Charge injection mechanism across the Au-poly(3-hexylthiophene-2,5-diyl) interface

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The nature of charge injection has been investigated across the Au-poly(3-hexylthiophene-2,5-diyl) (P3HT) interface of two kinds: P3HT on Au (bottom contact) and Au on P3HT (top contact). The *J-V* characteristics of a Au(bottom)/P3HT/Au(top) sandwich cell are analyzed by using the Fowler–Nordheim model and the hole barrier height at the top and bottom contacts has been estimated. The top contact showed a higher barrier height in comparison to the bottom contact. The quenching of photoluminescence spectra and the disappearance of characteristic P3HT peaks from the absorption spectra for the top contact supports that the ionically sputtered gold atoms on the polymer give rise to greater density of interfacial trap sites than those at bottom interface. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2734955]

I. INTRODUCTION

Organic electronic materials are particularly well suited for constructing cheap and solution-processable electronic devices.[1,2] A fundamental understanding of the mechanism of charge injection from a metal electrode to a π-conjugated organic system is essential to the design and operation of such devices.[3,4] Hence, polymer/metal interfaces play an important role in determining the device performance. The charge injection process depends on the magnitude of the energy barrier that the charge has to be overcome, while passing through the interface.[4] These barriers arise due to mismatch between the Fermi level of metal electrode and the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) levels of the conjugated polymer.[5,6] The alignment of energy levels at the interfaces suggests two distinct alignment regimes: vacuum level alignment and the alignment of the Fermi level. The former gives rise to the built-in potential while the latter leads to the formation of an interfacial dipole by means of diffusive charge transfer across the metal-polymer interface; the degree of charge transfer is reflected by the bending of energy bands of polymer with respect to the Fermi level of metal. This is expected to occur whenever there is a difference between the work function of the metal and polaronic bands of the conjugated polymer.[5,6] If the earlier conditions are not fulfilled then there is no charge transfer and only vacuum level alignment occurs. The interface between metal and polymer could be further broadly classified into two classes; one is polymer-on-metal (POM) and the other is metal-on-polymer (MOP), which is conventionally termed as the bottom and top contact, respectively.[7] Usually, the top contact is deposited by thermal evaporation of metal at high vacuum (10^{-6} mbar). It is assumed that the metal atoms can readily diffuse through the top surface of the polymer film and form a graded interface, which is morphologically different from the bottom contact.[8] Although, the electronic nature of the top and bottom contacts are studied well during investigation of the polymer light emitting diode,[9–11] the effect due to the difference in morphology could not be studied because of the use of dissimilar electrode materials.

In this article, we have investigated the behavior of poly(3-hexylthiophene-2,5-diyl) (P3HT) sandwiched between the top and bottom electrodes of gold. Due to the use of similar materials for the top and bottom electrodes, it is relatively easier to find out the difference between the injection-properties of the two electrodes.

II. EXPERIMENT

Sandwich cells of Au/P3HT/Au are fabricated by first ionically sputtering gold, while using a JEOL JFC-1500 ion sputtering device, on a cleaned glass substrate in the form of a strip having a width (w) of 1 mm. It is followed by spin coating of P3HT (thickness ≈ 0.25 μm) under ambient atmosphere from a 5% solution (w/v) in chloroform and this is further followed by sputtering of the top gold electrode in the form of strip ($w = 1$ mm) but oriented perpendicular to the bottom gold strip. The electronic grade regioregular P3HT used in this study is obtained from Aldrich, which has average molecular weight (17 500). The P3HT further purified in a Soxhlet extractor to remove low molecular weight impurities. The thickness of thin film is measured by a DEKTAK SURFACE PROFILER. The sputtering was performed at a rate of 1.5 Å/s approximately and at a pressure of 10^{-3} mbar. The effective cross-sectional area of the device is 1 mm^2. The *J-V* characteristics are measured at room temperature by a Keithley 6517 electrometer and at a pressure of 10^{-6} mbar. All the measurements are repeated a number of times on various samples of the same batch to check the reproducibility of the results. Samples for four-probe conductivity ($\sigma_{4\text{Probe}}$) are fabricated by evaporating four gold strips, having a width of 1 mm and separated by 50 μm, on a cleaned glass substrate by shadow masking. P3HT was latter spin coated under ambient atmosphere, while the measurement was performed under vacuum (10^{-6} mbar) after

