

Electronic Interaction and Electric Property in Vacuum Codeposited Films of Naphthalene Tetracarboxylic Derivatives and Metals

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Abstract

Strong and singular electronic interaction between naphthalene tetracarboxylic dianhydride (NTCDA) and indium was investigated using various spectroscopic and electric techniques. Doping indium into NTCDA by codeposition caused remarkable changes in the electronic absorption and electron spin resonance spectra, which were attributed to a partial charge transfer from the metal to the carbonyl oxygen. X-ray diffraction and infrared absorption measurements revealed that these electronic interactions prevent aggregation of the organic molecules, resulting in formation of microscopically mixed and amorphous-like films. In addition, indium doped NTCDA showed very high conductivity exceeding 10^{-2} S/cm, and some stability in under atmospheric condition.

Introduction

Organic electronic devices, such as organic light emitting diodes (OLEDs) or organic field-effect transistors (OFETs), inevitably have an interface between an organic film and the metal electrode. However, energetic and electrical properties of organic/metal interfaces have not been clarified sufficiently. Recently, a series of photoelectron spectroscopic studies have been reported and revealed that some metals induce an electronic interaction at the interface.¹⁻⁵ This interaction is observed when depositing a metal on an organic film, and is usually accompanied by the diffusion of the metal into the organic layer. Studies on the diffusion of metal can be linked to metal doping into organic semiconductors. For example, alkali metal doping into an interface is known to be an efficient way to improve OLED performance.^{6,7}

In this paper, we have investigated the electronic interaction between organic molecules and metals using co-deposited films, which not only includes the interaction at the interface, but the interaction within the whole film. While measurement methods to obtain interfacial information are generally limited, co-deposited films enable us to use various

spectroscopic techniques to investigate electronic interactions at the interface. In addition, co-deposited films can be regarded as being heavily doped organic semiconductors. From this viewpoint, we also evaluated electrical conductivity of the codeposited films including strong electronic interaction.

An organic semiconductor used here is naphthalene tetracarboxylic dianhydride (NTCDA), which is a promising compound for use in field-effect transistors⁸ and photocurrent multiplication devices.⁹

Experiment

The chemical structures of the compounds used are shown in Figure 1 (NTCDA and its variants, naphthalene-1,4:5,8-bis(dicarboximide) (NTCDI) and N,N'-bis(2-ethyl-6-methylphenyl)-naphthalene-1,4:5,8-bis(dicarboximide) (Ph-NTCDI)). The organic molecules and metal films were co-deposited on a cleaned glass substrate using separate sources at a pressure of 10^{-5} torr. The film thickness was 300 nm. Typically, the deposition rate of the organic molecules and the metal were 0.2 nm/s and 0.01 nm/s, respectively. The chamber was flushed with dry nitrogen gas after deposition had finished, and all measurements were carried out under atmospheric conditions.

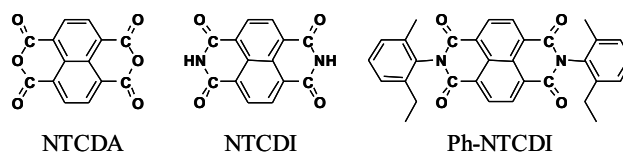


Figure 1. Chemical structures of naphthalene tetracarboxylic derivatives used.

The electronic characteristics of the co-deposited films were measured using UV-VIS spectrophotometry and electronic spin resonance. The film structures were evaluated using a Fourier transform infrared spectrometer and X-ray

diffractometer. The FT-IR spectra were measured using the attenuated total reflection (ATR) method for samples deposited on highly oriented pyrolytic graphite (HOPG) substrates.

The electrical characteristics were evaluated from current-voltage characteristics using a pair of parallel gold electrodes deposited on a glass substrate (gap = 100mm, length = 6mm).

