Resistance Measurements of Microcrystals of Single-component Molecular Metals Using Finely Patterned Interdigitated Electrodes

Hisashi Tanaka,*[1] Shigeo Hara,[1] Madoka Tokumoto,[1,2,5] Akiko Kobayashi,[3] and Hayao Kobayashi[4,5]
[1]*Nanotechnology Research Institute (NRI), AIST, 1-1-1 Umezono, Tsukuba 305-8568*
[2]*National Defense Academy, 1-10-20 Hashirimizu, Yokosuka 239-8686*
[3]*Department of Chemistry, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550*
[4]*Institute for Molecular Science, 38 Myodaiji, Okazaki 444-8585*
[5]*JST-CREST, Kawaguchi 332-0012*

(Received May 9, 2007; CL-070501; E-mail: hisashi.tanaka@aist.go.jp)

Two-probe resistance measurements on the micro-crystalline samples using finely patterned interdigitated electrodes revealed single-component molecular conductors, $[Au(tmdt)_2]$ and $[Ni(dmdt)_2]$, to be metallic down to liquid helium temperature.

Single-component molecular conductors are novel molecular crystals with high conductivity, even though they consist of single neutral molecular species.[1,2] As reported before, $[Ni(tmdt)_2]$ (tmdt = trimethylenetetrathiafulvalenedithiolate) is the first single-component molecular metal.[1] Observation of magnetic quantum oscillations in a small single crystal of $[Ni(tmdt)_2]$ using a microcantilever gave a rigorous proof of the metallicity of this single-component molecular crystal.[3] An isostructural gold analogue, $[Au(tmdt)_2]$ is also a very unique system which undergoes an antiferromagnetic transition at 110 K ($=T_N$) without loss of its high conductivity.[4] Although the high conductivity of compressed pellet of crystalline powder sample below T_N and the first-principles band structure calculation strongly suggest $[Au(tmdt)_2]$ to be the first antiferromagnetic molecular metal with T_N higher than 100 K,[4,5] metallic temperature dependence of resistivity has not been observed yet. The size of the crystals grown by conventional electrochemical oxidation using "H" shaped glass cells and platinum electrodes was too small to perform single-crystal four-probe resistivity measurements.

Considering the fact that even $[Ni(tmdt)_2]$ with stable metallic state down to very low temperatures exhibited a semiconducting temperature dependence of the resistivity at least at low temperatures on the crystalline powder sample,[2] the resistivity measurement on single crystal has been considered to be essential to prove the metallic nature of the system. However, the growth of single crystals of single-component molecular conductors with the size sufficiently large for the single-crystal four-probe resistivity measurements is extremely difficult in most cases. Therefore, we tried to develop a simple method to measure resistance on microcrystals by i) electrochemically growing small crystals directly on a finely patterned interdigitated electrodes (Figure 1), and ii) measuring the two-probe resistance, of as-grown crystals, between a pair of interdigitated electrodes. We used the gold or platinum electrodes commercially available from BAS Inc. The gap between interdigitated electrodes was 5 μm, and the width of electrode was 10 μm (Figure 1b). Metal complexes were synthesized according to the previous reports.[1,2,6] All syntheses and crystal growth procedures were performed under a strictly inert atmosphere. 10 mg of $(Me_4N)_2[Ni(dmdt)_2]$ (or 10 mg of $(Me_4N)[Au(tmdt)_2]$) and 100 mg of $(n\text{-}Bu_4N)PF_6$ were dissolved in 20-mL acetonitrile. Applying direct current between interdigitated electrodes and external counter electrode (ϕ100-μm copper wire) in the acetonitrile solution for 15–30 min, many small crystals grew and bridged the interdigitated electrodes. Sometimes, microcrystals covered the whole area of electrodes. In the case of $[Ni(dmdt)_2]$, very tiny black crystals (3–4 μm in length and 1 μm in width) were grown and covered the gold interdigitated electrodes area by applying 0.4-μA current, as shown in Figure 1b. On the other hand, as for $[Au(tmdt)_2]$, very small microcrystals (less than 2 μm in length) were grown on the platinum interdigitated electrodes by applying 0.5-μA current.

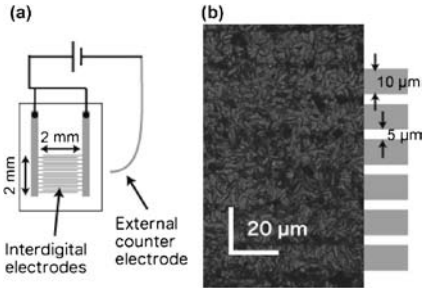

Figure 1. The schematic figure of interdigitated electrodes (a) and the picture of $[Ni(dmdt)_2]$ microcrystals grown on the gold electrodes (b). (a) Current is applied between the interdigitated electrodes and external counter electrode (cupper wire). The size of interdigitated electrodes area is $2 \times 2\,mm^2$ (b) Very tiny black microcrystals covered the interdigitated electrodes area. The width of interdigitated electrodes and gap were 10 and 5 μm respectively.

