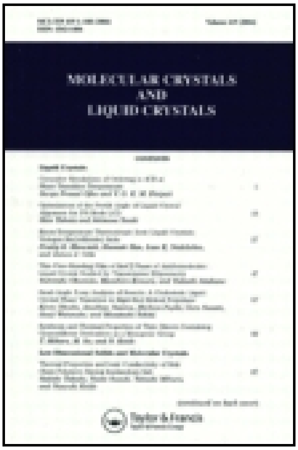

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Atmospheric Doping Effect on the Interfacial Electronic Structure of Titanyl Phthalocyanine Film

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The effect of oxygen doping on titanyl phthalocyanine (TiOPc) films was investigated by ultraviolet photoelectron spectroscopy (UPS). The energy of the electronic levels of TiOPc films probed by UPS was clearly different between the film deposited in ultrahigh vacuum (UHV) and in O_2 atmosphere. The film deposited in UHV showed downward band bending characteristic of n-type semiconductor. On the other hand, the film deposited under O_2 atmosphere showed upward band bending characteristic of p-type semiconductor. Such trends are in excellent correspondence with reported field effect transistor characteristics.

Keywords: organic semiconductor; oxygen doping; titanyl phthalocyanine; ultraviolet photoelectron spectroscopy

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INTRODUCTION

It is well known that the electrical conductivities of organic semiconductors are sensitive to the ambient atmosphere like O_2 [1–9]. According to these reports, exposure to O_2 increases the conductivity, probably due to *p*-type doping by oxygen. However, detailed study on the change in the electronic structure by the effect of oxygen has not yet been reported. Such study from the viewpoint of the electronic structure is important since it will give direct evidence for this mechanism and detailed and quantitative information about the doping effect of oxygen. Such atmospheric effects are important for the operation of organic devices such as organic light emitting diodes and organic field effect transistors (OFETs), because these devices are normally operated in the ambient condition or under encapsulation in inert gases.

Titanyl phthalocyanine (TiOPc; see Fig. 1), is also known to be sensitive to ambient gases such as O_2 and NO_2 [10–12]. For this material, Tada *et al.* recently investigated the effect of atmosphere on the electrical properties in detail by fabricating OFETs [12]. Their results revealed that TiOPc film deposited in ultrahigh vacuum (UHV) condition exhibited an *n*-type semiconducting behavior, while the exposure of the film to O_2 causes a clear conversion from *n*-type to *p*-type behavior.

In this work, we studied the interfacial electronic structure of TiOPc film prepared under UHV and O_2 atmosphere by ultraviolet photoelectron spectroscopy (UPS). We have been studying the

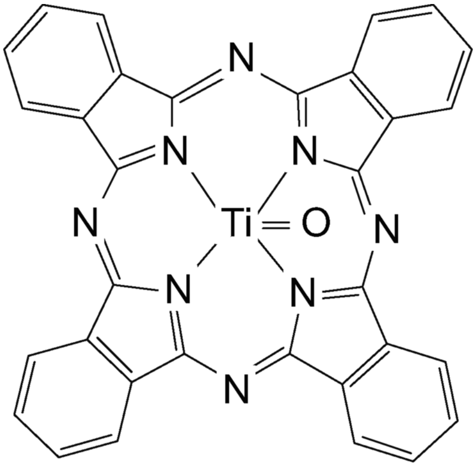

FIGURE 1 Molecular structure of titanyl phthalocyanine (TiOPc).

electronic structure of various TiOPc film/metal interfaces including possible band bending. The results showed excellent correspondence with the results of the reported OFET studies, confirming the effect of O_2 as p-type dopant.

EXPERIMENTAL

The sample of TiOPc was purchased from Aldrich and purified by repeated vacuum sublimation. We used Au and highly oriented pyrolytic graphite (HOPG) as the substrates. The HOPG substrate was cleaved in air just before loading into the sample preparation chamber (base pressure: 8×10^{-7} Pa). The Au substrate was an Au foil cleaned by Ar^+ ion sputtering in the same chamber. TiOPc films were prepared by vacuum deposition on the substrates in the preparation chamber and transferred to the analysis chamber (base pressure: 2×10^{-7} Pa) without breaking UHV conditions. The thickness of the TiOPc films was monitored with a quartz crystal microbalance. The deposition rate was about 0.3 nm/min. The UPS measurements were performed under UHV using He I resonance line ($h\nu = 21.2\,\text{eV}$). O_2 gas was introduced through a variable leak valve attached to the preparation chamber.