Results and Discussions

1. Spectral Investigations on the Electronic Interactions

We examined the electronic interaction using various spectroscopic techniques. Figure 2 shows the electronic absorption spectra with various co-deposition ratios of In. NTCDA shows two peaks at $\lambda = 367$ nm and 388 nm based on the π - π^* transition. On the other hand, co-deposition with In led to remarkable spectral changes. As the concentration of In increased, the original peak decreased, and two peaks at $\lambda = 443$ nm and 748 nm emerged that had an isosbestic point. These spectral changes indicate an obvious change of the electronic states.

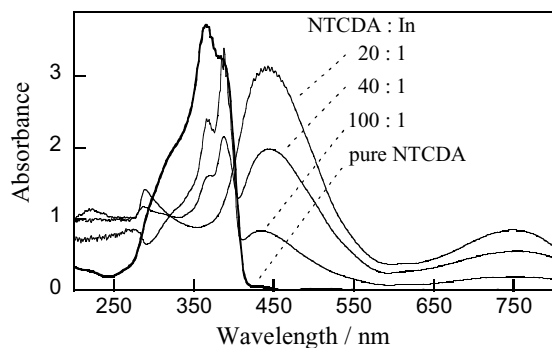


Figure 2. UV-VIS absorption spectra of co-deposited films of NTCDA and In with various co-deposition ratios.

ESR measurements were performed to clarify the nature of the electronic states. The co-deposited films gave a clear ESR signal at room temperature under atmospheric condition, as shown in Figure 3. In contrast, no signal was observed in the pure NTCDA and In films. This result means that unpaired electrons exist and different electronic states emerge by co-deposition with In. Although the line width is broad, the symmetric line shape with no hyperfine splitting suggests that the non-paired electrons are not distributed within the π -conjugated part. Thus, the electronic interactions reported at organic/metal interfaces in ultra high vacuums were clearly observed in the co-deposited films under atmospheric conditions.

The environment of each NTCDA molecule in the co-deposited film was examined using FT-IR absorption spectra to confirm the mixing properties. Figure 4 shows the FT-IR spectra of various co-deposition ratios, which are normalized by the invariable peak at 1520 cm^{-1} . The pure NTCDA film

showed a distinct peak at 1770 cm^{-1} , resulting from the C=O stretch and a peak at 1580 cm^{-1} , resulting from the C-O stretch. However, both peaks were weakened in the co-deposited films, and instead, a broad peak around 1650 cm^{-1} appeared. This result means In atoms exist near the carbonyl groups of the NTCDA, and so affect the molecular vibration, and also that all the molecules participate in the interaction, because the peaks of carbonyl groups are all changed.

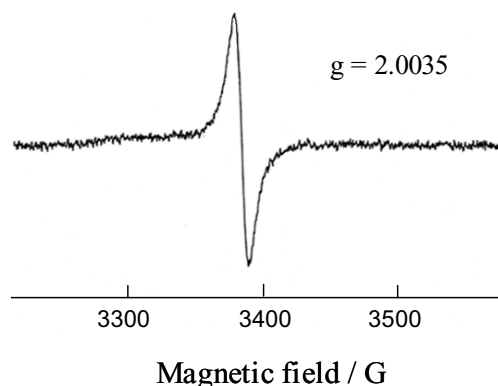


Figure 3. ESR spectrum of a co-deposited film of NTCDA and In at room temperature under atmospheric condition.

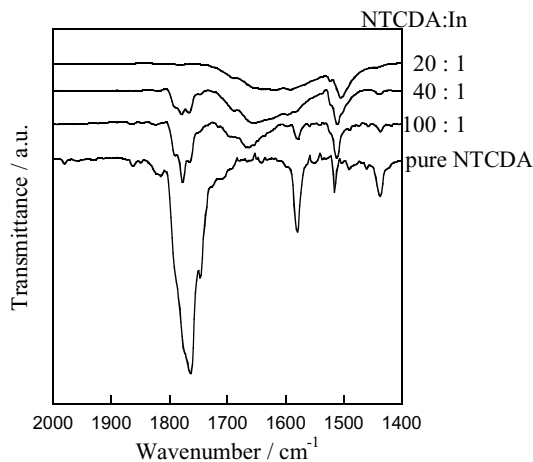


Figure 4. FT-IR absorption spectra of co-deposited films of NTCDA and In with various co-deposition ratios.

