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# Structural and Transport Studies of BEDO-TTF-Arachidic-Acid Conducting Langmuir-Blodgett Films

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We studied the structure and the electrical conduction of mixed Langmuir-Blodgett (LB) films of BEDO-TTF and arachidic acid (C20) on mylar and glass substrates. By the X-ray diffraction, the layered structure similar to the mixed LB films with behenic acid (C22) and stearic acid (C18) was found with periodicity of 6.2 nm, which is between those for C22 and C18. The conductivity of 40 S/cm was obtained at room temperature and metallic conduction was achieved down to ~80 K for the LB film of the optimum thickness of 13 layers. For the thick films, the conductivity showed hysteresis in the temperature region of 30-270 K, probably because of the mismatch of the thermal contraction between the films and the substrate. Similar to the case of C18, the BEDO-TTF/C20 film exhibited a decrease in conductivity with log *T* at low temperature, due to the weak localization effect as evidenced by the negative magnetoresistance at low temperatures. By applying hydrostatic pressure up to 1 GPa, the conductivity increased twice, but the temperature dependence did not change significantly.

Key words: Langmuir-Blodgett films, BEDO-TTF, mylar substrate, metallic conductivity, localization

## 1. INTRODUCTION

Metallic conduction and superconductivity in charge transfer salts made of BEDT-TTF molecules have been attracting attention from viewpoints of basic science in terms of the two-dimensional (2D) electronic system and the competition with the insulating states [1,2]. In view of application, fabrication of the metallic thin films is desirable in order to make use of the electronic function of the BEDT-TTF charge transfer salts toward the growing area of molecular electronics. For this purpose, Langmuir-Blodgett (LB) technique is favorable since it does not require heat which may decompose the molecules. Moreover, the thickness and molecular arrangement can be controlled by the layer-by-layer deposition.

Efforts to develop metallic LB films down to the low temperature continued last two decades [3,4], and finally reached the BEDO-TTF (oxygen-analog of BEDT-TTF, shown in Fig. 1(a)) and fatty acid system. The LB film made with BEDO-TTF and behenic acid (C22) showed metallic conduction down to 14 K [5]. The BEDO-TTF and fatty acid system is promising because the 2D ordered structure is spontaneously formed in the Langmuir film due to the strong self-aggregation nature of BEDO-TTF molecules [6]. Moreover, the charge transfer between the BEDO-TTF and the fatty acid occurs with help of oxygen [7]. It discards any secondary charge doping processes, which often introduce disorders into the film unfavorable for metallic conduction. Coherent 2D electron transport in the BEDO-TTF and stearic acid (C18) system has been demonstrated by the negative magnetoresistance in terms of the two-dimensional weak localization [8].

In this paper we report the fabrication and structural and transport measurements down to 0.7 K of the BEDO-TTF/arachidic acid (C20, shown in Fig. 1(b)) LB film deposited on mylar and glass substrate at ambient and applied pressure. The layered structure was observed by the X-ray diffraction. The metallic conduction was achieved down to ~80 K. Below 80 K, the conductivity decreased due to the weak localization as evidenced by the negative magnetoresistance. By applying hydrostatic pressure up to 1 GPa, the conductivity increased twice, but the temperature dependence did not change significantly.

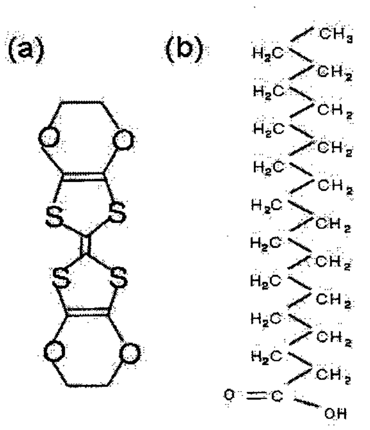

Fig. 1. BEDO-TTF molecules (a) and arachidic acid (C20) molecules.