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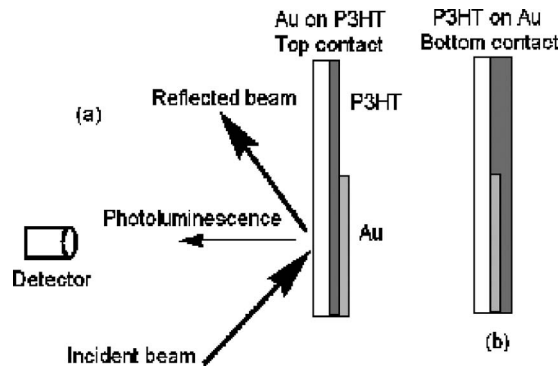
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FIG. 1. A schematic of photoluminescence setup for two kinds of samples: (a) top contact and (b) bottom contact.

waiting for 6 h. It is common in P3HT that the doping level decreases upon exposure to vacuum. That is why we have taken electrical measurements in vacuum (10^{-6} mbar) after waiting for 6 h. It has minimized the possibility unwanted dopants.

Two varieties of the sample (top and bottom contact) for photoluminescence (PL) spectra were prepared in the following manner. For the case of the top contact, P3HT film was spin coated on glass slide and half of the film was covered by ionically sputtered layer of gold having a thickness of 100 Å. To fabricate the bottom contact test structure, half of the glass substrate was covered by 100 Å thin gold coating, followed by spin coating of P3HT. Schematic illustrations of the experimental setup for measuring the photoluminescence spectra are shown in Fig. 1. For measuring the absorption spectra, a gold coated glass substrate (Au thickness =100 Å) was used as reference.

III. RESULTS AND DISCUSSIONS

Figure 2 shows the J-V plot for a Au/P3HT/Au device having a film thickness of 2500 Å. The device shows rectification as it switches on at around 22 V in the forward
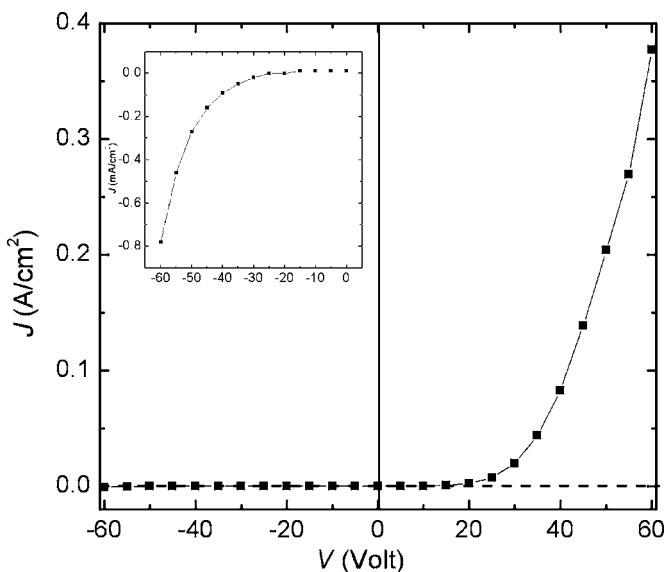

FIG. 2. J-V characteristics of the Au/P3HT/Au sandwich cell. The inset shows reverse data on an expanded scale.

biased region, i.e., the bottom contact is at a higher potential with respect to the top. The coefficient of rectification is found to be about 480 at 60 V. The inset shows J-V characteristics of the reverse biased region (i.e., the top contact is at a higher potential with respect to the bottom) in its appropriate scale. A comparison between the two plots in Fig. 2 indicates that the nature of the charge injection process across the two contacts is probably identical, although a reduction of J by three orders of magnitude, in the case of reverse bias, is observed (see inset of Fig. 2). The total device resistance calculated from the value of σ_{4Probe} conductivity for P3HT (2.5×10^{-6} S/cm) is found to be $R_{bulk} \cong 1.00$ kΩ. The four probe conductivity measurement techniques have been followed as explained by Qiu *et al.*[12] As explained by Qiu *et al.*,[12] the P3HT thin films are prepared from a 1% solution (w/v) at a spin rate 1500 rpm. Au four-line testing chips are used for P3HT. The thickness of P3HT thin film is measured by a Dektak Surface Profiler. A large series resistance (10 MΩ) is used because of a smaller current, so that the voltage reading across the series is large enough to be accurate. The direct current voltage output from the power supply is set between 10 and 60 V.

