

Highly-conductive LB films of Dioctyldimethylammonium-Au(dmit)₂ SaltMasato Takagi, Yuuki Takigawa, Shin-ichi Morita[†],
Yasuhiro F. Miura* and Michio SugiGraduate 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

The resistance of the Langmuir-Blodgett (LB) films of dioctyldimethylammonium-Au(dmit)₂ (2C₈-Au(dmit)₂) salt was measured along the film plane using electrode gaps of 0.5 mm and 5 μm in the temperature range of 7-290 K. In case the electrode gap is 0.5 mm, the LB film shows an activation-type behavior in the temperature range measured, while in case that is 5 μm, a distinct metallic temperature dependence of the resistance is observed in the temperature range of 48-290 K. By the infrared (IR) spectroscopy, it has been revealed that the order of the hydrocarbon chains decreases noticeably in the first 60 min of the electrochemical oxidation, which corresponds well with the stage of the increase in the conductivity. We hypothesize that the activation-type behavior of the resistance obtained by the electrode gap of 0.5 mm is due to random potentials set up by grain boundaries and/or defects and that the metallic nature inside the crystallites emerges by narrowing the electrode gap.

Key words: Langmuir-Blodgett (LB) films, Au(dmit)₂ complexes, Electrochemical oxidation, AC resistance, Infrared (IR) spectroscopy

1. INTRODUCTION

Fabrication of two-dimensional (2D) molecular assemblies that have metallic or even superconducting property is one of our ultimate goals in the research area of molecular electronics because it may allow us to step forward from conductive molecular sheets to conductive molecular wires.

We have already reported that the LB system based on ditetradecyldimethylammonium-Au(dmit)₂ [2C₁₄-Au(dmit)₂] 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 [1]. Furthermore, the ac magnetic susceptibility and resistance suggest the existence of a superconducting phase below 4 K [2-4].

Recently, we have also reported that the LB system based on the dioctyldimethylammonium-Au(dmit)₂ [2C₈-Au(dmit)₂, Fig. 1] salt exhibits a high conductivity up to 17 S/cm at room temperature without any secondary treatment, which is different from the analogous systems with longer alkyl chains [2C₁₄-Au(dmit)₂ and 2C₁₈-Au(dmit)₂ LB systems] [5]. Furthermore, the conductivity increases by the electrochemical oxidation, reaching 50 ± 23 S/cm at room temperature [5].

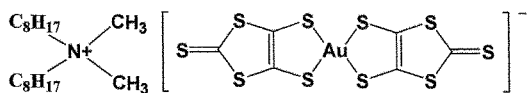


Fig. 1. Molecular structure of the 2C₈-Au(dmit)₂ salt.

Since charge-transfer complexes and radical salts tend to form domains in spite of the introduction of the alkyl chains [6], the resistance should be measured using an electrode gap of that dimension in order to evaluate the intrinsic electrical conduction. In this paper, we report on the AC resistance measured using electrode gaps of 0.5 mm and 5 μm together with some preliminary results of the infrared spectra.

2. EXPERIMENTAL

2.1 Sample Preparation

The 2C₈-Au(dmit)₂ salt (Fig. 1) was synthesized following the procedure of Steimecke *et al.* [7] 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, they were compressed up to 25 mN/m and transferred onto a 0.1-mm thick poly(ethylene terephthalate) (PET) film or 0.5-mm thick quartz plate. The PET film was a sample batch (Type S100) provided by Mitsubishi Polyester GmbH and the surface 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 prior to the 2C₈-Au(dmit)₂ transfer. The electrode-coated quartz plate is a BAS Type 011064 Micro-Electrode with an inter-digitated gap of 5 μm and the surface was hydrophobized by keeping them in a container filled with the vapor of 1,1,1,3,3,3-hexamethyldisilazane for more than a day. A NIMA Type 622 trough system was used.

The as-deposited films were immersed in an

[†]Present address: Department of Chemistry, The University of Georgia, Athens, GA 30602-2556, U.S.A

aqueous solution of LiClO₄ (0.1 M) and electrochemically oxidized by a constant current of 0.8 μ A. The gold electrode underneath the 2C₈-Au(dmit)₂ layer was used as the working electrode. The counter electrode was of platinum. The details of the sample preparation are given in our previous papers [1-4].

2.2 Characterization

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.

Infrared (IR) absorption spectra were measured at 4 cm⁻¹ resolution using a JASCO FT-IR Spectrometer. In order to obtain spectra with a high signal-to-noise ratio, 128 interferograms were co-added. The as-deposited film or the electrochemically-oxidized film taken out from the electrolyte and dried by nitrogen gas was set in the spectrometer equipped with a reflection attachment, JASCO RF-81S. The reflection absorption spectra were measured utilizing the interface of the LB films of 2C₈-Au(dmit)₂ salt and gold. A non-polarized incident, which is tilted 12 degrees from the surface normal, was used.