## 2. EXPERIMENTAL

BEDO-TTF molecules were synthesized by the method described elsewhere [9]. The arachidic acid (C20) with purity 99 % was purchased with Merck Co. and used as received. Separate chloroform solutions of each material were prepared with molar concentration of

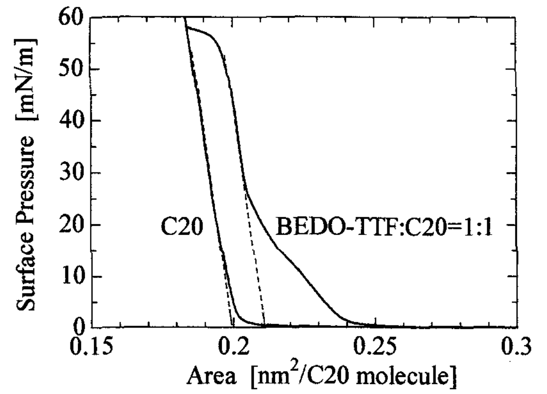

Fig. 2. The surface pressure-area isotherms of Langmuir films of pure C20 and 1:1 mixture of BEDO-TTF and C20.

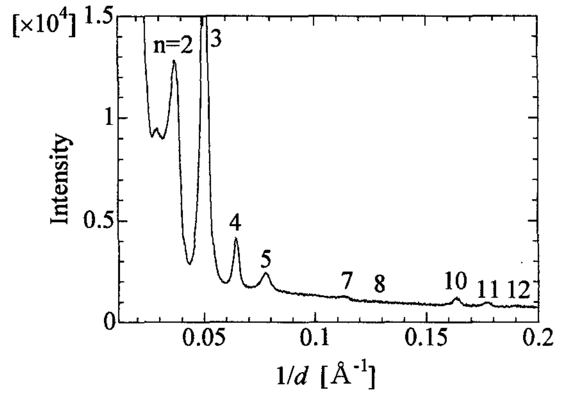

Fig. 3. The X-ray diffraction pattern from the BEDO-TTF/C20 LB film of 15 layers.

~$1\times10^{-3}$ mol/l. The substrate was either mylar (polyethylene-terephthalate, thickness 0.1 mm) or white-cut glass (thickness 0.7 mm). The surface roughness of the mylar film is ±20 nm and that of the glass is ±2 nm found by the atomic force microscopy. The substrate was sonicated once in ethanol and twice in ultra-pure water and was treated with ozone. Then four gold strips were thermally evaporated with separation of 0.6 mm. The thickness of the gold film was ~70 nm. Then the substrates were rinsed in ethanol and ultra-pure water and treated again with ozone before the LB film deposition.

The LB films were deposited by the vertical dipping method with a Langmuir trough equipped with a Wilhelmy balance and teflon moving walls (USI systems). Ultra-pure water subphase with pH=5.5 was prepared by a Milli Q system (Millipore) at 21℃. A mixed solution of BEDO-TTF and C20 with molar ratio of 1:1 was spread onto the water surface. Then, the moving walls compressed the molecules at a speed of 0.35 mm/sec until the surface pressure reached 30 mN/m. Then the LB film was deposited. Since the substrate is hydrophilic, the deposition started at the first upward stroke of the substrate immersed in the subphase. Then the number of layers increased at each downward and upward stroke. Resulting LB films were Y-type films. The dipping speed of the substrate was 5mm/min for mylar and 17 mm/min for glass. The transfer ratio of the film was about 0.15. It is probable that the LB films were deposited only between each Au electrode.

The X-ray diffraction was measured with the advanced thin film X-ray system (RIGAKU ATX-G) under a grazing incidence of X-ray (CuKα, $\lambda$=1.5418Å)

The electrical conductivity measurements were performed with the dc four-probe method. Four platinum wires (30 μm) were attached on the gold strips with graphite paste. Applied current was 1 μA and the current-voltage linearity was checked at several temperatures. The low temperature measurements were carried out with a glass dewar down to 4.2 K and a metal $^3$He cryostat down to 0.7 K. The temperature was measured with a calibrated Cernox thermometer. Typical cooling rate was 1 K/min. The magneto-conductance was measured with a 9 T superconducting magnet.