The maximum values of resistance (V/I) that have been obtained for forward and reverse biases are 0.016 and 7.7 MΩ at 60 V, respectively. Therefore, it is quite clear that the current is mostly limited by the top and bottom contacts and this might be due to the presence of hole barriers at the two contacts.[13,14]

The magnitude of the hole-injection barrier height could be determined by the Fowler–Nordheim (FN) model, which treats the tunneling of electrons from metal through a triangular barrier into unbound continuum states. The FN curves for our devices can be fitted into a straight line at higher electric fields and deviation from a straight line is mainly attributed to thermionic emission at lower electric fields. The use of the FN model is invoked here because for room temperature, $k_B T < \varphi_B$, where φ_B is the barrier height, T is the temperature, and k_B is the Boltzmann constant, and the effect of image charge[13] is ignored. According to this model, when the field emission dominates, the J-V characteristics are described by the following relation:

$$J = AE^2 \exp\{[-8\pi(2m^*)^{1/2}\varphi_B^{3/2}]/(3hqE)\}, \quad (1)$$

where m^* is the effective carrier mass, E is the magnitude of the applied electric field, and $A (=q^3/8\pi h\varphi_B)$ is a rate coefficient that contains a tunneling prefactor and rate of backflow current,[15] and it is expressed in A/V^2. In terms of the natural logarithm, Eq. (1) could be rewritten in the following manner:

$$\ln(J/E^2) = \ln A - \kappa(1/E). \quad (2)$$

A plot of $\ln(J/E^2)$ vs $(1/E)$ follows a straight line having a slope $-\kappa$, where the constant κ is related to φ_B through the relation: $\kappa = [[8\pi(2m^*)^{1/2}\varphi_B^{3/2}]/(3hq)$, from which the barrier height could be determined. Such a plot is referred as the FN plot.

Figure 3 shows the FN plots of a Au/P3HT/Au sandwich cell while the positive bias is applied at the bottom and top electrodes (inset). From the slopes of the straight line portion
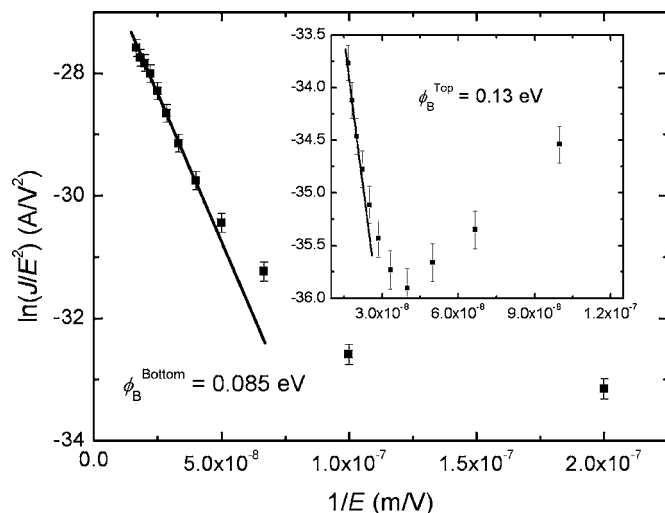
FIG. 3. FN plot for forward biased data shown in Fig. 2. The inset shows an identical plot for the reverse biased data. The straight lines are fits made by Eq. (2) to determine the hole-barrier height.

