

Electrical Properties of the Dialkyldimethylammonium-Au(dmit)<sub>2</sub> LB FilmsMasaaki Kitao<sup>1</sup>, Haruki Matsui<sup>1</sup>, Shin-ichi Morita<sup>1,†</sup>, Yasuhiro F. Miura<sup>1\*</sup>, Michio Sugi<sup>1</sup>,  
Masato Hedo<sup>2</sup> and Yoshiya Uwatoko<sup>2</sup><sup>1</sup>Graduate School of Engineering, Toin University of Yokohama

1614 Kurogane-cho, Aoba-ku, Yokohama, 225-8502 JAPAN

Fax: +81-(0)45-974-5290, \* e-mail: yfmiura@toin.ac.jp

<sup>2</sup>ISSP, University of Tokyo, 5-1-5 Kashinoha, Kashiwa 277-8581 Japan

The resistance of the Langmuir-Blodgett films based on ditetradecyldimethylammonium-Au(dmit)<sub>2</sub> (2C<sub>14</sub>-Au(dmit)<sub>2</sub>) salt was measured along the film plane using electrode gaps of 0.5 mm and 5 μm in a wide temperature range of 27-290 K. In case the electrode gap is 0.5 mm, the LB film shows a weak metallic behavior from room temperature down to around 200-250 K with a positive temperature derivative of the resistance, but it shows a negative temperature derivative of the resistance below the temperature. However, in case the electrode gap is 5 μm, the metallic temperature dependence of the resistance extends down to the lower temperature range of 58-106 K. The atomic force microscopy (AFM) has revealed that the LB film consists of crystallites, which are 1-5 μm in lateral sizes and 4-20 nm in thickness. We hypothesize that the broad minimum of the resistance vs. temperature plot emerges in a crossover region, where metallic nature inside the crystallites are competing with the random potentials set up by grain boundaries and/or defects, and then, the metallic temperature dependence extends down to the lower temperature by narrowing the electrode gap.

**Key words:** Langmuir-Blodgett films, Au(dmit)<sub>2</sub> complexes, Electrochemical oxidation, Electrical conductivity, Atomic force microscopy (AFM)

## 1. INTRODUCTION

Since the Langmuir-Blodgett (LB) technique allows us to assemble organic molecules into tailored two-dimensional (2D) molecular sheets with fairly low energy cost, the technique has attracted a great deal of attention [1]. Among various functions of 2D assemblies of organic molecules, realization of highly conductive LB systems is one of the important subjects [2].

The metal(dmit)<sub>2</sub> complex, where metal=Au, Ni, Cu, Zn, Pt or Pd and H<sub>2</sub>dmit=4,5-dimercapto-1,3-dithiole-2-thione, has been regarded as a good candidate for fabricating the conductive LB systems because the bulk salts exhibit a wide variety of electrical properties ranging from semiconductors to superconductors [3]. We have already reported that the Langmuir-Blodgett (LB) films of dialkyldimethylammonium-Au(dmit)<sub>2</sub> (2C<sub>n</sub>-Au(dmit)<sub>2</sub>, n=8, 10, 12, 14, 16, 18, Fig. 1) salts show high in-plane conductivity of 10<sup>0</sup>-10<sup>2</sup> S/cm. Among them, the LB system based on ditetradecyldimethylammonium-Au(dmit)<sub>2</sub> [2C<sub>14</sub>-Au(dmit)<sub>2</sub>] salt exhibits a high lateral conductivity of 40-100 S/cm at room temperature with a metallic temperature dependence of the conductivity in the range of 230-300 K after electrochemical oxidation [4]. Furthermore, the ac magnetic susceptibility and resistance suggest the existence of a superconducting phase below 4 K [5-7].

