

Structural Characterization of Langmuir-Blodgett Films of the Dioctadecyldimethylammonium-Au(dmit)₂ Salt Studied by Infrared Spectroscopy and Atomic Force Microscopy

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The structure of the Langmuir-Blodgett (LB) films based on the dioctadecyldimethylammonium-Au(dmit)₂ (2C₁₈-Au(dmit)₂) salt has been investigated by infrared spectroscopy and atomic force microscopy (AFM). Although we normally utilize electrochemical oxidation process as the post-treatment to render the LB film conductive, the infrared spectra in the fingerprint region suggest that the oxidation of the Au(dmit)₂ moiety already seems to start at the air/water interface. The morphology of the LB films changes from a quasi-three-dimensional (Q-3D) structure to a two-dimensional (2D) one during the time for which the salt is kept at the air/water interface before compression.

Key words: LB films, Au(dmit)₂, infrared spectroscopy, atomic force microscopy (AFM)

1. INTRODUCTION

A great deal of attention has been paid to the fabrication of the mono- and multi-layered systems using the Langmuir-Blodgett (LB) technique, which allows us to assemble organic molecules into organized two-dimensional molecular sheets utilizing the interface adsorption phenomena. Among the research activities for fabricating LB systems with various functions, the development of conductive LB films has become a growing area over the past two decades [1,2]. As the film-forming material, the sulfur-rich anion, metal(dmit)₂ (where H₂dmit = 4,5-dimercapto-1,3-dithiol-2-dithione and metal = Ni, Au, Pd, Pt) is one of the intriguing candidates because its salts exhibit wide varieties of electronic properties ranging from semiconductors to superconductors [3-5].

We have already reported that the dioctadecyldimethylammonium-Au(dmit)₂ (2C₁₈-Au(dmit)₂, Fig. 1) salt forms Langmuir films of good quality at the air/water interface without using matrix molecules and that the electrochemically-oxidized LB film of the 2C₁₈-Au(dmit)₂ salt shows the room-temperature conductivity (σ_{R.T.}) as high as 2 S/cm along the film plane [6].

Since the macroscopic conductivity of the LB system is often limited by the grain boundaries and/or defects, the improvement of the higher-order structure is important to increase the conductivity. In general, for optimizing the film-forming conditions in the LB technique, several key conditions should be taken into account (e.g., species of ions, pH, subphase temperature, spreading solvent, compression speed of the film forming materials). Furthermore, some earlier works suggest

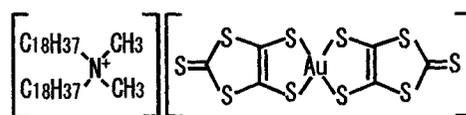


Fig. 1. The structure of 2C₁₈-Au(dmit)₂ salt.

that these film-forming parameters should be carefully treated in the time-domain because the film-forming materials do not always reach their thermodynamically-stable states immediately after the application of the spreading solution at the air/water interface [7-9]. Ikegami and coworkers also utilized the air/water interface as an active reaction field for the DCNQI (N, N'-dicyanoquinodimine) LB systems, and pointed out that the air/water interface may provide an active reaction field for the CT complexes and radical salts in general [10-12].

As for the metal(dmit)₂ LB systems, Gupta and coworkers have already reported that the occupied areas of the dialkyldimethylammonium-metal(dmit)₂ (metal = Pt, Pd, or Ni) salts increase with increasing the "waiting time (T_w)" [13, 14], which is defined as the time for which the salt is kept at the air/water interface, and the quality of the LB films is greatly improved in terms of the surface roughness. The effect of T_w upon the structure, however, has not been investigated comprehensively and the origin of the "spreading effect" has not been touched upon in these works. In this paper, we focus on the structure of the 2C₁₈-Au(dmit)₂ LB films fabricated with various values of T_w and report the

analyses by infrared spectroscopy and atomic force microscopy (AFM).

2. EXPERIMENTAL

The dioctadecyldimethylammonium-Au(dmit)₂ (2C₁₈-Au(dmit)₂, Fig.1) salt was synthesized following the procedure of Steimecke *et al* [15]. The 2C₁₈-Au(dmit)₂ salt was twice recrystallized in a mixture of acetonitrile and benzene and dried under reduced pressure for 12 h.

