Effect of High Pressure on Resistance in Au(dmit)$_2$ LB Films

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Abstract. The high pressure effect on resistance of the LB film of ditetradecyltrimethylammonium-Au(dmit)$_2$ $[2C_{14}N^+Me_2-Au(dmit)_2]$ salt has been investigated; the measurements were performed down to 0.8 K and pressures up to 1.03 GPa using a clamp-type pressure cell. The resistance gradually decreases with increasing pressure reaching a 57% smaller value at 1.03 GPa compared to the ambient one. The resistance increases with decreasing temperature for three different conditions of the measurement: at 0 GPa and under pressure (clamped at 0.80 GPa and 1.03 GPa) in the temperature range of 18–295 K. Over the whole temperature range, the higher the pressure is, the lower the sheet resistance is, indicating that the application of pressure is effective to reduce the sheet resistance. Although we have already reported the magnetic anomaly suggesting the Meissner state in the LB film below 3.9 K, no resistance drop is observed even if the resistance was measured down to 0.8 K.

1. Introduction
The Langmuir-Blodgett (LB) technique is a powerful technique that allows us to assemble organic molecules into organized two-dimensional (2D) molecular sheets [1]. Among the various objectives of fabricating functional LB films, the development of highly conductive LB systems is important, because it may open up the possibility of a variety of future applications [2]. So far, several LB systems have been reported to have metallic conducting properties; they are based on either Au(dmit)$_2$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) salts [3-7] or bis(ethylenedioxy)tetrathiafulvalene (BEDO-TTF) molecules [8-10].

We have already reported that the LB film based on the ditetradecyltrimethylammonium-Au(dmit)$_2$ salt [Fig. 1, $2C_{14}N^+Me_2-Au(dmit)_2$ salt] exhibits a high room-temperature conductivity of 40 S/cm with a metallic temperature dependence of resistance after
electro-oxidation [6,7]. Furthermore, our ac magnetic susceptibility measurement suggests the existence of a superconducting phase below 3.9 K [11]. However, resistance drop on cooling has not yet been observed reproducibly for the LB film.

We have already reported that the 2C_{14}N’Me_{2}-Au(dmit)_{2} LB film consists of domains of 5.20 ± 1.52 μm [12]. In such an inhomogeneous system, it is possible that the superconductivity is localized and global superconductivity, which shows macroscopic zero resistance, is not realized.

There exist several theoretically-derived threshold resistances for realizing global superconductivity in disordered superconductors. In a disordered 2D system, where superconductivity is competing with Anderson localization, the sheet resistance (R_{\parallel}) should satisfy R_{\parallel} < h/e^2 = 25.5 kΩ, where h = Planck constant and e = elementary charge [13]. In a 2D system, where 2D superconducting domains are linked with thin insulating regions, R_{\parallel} should satisfy R_{\parallel} < h/4e^2 = 6.4 kΩ, where h = Planck constant and e = elementary charge [14].

The R_{\parallel} value can be reduced by improving the order in the film. But the application of pressure may be another way to reduce the R_{\parallel} value. While the application of high pressure is an established method to induce metallic and superconducting states in various molecular crystals [15], studies on resistance of LB films under pressure are not common and limited to those by ourselves [5, 16, 17]. In this paper, we report on resistance of the LB film of the 2C_{14}N’Me_{2}-Au(dmit)_{2} salt measured under high pressures up to 1.03 GPa using a clamp-type pressure cell.

2. Experimental

2.1. Sample preparation

The ditetradecyldimethylammonium-Au(dmit)_{2} salt [2C_{14}N’Me_{2}-Au(dmit)_{2} salt, Fig.1] was synthesized in accordance with the procedure of Steimecke et al. [12,18]. The 2C_{14}N’Me_{2}-Au(dmit)_{2} salt was dissolved in a 1:1 mixture of benzene and acetonitrile (0.25 mM) and spread on the surface of pure water. After keeping the salts on the water surface for 5 min, they were compressed to 25 mN/m, and then, the floating film was transferred onto a PET (polyethylene terephthalate) substrate (Mitsubishi Plastics, Type S100-100) by the horizontal lifting method (Langmuir-Schafer method). Twenty layers were deposited onto the substrate. A commercially available LB trough (NIMA Technology Ltd., Type 622) was used.