In general, charge-transfer (CT) complexes and radical salts tend to form domains, which are several microns in lateral sizes, at the air/water interface in spite

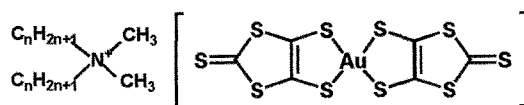


Fig. 1. Molecular structure of the 2C<sub>n</sub>-Au(dmit)<sub>2</sub> salt.

of the introduction of alkyl chains in the molecular systems. Thus, in order to evaluate the intrinsic electrical properties of the LB films, the resistance should be measured using an electrode gap equal to the domain size or even smaller one. So far, in our series of works on the conductive LB films of the 2C<sub>n</sub>-Au(dmit)<sub>2</sub> (n=8, 10, 12, 14, 16, 18) salts, the electrode gap for measuring the conductivity is 0.5 mm. In this paper, we report on the resistance of the 2C<sub>14</sub>-Au(dmit)<sub>2</sub> LB films measured using an inter-digitated electrode gap of 5 μm in the temperature range of 27-290 K together with the morphological studies by atomic force microscopy (AFM).

## 2. EXPERIMENTAL

## 2.1 Sample Preparation

The 2C<sub>14</sub>-Au(dmit)<sub>2</sub> salt (Fig. 1, n=14) was synthesized following the procedure of Steimecke *et al.* [8] and spread on the surface of pure water (17°C) using a 1:1 mixture of acetonitrile and benzene. After keeping the salts on the water surface for five minutes,

<sup>†</sup>Present address: Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, U.S.A

they were compressed up to 25 mN/m and transferred onto a 0.5-mm thick electrode-coated quartz plate, 0.1-mm thick poly(ethylene terephthalate) (PET) film or Si(100) substrate. A NIMA Type 622 trough was used. Twenty layers were deposited unless otherwise stated. The electrode-coated quartz plate is a BAS Type 011064 Mirco-Electrode with an inter-digitated gap of 5  $\mu\text{m}$  [Figs. 2(a) and 2(b)]. The PET-film substrate was a sample batch (Type S100) provided by Mitsubishi Polyester GmbH. The Si(100) substrate was cut from a commercially available wafer (*n*-type, 1-10  $\Omega \cdot \text{cm}$ ). The PET substrate was hydrophobized by five layers of the LB film of cadmium arachidate. Then, gold was vacuum-evaporated through a mask to form four electrode strips separated by a gap of 0.5 mm, as shown in Fig. 2(c). The electrode-coated quartz plate and the Si(100) substrate were hydrophobized by keeping them in a container filled with the vapor of 1,1,1,3,3,3-

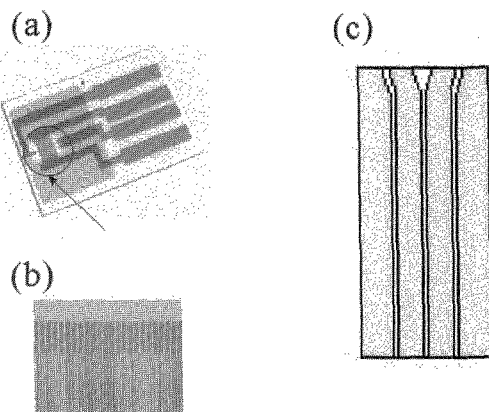


Fig. 2. (a) The electrode-coated quartz plate with an inter-digitated electrode gap of 5  $\mu\text{m}$ ; the inter-digitated area is surrounded by the open circle and the arrow (BAS Type 011064). (b) The area with the inter-digitation. (c) The 0.1-mm thick PET substrate coated by four gold strips with a gap of 0.5 mm.

hexamethyldisilazane for more than a day.

The as-deposited films were immersed in an aqueous solution of  $\text{LiClO}_4$  (0.1 M) and electrochemically oxidized by a constant current of 0.8  $\mu\text{A}$ . The gold electrode underneath the  $2\text{C}_{14}\text{-Au(dmit)}_2$  layer was used as the working electrode. The counter electrode was platinum. The details of the sample preparation are in our previous papers [4-7, 9].

### 2.2 Measurement of electrical resistance

For monitoring the resistance during the electrochemical oxidation process, the samples were taken out from the electrolyte and dried by nitrogen gas, and then, the resistance were measured by a *dc* two probe method using a SANWA AU-32 multimeter or Keithley Type 2001 digital multimeter at room temperature.

