore charge-transfer and/or dipole interactions are observed between metals and organic molecules with –CN substituents.¹⁶

In a previous work, we showed that the single-layer organic diode is a simple but effective device for characterizing the electrical properties of arylamine molecular films.¹⁷ We observed a linear dependence between the first molecular oxidation potential (E°) and diode turn-on voltage (V_t). However, when diodes were made from polyarylamines with –CN terminal

groups such as CN-4AAPD (Figure 1), the turn-on voltage was much greater than predicted by E° .¹⁷ Cyclic voltammetry measurements indicate that adding –CN groups only slightly increases the first oxidation potential of the arylamines. Consequently, the present work was motivated to study the mechanism(s) leading to the high V_t in order to develop arylamine-based organic electronics, such as molecular scale charge storage.¹⁸

Here, we demonstrate the use of single-layer organic diodes to quantitatively characterize the arylamine/metal interfaces. Our strategy is to insert an interfacial modification layer between the metal anode and the arylamine film. The interface is then examined by analyzing current–voltage (I – V) curves with and without the anode interfacial layer. We show that the arylamine/metal interfaces depend on the anode metal and peripheral substituent groups. The device conduction mechanism is also briefly discussed.

Experimental Section

Figure 1 shows the molecular structure of the arylamines examined and the device configurations. Two arylamines were used as both the hole transport material and the interfacial modification layer. The synthesis, film growth, and electrochemical characterization of material 4AAPD have been described elsewhere.^{19,20} The synthesis and electrochemical characterization of CN-4AAPD will be reported elsewhere. As can be readily seen, the CN-4AAPD molecule has the same molecular size as that of the 4AAPD, except four anisyl groups in the periphery are replaced with cyano groups. The cyano groups are electron withdrawing, yielding a slightly higher E° for CN-4AAPD (0.65 V vs SCE) than observed for 4AAPD (0.49 V vs SCE).

The diodes have a structure of GaIn(cathode)/arylamine/coinage metal (anode). They were fabricated by subsequent depositions of anode and organic layer(s) onto clean glass microscope slides without breaking the vacuum. The anodes (Au, Ag, and Cu) were 100-nm-thick films vapor deposited at a pressure of about 1×10^{-6} Torr with a deposition rate of 0.2

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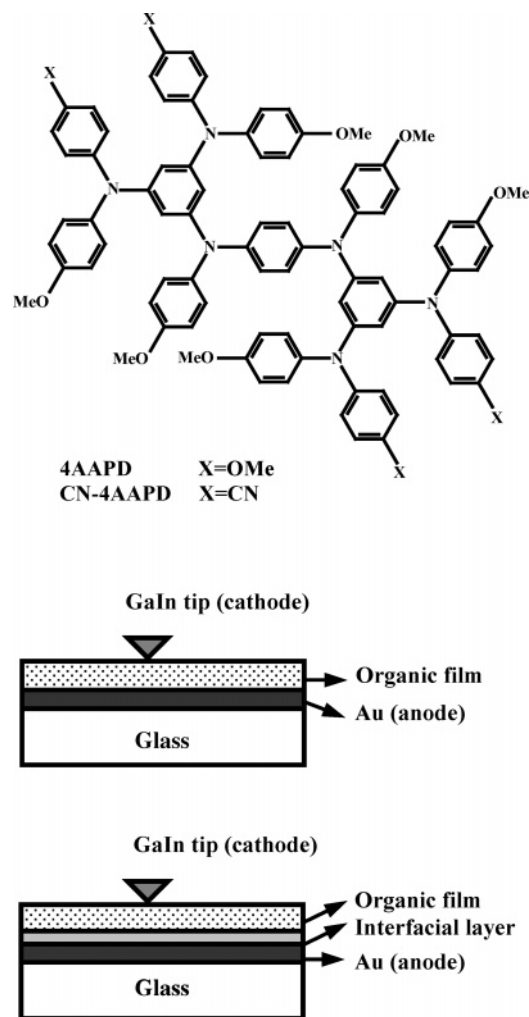


Figure 1. Schematic molecular structure of the arylamines used and the device configurations studied.

nm/s. The organic films were then deposited onto the anode at a rate of 0.5 Å/s. The film thickness and deposition rate were measured by a quartz crystal microbalance. A micrometer controlled liquid GaIn (as purchased from Aldrich) tip with a diameter of about 100 μm was used as the cathode, which provides a nondamaging soft contact to the organic layer.

