Time dependent parallel resistance in an organic Schottky contact

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ABSTRACT

The DC characteristics of a Schottky contact between regioregular poly (3-hexylthiophene) and aluminum are studied in forward and reverse bias regimes. Current-voltage curves of the junction in reverse bias show a resistive path in parallel with the expected Schottky contact. This is the sign of a nonuniform junction between the metal and semiconductor that exhibits ohmic behavior in some regions. Reduction of this parallel resistance and degradation of the Schottky junction are observed over a period of two weeks. Accumulation of undesired ions in the polymer or diffusion of aluminum atoms into the semiconductor are two possible mechanisms which may explain the time dependent behavior of these Schottky junctions.

INTRODUCTION

Since Schottky diode structures are used to build various organic electronic devices such as organic light-emitting diodes (OLEDs), their electrical characteristics are widely studied [1,2,3]. The main concern in an OLED is the forward bias characteristic, which makes the device emit light. However, the reverse bias characteristic of a Schottky contact can theoretically be used to obtain the barrier potential. Also the variation of reverse current with temperature reveals the carrier transport mechanism through the junction [4]. Such information can be obtained only if the device shows nearly ideal junction characteristics. In this paper we discuss some of the important factors that make a junction nonideal. Also the voltage-current characteristics of a Schottky contact between a metal and a conducting polymer are presented and aging effect on the DC characteristics is studied.

BACKGROUND

The carrier density in an undoped organic semiconductor is so low that a junction between a metal and an organic semiconductor is usually modeled as a metal-insulator junction [3]. On the other hand, the dopant density in an organic semiconductor which has been exposed to air is usually so high [5] that band bending occurs at the metal-semiconductor interface and creates a Schottky junction [4]. From thermionic emission theory the current in a Schottky diode in the forward bias regime is expressed by [4]:

$$I_F = I_S\left[\exp\left(\frac{qV}{nkT}\right)\right] \qquad \text{(for } V>0\text{)} \qquad (1)$$

where I_F is the current passing through the diode, I_S is the saturation current, q is the unit charge, V is the applied voltage, k is the Boltzman constant, T is the temperature and n is an empirical constant known as the ideality factor. The reverse current, I_R, in an ideal Schottky diode is constant (equal to I_S) and depends only on the physical parameters of the Schottky junction at a given temperature:

$$I_R = I_S = I_{S0} \exp\left(-\frac{q\varphi_b}{kT}\right) \qquad (\text{for} \quad V<0) \qquad (2)$$

where I_{S0} is the saturation current with zero barrier, which is itself also a function of temperature, and $q\varphi_b$ is the barrier height of the Schottky junction.

In practice the reverse current of a Schottky diode is a nonlinear function of the bias voltage. Existence of an interfacial layer between the metal and semiconductor is the main reason for this behavior. If the interfacial layer is an insulator, the barrier height, $q\varphi_b$, is altered by the bias voltage [4]. Also the height of the barrier is reduced with increase of the interfacial layer thickness and results in an increase of I_S in Equations 1 and 2 [4]. Formation of an oxide layer as an interfacial layer is very probable, particularly when a low work function metal such as aluminum is used for Schottky diode fabrication.

Sometimes the interfacial layer is not an insulator. For example, diffusion of metal ions into the semiconductor is reported [6] in a Schottky junction between an organic semiconductor and a metal. Insertion of ions into an organic semiconductor increases the density of localized states that increases the tunneling current [4]. This tunneling current affects the ideality factor, n, in Equation 1. The higher the tunneling current the larger is the value of n. This results in lowering of the rectification ratio.

If the tunneling current becomes the primary contributor of current both in the forward and reverse bias regimes the I-V curve of the device exhibits a resistive behavior. In such an instance the junction is called ohmic.

