

Ultraviolet Photoelectron Spectroscopy and Surface Potential of π -conjugated Langmuir-Blodgett Films on Gold Metal Electrode

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The interfacial electronic structure of π -conjugated Langmuir-Blodgett (LB) films [octasubstituted palladiumphthalocyanine (PcPd) and perylene-tetra-carboxyldiimide derivative (PTCDI-Spent)] deposited on Au electrodes was examined by ultraviolet (UV) photoelectron spectroscopy (UPS), and the results were compared with those obtained by the surface potential measurement in a dark vacuum vessel. As the number of deposited layers increases, the energy shift was observed in the UPS spectra, which were found to correspond well with the surface potential change. This result indicates that excess electronic charges are transferred from LB-films to the Au electrodes until a thermodynamic equilibrium is established at the metal-film interface, resulting in the formation of an electrostatic double layer within the range of 1 to 2 nanometers in thickness. The contribution of layers sandwiched between the metal and the PcPd molecular film to the UPS spectra was also examined.

KEYWORDS: Langmuir-Blodgett film, electrostatic phenomena, space charge, surface potential, UPS

1. Introduction

Recently, there has been much interest in electronically organic materials in association with electronic device applications, and many organic electronic devices have been proposed. Among these are tunnel junctions, molecular rectifying diodes,^{1–3)} photovoltaic cells,^{4–6)} and electroluminescent devices,^{7–9)} in which the construction of well-defined structures by incorporating almost pinhole-free thin films that possess functionalized molecules between metal electrodes is essential. Until now, various π -conjugated Langmuir-Blodgett (LB) films such as phthalocyanine^{10–12)} and perylene derivative¹³⁾ have been synthesized, and the current–voltage (I – V) characteristics of the elements using these LB films have been examined. However, these studies are not sufficient. It is also essential to clarify the interfacial electronic phenomena occurring at the interface, because the function of these organic devices originates at the electrode/film and film/film interfaces. As has been pointed out by many investigators, when an organic film is in contact with metal electrodes, electrons are transferred from electrode to film (or from film to electrode) at the metal/film interface and the organic films are charged.^{14–17)} Thus information on the interfacial electronic structure of organic films which takes into account of electrostatic phenomena is important for a better understanding of the device operation. It is helpful to study the electrostatic phenomena of organic films with thickness smaller than the thickness of the electrostatic double layer.^{18,19)} In our previous study,¹⁷⁾ using a Kelvin probe method for the surface potential measurement, surface potentials of octasubstituted palladium-phthalocyanine (PcPd) and perylene-tetra-carboxyl diimide derivative (PTCDI-Spent) LB films on Au electrodes were measured at various temperatures in a dark vacuum vessel. It was concluded that excess electronic charges are transferred from these LB films to Au electrodes and an electrostatic double layer on the order of nanometers in thickness is formed at the metal/film interface. Similarly, the surface potential created at the interface between PcPd

and PTCDI-Spent LB films was measured. Based on these conclusions, and taking account of the electrostatic phenomena at the metal/film and film/film interfaces, we presented a model of the energy diagram of the PcPd/PTCDI-Spent double layer films sandwiched between two Au electrodes. However, this is still not sufficient to fully understand the interfacial electronic phenomena. Thus, in this study, we carry out the ultra-violet (UV) photoemission spectroscopy (UPS) to further clarify the electronic structure of the PcPd (and PTCDI-Spent) molecular film/Au interface. Finally, we compare the UPS spectra of these molecular films with the results obtained by the surface potential measurement.

2. Experimental

Three types of LB film (denoted as PcPd, PTCDI-Spent, and PolC5F), whose chemical structures are shown in Fig. 1, were used in this study. PTCDI-Spent has a large electron affinity and ionization potential, whereas PcPd has a small electron affinity and ionization potential. PolC5F, which was synthesized from 1H-1H-5H-perfluoro-1-pentanol and poly(octadec-1-en-co-maleicanhydride) by a method similar to