For measurements under pressure, a Be-Cu clamp type pressure cell (UNIPRESS) was used. We used a 1:1 mixture of Fluorinat FC70 and FC77 as the pressure transmitting medium. We found almost no noticeable degradation of the conductivity in the case of Fluorinat, however, in the case of the daphne 7373 oil which was used for the $2C_{14}$-Au(dmit)$_2$ system [10], the conductivity of the BEDO-TTF/C20 LB film decreased rapidly just by dipping (1/50 by 2 hours). The pressure values were calibrated with an In-Sb pressure gauge at room temperature. During cooling, the pressure values decreased by c.a. 0.3 GPa from those room temperature.

## 3. RESULTS

### 3.1 Surface pressure-area isotherms

In Fig. 2, we show surface pressure-area isotherms of Langmuir films of pure C20 and 1:1 mixture of BEDO-TTF and C20. For the C20 film, Cd$^{2+}$ was added to the subphase to stabilize the film. The occupied area per C20 molecule increased only 0.01 nm$^2$ by the association of the BEDO-TTF molecules to the C20. This result indicates that the occupied area is determined mainly by the lateral packing of the fatty acid, similar to the BEDO-TTF/C22 LB film [5]. It is possible that the BEDO-TTF/C20 LB film also adopts the double-layered structure similar to the case of the BEDO-TTF/C22 and BEDO-TTF/C18 LB films [5,8].

### 3.2 X-ray analysis

In order to find the layered structure directly, we performed low-angle X-ray diffraction analysis. Diffractions peaks corresponding to the indices $n$=2,3,4, 5,7,8,10,11,12 were identified, as shown in Fig. 3. From the Bragg condition, $n/d=(2\sin\theta)/\lambda$, the periodicity of the layer is deduced as $d$=6.2 nm. The periodicity of 6.2 nm is reasonable considering the doubled unit of the BEDO-TTF and C20 molecules. The value is just between those reported for the BEDO-TTF/C22 ($d$=6.6 nm) and BEDO-TTF/C18 ($d$=5.8 nm) LB films [5,8].

### 3.3 Layer dependence of conductivity

Figure 4 shows the evolution of the conductivity of a BEDO-TTF/C20 LB film on a mylar substrate with the increase of the number of layers. The conductivity of the films is calculated based on the estimated thickness

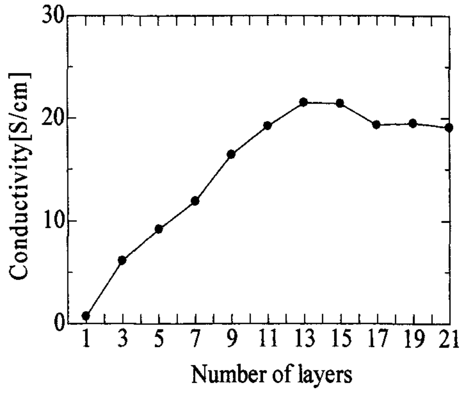

Fig. 4. The evolution of the conductivity of a BEDO-TTF/C20 LB film on a mylar substrate with increase of the number of layers.