FIG. 4. Energy band diagram for the Au/P3HT/Au sandwich cell.

of the FN plots, φ_B for hole injection is estimated to be 0.085 eV±0.5% for the bottom Au/P3HT interface and 0.13 eV±0.5% for the top P3HT/Au interface (see inset of Fig. 3). It should be noticed that the fitting of the FN model could only be done at high electric fields to avoid the contribution of thermionic emission. This practice is also observed in other articles where authors[16–18] use to truncate the FN curves, when a slight curvature starts to appear near the lower electric field intensities, in order to estimate the barrier height. It is interesting to note that the difference in barrier height of pre- and postdeposited gold electrodes might lead to rectifying the behavior of the Au/P3HT/Au device.

This result instigates us to find out the origin for the difference of the hole-barrier height at the two interfaces. Usually, sputtered gold has a work function of 5.1 eV.[18,19] From SCLC analysis of the hole only thin film devices,[20] cyclic voltametry,[21] and photoelectron spectroscopy[22] the HOMO level of P3HT is estimated to be in the range of 5.1–5.2 eV. A hole barrier height of 0.085 eV±0.5% at the bottom interface suggests that the HOMO level of the polymer should be located around 5.2 eV as shown in Fig. 4. This agrees well with the previous articles.[20–22] Moreover, a band gap of 2.1 eV for P3HT places the LUMO level at around 3.1 eV. On the other hand, a barrier height of 0.13 eV±0.5% for the top P3HT/Au interface suggests that the work function of the top gold electrode should be located at 5.07 eV (see Fig. 4). The difference of the work function for the pre- and postdeposited gold is not a new result. Kahn *et al.*[23] have shown that uncontrolled contamination of the gold electrode could decrease the work function as low as 4.7 eV. In the case of the Au/P3HT/Au sandwich cell, the distribution of gold atoms at the top and bottom interface is quite different from each other. While the bottom contact is sharp, the top contact could be graded due to possible diffusion of the sputtered gold atoms through a few layers of the P3HT film. In other words, the surrounding in which the diffused gold atoms are residing at the top interface is not similar to that of the bottom contact. At this point, it is very difficult to visualize what
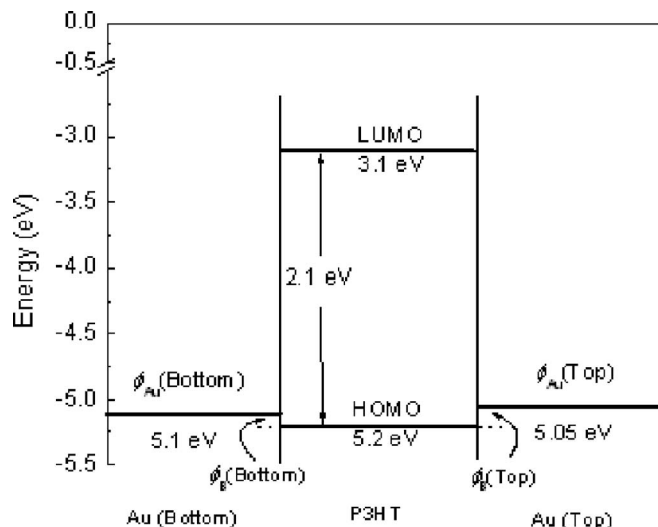
kind of interaction between the diffused gold atoms at the top interface and the π-conjugated chain could lead to a possible decrease of work function, Nevertheless, such a decrease of work function is a possibility.