The I – V curves were measured with a modified PAR-273 potentiostat (EG&G Instruments). All measurements were made in ambient conditions immediately after the samples were fabricated. The value of V_t is averaged from more than 25 measurements taken on different samples and at various positions. The error bars represent the standard deviation of the data set. The I – V curves did not show any hysteresis and were very reproducible at a given spot on the film. The film morphology was measured with a Digital Instruments DI3100 atomic force microscope in tapping mode. Self-assembled monolayers (SAMs) of 1-decanethiol were grown on a clean gold surface by immersion in a 1 mM solution in pure ethanol for 24 h. After removing the gold surface from the alkanethiol solution, it was thoroughly rinsed with ethanol and blown dry with nitrogen gas. We choose 1-decanethiol because it is the shortest alkyl chain thiol that produces well-ordered monolayers on Au surfaces.

Results and Discussion

Figure 2 shows typical I – V curves of the 4AAPD and CN-4AAPD diodes at different layer thicknesses. Under forward

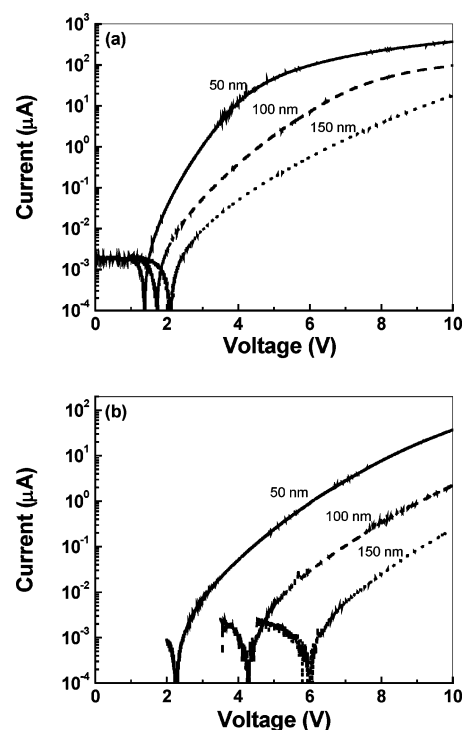


Figure 2. Typical I – V curves of (a) GaIn/4AAPD/Au and (b) GaIn/CN-4AAPD/Au diodes with different arylamine layer thicknesses.

bias, the current exhibits nonlinear behavior after the applied voltage exceeds a threshold point, the turn-on voltage V_t . Below V_t and in reverse bias (even to our highest accessible voltage -10 V), the samples only show leakage current (about 0.1 nA). The thickness dependence of V_t suggests that the current is electrical field mediated because the I – V curves collapse onto a common curve when current is plotted against V/cm (see the Supporting Information). Note that V_t of the CN-4AAPD diode is extraordinarily larger than that of the corresponding 4AAPD devices, although the oxidation potential of CN-4AAPD is only 0.16 V higher than that of 4AAPD. For example, V_t of the 150 nm CN-4AAPD diode is almost 4 V higher than that of the 4AAPD device. Even for the 50 nm diodes, the difference is still about 1 V. This suggests that there is an additional energy barrier to current flow in the CN-4AAPD diodes.

The only structural difference between the two arylamines is the presence of four $-\text{CN}$ groups in CN-4AAPD. This suggests that the interactions between the methoxy ($-\text{OCH}_3$) groups and $-\text{CN}$ groups with the Au surface may be very different and the cause of the large difference in V_t . To test this hypothesis, experiments were done by depositing a thin interfacial layer of one arylamine followed by a thick layer of the other arylamine. Figure 3 shows representative I – V curves of the 4AAPD and CN-4AAPD diodes with interfacial layers of varied thickness. When CN-4AAPD is used as the interfacial layer, V_t of the 4AAPD diodes increases from about 1.4 to 2.8 V as the CN-4AAPD interfacial layer increases from 0 to 10 nm. However, when 4AAPD is used as the interfacial layer in CN-4AAPD diodes, V_t is reduced from 2.5 to 1.3 V as the 4AAPD interlayer increases from 0 to 5 nm. The difference between the highest and the lowest V_t is more than 1 V. The CN-4AAPD layer obviously increases the hole injection barrier between the Au anode and the arylamine film.