Prior to the LB film deposition of the 2C_{14}N’Me_{2}-Au(dmit)_{2} salt, the PET substrate, which was 0.1 × 13 × 38 mm³ in size, was pre-coated with 20-

Fig. 2. The schematic representation of the LB film of the 2C_{14}N’Me_{2}-Au(dmit)_{2} salt for resistance measurement under pressure. (a) Cross section; (b) Top view.

Fig. 3. Experimental setup for applying pressure to the 2C_{14}N’Me_{2}-Au(dmit)_{2} LB film. The LB film attached to the plug is set to the Teflon cap of outer diameter of 8 mm (inner diameter: 7 mm) filled with the pressure medium of Daphne Oil 7373.
layered LB film of cadmium-arachidate, and then, four gold electrode strips with gaps of 0.2 mm were deposited on the substrate by vacuum evaporation. The as-deposited LB film was immersed in LiClO4 (aq.) and electro-oxidized with a constant current of 0.8 μA. The gold electrode underneath the LB layer and a platinum rod set in the electrolyte were used as the working and counter electrodes, respectively. A positive potential was applied to the gold electrode. The details of the sample preparation are in our previous papers [7, 12].

2.2. Resistance measurement under pressure

The electro-oxidized LB film, whose original size was $0.1 \times 13 \times 38 \text{ mm}^3$, was cut by scissors into a small fraction of $0.1 \times 3 \times 7 \text{ mm}^3$, as schematically shown in Figs. 2(a) and 2(b). Thin gold wires (50 μm in diameter) were attached to gold electrodes deposited underneath the LB film by a silver paste (Fujikura Kasei Co. Ltd., DOTITE: Type D-550) and the resistance was measured along the film plane by DC or AC two probe method, as shown in Figs. 2 (a) and 2(b).

The LB film with the dimension of $0.1 \times 3 \times 7 \text{ mm}^3$ was placed on a sample stage, which is made of a filter paper (Toyo Roshi Kaisha, Ltd., Advantec Type No. 1) vacuum impregnated with STYCAST 1266 epoxy encapsulant (Henkel AG & Co. KGaA), as shown in Fig. 3. The sample stage was further attached to a plug, which was made from beryllium copper, using STYCAST 2850 FT epoxy encapsulant (Henkel AG & Co. KGaA), and then, copper wires (0.1 mm in diameter) were attached to the gold wires using the silver paste, as shown in Fig. 3. The plug with the LB film was attached to a Teflon cap filled with Daphne Oil 7373 (Idemitsu Kosan Co. Ltd.).

The sample holder, in which the LB sample was set using the pressure medium of Daphne Oil 7373, was inserted in a beryllium copper cylinder body (indicated as “B” in Fig. 4) with a lock nut for clamp (indicated as “A” in Fig. 4), and placed on the stage of hydraulic press, as shown in Fig. 4. The pressure was gradually applied to the clamp-type pressure cell using the hydraulic press and clamped by the lock nut at 298 K and it was brought to cryostat to measure temperature dependence of resistance. The temperature dependence of resistance of the LB film cut from the same sample batch was also measured at 0 GPa (in vacuum) for comparison.

3. Results and Discussion

The resistance was first measured with increasing the pressure from ambient pressure up to 0.80 GPa at 298 K. Then, the pressure cell was clamped at 0.80 GPa and was cooled down to measure the temperature dependence of resistance. After the pressure cell was warmed up to 298 K, the resistance was further measured with increasing the pressure up to 1.03 GPa. Finally, the pressure cell was clamped at 1.03 GPa and was cooled down to measure the temperature dependence of resistance again [19].

Figure 5 shows the resistance of the $2C_{14}N’Me_2$-Au(dmit)$_2$ LB film plotted against pressure; the

![Fig. 4. Photo of the cylinder body (B) with the screw attached for clamp (A), which have been set at the stage of hydraulic press.](image)

![Fig. 5. Resistance at 298 K plotted against pressure; the first and secondary sequences of measurements are shown by open circles and squares, respectively.](image)
resistance was measured along the film plane by DC two probe method at 298 K. The resistance gradually decreases with increasing pressure reaching a 57% smaller value at 1.03 GPa compared to the ambient one.

