

Enhanced hole transport from Au to Zn-phthalocyanine by an insertion of a thin *n*-type layer

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A thin C₆₀ or bathocuproine (BCP) layer of 5 nm thickness is inserted to the Au/Zn-phthalocyanine (ZnPc) interface of a Au/ZnPc/In/Al Schottky-junction cell, and the effect of the insertion on the dark current is investigated. The forward dark current density is increased from 0.5 mA/cm² to 9.7 and 9.2 mA/cm² by the insertions of the C₆₀ and BCP layers, respectively. The increase is not attributed to a change in the barrier height for the hole injection, but to a decrease of the concentration of trapped negative charges on the ZnPc surface. © 2006 American Institute of Physics. [DOI: 10.1063/1.2168500]

In organic semiconductor devices, such as light-emitting diodes, solar cells, and transistors, the electrode/organic interface has a critical importance because it strongly affects the charge-transport properties of the devices. Many types of interface modifications have been reported which improve the device characteristics, e.g., insertion of a thin organic or inorganic layer to the interface,^{1–4} and chemical treatment of the electrode surface.⁵

In this letter, the effect of an interface modification on the dark current is studied for a Au/ZnPc/In/Al Schottky-barrier system in which the Schottky barrier is formed at the ZnPc/In interface. In our previous study of the inner electric field of Au/ZnPc/In/Al,⁶ it was shown that an anomaly occurs at the Au/ZnPc interface, which quenches the inner electric field of the ZnPc layer under the forward bias condition. Because of this anomaly, the forward dark current is strongly suppressed. The similar suppression of the forward dark current is observed when Cu-phthalocyanine is used instead of ZnPc. In the present study, the Au/ZnPc interface is modified by an insertion of a thin layer of C₆₀ or bathocuproine (BCP) both having a *n*-type nature. The inserted *n*-type layer at the Au/ZnPc interface is expected to block the hole transport from Au to ZnPc. Nevertheless, a strong enhancement of the forward current will be observed by the insertion, which provides a new method to enhance the hole transport from Au electrode to a *p*-type organic semiconductor.

ZnPc and BCP were purchased from Kanto Chem. Co. Inc. and Aldrich Chem. Co., respectively, and were used after subliming three times in a vacuum. C₆₀ was purchased from MER Corp. and was used after subliming two times in a vacuum. Au of 99.95% purity, Al and In of 99.99% purity were purchased from Nilaco Corp.

Figure 1 shows the arrangement of the thin films in the Au/C₆₀(or BCP)/ZnPc/In/Al Schottky-junction cell. The thin films were stacked by vacuum deposition under a pressure of 1×10^{-4} Pa. The film thicknesses were 13 nm for Au, 5 nm for C₆₀ and BCP, 100 nm for ZnPc, 20 nm for In, and 25 or 30 nm for Al. The speeds of the evaporation were

0.02 nm/s for Au, 0.02 nm/s for C₆₀, 0.03 nm/s for BCP, 0.1 nm/s for ZnPc, 0.01 nm/s for In, and 0.07 nm/s for Al. The film thickness and the deposition rate were monitored by a quartz oscillator (ULVAC CRTM5000 or CRTM6000). The size of the quartz substrate was $9 \times 24 \times 1$ mm³, and the effective area of the devices was 0.3 cm².

The dark current density J_{dark} was measured using a resistance r connected in series to the cell as shown in Fig. 1. The value of r was chosen between 10 Ω and 10 kΩ so as to be small enough compared to the resistance of the cell. Measurement of the capacitance C_p was carried out by a method described elsewhere,⁷ in which a sinusoidal voltage $V_0 \sin \omega t$ with $V_0 = 0.05$ V was applied to the device and the resulting current was detected using a digital oscilloscope. The measurements of J_{dark} and C_p at room temperature were carried out with the sample in the air. For the J_{dark} measurement at a variable temperature, the sample was kept in a vacuum in order to prevent the adsorption of moisture. No difference was observed between the values of J_{dark} in a vacuum and in the air at room temperature.

