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Direct Formation of Micro-/Nanocrystalline 2,5-Dimethyl-*N*,*N*′-dicyanoquinonediimine Complexes on SiO_2/Si Substrates and Multiprobe Measurement of Conduction Properties

Hiroshi M. Yamamoto,*,[†,‡] Hiromi Ito,[†,‡] Kunji Shigeto,[†] Kazuhito Tsukagoshi,[†] and Reizo Kato[†,‡]

RIKEN, JST-CREST, Hirosawa, Wako, Saitama, 351-0198 Japan

Received October 21, 2005; E-mail: yhiroshi@riken.jp

The formation of nanosized single crystals of $(\text{DMe-DCNQI})_2X$ complexes (X = Cu, Ag; DMe-DCNQI = 2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine) directly on silicon substrates is performed using two simple wet processes. Electrode-bridging measurements of the prepared samples reveal differences between the conduction properties of micro- and nanocrystals and bulk crystals of these complexes.

The differences in physical properties between micro- or nanosized materials and the corresponding bulk materials are attracting wide interest.[1] Molecular conductors exhibit many types of phase transitions and conduction phenomena, including the photoinduced insulator−metal transition,[2] humidity sensing behavior,[3] superconductivity,[4] ferroelectricity,[5] and giant negative magnetoresistance.[6] However, size effects have yet to be studied for molecular conductors, primarily due to a lack of techniques for processing these soft materials in crystalline form at sufficiently small scales. Crystals of molecular conductors are ionic and as such are usually insoluble and nonvolatile. The fabrication techniques commonly used for organic field-effect transistors, such as spin-coating or evaporation, are therefore not applicable to these materials. Such materials are also too soft to be processed by methods such as sputtering, etching, or milling. Direct crystal growth on the electrode therefore appears to be a promising method for the fabrication of micro- or nanosized crystals of molecular conductors for physical measurements.[7] To investigate the change in physical properties of molecular conductors with size and gate voltage,[8] our group has developed a procedure for multiprobe measurement of single crystals on Si substrates. This communication presents the fabrication and measurement of single crystals of $(\text{DMe-DCNQI})_2\text{Ag}$ and $(\text{DMe-DCNQI-}d_7)_2\text{Cu}$ prepared directly on SiO_2/Si substrates by simple wet processes.

Two alternative methods, chemical and electrochemical, are presented here for the growth of single crystals of molecular conductors directly on a substrate. In the chemical method, Ti (2 nm), Au (15 nm), and Ag (30 nm) are evaporated onto a SiO_2 (200 nm)/doped-Si substrate to form an electrode, the pattern of which is drawn by electron beam lithography using poly(methyl methacrylate)/methyl methacrylic acid as resists. The substrate is then immersed in a solution of 5 mL of CH_3CN and DMe-DCNQI (ca. 5 mg) in a glass cell, and the subsequent oxidation−reduction reaction between Ag and the acceptor molecule results in crystal growth. Immersion in this solution for 5 min is sufficient to grow $(\text{DMe-DCNQI})_2\text{Ag}$ needle crystals large enough to bridge the gap between electrodes (Figure 1 inset), as confirmed by observation under an optical microscope. The typical size of the crystals is 1−100 μm in length and 100 nm−10 μm in width and thickness. Although the direction of crystal growth is initially random, growth becomes preferentially oriented parallel to the substrate surface due to the mechanical instability of standing crystals under solvent flow across the surface and by the rapid drop in concentration of Ag^+ and $\text{DCNQI}^{\bullet -}$ away from the electrode surface. After removal of the substrate from the solution and drying, the electrodes are cut by laser ablation to form a circuit including the single crystal. In the electrochemical method, the electrode is prepared by deposition of Ti (2 nm) and Au (10 nm) while the substrate is immersed in a CH_3CN solution of DMe-DCNQI and a supporting electrolyte ($AgClO_4$). The cathodic probe is attached to the gold electrode on the substrate, and the anodic probe is brought into contact with the gate electrode (i.e., doped Si). The post-growth processes are similar to those performed in the chemical process. Formation of $(\text{DMe-DCNQI})_2\text{Cu}$ single crystals is performed by the same procedure using Cu instead of Ag (chemical case) or using $(NEt_4)_2[CuBr_4]$ instead of $AgClO_4$ (electrochemical case).

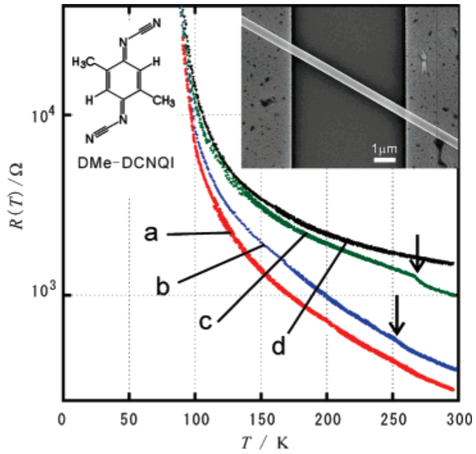

Figure 1. Variation in resistance of $(\text{DMe-DCNQI})_2\text{Ag}$ crystal with temperature from two-probe measurements (a) before and (b−d) after irradiation for 8 h (b), 16 h (c), and 24 h (d). The arrows indicate additional increase of resistance induced by the irradiation. (Inset) Crystal of $(\text{DMe-DCNQI})_2\text{Ag}$ bridging two Au electrodes.

