

Study on Structure and Electrical Properties of Alkylammonium-Au(dmit)₂ LB Films

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The ditetradecyldimethylammonium-Au(dmit)₂ (2C₁₄-Au(dmit)₂) salt can be transferred onto solid substrates reproducibly up to 160 layers. The conductance of the 2C₁₄-Au(dmit)₂ film of single layer does not increase by the electrochemical oxidation and is less than 10⁻⁷ S. As for the samples with thickness more than two layers, the conductance increases with increasing the time of the electrochemical oxidation (*T*_{ox}) reaching the maximum conductance, *G*_{max}, and, then, decreases gradually. The *G*_{max} increases from 10⁻⁶ S up to 10⁻³ S with increasing the thickness in the range of 2-4 layers obeying *G*_{max} ∝ *N*^{2.9}. We postulate that the macroscopic conduction paths are formed by the accumulation of the molecular layer in the thickness range of 2-4 layers. In the thickness range of 4-40 layers, the *G*_{max} is approximately proportional to *N* (the least-square fitting gives *G*_{max} ∝ *N*^{1.3}), indicating that the molecular layers can be oxidized uniformly to give a uniform conductivity. In the range of 40-160 layers, however, *G*_{max} is almost constant with the average value of 2.04 × 10⁻² S, indicating that the surface layers cannot be oxidized effectively and do not contribute to the macroscopic conduction significantly if the total number of layers is more than *ca.* 40.

Key words: Langmuir-Blodgett films, Au(dmit)₂ complexes, Electrochemical oxidation, Electrical conductivity, Atomic force microscopy (AFM), UV/visible spectroscopy

1. INTRODUCTION

The Langmuir-Blodgett technique has attracted a great deal of attention, because it allows us to assemble functional molecules into tailored two-dimensional (2D) molecular sheets [1]. Among various trials for fabricating functional LB systems, realization of highly conductive LB systems is one of the important subjects [2].

The metal(dmit)₂ complex, where metal=Au, Ni, Cu, Zn, Pt or Pd and H₂dmit=4,5-dimercapto-1,3-dithiole-2-thione, has been regarded as a promising candidate for fabricating conductive LB systems because the bulk salts exhibit a variety of electronic properties ranging from semiconductors to superconductors [3]. We have already reported that the Langmuir-Blodgett (LB) films of dialkyldimethylammonium-Au(dmit)₂ (2C_{*n*}-Au(dmit)₂, *n*=8, 10, 12, 14, 16, 18, Fig. 1) salts exhibit high in-plane conductivity in the range of 10⁰-10² S/cm. Among them, the LB system based on ditetradecyldimethylammonium-Au(dmit)₂ [2C₁₄-Au(dmit)₂] salt exhibits a high lateral conductivity of 40 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, on the water surface, charge-transfer (CT) complexes and radical salts tend to form domains, which are several microns in lateral size in spite of the introduction of alkyl chains in the molecular systems. Therefore, in order to evaluate the intrinsic electronic properties of the LB systems, the resistance should be measured using an electrode gap equal to the domain size or even smaller one. At the earlier stages of our

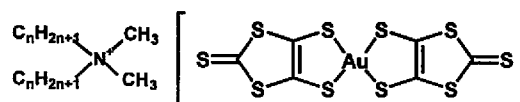


Fig. 1. Molecular structure of the 2C_{*n*}-Au(dmit)₂ salt.

studies on the 2C_{*n*}-Au(dmit)₂ LB films (*n*=8, 10, 12, 14, 16, 18), the electrode gap for the resistance measurement was 0.5 mm. Recently, however, we have reported the resistance measured by an inter-digitated electrode gap of 5 μm by an *ac* two-probe method. The resistance measured by the electrode gap of 5 μm has a metallic behavior more pronounced and it extends down to 58 K [8], while the resistance measured by the gap of 0.5 mm shows a weak metallic behavior in the range 230-300 K [4]. The atomic force microscopy (AFM) has revealed that the LB film consists of crystallites, which are 1-5 μm in lateral size and 4-20 nm in thickness [8]. We assume that the broad minimum of the resistance vs. temperature plot emerges in a crossover region, where metallic nature inside the crystallites is competing with the random potentials set up by grain boundaries and/or defects, and then, the metallic temperature dependence extends down to lower temperatures just by narrowing the electrode gap. Here, at this stage, one of the intriguing subjects is the formation of the conduction path and its dimensionality. In this paper, we report on the conductance of the 2C₁₄-Au(dmit)₂ LB films of 1-160 layer(s) and discuss the macroscopic conduction-path formation in the thin-film system.