Molecular orbital (MO) calculations of a TiOPc molecule were performed by density functional theory (DFT) method with B3LYP/6-31G(d). The simulated spectrum was obtained by convoluting delta functions at MO energies with a Gaussian function with 0.6 eV FWHM.

RESULTS AND DISCUSSION

In Figure 2, we show the UPS spectrum of the TiOPc film of 10 nm thickness deposited on Au substrate. The abscissa is the binding energy relative to the Fermi level of the substrate. The low kinetic energy cutoff corresponds to the energy of the vacuum level. In the figure, we also show the simulated spectrum by DFT calculation. The simulated spectrum is in good agreement with the observed spectrum when we take account of the smooth background by secondary electrons. The UPS spectrum in this region show three bands labeled A, B, and C. These bands can be assigned as follows. Band A is related to π MO distributed on the inner macrocycle containing N atoms, which is shown in the inset. Band B and C are mainly related to the π MOs distributed in the benzene rings. The UPS spectral structures and its assignments basically correspond with those in previous studies of various phthalocyanines [13,14].

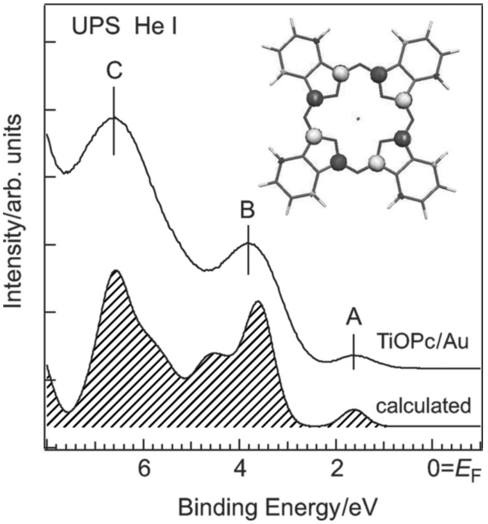

FIGURE 2 Comparison of the UPS spectrum of TiOPc film of 10 nm thickness deposited on Au substrate (top spectrum) and spectrum calculated by DFT method (bottom spectrum). Inset shows the simulated HOMO orbital.

Figure 3 shows the variation of the energy of the HOMO level relative to Fermi level of the HOPG substrate (ε_V^F) as a function of TiOPc thickness up to 40 nm. The value of ε_V^F was obtained as the binding energy of the onset of peak A. From these data, we can show schematically the electronic structure of the TiOPc/HOPG interface as shown in Figure 4. For the film deposited in UHV, as seen in Figure 3 and Figure 4(a), the HOMO level shifts downward increasing layer thickness up to ~20 nm, indicating the formation of positive space charge region. The saturated position of leading edge of the HOMO is about 1.2 eV below the Fermi level of HOPG. In addition, the position of the lowest unoccupied molecular orbital (LUMO) in thick film is estimated to be closer to the Fermi level of the substrate, when we suppose that the reported optical gap of about 1.7 eV provides the HOMO-LUMO gap [15]. There results suggest that the TiOPc film deposited in UHV exhibits an n-type semiconducting behavior, and the major carriers are electrons in this TiOPc film. This is consistent with the results of field effect measurements by Tada *et al.* [12]. We suppose that residual impurities in the TiOPc film, which could not be removed by purification by sublimation, works as unintentional donor dopant. In this case, the alignment between the Fermi level of the substrate and the Fermi level of the TiOPc film was not