Figure 6(a) shows the temperature dependence of sheet resistance of the 2C\textsubscript{14}N+Me\textsubscript{2}-Au(dmit)\textsubscript{2} LB film measured at 0 GPa and under pressure (clamped at 0.80 GPa and 1.03 GPa) by AC two probe method (17 Hz). Resistance increases with decreasing temperature for all of the three different conditions of the measurement in the temperature range of 18\textdegree - 295 K, as shown in Fig. 6(a). Furthermore, over the whole temperature range, the higher the pressure is, the lower the sheet resistance is, indicating that the application of high pressure to the LB film is effective to reduce the sheet resistance.

We have already reported that the 2C\textsubscript{14}N+Me\textsubscript{2}-Au(dmit)\textsubscript{2} LB film shows metallic temperature dependence down to a certain temperature when measured at 0 GPa [6,7]. However, it should be noted here that some sample batches do not show the metallic behaviour when the electrode gap for the measurement is as wide as 0.2 - 0.5 mm; this is possibly due to disorders such as grain boundaries and defects. As for this sample batch, the metallic behaviour is not observed at 0 GPa and the pressure application does not induce the metallic behaviour, although it reduces the sheet resistance, as shown in Figs 6(a).

Figure 6(b) shows the Arrhenius plot of sheet resistance (R\textsubscript{\textcircled{\text{Ω}}}). Logarithm of R\textsubscript{\textcircled{\text{Ω}}} plotted against the inverse of temperature is sublinear for all of the three different conditions of the measurement: measured at 0 GPa and under pressure (clamped at 0.80 GPa and 1.03 GPa). Since the pressure in the clamp-type cell gradually decreases on cooling, the interpretation of the temperature dependence of resistance is not straightforward. For instance, the pressure at around 7 K is ca. 20% lower than that at 298 K, when Daphne Oil 7373 was used as the pressure medium [20]. However, we hypothesise that the resistance behaviours under pressure, which are deviated from the simple activation-type one, are intrinsic because the decrease of pressure on cooling would give a superlinear behaviour for the
sample with the simple activation-type property and resistance measured in vacuum also has a similar sublinear behaviour.

Deviations from the simple activation-type behaviour have been reported for several conductive LB films. In those literatures, at lower temperature regions, 2D variable range hopping (VRH) regime [4], thermal-fluctuation-induced tunnelling (TFIT)[5], and 2D weak localization [20] have been taken into account to interpret the resistance behaviours in the heterogeneous LB systems. As for the present LB system, more investigations are necessary to elucidate the conduction mechanism.

As stated in introduction section, for disordered superconductors, there exist some theoretical values of threshold sheet resistance ($R_\square$) for realizing global superconductivity. In Fig. 6(a), the two different thresholds are shown by dotted line ($R_\square < h/e^2 = 25.5 \, k\Omega$) and dashed line ($R_\square < h/4e^2 = 6.4 \, k\Omega$), which are the cases when superconductivity is competing with Anderson localization [13] and when 2D superconducting domains are linked with thin insulating regions [14], respectively.

We have tentatively performed the resistance measurement of the $2C_{14}N^+Me_2-Au(dmit)_2$ LB film in the temperature range of 0.8–18 K at ambient pressure and under pressure (clamped at 0.80 GPa and 1.03 GPa), although the data are not shown in Fig. 6(a). None of the $R_\square$ values of the three different conditions of measurement satisfies those two thresholds at the lower temperatures and no resistance drop is seen even if the measurement has been performed down to 0.8 K. We consider that it is necessary to reduce the $R_\square$ values by improving the order in the LB film and applying higher pressures.

4. Conclusion and Future Directions

The resistance of the $2C_{14}N^+Me_2-Au(dmit)_2$ LB film decreases with increasing pressure at room temperature; it reaches a 57% smaller value at 1.03 GPa compared to the ambient one. The temperature dependence of resistance of the LB film was measured at ambient pressure and under pressure (clamped at 0.80 GPa and 1.03 GPa). In the temperature range of 18–295 K, the higher the pressure is, the lower the sheet resistance is, indicating that the application of high pressure to the LB film is an effective method to reduce the sheet resistance ($R_\square$). All the three behaviours of the temperature dependence of the sheet resistance are of sublinear. Since the decrease of pressure inside the pressure cell on cooling cannot explain the sublinear behaviour in the Arrhenius plot, we hypothesise that it reflects an intrinsic property of conduction in the film and studies on electronic transport properties in the LB film are now in progress.