2. EXPERIMENTAL

2.1 Sample Preparation

The 2C₁₄-Au(dmit)₂ salt (Fig. 1, $n=14$) was synthesized following the procedure of Steimecke *et al.* [9] and spread on the water surface (17°C, Milli-Q SP Reagent Water System) 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 quartz plate or poly(ethylene terephthalate) (PET) film by the horizontal lifting method. A NIMA Type 622 trough was used. The quartz plate is an Oken Suprasil P-20 and used for the samples for measuring the UV/visible absorption spectra. The PET film was a sample batch (Type S100) provided by Mitsubishi Polyester GmbH. The PET substrate surface was hydrophobized by the coating of five layers of the LB film of cadmium arachidate. Then, gold was vacuum-evaporated through a mask to form electrode strips separated by a gap of 0.5 mm. The PET substrate was used for the samples for measuring the electrical resistance. The quartz plate 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.

The LB films deposited on the PET substrates were immersed in an aqueous solution of LiClO₄ (0.1 M) and electrochemically oxidized by a constant current of 0.8 μ A. The gold electrode underneath the 2C₁₄-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, 8].

2.2 Resistance Measurement

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 Keithley Type 2001 digital multimeter at room temperature. The resistance was measured along the film plane using the gold electrode strips underneath the LB films.

2.3 Spectroscopic Measurement

UV/visible absorption spectra of the as-deposited LB films of 1-160 layer(s) deposited on the quartz plate were measured by a Shimadzu UV-2100 spectrometer.

3. RESULTS AND DISCUSSION

Figure 2(a) shows the UV/visible absorption spectra of the as-deposited 2C₁₄-Au(dmit)₂ LB films of 1-160 layers. Distinct absorption peaks are seen at 277 nm and 475 nm and the absorbance linearly increases with increasing the number of layers up to 160 layers, as shown in Fig. 2(b), suggesting the reproducible film deposition.

Figures 3(a) shows the conductance of the LB systems of 4, 8, 12, 16 and 20 layers plotted against time of the oxidation, T_{ox} ; the plotted values are of averages of 8 different samples. Figure 3(b) also shows the conductance of the LB systems of 20, 40, 80 and 160

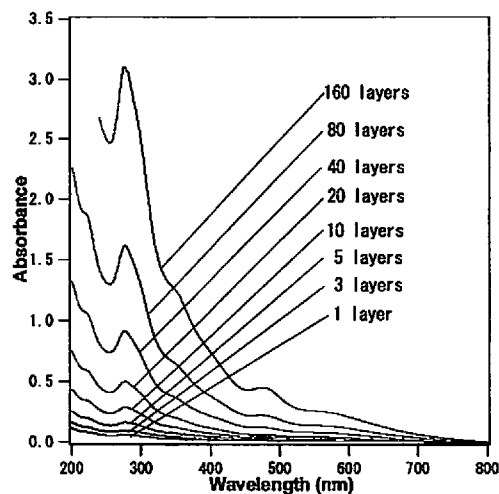


Fig. 2 (a) UV/visible absorption spectra of the as-deposited 2C₁₄-Au(dmit)₂ LB films of 1-160 layers.

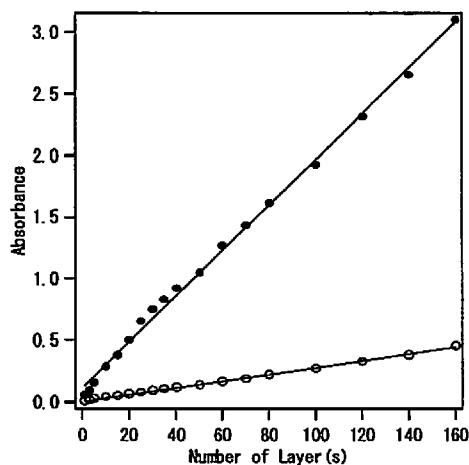
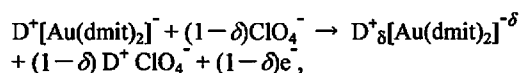


