

## Chemical Reaction between an LB Film of an Organic Electron Donor and That of an Organic Acceptor

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In fabrication of metal-semiconductor (MS) and metal-insulator-semiconductor (MIS) devices employing conductive Langmuir-Blodgett (LB) films, chemical reactions between the materials used in the metal and semiconductor layers should be controlled because they may largely modify the electrical properties in the thin molecular layers. In this context, MS- and MIS-structured LB samples have been prepared and characterized by infrared spectroscopy to detect possible chemical reactions. LB films of an electron acceptor,  $C_{18}TCNQ$ , have been employed for the semiconductor layer because the absorption band due to  $C\equiv N$  stretching indicates the valence state of the molecule. LB films with an electron donor, BO, has been employed for the metal layer. It has been found that an insertion of four layers of cadmium arachidate between the metal and semiconductor layers inhibits a chemical reaction, whose occurrence in the MS-structured samples has been suggested.

Key words: Langmuir-Blodgett films, chemical reaction at interface, electron acceptor, electron donor, FT-IR

### 1. INTRODUCTION

The pioneering work of Barraud and his co-workers [1] opened a new class of organic thin-film materials: conductive Langmuir-Blodgett (LB) films. To date, types of LB films exhibiting semiconduction and metallic conduction have been developed. The materials used in these conductive LB films may be chemically active, for carrier generation in organic materials is strongly correlated with formation of radicals. In particular, electron donors and acceptors may react with each other.

In general, Metal-Semiconductor (MS) and Metal-Insulator-Semiconductor (MIS) junctions are keys of electronic devices such as transistors and diodes. In fabrication of such devices employing conductive LB films, therefore, chemical reactions between the materials used as metal and semiconductor may take place. Accordingly, characterization of the junctions between LB films of donors and acceptors is an essential issue in this research field. Another interesting point is that reactions at donor-acceptor interfaces may be used

as a new method of carrier doping that can control the electrical properties in ultrathin semiconductor films without introducing topological disorders.

In these contexts, we have prepared MS- and MIS-structured LB samples and characterized them by infrared (IR) transmission spectroscopy. LB films of 2-octadecyl-7,7,8,8-tetracyanoquinodimethane ( $C_{18}TCNQ$ ) have been employed for the semiconductor layer in this work because its absorption band due to the  $C\equiv N$  stretching mode is known to be highly sensitive to the valence state of the molecule [2,3]. The fact that this material can work as an active layer of field-effect transistors [4,5] is another reason why we have employed it. As the metal layer, LB films based on the 1:1 mixture of bis(ethylenedioxy)tetrathiofulvalene (BO) and fatty acid [6-10] have been employed because of its metallic conduction and the absence of absorption bands in the  $C\equiv N$  stretching region of its IR spectrum. LB films of cadmium arachidate (CdA) have been sandwiched by these two layers as the inert dielectric layer of the MIS structure.

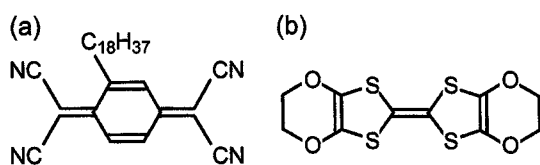


Fig. 1 Chemical structures of (a)  $C_{18}TCNQ$  and (b) BO.

### 2. EXPERIMENTAL

$C_{18}TCNQ$  and arachidic acid (AA) were purchased from Hayashibara Co. and Fluka Co., respectively, and used without further purification. BO was synthesized according to the literature [11] except that 5,6-Dihydro-[1,3]dithiolo[4,5-*b*][1,4]dioxine-2-thione

[12] and  $\text{P}(\text{OEt})_3$  was used instead of 5,6-Dihydro-[1,3]dithiolo[4,5-*b*][1,4]dioxine-2-selone and  $\text{P}(\text{OMe})_3$ , respectively.  $\text{C}_{18}\text{TCNQ}$  was dissolved in spectroscopic grade toluene with the concentration of  $1 \times 10^{-3}$  mol/l. AA and BO were dissolved in spectroscopic grade chloroform, respectively, with the concentration of  $1 \times 10^{-3}$  mol/l. Lauda Filmwaage trough were used to contain aqueous subphases, which were kept at 20 °C.