To provide additional insight into the difference in barrier height at POM and MOP interfaces, the PL spectra is measured for two kinds of test structures that mimic the top and bottom contacts, as described in the Sec. II. The PL measurements are carried out as shown in Fig. 1. It is well known[24–26] that PL emission maxima can be used to estimate the degree of π conjugation in the polymer. As the degree of conjugation decreases, the PL-emission maxima shift to a shorter wavelength. Besides, the magnitude of PL intensity is a relative measure for the number of excitons that undergoes radiative decay. Figures 5(a) and 5(b) show the PL spectrum of the top contact on P3HT for two values of film thickness. The corresponding PL spectrum for the bottom contact is shown as an inset of Figs. 5(a) and 5(b). It could be noticed that the PL intensity showed a greater degree of quenching for the top contact with decreasing film thickness, while this quenching phenomenon is relatively low in the case of the bottom contact (see insets of Fig. 5). In particular, the PL intensity is quenched by nearly two orders of magnitude, for the case of the thinnest P3HT film [Fig. 5(a)]. It is worth it to mention here that there is, effectively, no shift in PL emission maxima in both cases of the top and bottom contacts. This finding clearly shows no shortening of the conjugation length of P3HT chains due to top-sputtered gold atoms.[25] However, a minute difference in the position of the peak could be neglected as it is due to the metal quenching effect.[24] The difference in the degree of quenching of PL intensity in both cases suggests a different nature of the contacts. One of the obvious reasons for PL quenching might be the creation of trap sites near the top contact due to the diffusion of energetic gold into a few layers near the surface of P3HT film. These diffused gold atoms would try to adjust its position between the interstitial spaces present between chains leading to the distortions in the π conjugation. As a consequence, the crystallinity of regioregular P3HT chains would suffer, resulting into the formation of trap sites. When the interface
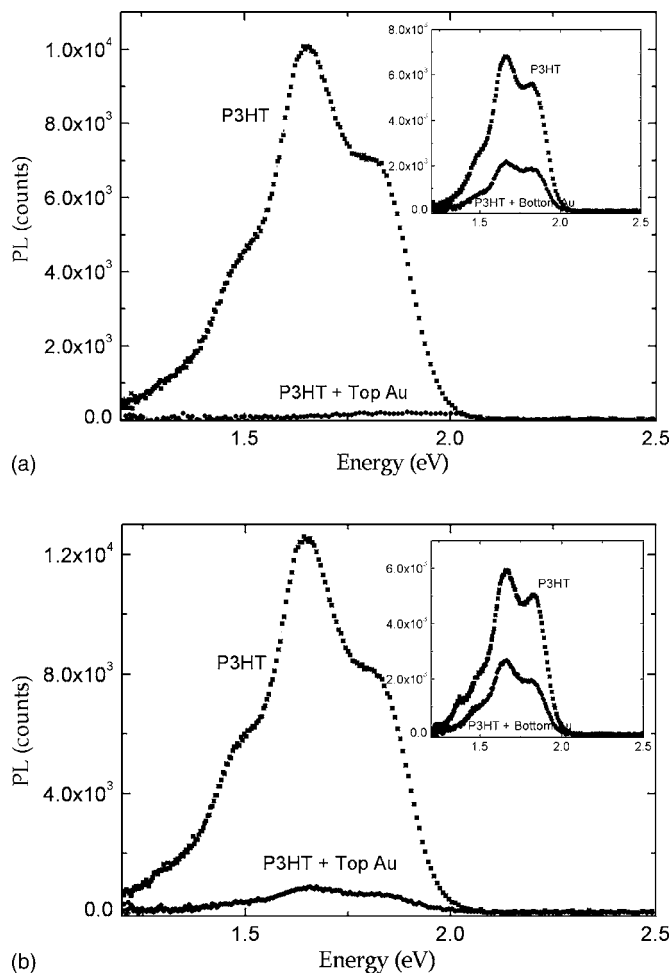
FIG. 5. PL data for top contact with varying P3HT film thickness (t): (a) $t \approx 100$ Å and (b) $t \approx 500$ Å. The inset shows the PL spectra for the case of bottom contact.

FIG. 6. Absorption data for (a) top contact and (b) bottom contact at various thickness values of P3HT films.

is excited optically, the excitons could get localized in these trap sites before it could exhibit radiative decay. On the other hand, the presence of a relatively lower number of trap sites at the bottom contact provides lesser quenching with respect to the top contact. Besides the PL spectra, the difference in the nature of the contacts is more clearly outlined in the absorption spectra for the top and bottom contacts, as described later.

The absorption spectrum for the top and bottom Au-P3HT interface, at various values of polymer film thickness, is shown in Fig. 6. For the case of the top contact [see Fig. 6(a)] no characteristic peak of P3HT is observed for the thinnest film, whereas such an unusual feature is absent in the case of the bottom contact [see Fig. 6(b)]. For films of intermediate thickness, there is a signature for the emergence of peak in the energy range of 2–3 eV, for the case of the top contact. This indicates that the diffusion of gold atoms could be confined within a layer of 100 Å. From all the earlier experiments it could be said that the electrical nature of the contact is different for the top and bottom and, hence, the charge injection properties.

