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Effect of an Insertion Layer in Organic-Semiconductor/Metal-Electrode Interfaces Studied with Electroabsorption Spectroscopy and UV Photoemission Spectroscopy

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A problem of current research for the organic material devices is to understand and to control an interface between organic materials and metal electrode. There were many researches for the understanding of the interface problems. An insertion of a thin layer of the organic-material/electrode-interface is a well known technique to improve the device ability. [1-3] The main focus of these studies was the lowering of the barrier height for carrier injection at organic/electrode interfaces. It should be note that there are other effects of insertion layer which also plays an important role in a device operation. In this study, we present an effect of an insertion layer which suppresses an interaction between organic-material and metal electrode.

As typical low molecular weight organic semiconductors and polymeric organic semiconductors (conducting polymers) we used phthalocyanines and poly(3-alkylthiophene)s in this study. Figure 1 indicates molecular structures of Zn-phthalocyanine (ZnPc) and poly(3-hexylthiophene).

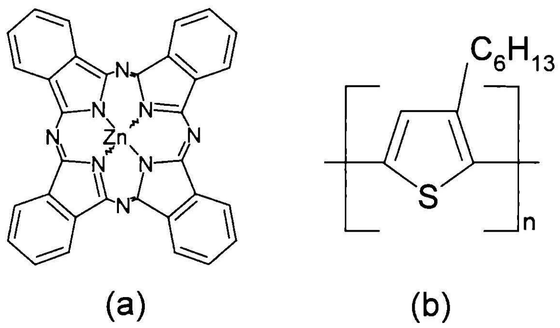

Fig. 1. Chemical structures of (a) Zn-phthalocyanince and (b) poly(3-hexylthiophene).

The effect of an interface modification is studied for a Au/ZnPc/In/Al Schottky-barrier system in which the Schottky barrier is formed at the ZnPc/In interface. It shows a typical rectification property in the current-voltage measurements. In the present study, we modified the Au/ZnPc interface with an insertion of a thin layer of bathocuproine (BCP). Figure 2 shows the arrangement of the thin films in the Au/BCP/ZnPc/In/Al Schottky-junction cell. The dark current density J_{dark} was measured using a resistance r connected in series to the cell. J_{dark} at external bias V_{bias} = + 2 V is 0.5 mA/cm^2 without the insertion and was increased to 9.2 mA/cm^2 by the insertion of the BCP layer. To reveal the cause of the increasing of J_{dark} through the insertion of BCP layer, we estimated the inner electric field in the ZnPc layer and the barrier height of Au/ZnPc interface.

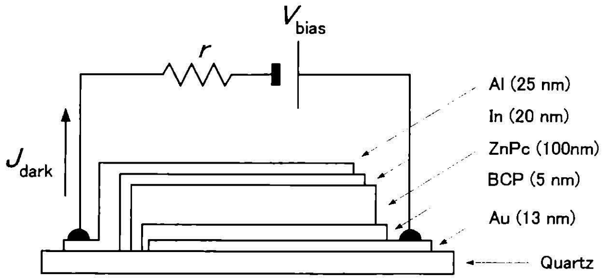

Fig. 2. The arrangement of the thin films in a Au/BCP/ZnPc/In/Al cell, and the electric circuit for the dark-current measurement. The bias direction shows in the figure corresponds to the forward bias direction.

For the estimation of the inner electric field of the ZnPc layer, we used the electroabsorption (EA) spectroscopy. Here we briefly describe the principle of the EA spectroscopy. Shown in Fig. 3 is the schematic drawing of the experimental arrangement for the EA experiment. Light from a halogen lamp passes through a monochromator. The exit intensity at wavelength λ, $I_0(\lambda)$, is focused onto the sample and the transmitted light is detected by a photomultiplier (PMT). The AC modulation is applied to the sample at frequency ω. The light striking the detector contains two signals: the DC is given by $I_0(\lambda)T(\lambda)$, where $T(\lambda)$ is the DC transmittance of the material while the modulated value at frequency ω is $I_0(\lambda)\Delta T(\lambda)$, where $\Delta T(\lambda)$ is the change in transmittance produced by the modulation. The AC signal from the detector is measured by a lock-in amplifier. Under these conditions the output of the lock-in amplifier is proportional to the EA signal. The 1F-EA intensity, which the EA intensity detected at the fundamental modulation frequency ω, is proportional to a multiplication of the inner electric field (E_0) and the modulation electric field (E_m).

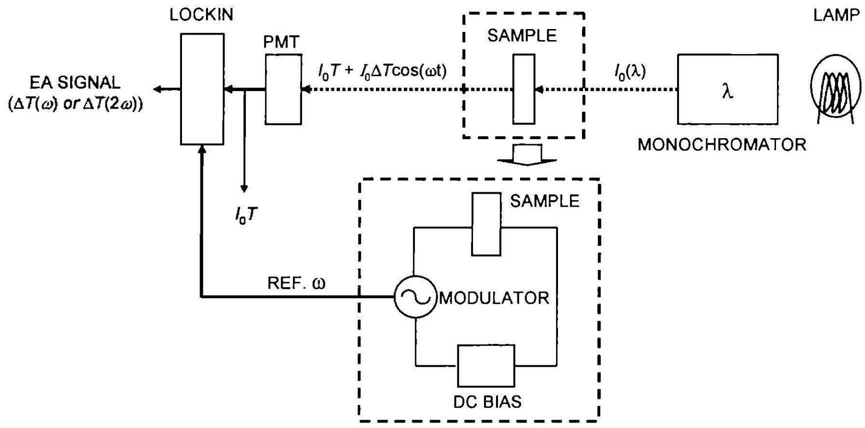

Fig. 3. Schematic diagram of the electroabsorption experimental apparatus.