As stated in introduction section, we have already reported that the ac magnetic susceptibility of the $2C_{14}N^+Me_2-Au(dmit)_2$ LB film suggests the existence of the Meissner state below 3.9 K. At this stage, however, the origin of the magnetic anomaly of the LB film is still an open question. One of the hypotheses to interpret the data is that superconductivity exists locally in the heterogeneous LB system, but due to disorders, global superconductivity is not observed. Studies are now in progress to reduce the $R_\square$ values by improving the order in the LB film and applying higher pressures toward the realization of global superconductivity in the LB film.

Acknowledgment

This work was supported in part by JSPS KAKENHI Grant No. 15K04655. We would like to thank Prof. Masato Hedo and Prof. Kazuyuki Matsubayashi for helpful guidance in resistance measurement under high pressure in early stages of this work.

References

[1] Ulman A 1991 An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to Self-Assembly (San Diego, CA: Academic Press)
[2] Nakamura T 1997 Handbook of Organic Conductive Molecules and Polymer, ed. Nalwa H S, vol 1, Chap. 14 (New York: Wiley)
[3] Nakamura T, Kojima K, Matsumoto M, Tachibana H, Tanaka M and Kawabata Y 1989 Chem Lett 18 367.
[4] Miura Y F, Takenaga M, Kasai A, Nakamura T, Matsumoto M and Kawabata Y 1991 Jpn J Appl Phys 30 3503.
[5] Isotalo H, Paloheimo J, Miura Y F, Azumi R, Matsumoto M and Nakamura T 1995 Phys Rev B 51 1809.
[6] Miura Y F, Okuma Y, Ohnishi H and Sugi M 1998 Jpn J Appl Phys 37 L1481.
[7] Miura Y F, Kitao M, Matsui H, Sugi M, Hedo M, Matsubayashi K and Uwatoko Y 2008 Jpn J Appl Phys 47 8884.
[8] Nakamura T, Yunome G, Azumi R, Tanaka M, Matsumoto M, Horiuchi S, Yamochi H and Saito G 1994 J Phys Chem 98 1882.
[9] Ogasawara K, Ishiguro T, Horiuchi S, Yamochi H and Saito G 1996 Jpn J Appl Phys 35 L571.
[10] Ohnuki H, Noda T, Izumi M, Imabukuro T and Kato R 1997 Phys Rev B 55 R10225.
[11] Miura Y F, Horikiri M, Saito S-H and Sugi M 2000 Solid State Commun 113 603.
[12] Miura Y F, Matsui H, Inoue K, Hoshino J and Ikegami K 2015 Synthetic Metals 207 54.
[13] Maekawa S and Fukuyama H 1981 J Phys Soc Jpn 51 1380.
[14] Fisher M P A 1990 Phys Rev B 36 1917.
[15] Ishiguro T, Yamaji K and Saito G (Eds.) 1997 Organic Superconductors, 2nd ed. (Berlin: Springer).
[16] Miura Y F, Isotalo H, Matsumoto M and Nakamura T 1993 Appl Phys Lett 63 1705.
[17] Miura Y F, Morita S, Saito S-H, Sugi M, Hedo M and Uwatoko Y 2002 Int’l J Nanoscience 1 627.
[18] Steimecke G, Sieler H J, Kirmse P and Hoyer E 1979 Phosphorus Sulfur 7 49.
[19] We have confirmed that the resistance behaviors measured by the dc or ac two-probe method are in good agreement with those measured by the dc or ac four-probe method. The effect of contact resistance is considered to be negligible when the resistance of the ultra-thin film is more than $10^2$-$10^3$ Ω as in the case shown in Figures 6(a) because the contact resistance is assumed to be around 1 Ω. This has been confirmed for the LB film under which four electrode strips are formed (please see Figure S1 in supplementary data), although it has been only confirmed for the ambient measurement. Measurements of the resistance under pressure using the dc or ac four-probe method has not yet been performed due to the limitation of the sample size but it is now in progress and will be published in a separate paper.
[20] Pressure at lower temperature in the clamp-type cell has been estimated utilizing the linear pressure dependence of critical temperature of superconductivity of lead [21]. The pressure at around 7 K is estimated as 0.64 GPa when it is clamped at 0.80 GPa at 298 K and it is estimated as 0.84 GPa when it is clamped at 1.03 GPa at 298 K.
[21] Boughton, R I, Olsen J L and Palmy C 1970 Progress in Low Temperature Physics, ed. Gorter C J, Vol 6, Chap. 4 (Amsterdam: North-Holland).