A KSV 5000 trough or a homemade trough whose dimension is the same as that of KSV-5000 was used. The 2C₁₈-Au(dmit)₂ salt was applied at the air/water interface from a 1:1 mixture of acetonitrile and benzene solution. The film at the air/water interface was compressed to 25 mN/m and transferred onto solid supports by the horizontal lifting method. The surface pressure (π) vs. area per molecule (A) isotherms were measured at a compression speed of 0.067 Å²/(s · molecule) at 17-20 °C. For both of the film deposition and π -A isotherm measurements the floating compounds were kept at the air/water interface for 5 – 180 min after applying the solution at the air/water interface and then the compression was performed.

A 1-nm-thick CaF₂ plate was used for infrared spectrum measurements. The CaF₂ plates were hydrophobized by the coating of 5-layered LB films of cadmium arachidate. An Si wafer hydrophobized by 1,1,1,3,3,3-hexamethyldisilazane was used as the substrate for the AFM observation. The AFM images were obtained by a SEIKO SPA-300 atomic force microscope (AFM) using a tapping mode with a force constant of 1.5 mNm⁻¹. Infrared transmission spectra were recorded using a JASCO FT/IR-300 spectrometer.

3. RESULTS AND DISCUSSIONS

3.1. The π -A isotherms

Figure 2 shows the π -A isotherms of the 2C₁₈-Au(dmit)₂ salt measured at 17 °C. “Waiting time (T_w)”, which is defined as the time for which the salt was kept at the air/water interface before compression, is varied in the range from 5 to 180 min. The area per salt at 25 mN/m, where the film deposition was performed, is 12 Å² when $T_w = 5$ min (curve a). Since the dioctadecyldimethylammonium moiety is known to occupy 40-50 Å² in a monomolecular films at the air/water interface, the occupied area of 12 Å² is unexpectedly small, suggesting the formation of a quasi-three dimensional (Q3D) structure. However, the π -A isotherm of the 2C₁₈-Au(dmit)₂ salt is found to expand remarkably with increasing T_w , as shown in Fig. 2. In case $T_w = 180$ min, the occupied area at 25 mN/m reaches 30 Å² and the limiting occupied area is in the range 40-50 Å² [16], which is in good agreement with the cross section of the dioctadecyldimethylammonium moiety in a monomolecular film at the air/water interface, indicating a formation of a two-dimensional (2D) structure.

3.2. The infrared spectra

Figure 3 shows the infrared transmission spectra of the as-deposited 2C₁₈-Au(dmit)₂ LB films of 20 layers fabricated with various values of T_w ($T_w = 5, 60, 90, 120,$

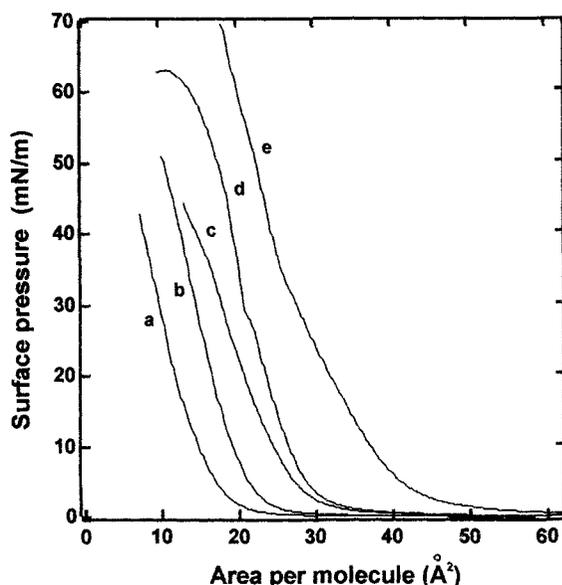


Fig. 2. The surface pressure (π) vs. area per molecule (Å²) isotherms of the 2C₁₈-Au(dmit)₂ salt measured at 17 °C, where “waiting time (T_w)” = (a) 5 min, (b) 30 min, (c) 60 min, (d) 90 min and (e) $T_w = 180$ min.