Langmuir films of  $\text{C}_{18}\text{TCNQ}$  were prepared by spreading its solution onto a pure-water subphase, compressed so that the surface pressure ( $F$ ) reaches to 25 mN/m, and then transferred directly on the front side of  $\text{CaF}_2$  plates (0.1 cm thick, IR grade, Oyokoken Co.) by the quasi-horizontal withdrawing method (Fig. 2 (a)). When successive  $\text{C}_{18}\text{TCNQ}$  layers were necessary, they were deposited by the horizontal lifting method with a collar [13].

Langmuir films of CdA were prepared by spreading the AA solution onto an aqueous solution of  $\text{CdCl}_2$  ( $4 \times 10^{-4}$  mol/l, also containing  $2 \times 10^{-5}$  mol/l of  $\text{KHCO}_3$ ) and compressed to  $F = 35$  mN/m. These films were transferred by the conventional vertical deposition method [13] except when they were transferred directly on  $\text{C}_{18}\text{TCNQ}$  films deposited in advance. In this exceptional case, a CdA layer was deposited by the quasi-horizontal immersing method (Fig. 2 (b)) and covered by another CdA layer transferred by the withdrawing process of the vertical deposition method.

The BO and AA solutions were mixed with the mixing ratio of 1:1 and spread onto a pure-water subphase to prepare BO-AA mixed Langmuir films, which were compressed to  $F = 22$  mN/m afterward. These films were transferred by the conventional vertical deposition method.

In the following, the prepared LB samples are labeled as  $l/m/n$ , where  $l$ ,  $m$  and  $n$  are the numbers of BO-AA, CdA and  $\text{C}_{18}\text{TCNQ}$  layers, respectively. The materials adsorbed on the back side of the substrate were removed before the IR transmission measurements that were performed by using a Perkin-Elmer Spectrum-2000

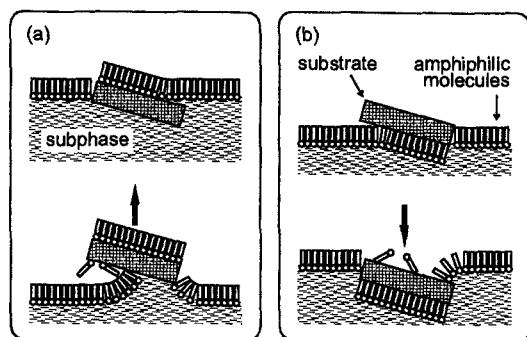


Fig. 2 Schematic illustrations of the deposition methods applied to some Langmuir films in this work: (a) quasi-horizontal withdrawing method, and (b) quasi-horizontal immersing method.

spectrometer. The baselines of IR spectra were corrected by subtracting the bare  $\text{CaF}_2$  spectrum adjusted with a multiplier from the recorded spectra.

A Langmuir film of the 1:1:1 BO-AA- $\text{C}_{18}\text{TCNQ}$  mixture was prepared by spreading the mixed solution onto a pure-water subphase and transferred on a  $\text{CaF}_2$  plate by the vertical deposition method. The IR spectrum of the obtained LB sample was recorded for comparison. All experiments were performed in air.