The temperature dependence of the resistance was

measured by an *ac* four-probe method using a LakeShore Model 370 AC Resistance Bridge combined with a LakeShore Model 3716 Scanner or by a *dc* four probe method using Keithley Type 2001 digital multimeter combined with a Keithley Type 220 programmable current source. The resistance was measured along the film plane using the gold electrode strips underneath the LB films.

### 2.3 Morphological observation

The surface of the  $2\text{C}_{14}\text{-Au(dmit)}_2$  film at the air/water interface was observed by Brewster angle microscopy (BAM) using a USI BAM system.

The surface structure of the  $2\text{C}_{14}\text{-Au(dmit)}_2$  films transferred on the hydrophobized Si(100) substrate was observed by a JEOL Model JSPM-4210 atomic force microscope (AFM) using a contact mode.

## 3. RESULTS AND DISCUSSION

In case the electrode gap is 0.5 mm, the conductivity at room temperature gradually increases with the oxidation until  $T_{\text{ox}}$  (oxidation time) in the range of 150-180 min but it turns to decrease with further oxidation [9]. However, in case the inter-digitated electrode gap of 5  $\mu\text{m}$  is used, the conductivity increases until  $T_{\text{ox}}$  in the range 60-80 min and it turns to decrease with further oxidation. The difference of  $T_{\text{ox}}$  values that realize the maximal conductivity is considered to be partly due to the difference of the areas of the LB films immersed in the electrolyte\* but further characterization is now in progress.

Figure 3 shows typical temperature dependence of the resistance measured by the electrode gaps of 5  $\mu\text{m}$

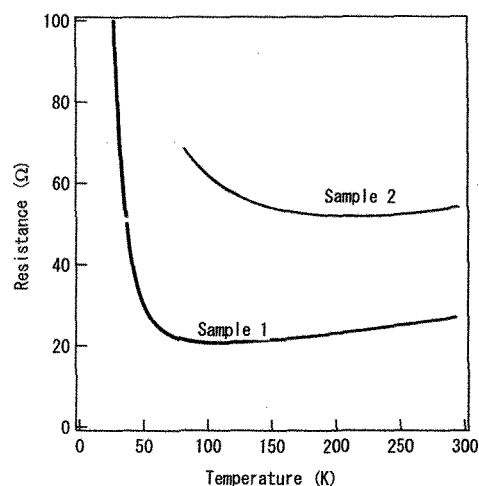


Fig. 3. Typical temperature dependence of the  $2\text{C}_{14}\text{-Au(dmit)}_2$  LB films measured with the electrode gaps of 5  $\mu\text{m}$  (Sample 1) and 0.5 mm (Sample 2).

\* The film areas immersed in the electrolyte are  $13 \times 10 \text{ mm}^2$  and  $2 \times 3 \text{ mm}^2$ , as for the samples of the electrode gaps of 0.5 mm and 5  $\mu\text{m}$ , respectively.

(Sample 1) and that of 0.5 mm (Sample 2). The values of the oxidation time ( $T_{\text{ox}}$ ) were  $T_{\text{ox}}=60$  min and