Since the arylamine/Au interface is shown to be very sensitive to $-\text{CN}$ and $-\text{OCH}_3$ groups, we inserted an alkanethiol SAMs on the surface of the Au anode before depositing the arylamine. As shown in Figure 4, both the 4AAPD and CN-4AAPD diodes

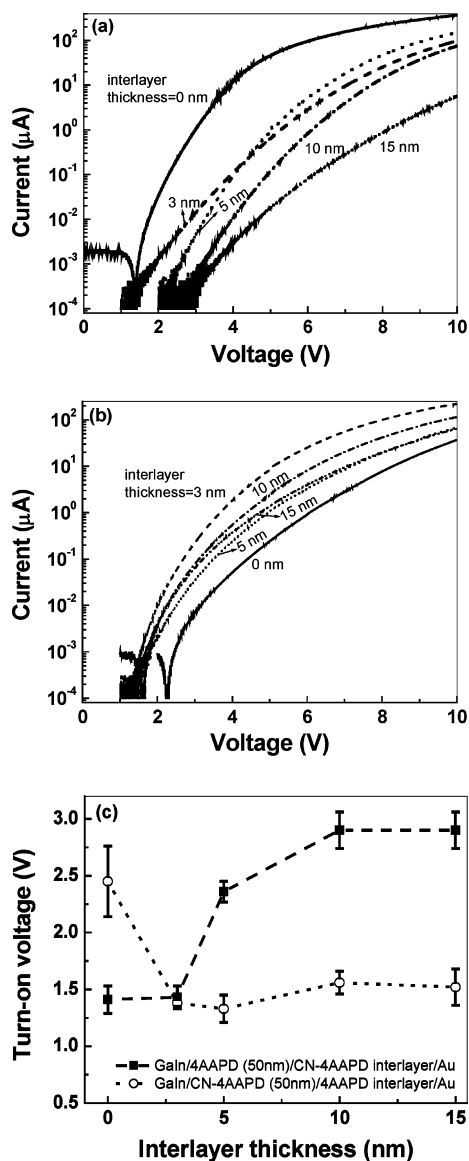


Figure 3. Effects of the anode modification layer on the charge-transfer interface. I - V curves of (a) GaIn/4AAPD (50 nm)/CN-4AAPD interlayer/Au and (b) GaIn/CN-4AAPD (50 nm)/4AAPD interlayer/Au diodes with various interlayer thicknesses. (c) Plot of average turn-on voltage versus the interlayer thickness. The lines are guides for the eye.

with 1-decanethiol SAMs interlayer have a much higher V_t than diodes without such a layer. For the 50-nm diodes, the device V_t is increased by about 0.5 and 2 V with the addition of a SAMs interlayer for 4AAPD and CN-4AAPD, respectively. The increase in V_t is consistent with the fact that alkanethiols monolayers reduce the work function of gold surfaces.^{11,21–23} Consequently, the hole-injection barrier is increased for both 4AAPD and CN-4AAPD diodes. The slope of Figure 4c is indicative of the threshold electrical field to turn on the device, while the y-intercept indicates the built-in potential between the anode and the cathode. The bigger the slope, the higher the electrical field needed to turn on the diode. The CN-4AAPD devices have a bigger slope than do the 4AAPD diodes. Note that the y-intercept value for CN-4AAPD on SAM/Au is evidently higher than that of the others. We believe these data support the notion that a large dipole layer forms at the arylamine/SAM interface in addition to the lower metal work function induced by the SAM.