The film structure and molecular arrangement of the co-deposited film were measured using XRD. NTCDA molecules are so planar and rigid that they aggregate in the deposited film, and show a sharp peak at $2\theta = 12.0^\circ$. However, the co-deposited film did not show such a clear peak. This result means that the co-deposited films were amorphous, in that both the NTCDA and the In did not aggregate.

The results of the FT-IR and XRD measurements assert that co-deposition with In prevents any aggregation or crystallization of NTCDA, and that this results in

microscopic-scale mixing. This suggests that the film structures are related to the electronic interactions identified by the UV-VIS absorption and ESR measurements. The electronic interactions acted as an affinity between the molecule and the metal in the deposition process, and this resulted in microscopically mixed amorphous-like films (Fig. 5).

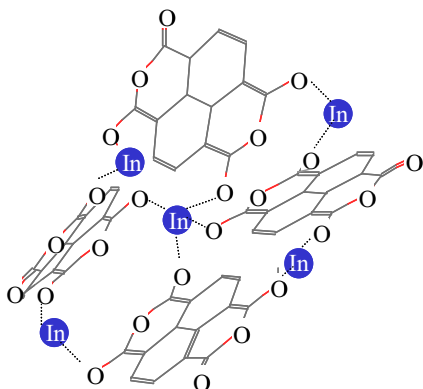


Figure 5. Structure model for the molecularly-mixed codeposited films composed of NTCDA and indium.

Similar results were obtained in the case of NTCDI having imide groups. On the other hand, no spectral changes were observed in Ph-NTCDI and indium codeposited films. This point will be discussed later.

2. Electrical Properties of the Codeposited Films

The electric conductivities of these co-deposited films are summarized in Table I. A pure NTCDA film showed low conductivity on the order of 10^{-8} S/cm. However, the co-deposited films of In showed very high electric conductivity of the order of 10^{-2} S/cm, which was about six orders of magnitude higher. This value is much higher than the reported conductivity on Li-doped film of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 5×10^{-6} S/cm).¹⁰⁾ On the other hand, the co-deposition with Ag and Au increased the conductivities of NTCDA films, but they were much smaller than that of the NTCDA/In co-deposited film.

Figure 6 shows the dependence of conductivity on the concentration of In. The conductivity increases with increasing concentration, but saturated between the deposition rate ratio of NTCDA : In = 40 : 1 and 20 : 1, latter being near equimolar ratio. If the increase of conductivity is merely due to low resistivity of metal, then the conductivity should increase monotonically with increasing metal concentration. The saturation suggests that the increase of conductivity is caused by electronic interaction between NTCDA and In. In addition, the ratio of NTCDA : In = 20 : 1 agreed with the concentration where the C=O stretch peak perfectly changed in the FT-IR spectra. This means that the excess of In, which does not participate in the interaction, does not contribute to the increase of conductivity.

This highly conductive state is not spoiled immediately, even if exposed to air. Figure 7 shows a change of conductivity with time under controlled atmospheric

condition (temperature 298K, humidity 40%). The conductivity decreased with time, but kept a high value more than 4×10^{-2} S/cm after 24 hours. This stability is much better than that of alkali metal doped BCP used as an injection layer of OLEDs.⁶⁾

Table I. Electric Conductivity of Pure Organic Films and Co-Deposited Film with Various Metals.