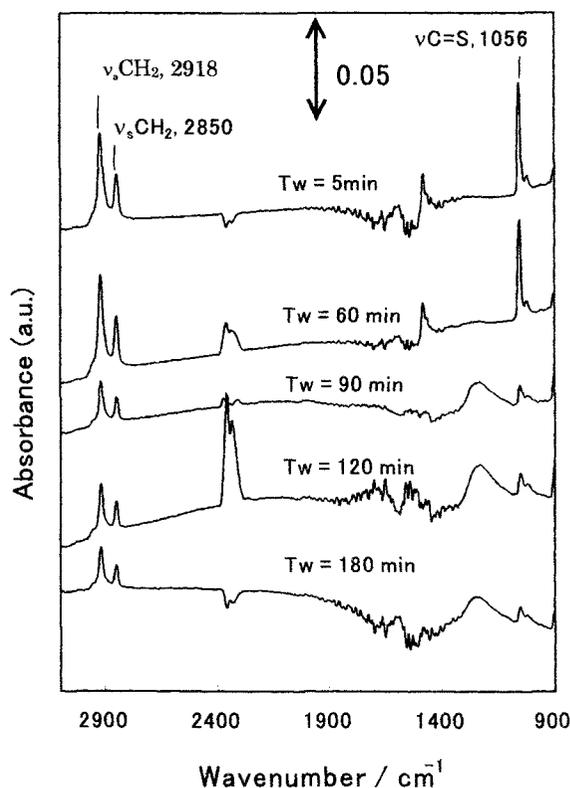


Fig. 3. The infrared transmission spectra of the 2C₁₈-Au(dmit)₂ LB film fabricated with various values of T_w . Assignments of the key bands: 2918 cm⁻¹, CH₂ antisymmetric stretching, ν_a (CH₂); 2850 cm⁻¹, CH₂ symmetric stretching, ν_s (CH₂); 1056 cm⁻¹, C=S stretching, ν (C=S).

and 180 min). Assignments for the infrared bands of the $2C_{18}\text{-Au(dmit)}_2$ LB film have not yet been fully established, however, some key bands for the LB film are as follows: 2918 cm^{-1} , CH_2 antisymmetric stretching; 2850 cm^{-1} , CH_2 symmetric stretching; 1056 cm^{-1} , C=S stretching.

The band intensities of the CH_2 antisymmetric stretching and the CH_2 symmetric modes do not change significantly until $T_w = 60$ min, however, they fall off markedly in the T_w range of 60-90 min, reaching roughly the half of those in case $T_w < 60$ min. On the other hand, the band shapes of the CH_2 antisymmetric stretching mode and CH_2 symmetric one and the intensity ratio of these bands do not change as a function of T_w , suggesting that the mobility and the orientation of the alkyl chain of the $2C_{18}\text{-Au(dmit)}_2$ LB film remain constant. The wavenumbers of the antisymmetric stretching and the CH_2 symmetric modes also do not change appreciably with changing T_w .

It should be also noted here that the infrared spectrum in the fingerprint region changes markedly as a function of T_w , as shown in Fig. 3. One of the distinct spectral changes is the intensity decrease of the C=S stretching band observed at around 1055 cm^{-1} . The band intensity of the C=S stretching mode compared with that due to the CH_2 antisymmetric and symmetric stretching modes drastically decreases with increasing T_w . Figure 4 shows the full width of the half height (FWHH) and the wavenumber of the C=S stretching mode, plotted against T_w . The FWHH of the band due to the C=S stretching mode is 14, 14, 17, 17, and 18 cm^{-1} for $T_w = 5, 60, 90, 120,$ and 180 min, respectively, as shown by the open circles in Fig. 4; the FWHH increases appreciably in the T_w range of 60-90 min. Furthermore, the broadening is accompanied by the appreciable red-shift of the band, which is from 1055 to 1053 cm^{-1} , as shown in Fig. 4. The earlier works suggest that the broadening accompanied by the slight red-shift is due to the oxidation of the metal(dmit)₂ moiety [15]. In fact, the infrared spectrum of the $2C_{18}\text{-Au(dmit)}_2$ salt oxidized by iodine coincides well with that of the as-deposited LB films fabricated in case $T_w = 180$ min. Thus, we consider that the chemical process proceeding at the

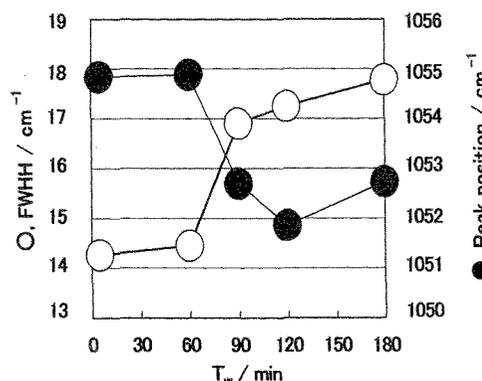


Fig. 4. The full width of the half height (FWHH) and the wavenumber of the C=S stretching mode, plotted against T_w .