EXPERIMENTAL DETAILS

To analyze the DC characteristic of an organic Schottky junction, regioregular poly (3-hexylthiophene) (rr-P3HT) is chosen as the semiconductor. rr-P3HT is known to be a very stable P-type organic semiconductor [7]. A schematic of the organic Schottky diode is shown in Figure 1. The structure of this diode is similar to that of a single layer OLED in which the organic semiconductor is sandwiched between a low and a high work function metal. A gold micro-electrode from Abtech Scientific Inc. (www.abtechsci.com) is used as the anode of the diode. The surface of the purchased micro-electrode is coated with a 0.5µm thick Si_3N_4 except at the electrode and the connection pad. A solution of 0.8 wt% of rr-P3HT, supplied by ADS

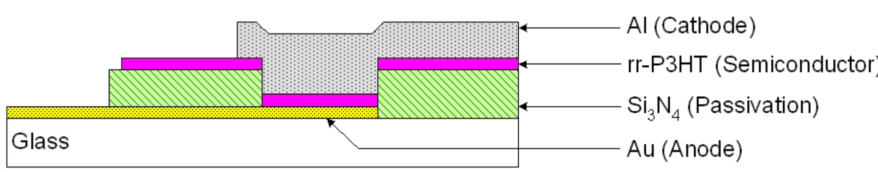

Figure 1. The side view of the organic Schottky diode made of rr-P3HT (not to scale)

(www.adsdyes.com), in chloroform is used to spin coat a 50nm thick film of semiconductor onto the micro electrode. Then the sample is heated to 100°C on a hot plate for 30 minutes to evaporate any residual solvent and anneal the semiconductor film [8]. The entire deposition process is done in a clean room without isolation between the sample and air.

The sample is then placed in a vacuum of 2×10^{-7} torr for 3 days to reduce the amount of adsorbed oxygen and moisture [9]. A 0.5μm thick aluminum cathode is then deposited on the sample by e-beam evaporation to form a Schottky contact.

The DC characteristics of the device are measured with a Solartron SI1287 electrochemical interface. All measurements are done in the absence of light in air.

RESULTS AND DISCUSSION

In Figure 2.a, the I-V characteristic measured between the aluminum and gold electrodes is plotted on a linear scale. The rectification behavior shows the formation of a Schottky contact between the aluminum and polymer. The inset plot, in Figure 2.a, shows the reverse bias characteristic of the junction. The linear relation between the current and voltage represents a resistance of 8×10^{8} Ω. Such a linear I-V behavior in reverse bias is the sign of either the existence of pinholes in the polymer or regions of ohmic contact at the aluminum-polymer interface. This resistance can be modeled as a parallel resistance, R_P, to a Schottky diode, D, in the simple equivalent circuit model proposed in Figure 3. Also a series resistance, R_S, is included in the model to represent the resistive effects of the contacts and the bulk semiconductor. With the assumption of $R_P \gg R_S$, the device would exhibit three distinct behaviors under different bias voltages. In reverse or low forward bias, the device characteristics should be dominated by R_P; at high forward bias, R_S should be the dominant component; and for biases between these two limits, the device's behavior would resemble that of the diode, D.

Therefore, to estimate the component values in the equivalent circuit of the device, the forward bias regime of the device is plotted in a semilog scale (shown in Figure 2.b). Three distinct regions, marked with R_P, D and R_S, can be identified. From this Figure,

