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The atmospheric effect on the ionization energy (I) of titanyl phthalocyanine (TiOPc) thin film was investigated by photoemission yield spectroscopy developed for the measurement of I for the same specimen both in vacuum and under gaseous atmosphere. The variation of I of TiOPc thin film induced by exposure to air was observed.

Keywords: atmospheric effect; ionization energy; photoemission yield spectroscopy; titanyl phthalocyanine

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INTRODUCTION

Recently, thin films of organic semiconductors are attracting considerable interest due to the possibility for application to various types of electronic devices such as organic light emitting diodes, organic thin film transistors (OFETs), and organic solar cells. It is well known that the ambient atmosphere significantly affects the electrical properties of organic devices [1–6]. As an example of detailed study of such effect, it was recently reported that the properties of the OFETs with titanyl phthalocyanine (TiOPc; see inset of Fig. 1.) film fabricated in high vacuum are drastically changed under oxygen atmosphere [7]. Our recent study by ultraviolet photoemission spectroscopy (UPS) also indicated that the electronic structure of the interface between the graphite

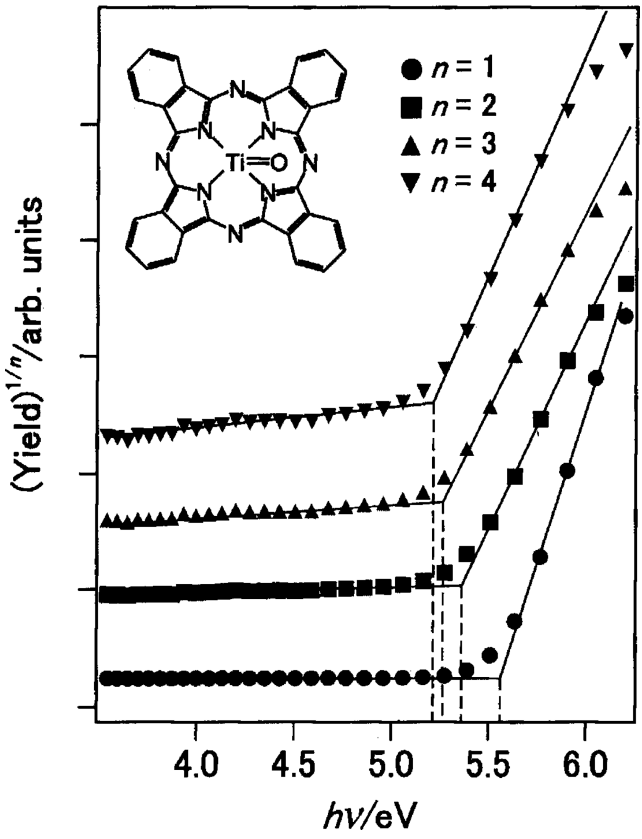

FIGURE 1 PYS spectrum of TiOPc film plotted to the 1, 1/2, 1/3, and 1/4 power as a function of $h\nu$. Vertical broken bars indicate the values of estimated I.

electrode and TiOPc film deposited in ultrahigh vacuum was different from that of the film deposited in oxygen atmosphere ($\sim 1 \times 10^{-2}$ Pa) due to *p*-type doping by oxygen [8], in good correspondence with the reported difference of the OFET characteristics [7]. However, high vacuum condition is needed for UPS measurements, and evacuation after the exposure was inevitable even for such measurements. Thus the real atmospheric effect on the electronic structure in ambient condition, which is important for the devices, could not be investigated in detail. Further, such an effect may be not so large, and the separate measurements for different samples may lead to large uncertainty due to the limited reproducibility of the sample preparation. Thus the development of an experimental method directly enabling the electronic structure both in high vacuum and under the presence of various atmosphere *for the same specimen* has been highly desired. We believe that so far no reliable quantitative experimental results were reported on the atmospheric effect on I.

Recently, we have developed photoemission yield spectroscopy (PYS) system applicable to the same specimen both in vacuum and ambient atmosphere conditions including the actual working condition of the devices. In this apparatus, monochromatic light of tunable photon energy is irradiated on the sample, and the number of electrons emitted by photoelectric effect is measured as the function of photon energy. The ionization energy I, which is a leading energy parameter of organic semiconductors, can be determined as the minimum photon energy to cause photoelectric emission, as described in detail later. In this paper, we present the first detailed study of the atmospheric effect on I by using this PYS method for TiOPc thin films. It was found that I of TiOPc thin film is dramatically changed by exposure to air.