### 3. RESULTS AND DISCUSSION

It was already reported that the alkylTCNQ molecules in LB multilayers deposited on  $\text{CaF}_2$  plates precoated by LB films of CdA are neutral [14-17]. Namely, the only signal assignable to the  $\text{C}\equiv\text{N}$  stretching mode in the observed IR spectra was located at  $2223\text{ cm}^{-1}$ , reflecting the neutral state of the TCNQ moiety. In this work, however, the precoating of  $\text{CaF}_2$  plates is avoided because it may disturb IR characterization of  $\text{C}_{18}\text{TCNQ}$  monolayers. Therefore, the valence state of  $\text{C}_{18}\text{TCNQ}$  deposited directly on  $\text{CaF}_2$  plates has been examined firstly. Although it has been confirmed that the only prominent signal in the  $\text{C}\equiv\text{N}$  stretching region of the IR spectrum observed for a multilayer (0/0/29) sample is located at  $2223\text{ cm}^{-1}$  (Fig. 3 (a)), a weak signal around  $2180\text{ cm}^{-1}$  has been found for single-layer (0/0/1) samples (Fig. 3 (b)). The latter signal reflects the reduced (negatively charged) state of the TCNQ moiety as described below. When the spectrum for the 0/0/29 sample is magnified (Fig. 3 (a)  $\times 29$ ), the same signal can be detected, too. Moreover, its absolute intensity has been found to be nearly independent of the layer number of  $\text{C}_{18}\text{TCNQ}$ . These results implies that some fractions of the bottom or the top layer of  $\text{C}_{18}\text{TCNQ}$  is reduced. Since room ambient is oxidative and since the signal around  $2180\text{ cm}^{-1}$  was not observed for the alkylTCNQ molecules deposited on

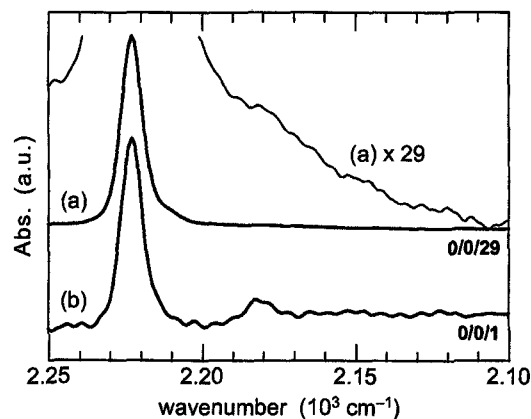


Fig. 3 Thick lines are the  $\text{C}\equiv\text{N}$  stretching region of the IR spectra observed for (a) 29-layer and (b) 1-layer samples of  $\text{C}_{18}\text{TCNQ}$ . These spectra are normalized by the peak intensity. The spectrum for the 29-layer sample is displayed also with magnification ( $\times 29$ ).

the precoated  $\text{CaF}_2$  plates [14-17], the substrate may be responsible for the detected reduction of the TCNQ moiety.

The  $\text{C}\equiv\text{N}$  stretching and fingerprint regions of the IR spectra observed for MS and MIS samples are shown in Figs. 4 and 5, respectively. Those of an LB film of the  $\text{BO-AA-C}_{18}\text{TCNQ}$  1:1:1 mixture and those of an LB film of the charge-transfer complex of BO and 2-decyl-TCNQ ( $\text{C}_{10}\text{TCNQ}$ ) [18], the latter of which was reported in Ref. [19], are also displayed in the same figures for comparison.

In addition to a prominent signal around  $2223\text{ cm}^{-1}$ , which corresponds to the neutral state of the TCNQ moiety, a distinct signal at  $2177\text{ cm}^{-1}$  is detected for 2/0/1 samples (Fig. 4 (a)). The latter signal is also detected for 2/2/1 (Fig. 4 (b)) and 2/4/1 samples (Fig. 4 (c)), but its intensity is decreased with increasing the layer number of CdA films inserted between the  $\text{C}_{18}\text{TCNQ}$  and  $\text{BO-AA}$  films. Furthermore, a weak signal around  $2145\text{ cm}^{-1}$  is notable in the spectrum for the 2/0/1 samples, but is hardly detected for the 2/4/1 samples. The signals around  $2177$  and  $2145\text{ cm}^{-1}$  well correspond to the bands due to  $\text{C}\equiv\text{N}$  stretching modes observed in the  $\text{BO-C}_{10}\text{TCNQ}$  complex LB films (Fig. 4 (e)) [19-20], in which most of the  $\text{C}_{10}\text{TCNQ}$  molecules are fully charged [20]. Therefore, the observed decreases in the intensities of these signals due to the insertion of CdA films suggest that reduction of  $\text{C}_{18}\text{TCNQ}$  due to BO takes place in the 2/0/1 MS