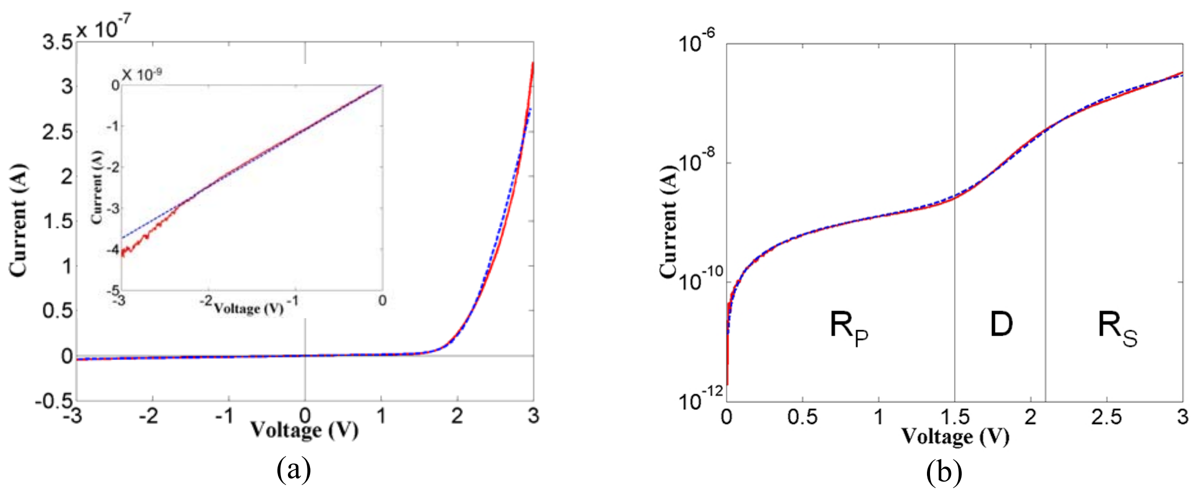

Figure 2. The I-V characteristic of a Schottky diode made of rr-P3HT (a) linear plot of I-V characteristic and (b) semilog plot of forward bias regime. The inset plot is the reverse bias regime in linear scale. The solid lines are the measured value and the broken lines are model results.

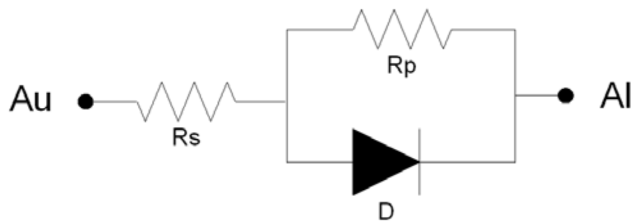

Figure 3. Proposed model including a series resistance (*Rs*) a nonideal Schottky junction (*D*) and a parallel resistance (*Rp*).

the values for R_P and R_S are extracted to be 8×10^8 Ω and 1.7×10^6 Ω, respectively. Applying least-squares method to fit an exponential curve to region *D* yields:

$$I = 5\times10^{-14}\exp(6.6\times V). \qquad (3)$$

The resulting model response is illustrated by the dashed line in Figure 2, which can be seen to fit reasonably well to the measured values, especially for voltages less than 2.5V. Comparing Equations 1 and 3 shows that I_S has a value of 5×10^{-14} A and the ideality factor, n, is approximately 5.8.

Since region *D*, in Figure 2.b, covers a small portion of the voltage range, this value of I_S may not be accurate enough to calculate the barrier potential. Nevertheless comparison between I_S and the reverse current of the device indicates that R_P dominates in the reverse bias regime and I_S is negligible. Also Equation 3 shows that the diode *D* in the model is not exhibiting ideal Schottky behavior. The very large ideality factor is a sign of a poor junction, with a relatively thick interfacial layer between the polymer and aluminum making the tunneling current more pronounced [4].

The I-V curve shown in Figure 2 is very repeatable for a fresh sample. However leaving the sample in air for eight days without any electrical connection, the device behavior degraded as

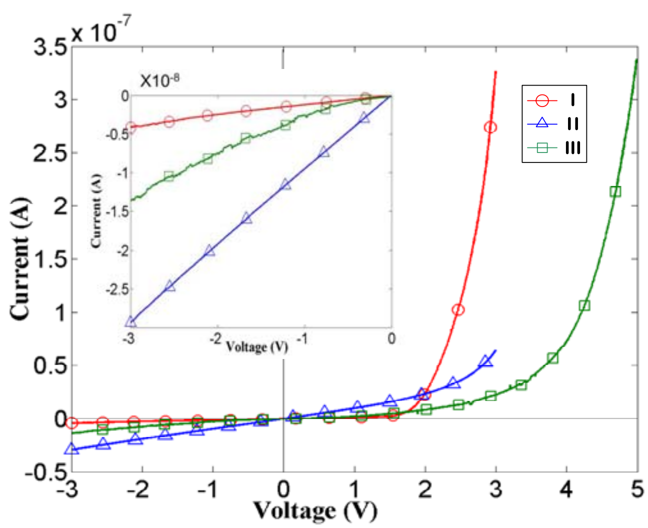

Figure 4. Linear plot of I-V characteristics of (I) fresh sample, (II) 8 days and (III) 13 days after the fabrication (after the burnt of some resistive contacts). The inset shows the reverse current.

shown in curve (II) of Figure 4. Using the same method to extract the component values of the model, *Rp* is found to be reduced to $1\times10^{8}\ \Omega$ and the current through *D* can be expressed by Equation 4:

$$I = 3\times10^{-11}\exp(2.4\times V) \qquad (4)$$

Therefore, I_S and n has increased to 3×10^{-11} A and 16, respectively. Since the maximum current used in the measurement is not very high, the effect of series resistance cannot be estimated.