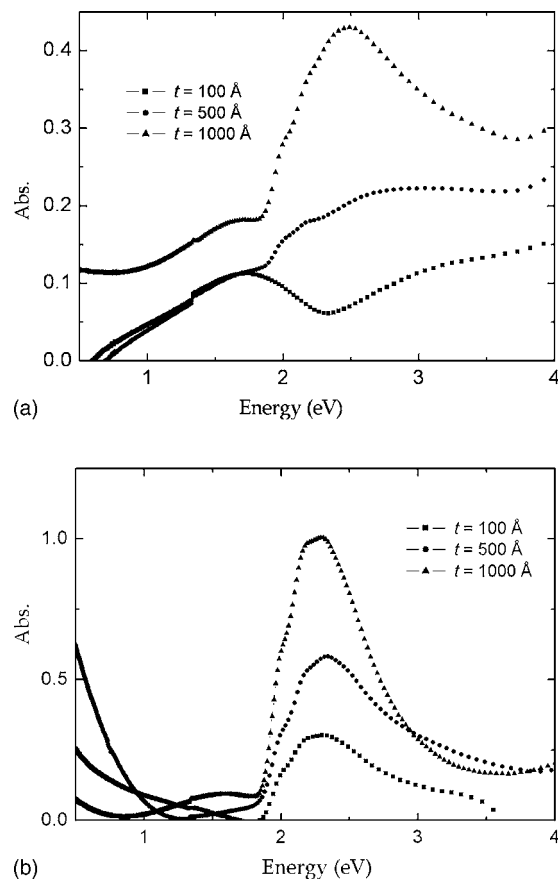The barrier height present at metal-polymer contacts (φ_B) could be of two types: the barrier height (φ_π) while the metal atoms could be in close vicinity of a π-conjugated polymer chain and the barrier height (φ_σ) while the metal atoms are in contact with the nonconjugated σ-bonded alkyl segments.[7] Therefore, the simplest approximation for the effective barrier height φ_B could be expressed as $\varphi_B = \varphi_\pi + \varphi_\sigma$. Nevertheless, it is not possible to estimate the percentage of gold atoms located at close proximity of a π-conjugated polymer backbone. The difference in the charge injection between the two contacts could be explained on the basis of difference in the trap site density and barrier height present at the two interfaces. Based on the PL and absorption data, we speculate that the ionically sputtered gold atoms cause more trap sites to appear at the top contact than the bottom. It is to be noted that the PL emission and absorption spectra do not show any shift in the peak position, which indicates that there is no breakage of the π-conjugated backbone into shorter chains.

The J-V characteristics, PL, and absorption spectrum suggest that the hole-barrier height of the top Au-P3HT interface is higher with respect to the barrier present at the bottom contact. The potential drop across the bulk is negligible, as estimated from the relative magnitudes of $R_{contact}$ and R_{bulk}. It could be readily understood that in the case of reverse bias, the hole faces a high barrier and a fairly good number of trap sites at the top P3HT/Au interface, and therefore less current is expected, though the nature of J-V dependence would remain identical to the forward bias condition. This understanding is in conformity with the data shown in

Fig. 2. Thus, the difference in barrier heights at the two interfaces gives rise to rectifying behavior of the Au/P3HT/Au device.

IV. CONCLUSION

The *J-V* characteristics of the Au (bottom)/P3HT/Au (top) sandwich cell has been measured and it has been found to show rectification. The resistance of the P3HT bulk and the total resistance of the cell have confirmed that the current injection is controlled mainly by the electronic nature of the top and bottom contacts. The hole-barrier heights at the two interfaces have been estimated by the Fowler–Nordheim model and it is found to be 0.085 eV±0.5% for the bottom and 0.013 eV±0.5% for the top contact. Such a difference of barrier heights is speculated due to a possible difference of work function between top and bottom sputtered gold. The difference in the nature of the contact has been confirmed by photoluminescence and absorption spectra of the top and bottom contacts and it suggests a higher trap site density near the top interface due to possible diffusion of the sputtered gold atoms. From these data a rough estimate for the thickness, through which the gold atom diffuses, has been obtained and it is found to be to be near 100 Å.

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