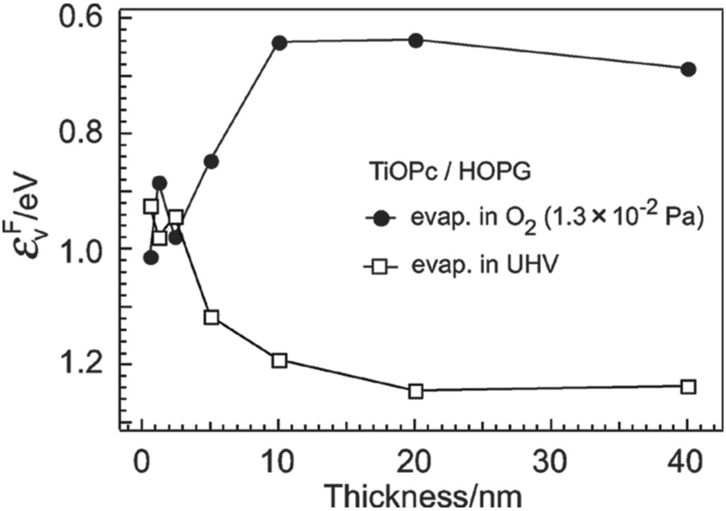

FIGURE 3 The dependence of the HOMO level position relative to the Fermi level of the HOPG substrate (ε_v^F) on the thickness of the TiOPc film. The open squares represent the results of the TiOPc film deposited in UHV condition, and the filled circles represent the results of the film deposited under O_2 atmosphere of 1.3×10^{-2} Pa.

observed, possibly because of insufficient charge density in the TiOPc film [16].

In Figure 3, the variation of ε_v^F of TiOPc film deposited under O_2 atmosphere (1.3×10^{-2} Pa) is also shown, and the deduced electronic structure of the TiOPc/HOPG interface is shown in Figure 4(b). Figure 3 and Figure 4(b) show upward shift of the HOMO level by about 0.3 eV with increasing layer thickness up to $\sim$10 nm, indicating the formation of negative space charge region, and we observed that the Fermi level alignment between the substrate and TiOPc film was achieved. These results indicate that the TiOPc film deposited in O_2 atmosphere has a *p*-type semiconducting behavior, and this is consistent with expected *p*-type doping by oxygen. This clear conversion of the electronic structure from *n*-type to *p*-type by the existence of O_2 well corresponds again to the results of the OFET measurements [12], and demonstrates that the bulk of TiOPc film could be actually doped by oxygen.

The results call for caution at the comparison between the experimental results obtained under UHV and other conditions. The basic understanding of the interfaces can often be obtained only from

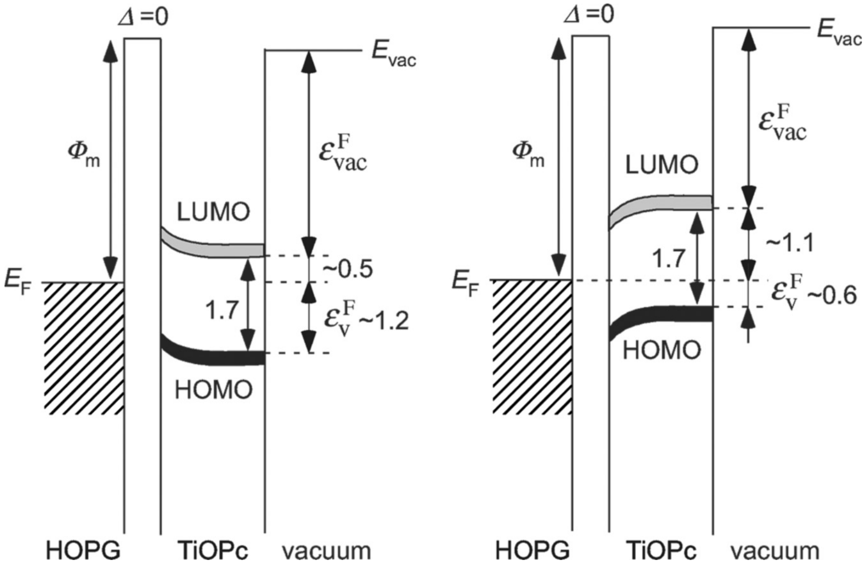

FIGURE 4 Schematic energy level diagrams (in eV) of TiOPc film deposited on HOPG substrate in UHV (a) and O_2 atmosphere of 1.3×10^{-2} Pa (b) E_{vac} denotes the vacuum level, and Δ is the shift of vacuum level at the interface due to the dipole layer formation, which is negligible in the present case. Φ_m is the work function of the HOPG substrate, which is 4.4 eV in the present case. The energy of the Fermi level (E_F) of the HOPG substrate was determined by Fermi level of the Au film deposited on it.

UHV experiments, but simple application of the knowledge obtained under UHV to real devices can be sometimes dangerous. In this sense, the present results are instructive for the further progress of the understanding of the organic interfaces.

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