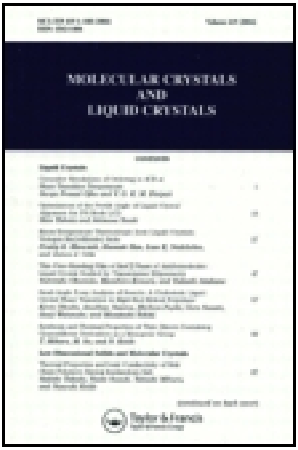

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Charge Exchange Phenomena and the Electronic Density of State at Metal/ Langmuir-Blodgett Film Interface

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CHARGE EXCHANGE PHENOMENA AND THE ELECTRONIC DENSITY OF STATE AT METAL/LANGMUIR-BLODGETT FILM INTERFACE

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Abstract Surface potentials of three kinds of polymeric LB films deposited on Au, Cr and Al electrodes were measured at room temperature as a function of the number of deposited layers. The potential depended on the thickness of LB films and the work function of base electrode. The density of electronic state in LB films was determined. It was found that the electrostatic phenomena in LB films at metal/film interface are explained by assuming the presence of interfatial states in the region 1 nm from the interface and the distribution of the molecular orbital.

INTRODUCTION

Organic thin film devices have been well studied in the field of electronics and photonics because of thier varieties of photo-reactive functions and their potentialities in nano-scale electronic applications. For use in electronic devices, it is essential to clarify the the electronic structure of organic films at the interface. In this report, we measured the surface potential built across three kinds of LB films due to the charge exchange at the film/electrode interface. We then estimated the distribution of electronic density of state in these LB films. [1-3]

EXPERIMENTAL

Three kinds of LB films (denote as PI, OCH_3-AzPAAD, and OCH_3-AzPI), whose chemical structures are shown in Fig. 1 were used in this study. [1-5] PI has the large electron affinity and it has a strong tendency to accept electrons. OCH_3-AzPAAD has the small ionization energy and it has a tendency to donate electrons. OCH_3-AzPI is obtained by the heat-treatment (thermal imidization) for more than one hour at a temperature of 150 $°C$ in a vacuum of the order of $10^{-6} Torr$. OCH_3-AzPI has a much larger electron affinity and a higher thermal stability than those of OCH_3-AzPAAD because of the high electron affinity and the chemical stability of imide group. The surface potential of LB films was measured with reference to the potential of clean base metal electrodes in the same maner as we previously reported.[1,2]

RESULTS AND DISCUSSIONS

Figure 2 (a) shows the relationship between the potential Vs across PI LB films on Au, Cr and Al electrode and the number of deposited layers. This result indicated that PI films acquired electrons from base electrode because of $Vs < 0$ and the