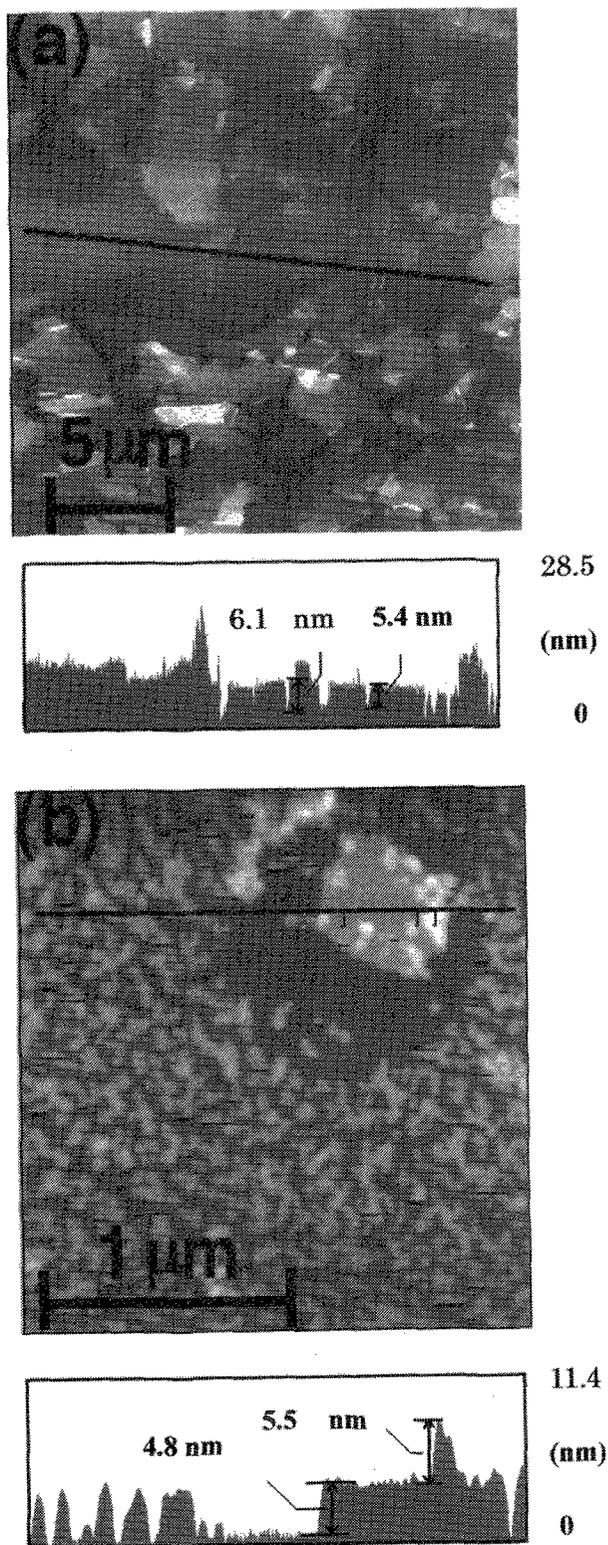


Fig. 5. Typical AFM images of "single-layered" LB films of the $2C_{18}\text{-Au(dmit)}_2$ salt deposited on hydrophobized Si wafers; (a) $T_w = 5$ min, (b) $T_w = 180$ min.

air/water interface is the oxidation of the Au(dmit)₂ moieties.

Although we utilize the electrochemical oxidation process for realizing the mixed-valence state ([Au(dmit)₂]^{δ-}, 0 < δ < -1) and we have obtained lateral conductivity as high as 10⁰-10¹ S/cm, an oxidation process already seems to start at the air/water interface. As shown in Fig. 3, broad bands also appear at 1240 cm⁻¹ and in the range greater than 1600 cm⁻¹ with increasing T_w. Our infrared absorption measurement using linearly-polarized light suggests that the transition dipole moments of the broad bands lie along the film plane and we postulate that the broad bands are the charge-transferred (CT) bands, although the macroscopic electrical conduction is not realized before the electrochemical oxidation. Studies are now in progress for determining the dopant species at the air/water interface.