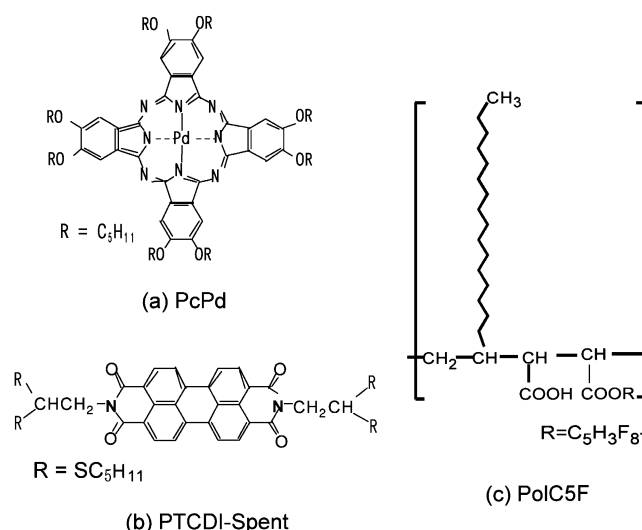


Fig. 1. Chemical structure of molecules used in this study. (a) PcPd, (b) PTCDI-Spent, and (c) PolC5F.

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Table I. Conditions of LB film deposition.

	Deposition temperature (°C)	Surface pressure (mN/m)	Dipping speed (mm/min)
PcPd	10	15	2
PTCDI-Spent	4	12	2
PolC5F	10	25	2

that described by Winter *et al.*,²⁰⁾ was used as an insulating layer. Au-covered silicon wafers (p^+ -doped with a native oxide layer), which were prepared by evaporation of 10 nm of Cr as an adhesion layer followed by 200 nm of Au, were used as substrates. Before LB film deposition, the substrates were treated with a 1 : 1 mixture of hexamethyldisilazane:chloroform for 12 h at room temperature for preparation of quality films. We then deposited the LB films onto an Au-evaporated electrode under the conditions listed in Table I. The UPS spectra were measured in a vacuum on the order of 10^{-9} Torr, using He I (21.21 eV) and He II (40.81 eV) radiation. Samples were not heat treated during the measurement. The measurements were performed using a Leybold-Heraeus hemispherical analyzer (EA11) at an overall resolution of about 50 meV. This resolution was determined from the FWHM of the Fermi edge of clean gold which was used as a reference. All substrates were biased at a voltage of -10 V.

3. Results and Discussion

Figure 2 shows the UPS spectra of a bare Au electrode, PcPd and PTCDI-Spent mono-molecular films deposited on a Au electrode. These spectra were obtained by irradiation of the incident light from the light source of the He I discharge with a photon energy $h\nu$ of 21.2 eV. The x-axis represents the kinetic energy of photoinduced electrons. On the left-hand

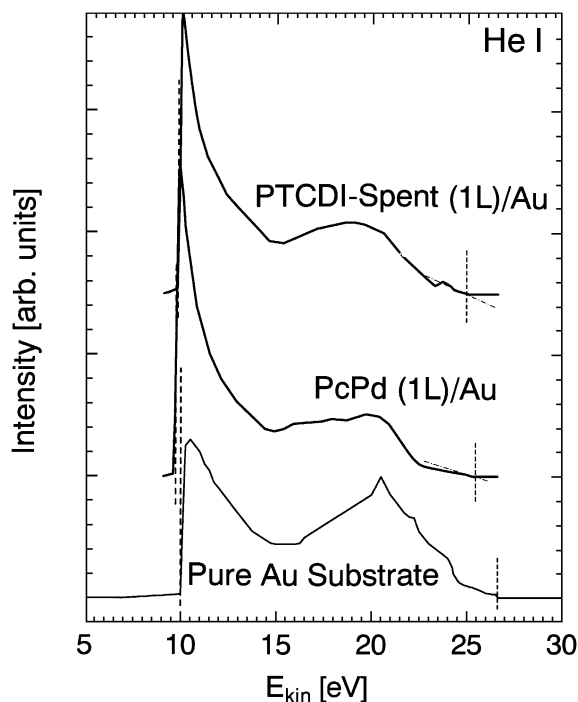


Fig. 2. UPS spectra of Au and PcPd, and PTCDI-Spent monomolecular films with respect to kinetic energy of photoelectrons induced by He I ($h\nu = 21.2$ eV).