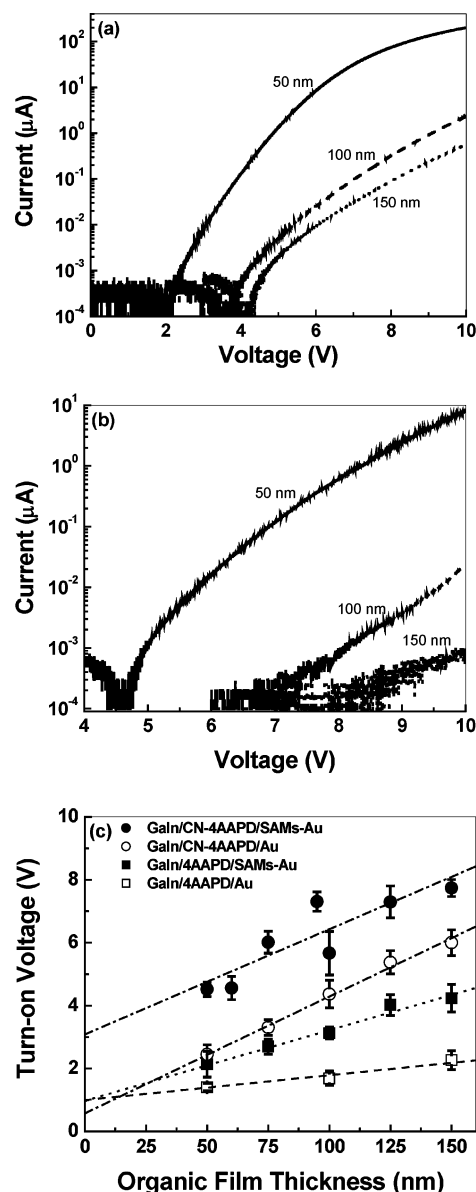


Figure 4. Effect of 1-decanethiol monolayer on the charge-transfer interface. Typical I - V curves of (a) GaIn/4AAPD/SAMs-Au and (b) GaIn/CN-4AAPD/SAMs-Au diodes with different organic layer thicknesses. (c) Thickness dependence of V_t for the 4AAPD and CN-4AAPD diodes fabricated on Au and SAMs-Au, respectively. The lines show the best linear fit.

We also characterized a series of 50-nm diodes of 4AAPD and CN-4AAPD fabricated on Ag and Cu. The turn-on voltage increases ~ 2 V when 4AAPD is replaced by CN-4AAPD on Ag and Cu electrodes. In the Au diode the increase is only 0.7 V when 4AAPD is replaced by CN-4AAPD. This trend suggests there may be a charge-transfer interaction between CN-4AAPD and Ag and Cu that contributed to the charge injection barrier at these interfaces. This is consistent with the fact that Ag and Cu are more reactive than Au and form charge-transfer salts with strong electron acceptors such as tetracyanoquinodimethane.²⁴ The fact that there is an increase in the turn-on voltage on Au (although smaller than on Ag and Cu surfaces) can be explained by the formation of a more polarized interfacial dipole layer between the cyano groups (versus the methoxy groups) at the gold surface. The surface morphology of arylamine molecular films also hints to the stronger intermolecular interactions (i.e., dipole-dipole) in the CN-4AAPD films. Figure 5 shows representative tapping mode AFM images of the 50-nm-thick