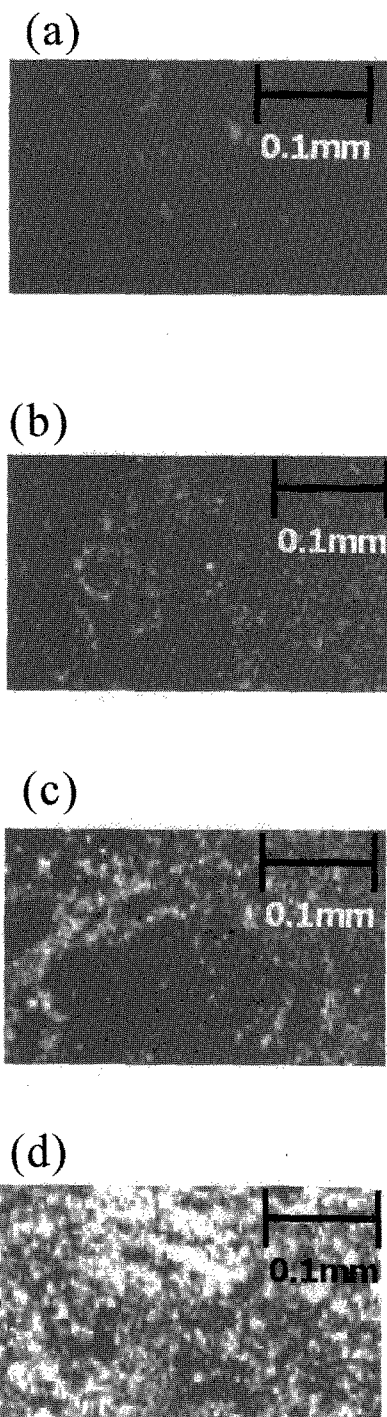


Fig. 4. Brewster angle microscopy (BAM) images of the  $2C_{14}\text{-Au(dmit)}_2$  film at the air/water interface recorded at the surface pressure of 0 mN/m (a), 10 mN/m (b), 25 mN/m and 40 mN/m.

$T_{\text{ox}}=150$  min, for Sample 1 and Sample 2, respectively. As shown in Fig. 3, the metallic behavior of the resistance of Sample 1 extends down to 106 K while that of Sample 2 is down to around 215 K. The broad minimum of the resistance vs. temperature plot differs from sample to sample but they were in the range of 200-250 K in case the electrode gap is 0.5 mm, while they were in the range of 58-106 K in case that is 5  $\mu\text{m}$ .

Figure 4 shows Brewster angle microscopy (BAM) images recorded with increasing the surface pressure in the range 0-40 mN/m. As shown in Fig. 4(a), even at 0 mN/m, some domains, which are 5-30  $\mu\text{m}$  in lateral sizes, are seen. It appears that the surface coverage by the domains increases with increasing the surface pressure up to 25 mN/m, as shown in Figs. 4(a), 4(b) and 4(c). We currently assume that the darker flat regions in Figs. 4(b) and 4(c) are also filled with the relatively thin film of the  $2C_{14}\text{-Au(dmit)}_2$  salt because the diffusion speed of the domains at the air/water interface is extremely slow in case the surface pressure is in the range 10-40 mN/m.

Figure 5 shows a typical atomic force microscopy (AFM) image of the  $2C_{14}\text{-Au(dmit)}_2$  film transferred on the Si(100) wafer by "one single transfer". The film consists of thin plate-like crystallites, which are 1-5 microns in lateral size and 4-20 nm in thickness. Thus, the electrode gap of 0.5 mm is two orders of magnitude larger than the lateral size of the crystallites, and the resistance measured by the 0.5-mm gap is possibly influenced by the random potentials set up by the grain boundaries and/or defects. We currently hypothesize that the narrower electrode gap of 5  $\mu\text{m}$  allows us to detect the intrinsic electronic properties of the LB system and that the metallic behavior extends down to around 106 K.

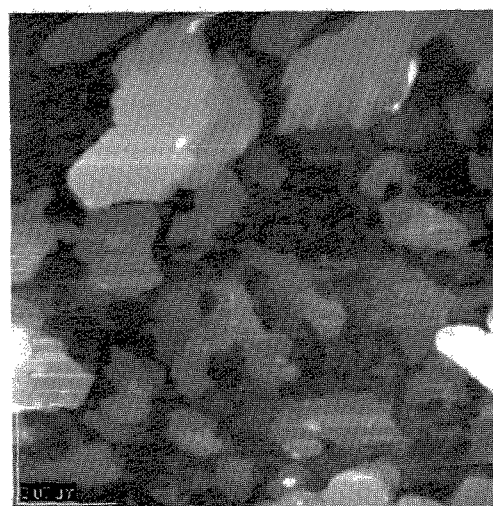
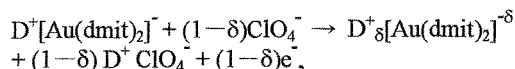


Fig. 5. Typical atomic force microscopy (AFM) image of the  $2C_{14}\text{-Au(dmit)}_2$  film transferred on the Si(100) wafer by "one single transfer".