Fig. 2(b) The absorbance of the peaks at 277 nm (●) and 475 nm (○) of the as-deposited 2C₁₄-Au(dmit)₂ LB films plotted against number of deposition.

layers plotted against T_{ox} ; the plotted values are of 4-9 different samples. The conductance tends to increase with increasing the number of layers up to 40 layers, as shown in Fig. 3(b), however, no appreciable increase is seen in the range of 40-160 layers. It appears that the layers approximately beyond 40th one, which are relatively distant from the electrode-coated surface of the substrate, do not contribute to the electrical conduction significantly. We have already pointed out that the ClO₄⁻ anions are incorporated in the film for the compensation of the charge during the electrochemical oxidation and the possible reaction is as follows:



where D^+ =ditetradecyldimethylammonium and δ =charge transfer ratio ($0 < \delta < 1$) [8]. We currently

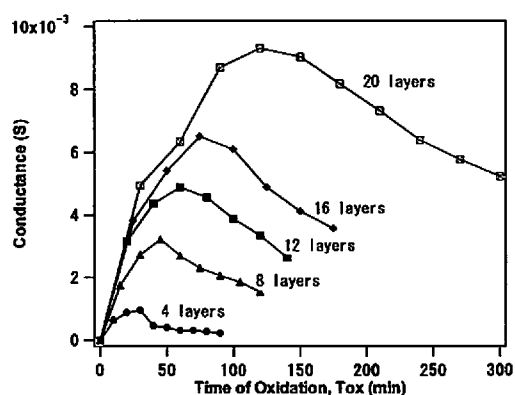


Fig. 3 (a) Conductance of the $2C_{14}$ -Au(dmit) $_2$ LB films of 4, 8, 12, 16 and 20 layers plotted against time of the oxidation, T_{ox} ; the values are of averages of 8 different samples.

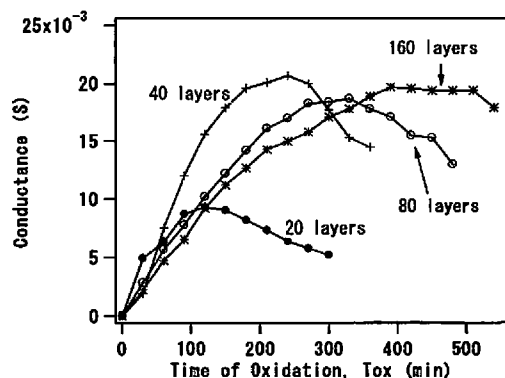


Fig. 3(b) Conductance of the $2C_{14}$ -Au(dmit) $_2$ LB films of 20, 40, 80 and 160 layers plotted against time of the oxidation, T_{ox} ; the values are of 4-9 different samples.

hypothesize that the LB layers approximately beyond 40th one, which are relatively distant from the electrode-coated surface of the substrate, cannot be oxidized effectively. In fact, as shown in Fig. 4, the oxidation time to obtain the maximum conductance, $T_{ox}(G_{max})$, plotted against the number of layer exhibits a sublinear behavior if the number of layer (N) is more than 40, indicating that the outermost layers can not be oxidized effectively if the distance between the molecular layers and the electrode is relatively farther.

Figure 5 shows the maximum of the conductance, G_{max} , plotted against the number of layer(s), N . If N is in the range of 2-4 layers, the G_{max} increases steeply with increasing N .[†] The least-squares fitting gives $G_{max} \propto N^{7.9}$. We have already reported that the atomic force microscopy (AFM) has revealed that the LB film consists of crystallites, which are 1-5 μ m in lateral sizes and 4-20 nm in thickness [8]. We

[†] The conductance of the $2C_{14}$ -Au(dmit) $_2$ LB film of single layer is below 10^{-7} S even after the electrochemical oxidation.