Composition	Conductivity (S/cm)
NTCDA/In	1.3×10^{-2}
NTCDA/Ag	1.2×10^{-5}
NTCDA/Au	1.2×10^{-5}
pure NTCDA	2.5×10^{-8}

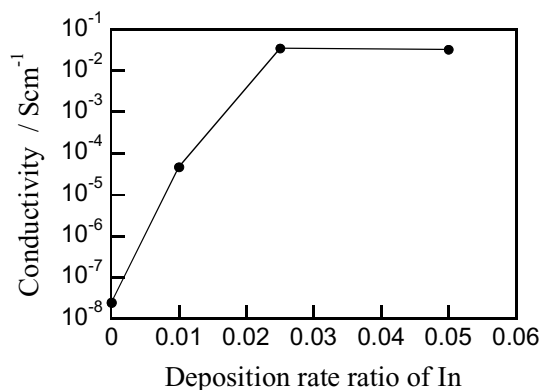


Figure 6. Dependence of electric conductivity on the In concentration (deposition rate ratio of In) in the NTCDA/In co-deposited films.

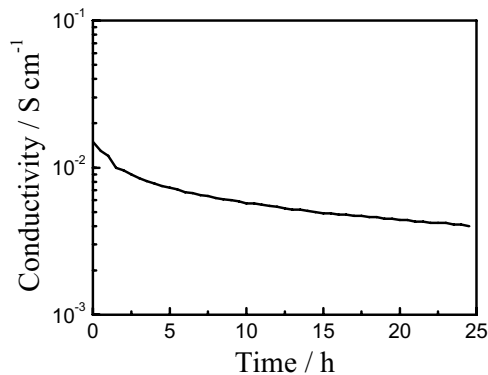


Figure 7. Typical conductivity change of a NTCDA/In film with time under controlled atmospheric condition. Temperature was 298K, humidity was 40%.

3. Discussion on the Interaction Mechanism

Thus, doping indium into NTCDA caused remarkable changes in the electronic states and film structure, in addition, drastic increase of electric conductivity. The fact that no interaction was observed in the case of Ph-NTCDI, which has bulky substituents, indicates that metal atoms need to approach the carbonyl oxygen for the interaction. Therefore, there is no doubt that the carbonyl groups play an essential role. The strong and broad absorption in the UV-VIS spectra suggests formation of a charge transfer (CT) state, which is supported by the existence of unpaired electrons that were observed in the ESR spectra. These results lead us to the conclusion that the electronic interactions in the co-deposited films are attributable to partial charge transfer from the metal to the carbonyl oxygen of the NTCDA in the ground state.

Such CT effects are similar to the known doping effect of alkali metals in conducting polymers and OLEDs. However, the electronic interactions observed in this study are dependent on the combination of the metals and organic molecules. We tried many metals, In, Mg, Ca, Al and Ga. They also indicated changes of absorption bands, however, indium shows the most significant interaction nevertheless it is not such an active (low work function) metal. In this sense, the interactions seem to be different from simple doping effects that involve a one-sided electron donation from the metal to a semiconductor, and rather, seem to involve some form of chemical interaction or bonding. The interacted states are supposed to be a metastable state, where the molecules and metal atoms are microscopically and randomly mixed owing to the affinity resulting from the electronic interaction.

Conclusion

We have investigated the electronic interactions in co-deposited films of NTCDA and indium. The strong interaction forms microscopically-mixed amorphous film including charge transfer states. The electronic interaction was attributed to a partial charge transfer from metal to the carbonyl oxygen in the ground state. In addition, the electric conductivity drastically increased due to high carrier

concentration so that an ESR peak can be observed under atmospheric condition.

These electronic interactions dependent on the chemical structure suggest a new guiding principle for controlling the electric property of organic semiconductors. For instance, control of p-type or n-type may be attained by different way from inorganic semiconductors (simple doping of donor or acceptor), *i.e.*, by chemical reaction peculiar to the combination of substituents of organics and metals.

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Biography

Ken-ichi Nakayama has worked as the assistant professor at Osaka University since 2000. He received the M. Eng. in 1997 and the Ph.D. Eng. in 2000 in Applied Chemistry from Osaka University. He is now investigating photo-electrical properties of organic semiconductors and their application. He is especially interested in structural and energetic properties of the organic/metal interface.