During the electrochemical oxidation, we postulate that the  $\text{ClO}_4^-$  anions are incorporated in the film for the

compensation of the charge as follows:



where  $D^+$ =ditetradecyldimethylammonium and  $\delta$ =charge transfer ratio ( $0 < \delta < 1$ ) [9]. The morphology of the film may change because of the rearrangement during the post treatment. In fact, we have already reported on the studies by the infrared (IR) spectroscopy that the order of the alkyl chains changes remarkably during the electrochemical oxidation [9]. Further studies on the morphology of the electrochemically-oxidized film are now in progress.

#### 4. CONCLUSION

The resistance of the Langmuir-Blodgett Films based on ditetradecyldimethylammonium-Au(dmit)<sub>2</sub> (2C<sub>14</sub>-Au(dmit)<sub>2</sub>) salt was measured along the film plane using electrode gaps of 0.5 mm and 5  $\mu$ m in a temperature range of 27-290 K. In case the electrode gap is 0.5 mm, the LB film shows a weak metallic behavior from room temperature down to around 200-250 K with a positive temperature derivative of the resistance, but it shows a negative temperature derivative of the resistance below the temperature. However, in case the electrode gap is 5  $\mu$ m, the metallic temperature dependence of the resistance extends down to the lower temperature range of 58-106 K. The atomic force microscopy (AFM) has revealed that the LB film consists of crystallites, which are 1-5  $\mu$ m in lateral sizes and 4-20 nm in thickness. We hypothesize that the broad minimum of the resistance vs. temperature plot emerges in a crossover region, where metallic nature inside the crystallites are competing with the random potentials set up by grain boundaries and/or defects, and then, the metallic temperature dependence extends down to lower temperatures by narrowing the electrode gap.

#### ACKNOWLEDGMENT

This work was supported in part by Grant-in-Aid for Scientific Research of MEXT (Ministry of Education, Culture, Sports, Science and Technology, Japan) under Grant No. 12750019, University-Industry Join Research Project for Private University: matching fund subsidy from MEXT, 2002-2007 and KAST (Kanagawa Academy of Science and Technology, Japan) under Grant No. 0012011.

#### REFERENCE

- [1] A. Ulman, "An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to Self-Assembly", Academic Press, San Diego (1991).
- [2] T. Nakamura, "Handbook of Organic Conductive Molecules and Polymers", Ed. by H. S. Nalwa, Wiley, New York (1997), Vol. 1, Chap. 14 (*Electrically Conductive Langmuir-Blodgett Films*), pp. 728-773.
- [3] "Organic Superconductors", Ed. by T. Ishiguro, K. Yamaji and G Saito, Springer Series in Solid-State Sciences, Springer, Berlin (1997).
- [4] Y. F. Miura, Y. Okuma, H. Ohnishi, T. Kawasaki and M. Sugi, *Jpn. J. Appl. Phys.*, **37**, L1481-L1483 (1998).
- [5] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi, *Solid State Comm.*, **113**, 603-605 (2000).
- [6] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi, *Synth. Met.*, **120**, 727-728 (2001).
- [7] Y. F. Miura, M. Horikiri, S. Tajima, T. Wakaita, S.-H. Saito and M. Sugi, *Synth. Met.*, **133-134**, 663-664 (2003).
- [8] G. Steimecke, H. J. Sieler, P. Kirmse and E. Hoyer, *Phosphorus Sulfur*, **7**, 49-55 (1979).
- [9] R. Watanabe, S. Morita, Y. F. Miura and M. Sugi, *Trans. Mater. Res. Soc. Jpn.* **30**, 135-138 (2005).

(Received March 31, 2006; Accepted April 10, 2006)