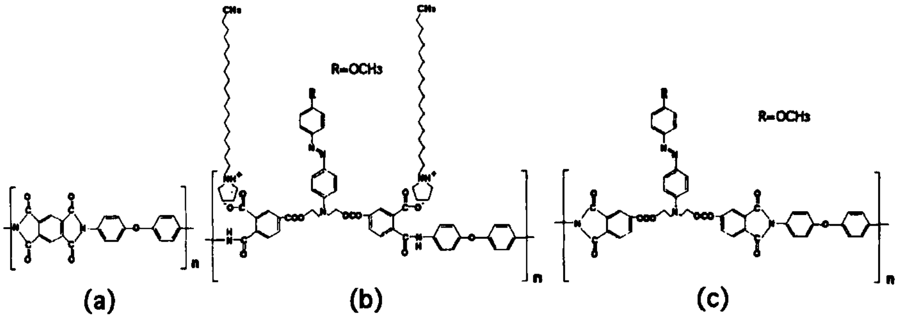


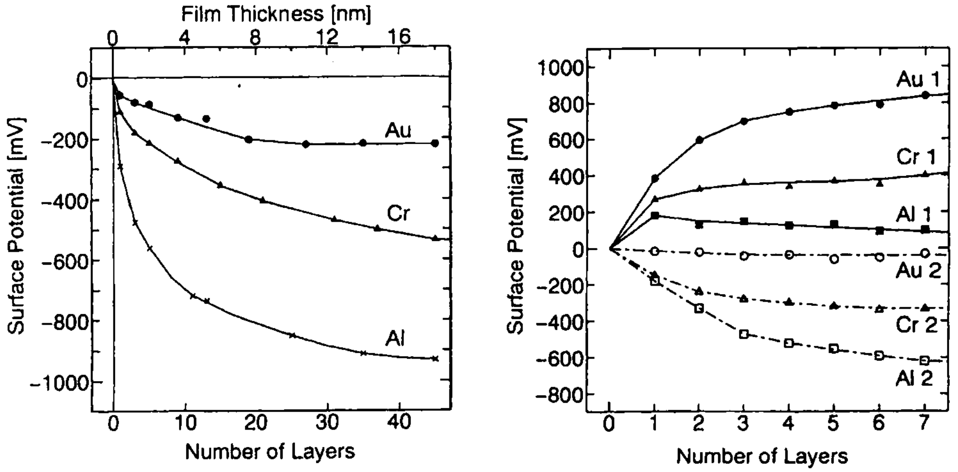
FIGURE 1 Chemical structures of molecule units used in this study. (a) PI, (b) OCH_3-AzPAAD, and (c) OCH_3-AzPI.

electrostatic layer with a thickness of the order of nms was formed at the metal/PI LB film interface.

Figure 2 (b) shows the relationship between the potential across OCH_3-AzPAAD (and OCH_3-AzPI) LB films on Au, Cr and Al electrodes and the number of deposited layers. It was found that OCH_3-AzPAAD LB film has a tendency to donate electrons to base electrode, whereas OCH_3-AzPI LB film has a tendency to accept electrons from base electrode. Very small fluctuation of the surface potential was observed as the number of deposited layers increases as a result of the Y-type deposition of LB films with a vertical component of permanent dipole moment. [5] However we neglected this fluctuation for simplicity in the analysis.

The difference in the saturated potential of LB films deposited on various electrodes coincided with the difference in the work function of these electrodes, in a manner reported in refs. 1 and 2. We therefore concluded that thermodynamic equilibrium was established at the metal/LB film interface, and determined that surface fermi level of PI, OCH_3-AzPAAD, and OCH_3-AzPI was about -5.0, -3.9, and -4.75 eV v.s. vacuum level, respectively.

When thermodynamic equilibrium is established at the interface, it is expected that the surface fermi level of LB films and the fermi level of metals are brought into coincident. Therefore, the electronic states of LB films whose electronic energy is higher than the fermi level of metal can donate electrons to metal, whereas the electronic states of LB films whose electronic energy is lower than the fermi level of metal can accept electrons as shown in FIG. 3. (a). [3] Thus, when these films accept electrons from metal, $-\rho(x)/e$ ($\equiv G(E_0, x, T)$) becomes the sum of the electronic accepting state below the energy E_0. Here, $\rho(x)$ is the spatial charge density as a result of electron transfer between metal and the films. Similarly, $+\rho(x)/e$ ($\equiv G(E_0, x, T)$) becomes the sum of the electronic donating state above E_0, when the films donate electrons to metal. It is instructive here to note that electronic state does not depend on the work function of electrode, whereas E_0 depends on the work function of electrode and the electrostatic potential Vs. Therefore, E_0 can be altered



(a) (b)

FIGURE 2 (a) Relationship between the surface potential of PI LB films and the number of deposited layers at room temperature.
(b) Relationship between the surface potential of OCH_3-AzPAAD and OCH_3-AzPI LB films and the number of deposited layers at room temperature. Au1, Cr1, and Al1 is the potential curve for OCH_3-AzPAAD, and Au2, Cr2, and Al2 is the potential curve for OCH_3-AzPI.

by choosing the base metal electrode material.