The EA signal from the ZnPc layer is identified spectroscopically and measured as a function of dc bias. For the both samples, the EA intensities in the reverse bias region increased following with the theoretical estimation that derived from the depletion layer approximation. Under the forward bias condition, on the other hands, the EA intensity of ZnPc in the Au/ZnPc system showed anomaly decrease. The EA intensity in the Au/BCP/ZnPc system was also showed the decrease of the EA intensity but its discrepancy between the theoretical values of the depletion layer approximation was smaller than that of Au/ZnPc system. These results indicate that the magnitude of the inner electric field in the ZnPc layer was suppressed in the forward bias region particularly in the Au/ZnPc system.

In order to estimate the barrier height of the carrier injection, the temperature dependence of the J_{dark} was measured. Figure 4 shows log J_{dark} vs. $1/T$ of the cells. It was found that the activation energy Ea of the Au/ZnPc system was lower than that of the Au/BCP/ZnPc system. This indicates that the energy barrier height for the hole injection from Au to ZnPc is increased through an insertion of BCP layer, which does not correlate with the increasing of J_{dark} through the insertion of BCP layer. Fig 5 shows UPS spectra of ZnPc and BCP around the Fermi level. The edge energy of the highest occupied molecular orbital of ZnPc and BCP was observed at about 1.0 eV and 3.0 eV from the Au Fermi edge, respectively. This result also supports that the barrier height of the hole injection from Au to BCP is larger than that of Au to ZnPc.

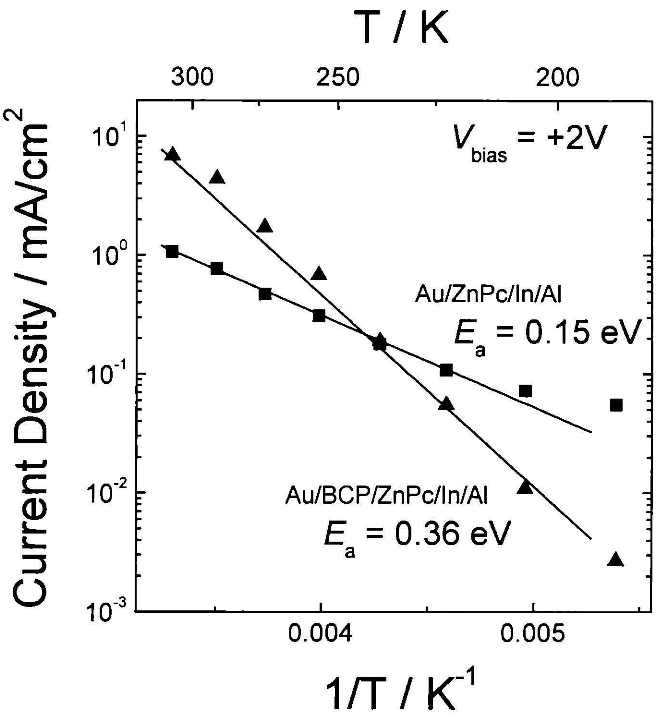

Fig. 4. The temperature dependence of the dark current density for Au/ZnPc/In/Al(■) and Au/BCP/ZnPc/In/Al (▲) with V_{bias} = +2V.

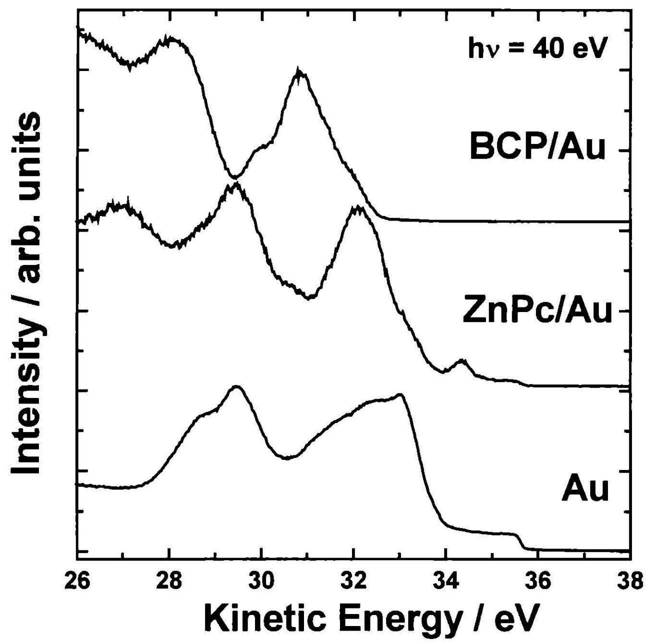

Fig. 5. Photoemission spectra of Au, ZnPc (5nm) on Au and BCP (5nm) on Au around the Fermi level.

If the carrier injection barrier at the Au/ZnPc interface is the only factor of the J_{dark} of the systems, the Au/BCP/ZnPc interface should show lower J_{dark} than the ZnPc/Au interface. This provably means that the effect of insertion of the BCP layer was not the lowering of the injection energy between Au and ZnPc but the prevention of an interaction between Au and ZnPc. The anomaly decrease of the inner electric field in the ZnPc layer under forward bias region at Au/ZnPc system is provably correlated with the interaction of Au and ZnPc.

These results suggest that the effect of an insertion of thin layer between the organic-material/metal-electrode is a control of an interaction between organic material and metal: in the present case the control of the interaction between ZnPc and Au. This effect is also important for the controlling of the organic semiconductor devices as well as the decreasing of the injection barrier height from the electrode to the organic materials. Similae studies have also been carried out in poly(3-alkylthiophene)s.

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