3. RESULTS AND DISCUSSION

The film-forming material, the 2C₈-Au(dmit)₂ salt, was synthesized as follows. A methanol solution (40 ml) of sodium methoxide (5.32 mmol) was added to a methanol solution (40 ml) of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (1.09g, 2.68 mmol). 20 ml methanol solution of sodium tetrachloroaurate (511 mg, 1.28 mmol) was added. Then a methanol solution (20 ml) of dioctyldimethylammonium bromide (439 mg,

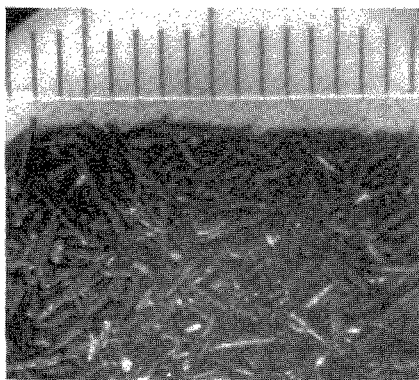


Fig. 2. The film-forming material obtained as black and shiny plate-like crystals.

1.28 mmol) was added. All the procedures were performed under N₂ flowing at 293 K. By performing the recrystallization in methanol solution for three times, the compound was obtained as black and shiny plate-like crystals, as shown in Fig. 2.

Figure 3 shows typical temperature dependence of the resistance measured by the electrode gap of 0.5 mm (Samples A1 and A2) and that of 5 μ m (Sample B1). So far, by the measurement of the electrode gap of 0.5 mm, the 2C₈-Au(dmit)₂ LB films have shown an activation-type behavior in the temperature range measured, as shown in Fig. 3 (Samples A1 and A2), while the film shows a distinct metallic behavior by the measurement of the inter-digitated electrode gap of 5 μ m (Sample B1). The metallic behavior of Sample B1 extends down to around 47 K.

We have already reported that the analogous LB

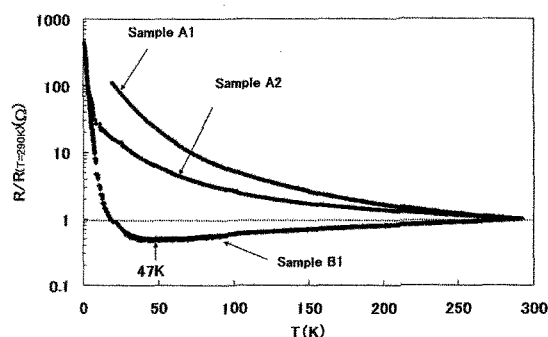


Fig. 3. Temperature dependence of the resistance, $R/R(T=290\text{ K})$, of the 2C₈-Au(dmit)₂ LB films measured with the electrode gaps of 0.5 mm (Sample A1 and Sample A2) and 5 μ m (Sample B).

system, 2C₁₄-Au(dmit)₂ LB system, consists of crystallites, which are 1-5 μ m in lateral sizes and 4-20 nm in thickness. We postulate that the 2C₈-Au(dmit)₂ LB system also consists of thin crystallites of similar dimensions and that the metallic nature inside the crystallites can not be seen by the measurement of the electrode gap of 0.5 mm, which is possibly two orders of magnitude larger than the domain size. We have already reported that the 2C₁₄-Au(dmit)₂ LB film shows a weak metallic temperature dependence in the range of 230-300 K by the measurement of 0.5 mm gap [1], while the 2C₈-Au(dmit)₂ LB film shows no metallic behavior with the same electrode gap.

Figure 4(a) shows infrared (IR) absorption spectra of the 2C₈-Au(dmit)₂ LB film in the region of 2800-3000 cm⁻¹ with T_{ox} (time for applying the constant electrical current of 0.8 μ A) in the range of 0-180 min. The distinct absorption bands located at around 2850 cm⁻¹ and 2920 cm⁻¹ are due to the CH₂ symmetric stretching mode (ν_s) and CH₂ antisymmetric one (ν_{as}), respectively. For each band, the absorbance decreases noticeably in the first 60 min, which corresponds well with the increase in conductance as shown in Fig. 4(b). The decrease in the two stretching modes is associated with the appreciable broadening, as clearly seen in Fig. 4(a). On the contrary, the two stretching modes of the 2C₁₄-Au(dmit)₂ LB system increase in absorbance associated with the appreciable sharpening in band