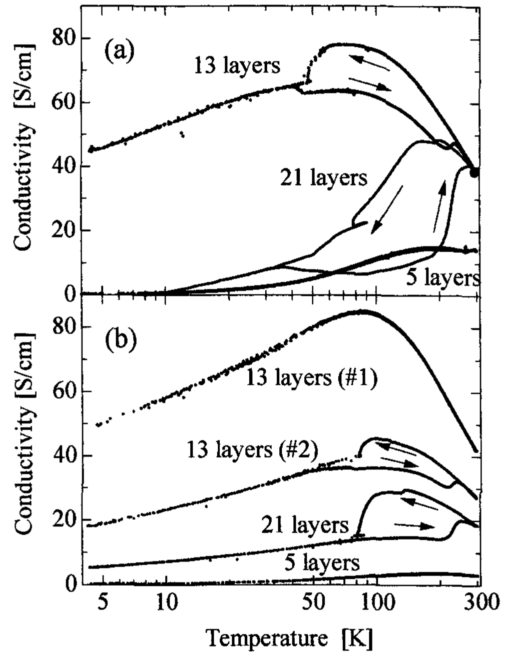

Fig. 5. The temperature dependence of the conductivity of the BEDO-TTF/C20 LB film of 5, 13, 21 layers on glass substrates (a) and mylar substrates (b).

of one BEDO-TTF/C20 unit layer of 3.1 nm according to the X-ray result. The conductivity increased up to 13 layers, and was constant or slightly decreased with further increase of the number of layers. In the case of glass substrate, we found the same result. At the thickness of 13 layers, the layered structure of the LB film is stabilized for the best electrical conduction.

The maximum value of the conductivity at room temperature was 40 S/cm. This is the same for the BEDO-TTF/C22 LB film, but slightly lower than BEDO-TTF/C18 LB film.

In Figs. 5(a) and 5(b), we show the temperature dependence of the conductivity of the LB films of 5, 13, 21 layers on glass (a), and mylar (b) substrates. Arrows indicate the direction of the temperature sweep.

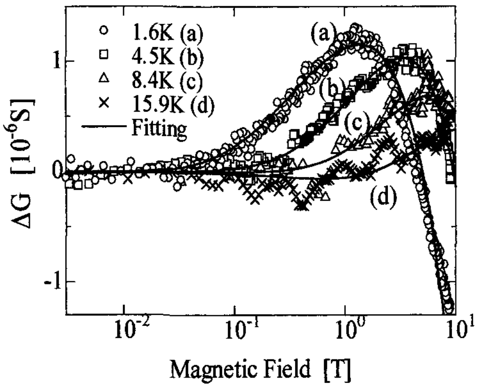

Fig. 6. Magnetoconductance of the BEDO-TTF/C20 LB film at low temperatures. Solid lines are fit to the equation (1) with parameters listed in Table I.

The metallic conduction was achieved from room temperature to 80 K for the LB film of the optimum thickness of 13 layers. In the 13 layer LB film, the decrease in conductivity in the low temperature region obeys the temperature dependence of log$T$ due to the localization effect similar to the BEDO-TTF/C18 LB film [8]. Down to 0.7 K, there was no sign of the occurrence of the superconductivity. A large hysteresis of the conductivity with respect to the temperature sweep appeared in the temperature range between 30 and 270 K. Difference in conductivity between cooling and heating processes, normalized with the conductivity value at room temperature, became larger with the increase of the number of the layers. For the film of 5 layers, no hysteresis was found for both substrates. At the same number of layers, the difference in conductivity was larger for the glass substrate than for the mylar substrate.

### 3.4 Magnetoconductance

Figure 6 shows the transverse magnetoconductance $\Delta G=G(B)-G(0)$ under the magnetic field $B$ applied perpendicular to the substrate of the LB film of 13 layers. The positive magnetoconductance (negative magnetoresistance) with conductance maximum at 1-2 T was observed below 10 K, similar to those reported for the BEDO-TTF/C18 LB film. In the 2D weak localization theory, the negative magnetoresistance is explained in terms of the reducing area of the coherent motion of electrons by the cyclotron motion under the magnetic field [8]. The magnetoconductance is written as,

$$\Delta G = A_1\frac{e^2}{2\hbar\pi^2}\left[\ln\left(\frac{B}{B_i}\right)-\psi\left(\frac{1}{2}+\frac{B}{B_i}\right)\right]-A_2B^{\alpha} \qquad (1)$$

where $B_i=\hbar/4eL_{Th}^2$, $\psi$ is the digamma function. $A_1$, $A_2$, and $\alpha$ are scaling parameters used in the fitting. The Thouless length $L_{Th}$ is the characteristic length in which the phase coherence of the electronic motion is preserved. The observed magnetoconductance is fitted with the parameters listed in Table I. These parameters are in fairly agreement with values for the BEDO-TTF/C18 and BEDO-TTF/C22 LB films [8,11].