EXPERIMENTAL

PYS measures photoemission yield Y defined as the total number of photoelectrons per an incident photon as a function of the incident photon energy $h\nu$. As mentioned above, the value of I can be determined as the threshold energy of photoelectron emission, which corresponds to the onset of the PYS spectrum.

Around the photoelectric threshold I is usually expressed as the following relation [9–11],

$$Y \propto (h\nu - I)^n \tag{1}$$

where n is a parameter depending on the shape of the density of electronic states at the upper edge of the occupied states of the sample. The square law ($n = 2$) and cube law ($n = 3$) are often used for fitting

the PYS spectra of metals and organic materials, respectively [9–11]. In this paper, we determined I of TiOPc film by analysis of the PYS spectra with the cube law following Reference [11], and plotted $Y^{1/3}$ as a function of $h\nu$. From the extrapolation of the linear part of $Y^{1/3}$ to $Y = 0$, the value of I was determined.

TiOPc sample with the quoted purity of 95% was purchased from Aldrich and purified by vacuum sublimation. The Au substrate was prepared *in situ* by depositing 100 nm thick Au film on Si (100) substrate with naturally oxidized surface. The TiOPc films were deposited on this Au substrate by vacuum evaporation in the PYS chamber. Deposition rate and thickness of the TiOPc film were monitored with a quartz microbalance and were adjusted to be about 0.01 nm/s and 100 nm, respectively. During the evaporation, the substrate was kept at room temperature and the pressure of the PYS chamber was less than 1×10^{-5} Pa.

Details of PYS system will be reported in detail elsewhere, and we will briefly summarize the important points. The photoemission yield was measured by using a monochromatic UV light source consisting of a deuterium lamp and a monochromator (JASCO) with a resolution of 3.9 nm (0.04–0.12 eV in the present wavelength region). The photon intensity distribution of this light source was calibrated with a photodiode (Hamamatsu Photonics S1337–1010BQ). A voltage of 200 V was applied between the negatively biased sample and a grounded ring-shaped electrode placed in front of the sample. Such voltage ensures the complete collection of the emitted photoelectrons, and may also cause amplification of the signal by the possible ionization of the atmospheric gas molecules by the collision of the accelerated electrons. The amount of the emitted electrons were measured as the photocurrent with a sub-picoampere ammeter (KEITHLEY 6430).

RESULTS AND DISCUSSION

The PYS spectrum near the photoelectric threshold of TiOPc thin film is plotted on various power law assumptions in order to establish the spectral characteristics. As mentioned above, there is the relationship, expressed in Eq. (1), between I and Y around the photoelectric threshold. Figure 1 shows the PYS spectrum of TiOPc film plotted to the 1, 1/2, 1/3, and 1/4 power as a function of $h\nu$. As shown in Figure 1, the 1/3 power law most closely represents the data. In this paper, we used 1/3 power law to determine I of TiOPc film.

Figure 2 shows the change of I of TiOPc film in a time sequence with varying atmospheric conditions in order to study the atmospheric effects on I of TiOPc film.

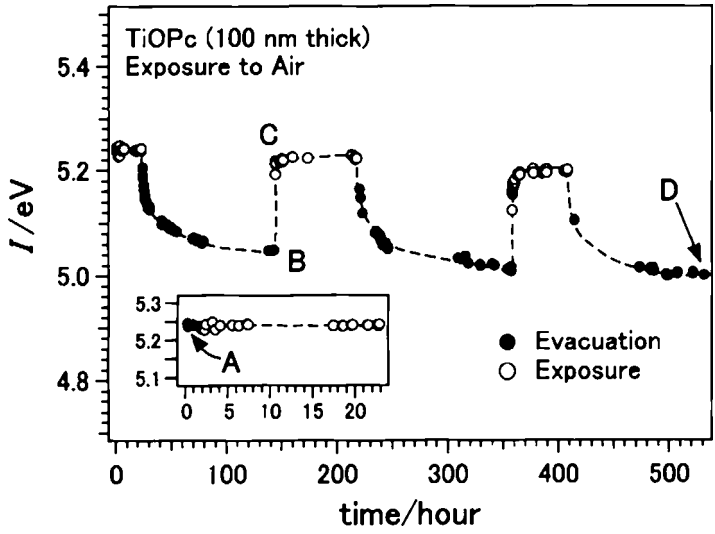

FIGURE 2 The dependence of the ionization energy I of TiOPc film in a time sequence with repeated cycles of introduction and evacuation of air of ambient pressure. Filled circles denote I measured in high vacuum, and open circles are I measured in air. Broken line is guide for eyes. The inset shows the change of I of TiOPc film at the first exposure to air. The molecular structure of TiOPc is shown in the other inset.