side, the cutoff was observed at $E_{\text{kinmin}} (=10$ eV) for the Au substrate, and the corresponding energy coincided with the biasing energy eV_{bias} . Thus, the Fermi energy of the Au substrate E_{F} was determined to be -4.6 eV using the following equation

$$E_{\text{F}} = E_{\text{kinmax}}^{\text{Au}} - h\nu + eV_{\text{bias}} \quad (1)$$

Here, $E_{\text{kinmax}}^{\text{Au}}$ is the onset energy (threshold energy) of the intensity in the UPS spectra, which is seen on the right hand side of this spectra. The spectrum differs in E_{kinmin} between the Au substrate and PcPd monomolecular film, as shown in Fig. 2. The electrostatic potential across the PcPd monomolecular film contributes to reduction of the electron energy applied between the sample and the spectrometer surface. Due to the presence of the surface potential at the Au/film interface, the onset energy shifts 0.3 eV with respect to the energy difference between the Fermi energy of Au and the ionization energy of PcPd molecule in PcPd films. Thus this energy difference $\Delta E (=0.3$ eV) corresponds to the electrostatic surface potential across the PcPd mono-molecular film on the Au substrate, possibly due to the displacement of electrons from PcPd to the Au substrate. Similarly, the onset energy shifts 0.2 eV for PTCDI-Spent monolayer films. Therefore the right-hand side onset energy (threshold energy) of intensity for LB films $E_{\text{kinmax}}^{\text{LB}}$ is subtracted ΔE from the $E_{\text{kinmax}}^{\text{LB}}$ value of the film without charge transfer at the metal/film interface. Taking into account the band bending ΔE in the PcPd LB film due to the interfacial electrostatic phenomena at the Au/PcPd LB film interface, the ionization potential of the monomolecular PcPd LB film was determined to be 5.4 eV using the following equation:

$$IP = h\nu - eV_{\text{bias}} - E_{\text{kinmax}}^{\text{LB}} - \Delta E. \quad (2)$$

Similarly, the ionization potential of the mono-molecular PTCDI-Spent film was determined as 6.1 eV. It should be noted here that the charging of the PcPd films is negligible possibly because the films have semiconductive properties. Figure 3 shows the UPS spectrum in the high energy range,

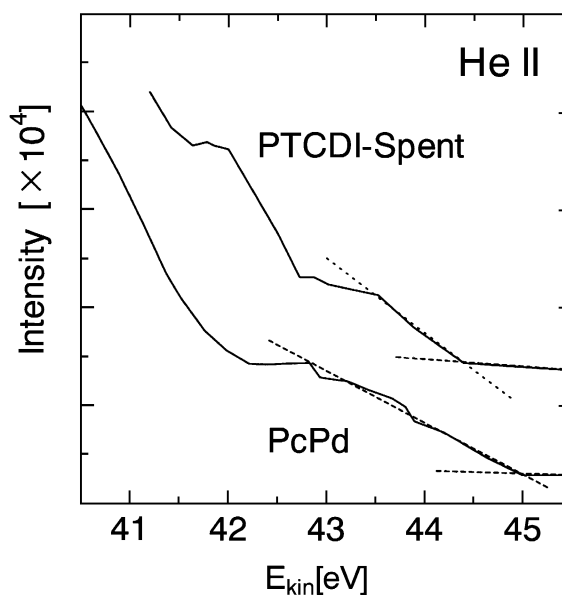


Fig. 3. The inset is the UPS spectrum induced by He II ($h\nu = 40.8$ eV). Biasing energy between the detector and the Au substrate is 10 V.

which is obtained by the excitation of the He II discharge with a photon energy $h\nu$ of 40.8 eV. The values of ΔE of PcPd and PTCDI-Spent are 0.3 eV and 0.2 eV, respectively, and the ionization potentials of the PcPd and PTCDI monomolecular films were determined to be 5.4 eV and 6.2 eV. Figures 4(a) and 4(b) show the energy diagram of the PcPd and PTCDI-Spent monomolecular films deposited on the Au substrate, respectively. Here, the HOMO-LUMO gap of the films was determined using the optical absorption spectra. The HOMO and LUMO levels are reduced at an energy of ΔE at the Au/monomolecular film interface. As a result, the Fermi level of the Au substrate E_F is located in the middle of the HOMO-LUMO gap for the PcPd monolayer films, whereas it is located at an energy level close to the LUMO state of the PTCDI-Spent for the PTCDI-Spent monolayer film.