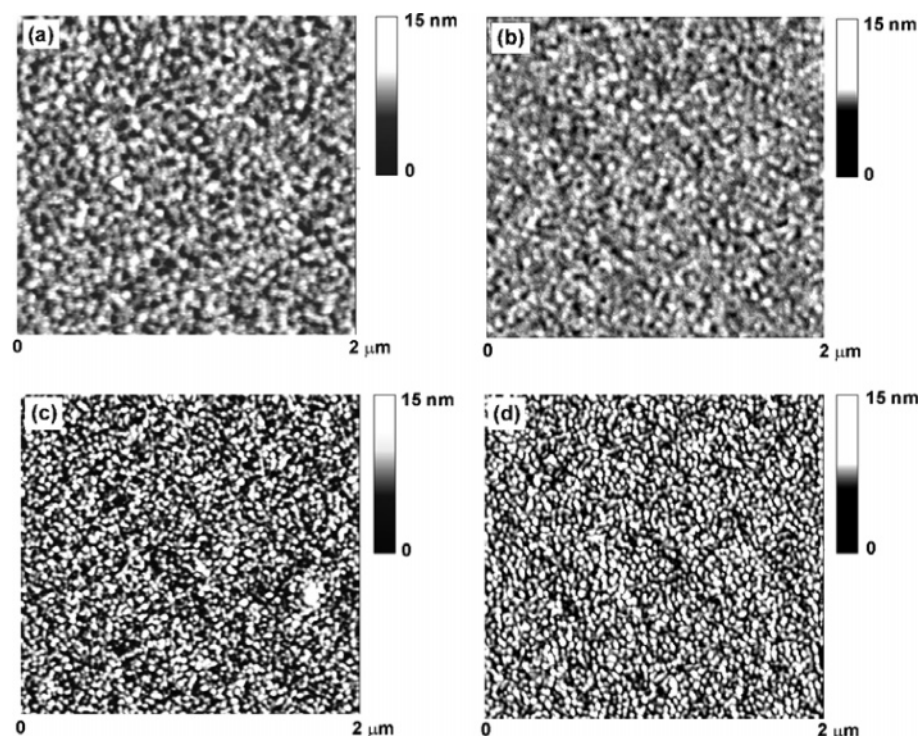


Figure 5. Tapping mode AFM images of the 50 nm films: (a) 4AAPD on Au, (b) 4AAPD on SAMs-Au, (c) CN-4AAPD on Au, and (d) CN-4AAPD on SAMs-Au substrates.

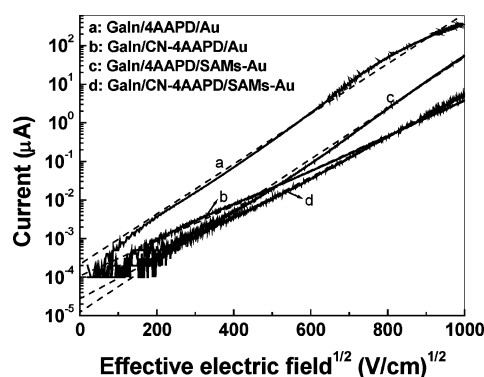


Figure 6. Semilog plot of current versus the square root of the effective electrical field for the 50-nm 4AAPD and CN-4AAPD diodes fabricated on Au and SAMs-Au. The dashed lines are the best linear fit.

arylamine films. Both 4AAPD and CN-4AAPD films are composed of small island-shaped domains. The films deposited on SAMs-Au are a little smoother than that on bare Au.

The conduction mechanism of our diodes is injection limited, which can be well characterized by the Richardson–Schottky (RS) thermionic emission model. The RS equation is $J = AT^2 \exp[-(\Phi_B - \beta E_{\text{eff}}^{1/2})/(k_B T)]$, where J is the current density, A is the Richardson constant, β is a constant with a value inversely proportional to the square root of the molecular permittivity, T is the temperature, Φ_B is the zero-field injection barrier, and k_B is the Boltzmann constant. As shown in Figure 6, for the diodes fabricated on both Au and SAM-Au anodes, the plot of $\log(I)$ versus $E_{\text{eff}}^{1/2}$ shows a linear behavior over a large range of current and electrical field. The slope and the y axis intercept are proportional to values of β and Φ_B , respectively. The diodes fabricated on SAM-Au have a lower y-intercept (i.e., higher Φ_B) than those fabricated on bare gold, suggesting that the SAMs introduce an extra injection barrier in the devices.

Conclusions

We demonstrate that the arylamine/metal interfaces can be characterized through analyzing the I – V data of single-layer organic diodes with the aid of the anode interfacial engineering approach. The diode turn-on voltage is very sensitive to the presence of arylamine/metal interfaces, thus the voltage can serve as a powerful probe for probing such interfaces. The arylamine terminal functional groups can have a critical influence on the interfaces. In contrast, the work function of the metal played only a minor role. Moreover, we show that there exists an additional energy barrier in diodes when CN-4AAPD was grown on SAMs. The conduction of our diodes is injection limited, which can be well described by the Richardson–Schottky thermionic emission model. We believe that our simple approach will be useful in studying the organic/metal interfaces of other kinds of organic semiconductors in real device situations.

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Supporting Information Available: Plots of current versus the effective electrical field for 4AAPD and CN-4AAPD diodes with different layer thickness. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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