Figure 3. (b) shows the relationship between $G(E_0, x, T)$ and the depth of energy E_0 of PI LB films. Curves 1, 2, 3, 4, 5, 6, 7 and 8 represent the relationship between $G(E_0, x, T)$ and E_0 at positions x=0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6 and 3.0 nm, respectively. It was found that the interfatial electronic states exist at the interface within the region of $1 \sim 2nm$ because $G(E_0, x, T)$ changes steeply as the distance from metal increases. It is interesting here to note that $G(E_0, x, T)$ steeply increases with the increment of the energy E_0 near LUMO (Lowest Unoccupied Molecular Orbital) of PI. Thus, we concluded that the LUMO states distribute with respect to energy in the order of several hundred meVs.

Figure 3. (c) shows the relationship between $G(E_0, x, T)$ and the depth of energy E_0 of OCH_3-AzPAAD. Two solid lines show the change of $G(E_0, x, T)$ for electron donating state, and one broken line shows the change of $G(E_0, x, T)$ for electron accepting state. It was found that the distribution of the electronic density of state was almost the same for $n > 1$. It should be noted here that $G(E_0, x, T)$ became zero around $E_0 = -3.8 \sim -3.9$eV, that is, around surface fermi level of OCH_3-AzPAAD. In contrast, $G(E_0, x, T)$ for the 1st layer (n=1) differed from that for $n > 1$, probably because of the existence of interfatial electron donating state or interfatial dipole layer.[6]

Figure 3. (d) shows the relationship between $G(E_0, x, T)$ and the depth of energy E_0 of OCH_3-AzPI. Curves for 1st, 2nd, 3rd, 4th, and 5th layer represent the relationship between $G(E_0, x, T)$ and E_0 at positions x=0.2, 0.6, 1.0, 1.4, and 1.8 nm,

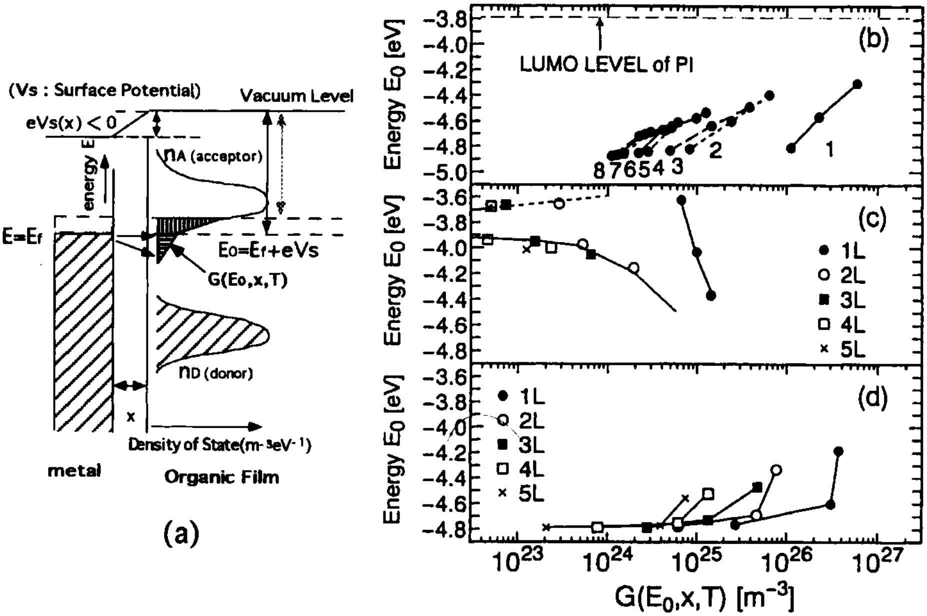


FIGURE 3 (a) Schematic illustration of distribution of electronic density of state and the sum of density of state $G(E_0, x, T)$. Relationship between $G(E_0, x, T)$ and the energy E_0 of (b) PI, (c) OCH_3-AzPAAD, and (d) OCH_3-AzPI.

respectively. It was found that the interfatial electronic states exist at the interface within the region of $1 \sim 2nm$ above the energy level of -4.8 eV. From FIG. 3 (c) and (d), it was concluded that the drastic change of electronic structure occurred after the thermal imidization of OCH_3-AzPAAD.

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