Table II summarizes the energy parameters of PcPd LB films deposited on the Au substrate. The energy difference in E_{kinmax} between the LB film and the Au substrate coincides with the energy depth of the onset energy which is measured with respect to the Fermi level of the Au substrate (see Fig. 3). It should be noted here that this energy difference corresponds to the energy depth of the HOMO of the LB films with respect to the Fermi level of the Au substrate. The ionization potential IP_{LB} is given by $-E_F + (E_{\text{kinmax}}^{\text{Au}} - E_{\text{kinmax}}^{\text{LB}}) - \Delta E$ from eqs. (1) and (2). ΔE increases as the number of deposited layers increases, and then saturates when the number of deposited layers is at least 6. The surface Fermi level of LB films and

Fermi level of the Au electrode coincide when a thermodynamic equilibrium is established at the interface.¹⁵⁻¹⁷⁾ Therefore ϕ_{LB} is given by $-E_F + \Delta E$, and the saturated value of ϕ_{LB} corresponds well to the work function of LB films. On the other hand, the ionization potential IP of PcPd LB films does not depend on the number of deposited layers. These results indicate that ΔE is induced due to the formation of the electrostatic double layer at the Au/LB film interface and not due to the chemical bonding at the interface. Table III summarizes the energy parameters of PTCDI-Spent LB films deposited on the Au substrate. ΔE gradually increases as the number of deposited layers increases and does not saturate, at least, for the first 10 layers; however, the ionization energy of the films is nearly constant, only, that of one-layer PTCDI-Spent film is somewhat smaller than that of the six- and ten-layer films. As illustrated in Fig. 4(b), the energy level of the LUMO of the PTCDI-Spent film is closer to the Fermi level of the Au electrode than that of the PcPd film. Perturbation, such as anion formation between the LUMO and filled Au states or surface rearrangement of the molecule, may induce a reduction of the ionization energy or formation of the interfacial electronic states at the first LB layer.^{19,21-23)}

Table IV summarizes the cyclic voltammetric behavior of the 10-layer PcPd and PTCDI-Spent LB films. We examined the cyclic voltammetric behavior of these films in acetonitrile solution (vs Ag/AgCl). The electron affinity A_c and ionization potential IP were calculated, assuming that the vacuum level of the referenced ionization potential of the Ag/AgCl electrode is 4.7 eV. The ionization potential of Ag/AgCl was estimated by the sum of the electromotive force of saturated Ag/AgCl solution based on the hydrogen scale NHE ($=0.2$ V) and the ionization potential of NHE ($=4.5$ eV). The ionization potential of the PTCDI-Spent film was determined by the sum

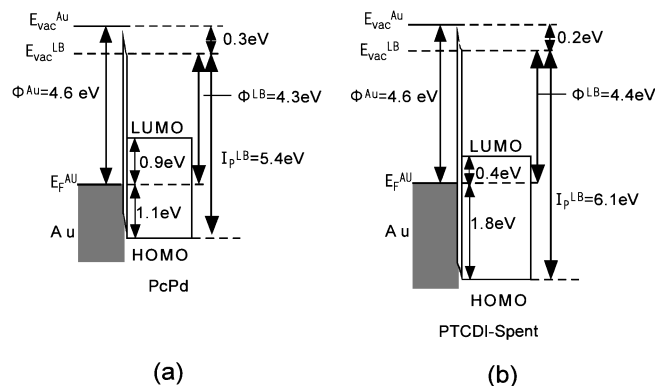


Fig. 4. Energy diagrams of (a) Au/PcPd monomolecular film interface and (b) Au/PTCDI-Spent monomolecular film interface.

Table IV. Cyclic voltammetric behavior of the 10-layer PcPd and PTCDI-Spent LB films.

	Energy level/V vs. satid. Ag/AgCl (E_2)	$4.7 + E_2/eV$
PcPd (A_c)	-1.20	3.5
PcPd (I_p)	+0.62	5.3
PTCDI-Spent (A_c)	-0.53	4.2
PTCDI-Spent (I_p)	—	6.4

Table II. Energy parameters of PcPD LB films deposited on Au.