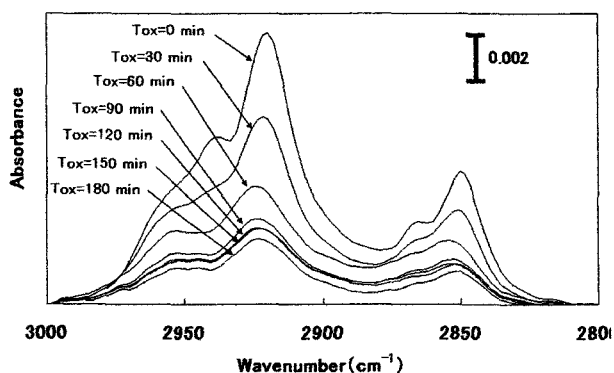


Fig. 4(a) Infrared (IR) absorption spectra of the $2C_8$ -Au(dmit) $_2$ LB film in the region of 2800 - 3000 cm^{-1} with T_{ox} (time for applying the constant electrical current of 0.8 μA) in the range of 0 - 180 min.

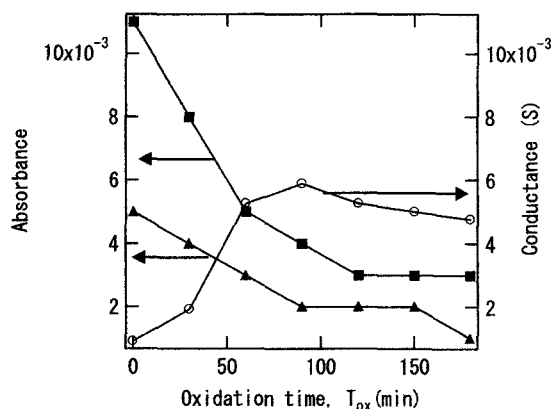


Fig. 4(b) The absorbance peaks at 2850 cm^{-1} (CH_2 ν_s , ▲) and at 2920 cm^{-1} (CH_2 ν_{as} , ■) together with the conductance (○) plotted against the oxidation time, T_{ox} .

shape [8]. It is considered that the alkyl chains in electrochemically-oxidized $2C_8$ -Au(dmit) $_2$ film have more disordered than those in the $2C_{14}$ -Au(dmit) $_2$ film and that the random potentials set up by disorders may limit the macroscopic conductivity in the $2C_8$ -Au(dmit) $_2$ LB film. Further studies on the IR spectra of the $2C_8$ -Au(dmit) $_2$ LB films are now under way together with the morphological studies by atomic force microscopy (AFM).

4. CONCLUSION

The resistance of the Langmuir-Blodgett films of dioctyldimethylammonium-Au(dmit) $_2$ [$2C_8$ -Au(dmit) $_2$] salt was measured along the film plane using electrode gaps of 0.5 mm and 5 μm in the temperature range of 7 - 290 K. In case the electrode gap is 0.5 mm, the LB film shows an activation-type behavior in the temperature range measured, while in case that is 5 μm , a distinct metallic temperature dependence of the resistance is observed in the temperature range of 48 - 290 K. The distinct absorption peaks located at

around 2850 cm^{-1} and 2920 cm^{-1} , which are due to the CH_2 symmetric stretching mode (ν_s) and CH_2 antisymmetric one (ν_{as}), respectively, decrease with the electrochemical oxidation with the pronounced broadening. In particular, the change is noticeable in the first 60 min in the post treatment, which corresponds well with the increasing stage in conductance. We hypothesize that the activation-type behavior of the resistance obtained by the electrode gap of 0.5 mm is due to random potentials set up by grain boundaries and/or defects and that the metallic nature inside the crystallites emerges by narrowing the electrode gap down to 5 μm .

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 Joint 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] Y. F. Miura, Y. Okuma, H. Ohnishi, T. Kawasaki and M. Sugi, *Jpn. J. Appl. Phys.*, **37**, L1481-L1483 (1998).
- [2] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi, *Solid State Comm.*, **113**, 603-605 (2000).
- [3] Y. F. Miura, M. Horikiri, S.-H. Saito and M. Sugi, *Synth. Met.*, **120**, 727-728 (2001).
- [4] Y. F. Miura, M. Horikiri, S. Tajima, T. Wakaita, S.-H. Saito and M. Sugi, *Synth. Met.*, **133-134**, 663-664 (2003).
- [5] Y. Takigawa, R. Watanabe, S. Morita, Y. F. Miura and M. Sugi, *Jpn. J. Appl. Phys.*, **45**, 394-396 (2006).
- [6] 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.
- [7] G. Steimecke, H. J. Sieler, P. Kirmse and E. Hoyer, *Phosphorus Sulfur*, **7**, 49-55 (1979).
- [8] R. Watanabe, S. Morita, Y. F. Miura and M. Sugi, *Trans. Mater. Res. Soc. Jpn.* **30**, 135-138 (2005).

(Received March 6, 2006; Accepted March 31, 2006)