The X-ray diffraction of $[Ni(dmdt)_2]$ was measured on the small crystals grown over the interdigitated electrodes area ($2 \times 2\,mm^2$, as shown in Figure 1a) with a Rigaku RINT-Ultima X system. The result is shown in the bottom of Figure 2. As compared with the calculated powder X-ray diffraction patterns based on the crystal structure (top of Figure 2),[3] only (h00) ($h = 1$, 2, and 4) and (0k0) ($k = 1$) peaks were observed. According to the calculation, there should be strong peaks of $(02\bar{1})$ and $(12\bar{1})$ around 26 degree. However, only a small hump was observed at the corresponding position. These results suggest that the microcrystals of $[Ni(dmdt)_2]$ grown on the electrodes have preferred orientations, that is, the most $[Ni(dmdt)_2]$ molecules are arranged with their side-by-side molecular axis perpendicular to the electrode surface. (see the

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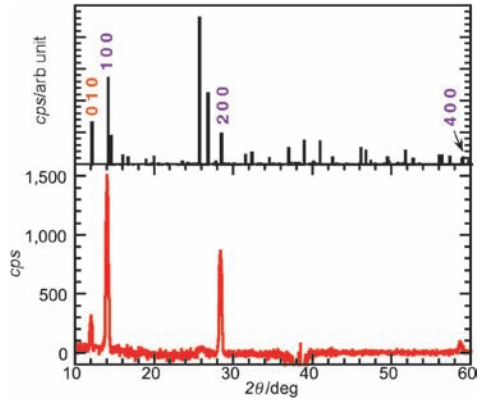

Figure 2. The calculated (top) and observed (bottom) X-ray diffraction patterns of [Ni(dmdt)$_2$]. The anomaly observed around 36–40 degree in the bottom chart is caused by the subtraction of the back ground due to the gold electrodes. The indexes of observed peaks were shown in the top chart. The calculated intensities of (300) and (0k0) ($k \geq 2$) peaks were so small that they could not be observed.

picture of Graphical Abstract) The weak (010) peak means a small part of molecules are arranged with their stacking direction axis perpendicular to the electrode surface. On the other hand, X-ray diffraction pattern of [Au(tmdt)$_2$] was almost identical with the calculated one based on the reported [Au(tmdt)$_2$] structure.[2] There was no obviously preferred orientation in the microcrystals of [Au(tmdt)$_2$] grown on the electrodes.

The temperature dependence of the resistivity of [Ni(dmdt)$_2$] and [Au(tmdt)$_2$] measured by a compressed pellet samples was not metallic in both cases as reported before (see the red broken lines in Figure 3).[2,4,6] The resistivity of [Ni(dmdt)$_2$] increased slightly with decreasing temperature, i.e. $\rho(3\,\mathrm{K})/\rho(300\,\mathrm{K}) = 2.3$, suggesting that the resistance at grain boundaries concealed their intrinsic properties.

The blue solid lines in Figure 3 represent the results of the resistance measurements of [Ni(dmdt)$_2$] (Figure 3a) and [Au(tmdt)$_2$] (Figure 3b) between a pair of interdigitated electrodes. The raw resistance values at room temperature ware 14 and 700 Ω, respectively. The normalized resistance behavior of different batches was almost reproducible as far as the contacts between crystals and electrodes were good enough. In this two-probe resistance measurement, many microcrystals bridging the interdigitated electrodes contribute to the electrical conduction. Nevertheless, both samples showed metallic properties down to the lowest temperatures. The resistivity became almost constant below about 10 K. The resistance ratio, $\rho(3\,\mathrm{K})/\rho(300\,\mathrm{K})$, of [Ni(dmdt)$_2$] was 0.29. This value is almost the same as the one obtained by four-probe measurement on the single crystal of [Ni(tmdt)$_2$].[1]

On the other hand, SQUID, ESR, and NMR measurements and the first-principles band structure calculation strongly suggested that [Au(tmdt)$_2$] undergoes an antiferromagnetic phase transition around 110 K.[2,4,6,7] As shown in Figure 3b, the resistance measurements on [Au(tmdt)$_2$] using interdigitated electrodes showed the metallic behavior down to about 10 K, and almost constant resistance at lower temperatures. The resistance ratio $\rho(3\,\mathrm{K})/\rho(300\,\mathrm{K})$ of [Au(tmdt)$_2$] samples was 0.43. These results clearly proved that [Au(tmdt)$_2$] is an antiferromagnetic metal below 110 K. That is, [Au(tmdt)$_2$] is the first

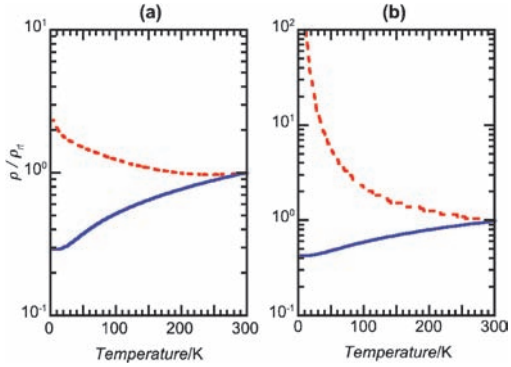

Figure 3. The normalized resistivity of powder samples (red broken lines) and microcrystal samples (blue solid lines) of [Ni(dmdt)$_2$] (a) and [Au(tmdt)$_2$] (b). Powder samples were compressed in pellet and measured by a four-probe method (Refs. 2 and 6).

antiferromagnetic molecular metal with T_N higher than 100 K. It should be noted that despite the large decrease in the susceptibility suggesting the disappearance of a considerably large part of the Fermi surfaces by the antiferromagnetic (or spin density wave) transition, the resistivity showed no anomaly around 110 K.

In summary, we developed a simple method for resistance measurement on as-grown micron-sized crystals. Recently, a resistivity measurement on a micro-sized single crystal was reported using finely fabricated electrodes on a silicon substrate by Yamamoto et al.[8] They achieved four-probe resistivity measurements by cutting unwanted electrode using laser ablation after crystal growth. They found the effect of crystal size on the electrical behavior which is different from the known bulk properties. On the other hand, our simple two-probe method using finely patterned interdigitated electrodes is effective to characterize the temperature dependence of resistance of new compounds whose large single crystals are hardly obtainable, and successfully confirmed the metallic nature of the ground state of single-component molecular conductors [Au(tmdt)$_2$] and [Ni(dmdt)$_2$].

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