Comparing Equations 3 and 4 shows that over 8 days the ideality factor has increased from 5.8 to 16, and I_s from 5×10^{-14}A to 3×10^{-11}A, which both point to the growth of an interfacial layer that results in increased tunneling current. This interfacial layer may have grown as a result of diffusion of oxygen and other contaminants to the metal-polymer interface [10]. Since the fabrication process is done in air and the sample is kept in air, it is not clear whether the contaminants are external, such as oxygen and moisture that have entered the device through pinholes in the aluminum layer [11], or whether they are residual contaminants introduced during fabrication. In addition, the diffusion of contaminants to the junction may increase the dopant concentration in the polymer. In regions where the doping level is very high, tunneling current would dominate and converts the Schottky contact to an ohmic one representing a parallel resistor, R_P, in the I-V characteristics. The change of R_P from $8\times10^{8}\ \Omega$ to $1\times10^{8}\ \Omega$ in eight days is likely due to the diffusion of more contaminants to the polymer that results in expansion of the highly doped regions. Also, it is possible that aluminum has diffused into the semiconductor in the form of ions and has become a dopant [6].

Therefore, the physical interface between the aluminum and semiconductor is expected to be composed of different regions as shown in Figure 5. In region A, a Schottky contact is produced with an interfacial layer. Section B shows a region of highly doped semiconductor that creates an ohmic contact instead of a Schottky contact. Such a non-uniform junction has been seen as the bright rings around dark spots in OLEDs [10].

After leaving this device in air for 13 days, the slope of the reverse current is so steep that the exponential behavior in the forward current is hardly recognizable in the ±3V range (not shown in Figure 4). This means that R_P, estimated to be approximately $1.7\times10^{7}\ \Omega$, has dropped drastically. This behavior is consistent with the recurrence of microscopic conductive paths in OLEDs with time [12].

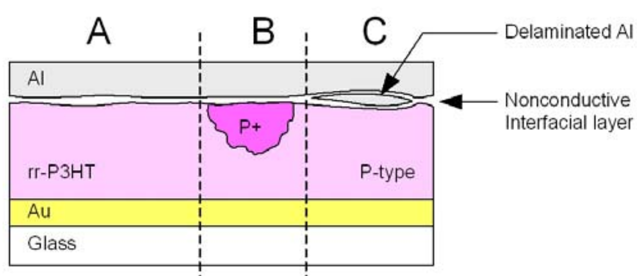

Figure 5. Non-uniform junction between the organic semiconductor and aluminum. Region A represents a nonideal Schottky contact with a non-uniform interfacial layer. Region B shows an ohmic contact with an interfacial layer. Region C represents an open circuit or a dark spot where there is essentially no electrical connection between the aluminum and the semiconductor.

By increasing the forward bias voltage to 5V, some of these resistive contacts can be burnt out [12]. This results in delamination of a thin layer of aluminum from the bulk aluminum layer, and makes an open circuit in these regions, similar to the dark spots in OLEDs [10]. This type of metal-polymer interface is shown in region C of Figure 5.

The I-V characteristic measured after this procedure is shown by curve III in Figure 4. Applying the model shown in Figure 3 results in $Rp=3.33\times10^{8}\ \Omega$, $Rs= 1.5\times10^{6}\ \Omega$ and for diode D the current-voltage relationship is expressed by Equation 1 with I_S of 1.35×10^{-10}A and n of 24.6.

However after a few days the resistive characteristic in the reverse bias regime reappears and is observed as a very straight line that could again be the result of creation of new ohmic regions.

CONCLUSION

We show that the reverse bias characteristic of an organic Schottky contact is different from that in crystalline semiconductors due to the presence of parallel ohmic paths. We see that this parallel resistance changes with time when the sample is fabricated and stored in air. The expansion of highly doped regions in the polymer by diffusion of contaminants to the junction may be responsible for reducing the parallel resistance. Also the growth of interfacial layer in the Schottky junction area causes degradation of the Schottky junction. The existence of resistive path and growth of interfacial layer reduces the rectification ratio of the device and makes it difficult to derive the barrier potential of the junction simply by studying the reverse bias characteristics. The importance of understanding the mechanisms of degradation in the interfacial layer and finding methods of eliminating these effects is critical to the successful implementation of Schottky junction based organic electronic devices.

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