3.3 The AFM images

Figure 5(a) shows a typical AFM image of the "single-layered" LB film deposited on an Si-wafer with T_w = 5 min. As shown by the profile along the solid line in Fig. 5(a), steps are in the range of 5-6 nm and the LB film seems to be composed of 6-nm-thick plate-like crystallites piled up to form a few layers. Figure 5(b) shows an AFM image of the LB film fabricated by a single deposition with T_w = 180 min. The surface of the film fabricated with T_w=180 is relatively smooth compare to that fabricated with T_w=5 min and the lateral sizes of the domains are getting smaller than those observed for the surface created with T_w=5 min. It should be also noted here that there are some extremely flat surface, which can be ascribed to the bare substrate surface.

As we have already mentioned, the occupied area of the 2C₁₈-Au(dmit)₂ is too small in case T_w = 5 min if we assume a formation of a monomolecular film at the air/water interface. The occupied area, however, tends to increase with increasing T_w. Therefore, a relatively smooth 2D structure is assumed for the floating film formed with larger values of T_w. We consider that the structure of the film at the air/water interface, which depends on T_w, affects the surface morphology of the films deposited on the hydrophobized Si-wafer substrates.

CONCLUSIONS

We have studied the structure of the LB films of the 2C₁₈-Au(dmit)₂ salt fabricated with various values of T_w by means of infrared spectroscopy and AFM. The infrared spectra in the fingerprint region suggest that the oxidation of the Au(dmit)₂ moiety already starts at the air/water interface before the electrochemical oxidation. The T_w-dependent spectral change is associated with morphological change of the surface of the LB films, which is from a quasi-3D structure to a 2D one. A comprehensive investigation including the correlation between electrical conductivity and the values of T_w is now in progress and will be published elsewhere.

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REFERENCES

- [1] T. Nakamura, *Handbook of Organic Conductive Molecules and Polymers*, ed. H. S. Nalwa, (Wiley, New York, 1997) 728.
- [2] M. R. Bryce and M.C. Petty, *Nature*, **374** (1995) 771.
- [3] *The physics and Chemistry of Organic Superconductors*, ed. G. Saito and S. Kagoshima (Springer, Heidelberg, 1990)
- [4] T. Nakamura, H. Tanaka, K. Kojima, M. Matsumoto, H. Tachibana, M. Tanaka and Y. Kawabata, *Thin Solid Films*, **179** (1989) 183.
- [5] L. M. Goldenberg, A. P. Monkman, C. Pearson, J. Gibson, M. R. Bryce and M. C. Petty, *Thin Solid Films*, **284-285** (1996) 512.
- [6] M. Horikiri, Y. F. Miura, Y. Araki, K. Ikegami and M. Sugi, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **198-200** (2002) 657.
- [7] T. Kato, K. Ohshima and K. Suzuki, *Thin Solid Films*, **178** (1989) 37.
- [8] T. Kato, *Langmuir*, **6** (1990) 870.
- [9] T. Kato, Y. Hirobe and M. Kato, *Langmuir*, **7** (1991) 2208.
- [10] K. Ikegami and T. Nakamura, *Jpn. J. Appl. Phys.* **37** (1998) L550.
- [11] K. Ikegami, M. Lan and T. Nakamura, *J. Chem. Phys.* **112** (2000) 881.
- [12] T. P. Majumder and K. Ikegami, *J. Chem. Phys.* **116** (2002) 10428.
- [13] D. M. Taylor, S. K. Gupta, A. E. Underhill and C. E. A. Wainwright, *Thin Solid Films*, **210-211** (1992) 287.
- [14] S. K. Gupta, D. M. Taylor, A. E. Underhill and C. E. A. Wainwright, *Synth. Met.* **58** (1993) 373.
- [15] G. Steimecke, H. J. Sieler, P. Kirmse and E. Hoyer, *Phosphorus & Sulfer* **7** (1979) 49.
- [16] K. Tajima, M. Takahashi and K. Kobayashi, *Thin Solid Films* **178** (1989) 381.

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