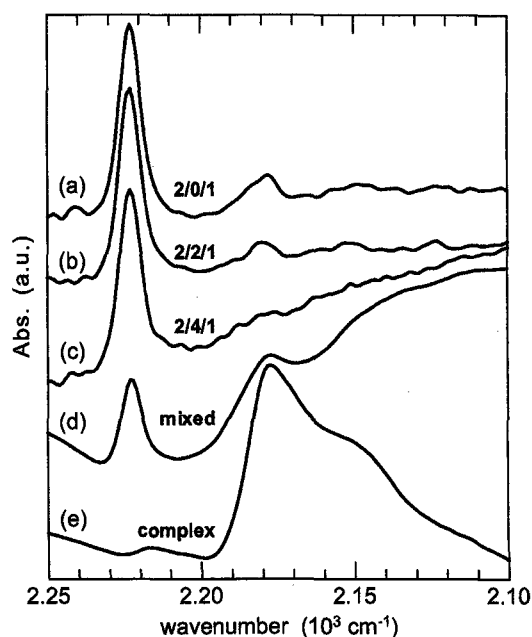


Fig. 4 The  $\text{C}\equiv\text{N}$  stretching region of the IR spectra observed for (a) a  $(\text{BO-AA})/\text{C}_{18}\text{TCNQ}$  hetero-structured film, (b)-(c)  $(\text{BO-AA})/\text{CdA}/\text{C}_{18}\text{TCNQ}$  hetero-structured films, (d) a  $\text{BO-AA-C}_{18}\text{TCNQ}$  mixed film, and (e) a  $\text{BO-C}_{10}\text{TCNQ}$  charge-transfer complex film [19]. See text for further information about the sample structure.

structure and that reduction is inhibited by the inserted CdA films. The signal around  $2177\text{ cm}^{-1}$  observed for the 2/4/1 samples may be ascribed to the reduction of the TCNQ moiety due to the substrates. Actually, further decrease in the intensity of this signal has *not* been observed for 2/6/1 and 2/8/1 samples, suggesting that an insertion of four CdA layers is sufficient to inhibit the reaction at the interface between the BO and  $\text{C}_{18}\text{TCNQ}$  films completely.

The absorption frequency of  $2177\text{ cm}^{-1}$  observed for the 2/0/1 samples suggests that the reduced  $\text{C}_{18}\text{TCNQ}$  molecules in these samples are fully charged as in the case of the  $\text{BO-C}_{10}\text{TCNQ}$  complex LB films [20]. However, the charge-transfer reaction takes place only in limited regions of the  $\text{C}_{18}\text{TCNQ}$  films and the most TCNQ moieties remain neutral, leading to the large signal at  $2223\text{ cm}^{-1}$ . Here, it should be noted that the oscillator strength of the  $2177\text{ cm}^{-1}$  band is larger than that of the  $2223\text{ cm}^{-1}$  band [15-17], which make the intensity ratio between these bands larger than the molar ratio of the reduced and neutral  $\text{C}_{18}\text{TCNQ}$ .

In the fingerprint region of the spectrum observed for the 2/0/1 samples (Fig. 5 (c)), the weak signal at  $1497\text{ cm}^{-1}$  (marked by \*) may be due to the  $b_{1u}$  mode of reduced TCNQ [15-17]. The signal at  $1547\text{ cm}^{-1}$  (marked by ‡) and that at  $1530\text{ cm}^{-1}$  (marked by †) in this spectrum are assignable to the  $b_{1u}$  and  $b_{2u}$  modes of neutral TCNQ [15-17], respectively, and their