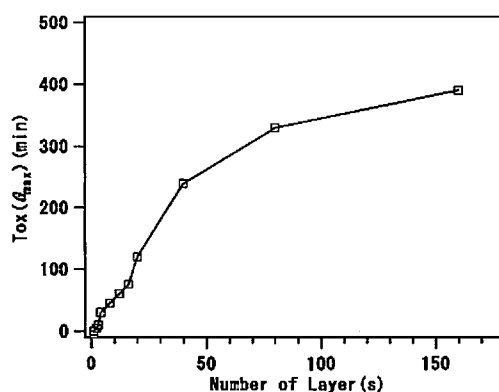


Fig. 4. The oxidation time to obtain the maximum conductance, $T_{ox}(G_{max})$, plotted against the number of layer. The data are of averages of 4-9 different sample batches.

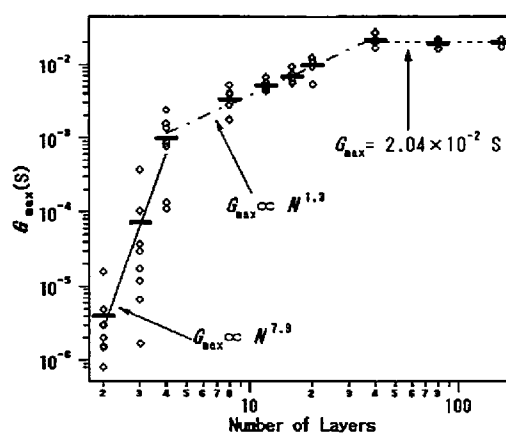


Fig. 5. The maximum of conductance, G_{max} , plotted against the number of layer(s), N . The data of 4-9 different sample batches are shown by open squares together with the averages shown by solid bars. The solid, dashed-and-dotted and broken lines are of the least square fitting in the range of $2 \leq N \leq 4$, $4 \leq N \leq 40$ and $40 \leq N \leq 160$, respectively.

hypothesize that the steep conductance increase with increasing N in the range of 2-4 layers is due to the formation of the macroscopic conduction paths and that the conduction paths include three-dimensional contacts of the plate-like crystallites created by the accumulation of layers.

In the range of 4-40 layers, the least-squares fitting gives $G_{max} \propto N^{1.3}$. The G_{max} is approximately proportional to N , indicating that the molecular layers in the range of 4-40 layers can be electrochemically oxidized uniformly to give a uniform conductivity. In the range of 40-160 layers, however, G_{max} is almost constant giving the average G_{max} value of 2.04×10^{-2} S, indicating that the surface layers can not be oxidized effectively and do not contribute to the macroscopic

conduction if the total number of layers is more than *ca.* 40. Studies on the temperature dependence of the resistance of the 2C₁₄-Au(dmit)₂ LB films of various thicknesses are now in progress and will be reported elsewhere.

4. CONCLUSION

The 2C₁₄-Au(dmit)₂ salt can be transferred onto solid substrates reproducibly up to 160 layers. The conductance of the 2C₁₄-Au(dmit)₂ film of single layer does not increase by the electrochemical oxidation and is less than 10⁻⁷ S. As for the samples with thickness more than two layers, the conductance increases with increasing the time of the electrochemical oxidation (*T*_{ox}) reaching the maximum conductance, *G*_{max}, and, then, decreases gradually. The *G*_{max} increases from 10⁻⁶ S up to 10⁻³ S with increasing the thickness in the range of 2-4 layers obeying *G*_{max} ∝ *N*^{7.9}. We postulate that the macroscopic conduction paths are formed by the accumulation of the molecular layer in the thickness range of 2-4 layers. In the thickness range of 4-40 layers, the *G*_{max} is approximately proportional to *N* (the least-square fitting gives *G*_{max} ∝ *N*^{1.3}), indicating that the molecular layers can be oxidized uniformly to give a uniform conductivity. In the range of 40-160 layers, however, *G*_{max} is almost constant with the average value of 2.04 × 10⁻² S, indicating that the surface layers cannot be oxidized effectively and do not contribute to the macroscopic conduction if the total number of layers is *ca.* more than 40.

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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] R. Watanabe, S. Morita, Y. F. Miura and M. Sugi, *Trans. Mater. Res. Soc. Jpn.*, **30**, 135-138 (2005).
- [9] G. Steimecke, H. J. Sieler, P. Kirmse and E. Hoyer, *Phosphorus Sulfur*, **7**, 49-55 (1979).

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