Number of layers	$E_{\text{kinmax}}^{\text{Au}} - E_{\text{kinmax}}^{\text{LB}}$	$E_{\text{kinmin}}^{\text{Au}} - E_{\text{kinmin}}^{\text{LB}}$ (ΔE)	$\Phi_{\text{LB}} - E_F + \Delta E$	Ionization potential IP_{LB}
1	1.1 eV	0.3 eV	4.3 eV	5.4 eV
6	1.5 eV	0.7 eV	3.9 eV	5.4 eV
10	1.5 eV	0.7 eV	3.9 eV	5.4 eV

Table III. Energy parameters of PTCDI-Spent LB films deposited on Au substrate.

Number of layers	$E_{\text{kinmax}}^{\text{Au}} - E_{\text{kinmax}}^{\text{LB}}$	$E_{\text{kinmin}}^{\text{Au}} - E_{\text{kinmin}}^{\text{LB}}$ (ΔE)	$\Phi_{\text{LB}} - E_F + \Delta E$	Ionization potential IP_{LB}
1	1.7 eV	0.2 eV	4.4 eV	6.1 eV
6	2.0 eV	0.3 eV	4.3 eV	6.3 eV
10	2.1 eV	0.4 eV	4.2 eV	6.3 eV

Table V. Energy parameter of the PcPd(1L)/Au, PcPd(1L)/PTCDI-Spent(4L)/Au, and PcPd(1L)/PolC5F(4L)/Au system.

Sample structure	$E_{\text{kinmax}}^{\text{Au}} - E_{\text{kinmax}}^{\text{LB}}$	$E_{\text{kinmin}}^{\text{Au}} - E_{\text{kinmin}}^{\text{LB}}$ (ΔE)	Ionization potential I_{P}^{LB}
PcPd(1L)/Au	1.1 eV	0.3 eV	5.4 eV
PcPd(1L)/PTCDI-Spent(4L)/Au	1.4 eV	0.6 eV	5.4 eV
PcPd(1L)/PolC5F(4L)/Au	3.3 eV	2.6 eV	5.3 eV

of the electron affinity and the optical energy gap (=2.2 eV) because no oxidation wave could be obtained by the cyclic voltammetry. There is a good agreement between the values indicated in the energy diagram as shown Fig. 4 and those tabulated in Tables II and III.

In our previous study, we measured the surface potential across PcPd LB films and PTCDI-Spent LB films on a Au electrode in a dark vacuum vessel at various temperatures. It was suggested that excess electronic charges are transferred from these LB films to the Au electrodes until a thermodynamic equilibrium is established at the metal/film interface, resulting in the formation of an electrostatic layer on the order of several nanometers. Figure 5 shows the relationship between the surface potential of the PcPd and PTCDI-Spent LB films deposited on the Au electrode and the number of deposited layers before heat treatment.¹⁷⁾ The surface potentials of PcPd LB films gradually increase as the number of deposited layers increases and then reach a constant saturation potential within the first 5 LB layers; whereas the surface potentials of PTCDI-Spent LB films gradually increase as the number of deposited layers increases and do not reach a constant saturation potential even when the number of layers is 15. These tendencies correspond well to the UPS results of ΔE summarized in Tables II and III. That is, ΔE of PcPd LB films saturate with first five layers because the thickness of electrostatic double layer is less than five molecular layers, whereas the ΔE of PcPd LB films does not saturate in the first 10 layers because the thickness of the electrostatic double layer is larger than the 15 molecular layer thickness. The potentials plotted in Fig. 5 are somewhat smaller than the

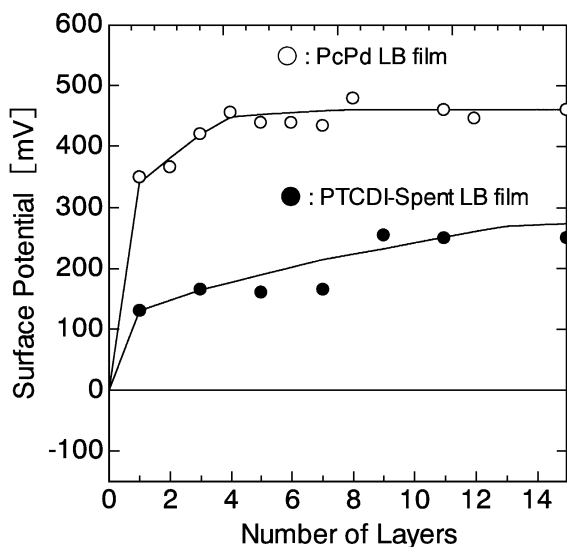


Fig. 5. Relationship between the surface potentials of PcPd and PTCDI-Spent LB films deposited on Au substrates measured in a dark vacuum vessel before heat-treatment.