Figure 2 shows the $J_{\text{dark}}-V_{\text{bias}}$ characteristics of the Au/ZnPc/In/Al cells at room temperature with and without an insertion of a thin layer of C₆₀ or BCP to the Au/ZnPc interface. J_{dark} at $V_{\text{bias}} = +2$ V is 0.5 mA/cm² without the insertion and is increased to 9.7 and 9.2 mA/cm² by the insertions of the C₆₀ and BCP layers, respectively. This is a remarkable result because C₆₀ is a *n*-type semiconductor so that C₆₀/ZnPc forms a *n-p* junction which should block the forward current. Also, BCP has a *n*-type nature and is usually

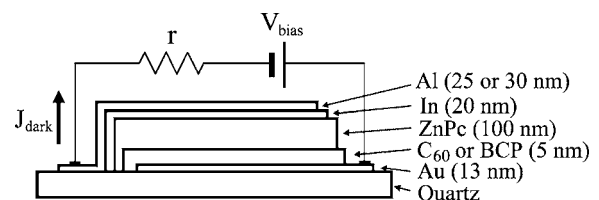


FIG. 1. The arrangement of the thin films in a Au/C₆₀(or BCP)/ZnPc/In/Al cell, and the electric circuit for the dark-current measurement. The bias direction shown in the figure corresponds to the forward bias direction.

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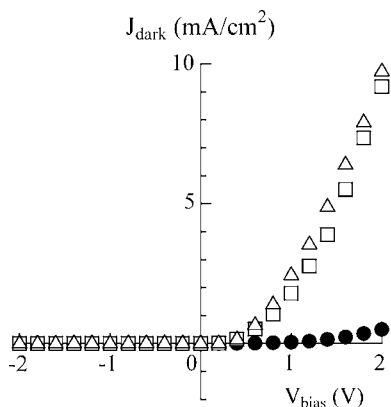


FIG. 2. Dark-current density vs bias voltage of Au/ZnPc/In/Al (●), Au/C₆₀/ZnPc/In/Al (△), and Au/BCP/ZnPc/In/Al (□).

used as an exciton blocking layer at the interface between a *n*-type semiconductor and electrode, rather than the interface for *p*-type semiconductor.^{2,3}

No significant enhancement of the short-circuit photocurrent I_{sc} is observed by the insertions of the C₆₀ and BCP layers. For Au/ZnPc/In/Al, I_{sc} was 8.5 nA/cm² with the illumination of 630 nm light of 1.4 μW intensity, and became 11.3 and 4.3 nA/cm² by the insertions of C₆₀ and BCP, respectively.

One possible origin of the increase of the forward J_{dark} by the insertion of C₆₀ or BCP may be a decrease of the energy-barrier height for the hole injection from Au to ZnPc. In order to estimate the barrier height, the temperature dependence of J_{dark} was measured. Figure 3 shows $\log J_{dark}$ versus $1/T$ of the cells. As seen in Fig. 3, $\log J_{dark}$ shows a linear dependence on $1/T$. From the slope of the linear dependence, the activation energy E_a defined by

$$J_{dark} \propto \exp(-E_a/kT) \quad (1)$$

was estimated, where k is the Boltzmann's constant. The estimated value of E_a is 0.15 eV for Au/ZnPc/In/Al, 0.26 eV for Au/C₆₀/ZnPc/In/Al, and 0.36 eV for Au/BCP/ZnPc/In/Al. This indicates that the energy-barrier height for the hole injection from Au to ZnPc is increased by an insertion of the C₆₀ or BCP layer, which does not correlate with the increase of the forward J_{dark} by the insertion observed in Fig. 2.

The increase of the forward J_{dark} by the insertion is related to the concentration of trapped charges at the Au/ZnPc interface region. Figure 4 shows the frequency dependence of the capacitance C_p of the cells with $V_{bias} = +2$ V. For

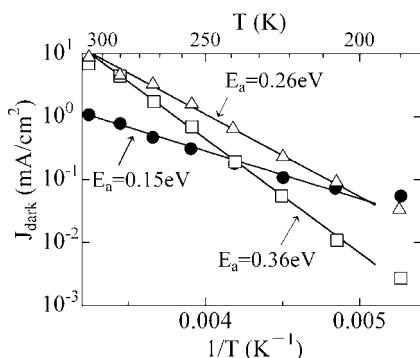


FIG. 3. Arrhenius plot of the dark-current density for Au/ZnPc/In/Al (●), Au/C₆₀/ZnPc/In/Al (△), and Au/BCP/ZnPc/In/Al (□) with $V_{bias} = +2$ V.

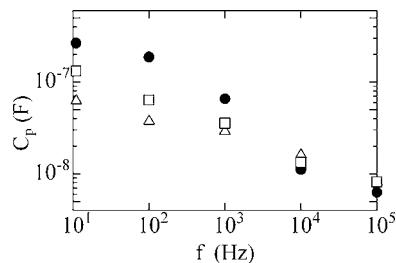


FIG. 4. Frequency dependence of the capacitance of Au/ZnPc/In/Al (●), Au/C₆₀/ZnPc/In/Al (△), and Au/BCP/ZnPc/In/Al (□) with $V_{bias} = +2$ V.