Table I. The parameters found in the fitting procedure of the magnetoconductance.

| Temperature [K] | $L_{Th}$ [nm] | $A_1$ | $A_2$ | $a$ |
|---|---|---|---|---|
| 1.6 | 82 | 0.078 | $0.70\times10^6$ | 0.94 |
| 4.5 | 38 | 0.089 | $0.15\times10^6$ | 1.3 |
| 8.4 | 24 | 0.100 | $0.14\times10^6$ | 1.07 |
| 15.9 | 17 | 0.104 | $0.18\times10^6$ | 0.80 |

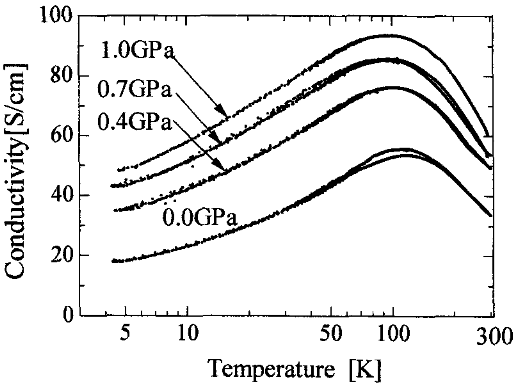

Fig. 7. The temperature dependence of the conductivity under pressures up to 1 GPa.

The Thouless length decreases with increasing temperature representing the increase in the scattering rate of electrons by phonons. The successful treatment with 2D localization theory represents the 2D coherent electron conduction occurs in the present BEDO-TTF/C20 LB films.

### 3.5 Conductivity under pressure

In Fig. 7, we show the temperature dependence of the conductivity of a LB film deposited on the mylar substrate (15 layers) under pressure. The hystersis was suppressed under a pressure of 0.4 GPa. By applying further pressure up to 1 GPa, the conductivity increased at most twice as much as that at ambient pressure. The hysteretic behavior was suppressed under pressure. However, the overall temperature dependence was almost unchanged with the application of pressure.

## 4. DISCUSSION

The thermal hysteresis in conductivity appeared for the thick film, and was more remarkable for glass substrate case than for mylar substrate case. Hysteresis phenomena in conductivity of organic conductors are often interpreted in terms of the microcracks during cooling [1]. Microcracks in the present LB film are possibly caused by the mismatch in the thermal contraction between the film and the substrate. The thermal contraction down to the liquid helium temperature is 0-0.1 % for the glass and 0.4-0.5 % for the mylar (estimated by the room temperature thermal expansion coefficient of $1.7\times10^{-5}$ /K [12]). The typical thermal contraction of the organic conductors made of TTF-like molecules is about 1 % [1], so that the LB film shrinks more than the substrate. Thermal contraction of thin films is governed by that of the substrate, however, thick films exhibit their own thermal contraction relative to the substrate. As a result, thick films tend to crack by cooling. This tendency is stronger in the case of glass substrate with larger thermal contraction difference. Such cracking of the LB films is suppressed under pressures.

## 5. CONCLUSION

We fabricated BEDO-TTF/arachidic acid LB films metallic down to 80 K. We have successfully deposited LB films on flexible mylar substrates, that is advantageous for the future application. The conductivity hit maximum at the thickness of 13 layers. A large thermal hysteresis in the temperature region of 30-270 K was observed for the thick film, which may be caused by the mismatch in thermal contraction between the LB film and the substrate. The 2D coherent transport is demonstrated by the presence of the negative magnetoresistance similar to the BEDO-TTF/C18 and BEDO-TTF/C22 LB films. Under pressure, the conductivity increased at most twice with suppression of the thermal hystersis, however, the over-all temperature dependence remained unchanged.

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