ΔE obtained by UPS measurement. One reason is that our sample was charged up during photoemission. Another reason is that the surface potential of non-heat-treated samples was unstable, and the potentials scattered with a deviation of about 0.1 V from sample to sample. Further, these potentials changed significantly by the heat treatment. For example, the saturated value of the surface potential of the PcPd LB film strongly depends on temperature and changes from 0.5–0.6 V to 0.25 V at room temperature during the heat treatment.¹⁷⁾ Therefore, we may argue here that the energy difference ΔE corresponds to the electrostatic energy. That is, ΔE corresponds to the surface potential reached due to the displacement of electronic charge at the metal/organic thin-film interface. Thus, we concluded that the saturation values of ϕ_{LB} in Tables II and III represent the work function of organic films.

Figure 6 shows the UPS spectrum of PcPd monolayer films deposited on a bare Au electrode, and those of the four-layer PTCDI-Spent film and the four-layer PolC5F film. These films are denoted as PcPd (1L)/Au, PcPd (1L)/PTCDI-Spent (4L)/Au, and PcPd (1L)/PolC5F (4L)/Au. Table V summarizes the energy parameters obtained from Fig. 6. The trace of these three samples is nearly the same in Fig. 6, indicating that photoinduced electrons are emitted from the overcoated PcPd monolayer film. ΔE of the PcPd (1L)/PTCDI-Spent (4L)/Au was 0.62 eV. It coincided with ΔE of PcPd monolayer film,

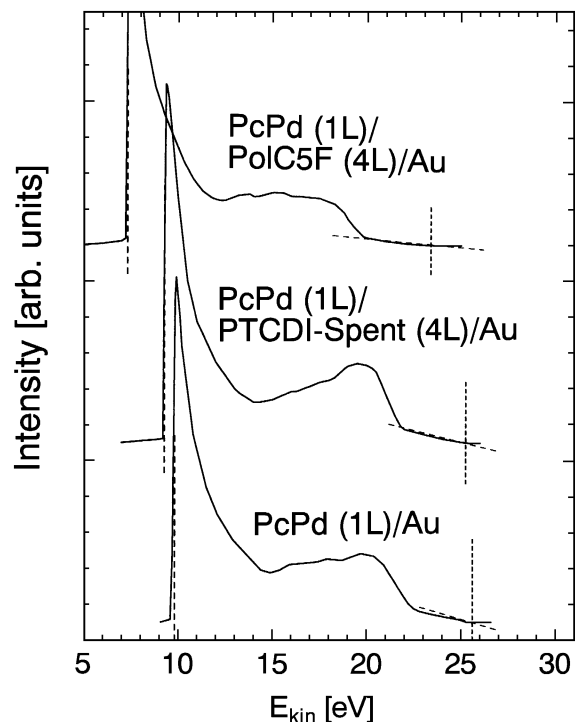


Fig. 6. UPS spectra of PcPd (1 layer), PcPd (1 layer)/PTCDI-Spent (4 layers), and PcPd (1 layer)/PolC5F (4 layers) films on Au substrate with respect to kinetic energy of photo-electrons induced by He I ($h\nu = 21.2$ eV).

whereas it was in good agreement with ΔE of PcPd multilayer film (see Table II). In our previous study, we measured the surface potential of PcPd LB films deposited on PTCDI-Spent LB films, where the PcPd monolayer film was positively charged and the potential V_s was 0.1 V to 0.2 V with respect to the PTCDI-Spent LB films. Therefore, it is estimated that the energy shift is the sum of ΔE of the PTCDI-Spent multilayer film (0.3–0.4 eV) and electron volts (0.1–0.2 eV). We therefore concluded that thermodynamic equilibrium is established even when PTCDI-spent molecular film is sandwiched between the PcPd film and the Au electrode, and the positive charge generated during the UPS measurement transfers to the Au substrate. In contrast, ΔE of PcPd (1L)/PolC5F (3L)/Au ($=2.64$ eV) became much larger than that of the PcPd monolayer film, indicating that the positive charge does not transfer to the Au substrate when the PolC5F film was sandwiched between PcPd and Au. Another reason is the contribution of the dipole layer originating from the fluorinated chains in PolC5F molecules. We therefore concluded that the energy shift in the low kinetic energy range of UPS spectra with respect to the Au substrate corresponds well with the electrostatic energy only when a π -conjugated ultrathin film is used.