The experiments of PYS were carried out the following procedure. (1) I of TiOPc film was measured in high vacuum ($\sim 1 \times 10^{-6}$ Pa) immediately after the deposition. (2) After 2 h, we measured I again, and in all cases found no change of I within 0.01 eV. (3) The TiOPc film was exposed to air, and monitored the change in I as a function of time. (4) The chamber was evacuated, and the change of I was monitored as a function of time. (5) The cycle of (3) and (4) are repeated further.

As shown in the inset of Figure 1, the value of ($I = 5.24$ eV) was measured *in situ* just after the deposition (labeled "A" in Fig. 1). It did not change after the first exposure to air of ambient pressure, and during the further exposure of 24 h. When the chamber was subsequently evacuated, however, I decreased by 0.19 eV within the following 120 h ("B"). At the second exposure to air, I immediately returned to the value measured in the term A at the first exposure to air ("C"). The following cycles of evacuation and exposure showed similar reversible change of I. The reversible change in the later part of the sequence may be ascribed to the adsorption and desorption of molecules, but the absence of change at the first exposure cannot be

explained by this factor only. These results indicate that some kind of irreversible change takes place at the first exposure to air. Furthermore, a gradual decrease of I through the repeated exposure-evacuation cycles was observed. For example I in vacuum at 530 h ("D") is smaller by 0.05 eV than I in vacuum at 120 h ("B").

We will briefly discuss the possible origins for the change of I caused by the exposure to air. The exposure of the TiOPc film to O_2 and H_2O showed similar effects on I to that by air, although the exposure to N_2 had little effect (experimental data are not shown here). The largest effect was obtained by the exposure to H_2O. We note that there are three kinds of experimental results common to air, O_2, and H_2O, i.e., (a) little change at the first exposure, (b) almost reversible change at each of the subsequent exposure-evacuation cycle, and (c) gradual change through the repeated exposure-evacuation cycles. The almost reversible change (b) is most probably due to the adsorption and the desorption of the gases like H_2O and O_2. Such adsorption is expected to modify the dipole layer at the surface, and the direction is interpreted as the formation of dipole layer (with the vacuum side negatively charged) at the adsorption of these gases. Such dipole layer may be formed for nonpolar O_2 molecule by some charge transfer to the TiOPc molecule with rather small ionization energy to electron accepting O_2 molecule or other possible origins. For H_2O molecule, similar mechanism and also the oriented adsorption of polar H_2O may also contribute, and this might be the possible origin of the larger effect of H_2O than O_2.

The finding of only little change of I at the first exposure (a) is a rather unexpected result. Since the effect of adsorption observed in (b) should be also operative at the first exposure, we can speculate that there is some irreversible mechanism cancelling the adsorption of the gases. This factor should contribute to form a dipole layer with the vacuum side positively charged. We may speculate that the first adsorbed layer strongly interacts with the TiOPc molecule to form such a layer, and this cannot be desorbed easily by subsequent adsorption-evacuation cycle. Other possible origins of such dipole layer at the first exposure are (2) the change of the electronic structure of TiOPc molecule by chemisorption of O_2 or H_2O and (3) the change of the electronic structure of TiOPc film induced by morphological change of the film surface by exposure to O_2 or H_2O gases. Finally, the slow change (c) is also a rather unexpected result, and should be connected with a rather slow process such as the change of molecular orientation mentioned in (3). However, the discussion made here is rather speculative, further studies by other techniques and also studies on other molecules/substrates are necessary for examining these mechanisms.

CONCLUSION

In this work, we have measured the ionization energy I of TiOPc thin film in vacuum and air by the PYS method, developed to directly measure I of the same specimen both in vacuum and ambient atmosphere conditions. The value of I of the *in situ* prepared TiOPc film changed little at the first exposed to air, but showed roughly reversible decrease and increase at the subsequent exposure-evacuation cycles.

These are the first reliable systematic examination of the atmospheric effect on the ionization energy of organic semiconductor, and some of the results were rather unexpected. Further systematic studies for related systems will give deeper insight on this important effect.

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