Au/ZnPc/In/Al, C_p increases steeply as the frequency is lowered from 10⁴ Hz, which is due to a dielectric relaxation of trapped charges.^{6,7} By the insertion of the C₆₀ or BCP layer to the Au/ZnPc interface, C_p in the frequency range between 10¹ and 10³ Hz decreases substantially. This indicates that the concentration of the trapped charges decreases by the insertion, which correlates with the increase of the forward J_{dark} by the insertion.

The concentration of the trapped charges may be related to the surface morphology of the thin films observed by atomic force microscopy (AFM). On the surface of a Au film of 13 nm thickness on a quartz substrate, full of dips of 2–3 nm depth were observed which may be the origin of the carrier traps, while such deep dips were rarely seen on the surface of a BCP film of 5 nm thickness deposited on the Au film. No reliable AFM observation was possible for a C₆₀ film on Au because of a fast clustering of C₆₀, which, however, was prevented by depositing a ZnPc film on C₆₀.

In our previous study of the inner electric field of Au/ZnPc/In/Al,⁶ it was shown that, when a forward bias voltage larger than 0.5 V is applied to the cell, most of the applied voltage is spent as a voltage drop at the Au/ZnPc interface and nearly no electric field is formed in the ZnPc layer. In other words, the Au/ZnPc interface, in effect, has a large resistance under the forward bias condition. As a result, the forward J_{dark} becomes small for Au/ZnPc/In/Al. This situation is illustrated in Fig. 5(a). By applying a forward bias voltage larger than the difference between the work functions of Au and In, a strong shift of the energy levels occurs at the Au/ZnPc interface. In order for such a shift to occur, a large dipole moment must be induced at the interface with negative charges on the ZnPc surface. The trapped charges detected in the present capacitance measurement in Fig. 4 are assumed to be these negative charges.

By the insertion of the C₆₀ or BCP layer, the concentration of the negative trapped charges is decreased substantially as observed by the present capacitance measurement. As a result, the energy-level shift at the surface of the ZnPc layer is reduced, as illustrated in Fig. 5(b), and the effective

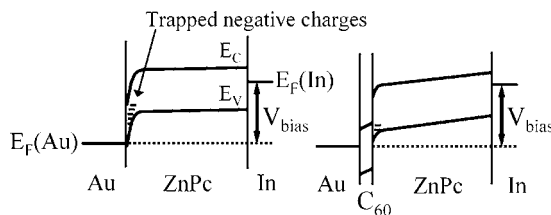


FIG. 5. The energy band diagrams of (a) Au/ZnPc/In/Al and (b) Au/C₆₀/ZnPc/In/Al, for the forward bias voltage larger than the difference between the work functions of Au and In.

resistance of the Au/ZnPc interface is also reduced. This explains the increase of the forward J_{dark} by the insertion observed in Fig. 2.

It is noted that, when an indium tin oxide (ITO) electrode is used instead of Au, the situation is different. For ITO/ZnPc(100 nm)/In/Al, J_{dark} at $V_{\text{bias}} = +2$ V was as high as 6.7 mA/cm². By the insertions of the C₆₀ and BCP layers of 5 nm thickness to the ITO/ZnPc interface, J_{dark} reduced to 1.1 and 4.2 mA/cm², respectively. Thus, the enhancement of the forward J_{dark} by the insertion of the C₆₀ or BCP layer is a phenomenon specific to the Au/ZnPc system.

In summary, by an insertion of a thin C₆₀ or BCP layer to the Au/ZnPc interface, the hole transport from Au to ZnPc is enhanced substantially under the forward bias condition. This is due to a decrease of the concentration of trapped charges at the surface of the ZnPc layer by the insertion, resulting in a decrease of the effective resistance of the Au/ZnPc interface. The present method to enhance the hole transport may be applicable to the devices having the Au/phthalocyanine (Pc) interface. For example, in the case

of Au/Pc/Au coplanar or sandwich cells for the conductivity measurement of Pc, the anomaly at the Au/Pc interface prohibits the correct estimation of the conductivity which may become possible by the insertion of the C₆₀ or BCP layers to the interfaces. In the case of organic transistors having a Au/Pc/Au configuration, an improvement in the device characteristics may be achieved by the present method.

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