4. Conclusions

In this study, we measured the UPS spectra of π -conjugated Langmuir-Blodgett films (octasubstituted palladiumphthalocyanine (PcPd), preylene-tetra-carboxyldiimide derivative (PTCDI-Spent)) deposited on Au electrodes. It was revealed that the energy shift of the low kinetic energy site with respect to the Au substrate corresponded well with the surface potential results obtained by a conventional Kelvin-probe method in a dark vacuum vessel using a π -conjugated film. It was suggested that excess electronic charges are transferred from these LB films to the Au electrodes until thermodynamic equilibrium is reached at the metal/ π -conjugated film interface, resulting in the formation of an electrostatic layer with a thickness on the order of 2 or 3 nanometers.

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- 1) M. Iwamoto, M. Wada and T. Kubota: *Thin Solid Films* **243** (1992) 472.
- 2) Y. Isono and H. Nakano: *J. Appl. Phys.* **75** (1994) 4557.
- 3) C. M. Fischer, M. Burghard, S. Roth and K. v. Klizing: *Appl. Phys. Lett.* **66** (1995) 3331.
- 4) C. W. Tang: *Appl. Phys. Lett.* **48** (1986) 183.
- 5) M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Anderson and R. H. Friend: *Nature* **395** (1998) 257.
- 6) C. M. Fischer, M. Burghard and S. Roth: *Synth. Met.* **76** (1996) 237.
- 7) C. W. Tang and S. A. VanSlyke: *Appl. Phys. Lett.* **51** (1987) 913.
- 8) T. Tsutui, C. P. Lin and S. Saito: *Mol. Liq. Cryst.* **256** (1994) 63.
- 9) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest: *Nature* **395** (1998) 151.
- 10) M. Burghard, M. Schmelzer, S. Roth, P. Haisch and M. Hanack: *Langmuir* **10** (1994) 4265.
- 11) C. C. Leznoff and A. B. P. Lever: *Phthalocyanines—Properties and Applications* (VCN, Weinheim, 1989).
- 12) G. Roberts: *Langmuir-Blodgett Films* (Plenum Press, New York, 1990) Chap. 7.
- 13) M. Burghard, C. M. Fischer, M. Schmelzer, S. Roth, M. Hanack and W. Gopel: *Chem. Mater.* **7** (1995) 2104.
- 14) L. H. Lee: *J. Electrostat.* **32** (1994) 1.
- 15) M. Iwamoto, A. Fukuda and E. Itoh: *J. Appl. Phys.* **75** (1994) 1607.
- 16) E. Itoh and M. Iwamoto: *J. Appl. Phys.* **81** (1997) 1790.
- 17) E. Itoh, H. Kokubo, M. Iwamoto, M. Burghard, S. Roth and M. Hanack: *Jpn. J. Appl. Phys.* **37** (1998) 577.
- 18) S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima and K. Yamashita: *Appl. Phys. Lett.* **67** (1995) 1899.
- 19) H. Ishii, K. Sugiyama, E. Ito and K. Seki: *Adv. Mater.* **11** (1999) 605.
- 20) C. S. Winter, R. H. Tredgold, A. J. Vickers, E. Khoshdel and P. Hodge: *Thin Solid Films* **135** (1985) 49.
- 21) D. Schlottwein and N. R. Armstrong: *J. Phys. Chem.* **98** (1994) 11771.
- 22) T. R. Ohno, Y. Chen, S. E. Harvey, G. H. Kroll and J. H. Weaver: *Phys. Rev. B* **44** (1991) 13747.
- 23) P. S. Bagus, C. J. Nelin and C. W. Bauschlicher: *J. Vac. Sci. Technol. A* **2** (1984) 905.