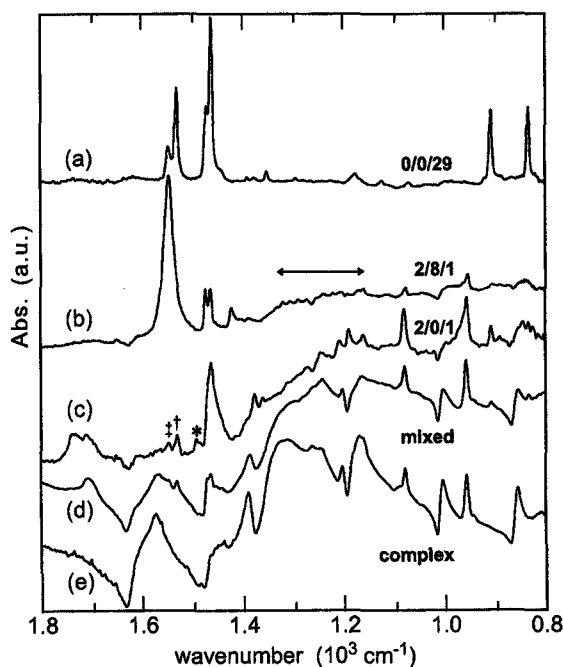


Fig. 5 The fingerprint region of the IR spectra observed for (a) a thick  $\text{C}_{18}\text{TCNQ}$  film, (b) a  $(\text{BO-AA})/\text{CdA}/\text{C}_{18}\text{TCNQ}$  hetero-structured film, (c) a  $(\text{BO-AA})/\text{C}_{18}\text{TCNQ}$  hetero-structured film, (d) a  $\text{BO-AA-C}_{18}\text{TCNQ}$  mixed film, and (e) a  $\text{BO-C}_{10}\text{TCNQ}$  charge-transfer complex film [19].

counterparts are seen in the spectrum for the 0/0/29 sample (Fig. 5 (a)). These results are consistent with the observations in the C=N stretching region of the IR spectrum observed for the 2/0/1 samples. Namely, the charge-transfer reaction takes place some regions of the C<sub>18</sub>TCNQ films in these samples, while the molecules in the rest parts of the films remain neutral.

The band around 1730 cm<sup>-1</sup> seen in the spectrum observed for the 2/0/1 samples is assignable to the C=O stretching mode of the half-ionized carboxylic group, like in the case of BO-behenic acid (BA) films [7]. This fact implies that the structure of the BO-AA films deposited in this work is similar to that of the BO-BA films. On the contrary, the carboxylic group in the CdA films is fully ionized and strongly absorb light at 1545 cm<sup>-1</sup>, masking the bands due to the TCNQ moiety in the 2/8/1 case (Fig. 5 (b)). In this case, the split of the CH<sub>2</sub> scissoring band (around 1470 cm<sup>-1</sup>) and the appearance of the (-CH<sub>2</sub>)<sub>n</sub> progression band (marked by ↔) are noted. These facts reflect a well-ordered packing structure of the alkyl chains in the CdA films.

The C=N stretching region of the IR spectrum observed for a BO-AA-C<sub>18</sub>TCNQ 1:1:1 mixed LB film (Fig. 4 (d)) shows that the reaction between C<sub>18</sub>TCNQ and BO takes place more efficiently in the mixed film than in the MS and MIS samples. In addition, the fingerprint region of that spectrum (Fig. 5 (d)) is closely similar to that observed for the LB films of the BO-C<sub>10</sub>TCNQ complex (Fig. 5 (e)) [19,20], while the spectral profile observed for the 2/0/1 samples is somewhat different from them. The difference may reflect the different stacking structure of BO, although the detailed characterization of the ternary mixed film is beyond the scope of the present work.

#### 4. CONCLUDING REMARKS

MS- and MIS-structured LB samples were prepared by employing C<sub>18</sub>TCNQ, BO-AA, and CdA films for semiconductor, metal, and insulator layers, respectively. The prepared samples were characterized by IR spectroscopy because the absorption band due to stretching of the C=N groups born by the TCNQ moiety is highly sensitive to the valence state of the molecule. Absorption bands corresponding to the fully charged TCNQ moiety, as well as that corresponding to the neutral TCNQ moiety, were found in the IR spectra recorded for the MS-structured samples. The former band is weakened when CdA films are inserted between the metal and semiconductor layers, indicating that the charge-transfer reaction at the MS interface is inhibited by the inserted CdA films.

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