The results of two-probe measurements with respect to temperature are shown in Figure 1 for the $(\text{DMe-DCNQI})_2\text{Ag}$ single crystal. The bulk crystal of $(\text{DMe-DCNQI})_2\text{Ag}$ is known to exhibit a rapid increase in resistivity below 100 K.[9] Similar behavior was observed in the present measurements. However, the weakly metallic behavior exhibited by the bulk crystal near room temperature was not observed in the present samples, probably due to the influence of contact resistance.

In addition to this apparent transition at 100 K, a slight and gradual increase in resistance at 260−290 K dependent on the duration of exposure to light in the ultraviolet−visible regime has also been reported.[10] This feature was also observed in the present experiments, as indicated by arrows in Figure 1.

Although the irradiation time in the present experiments (8−24 h) was not as long as that in Naito's study (5 days), a clear elevation

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[†] RIKEN.
[‡] JST-CREST.

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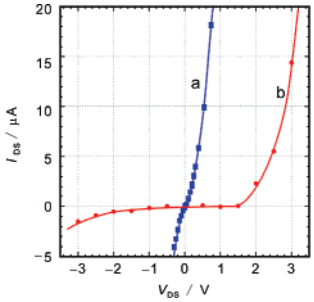

Figure 2. IV characteristics for $(DMe\text{-}DCNQI)_2Ag$ (a) before and (b) after irradiation of half of the crystal.

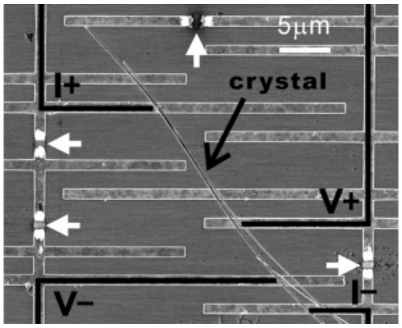

Figure 3. Scanning electron micrograph of four-probe circuit on a $(DMe\text{-}DCNQI\text{-}d_7)_2Cu$ nanocrystal of 100 nm in width and thickness and 60 μm in length. Electrodes were cut at the points indicated by white arrows.

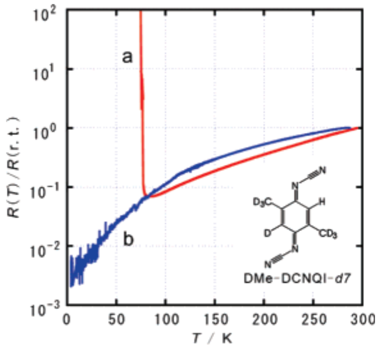

Figure 4. Temperature dependence of resistance for (a) bulk and (b) nanocrystalline $(DMe\text{-}DCNQI\text{-}d_7)_2Cu$.

of the anomaly temperature to above room temperature was observed after irradiation for 24 h. This shortening of irradiation time for emergence of this anomaly can be attributed to the relative smallness of the present crystals, which allows rapid photoexcitation of the entire sample. By irradiating half of the relatively long crystal (50−100 μm), as has also been reported by Naito's group, rectifying behavior was observed as shown in Figure 2. This is considered a consequence of the fact that the irradiation of $(DMe\text{-}DCNQI)_2Ag$ transforms the crystal from n-type to p-type, and a p−n junction is formed in the single crystal.

Analysis of $(DMe\text{-}DCNQI)_2Cu$ was performed using deuterated $(DMe\text{-}DCNQI\text{-}d7)_2Cu$, the anion radical salts of which have been shown to exhibit sharp metal−insulator transitions.[11] Four-probe measurements were performed using a circuit fabricated on a single crystal (Figure 3). The crystal exhibited a monotonic decrease in resistance down to the lowest temperature (Figure 4), without the expected jump at 80 K, indicating that this crystal retains its metallic character through the present temperature range. This is an example of the difference in transition behavior exhibited by nanosized and bulk crystal. It is notable that the contact resistances in these measurements were very low, despite the small contact area (about 1 kΩ for 0.1 μm^2 contact area).

The size effects revealed by the present experiments have many possible explanations. However, as most of the mass of the nanocrystal forms part of the surface of the material, the physical and/or chemical conditions at such small scales can be expected to differ from those exhibited by bulk crystal. The effects of differences in thermal contraction rates between the substrate and the molecular crystal and of differences in work function between the electrode and the molecular conductors, which results in partial doping of the crystal, are also predicted to be important factors. More detailed studies of these size effects are therefore necessary to clarify their origins.

In summary, two wet processes have been developed for the fabrication of conductive molecular devices on silicon substrates. For $(DMe\text{-}DCNQI)_2Ag$, phase transitions were confirmed for the microcrystals, but $(DMe\text{-}DCNQI\text{-}d7)_2Cu$ did not show any sign of phase transition at 80 K that is expected by the bulk measurement. In addition, rectifier was successfully fabricated on the substrate. The methods are simple, fast, convenient, and low-cost, and as such they are expected to open the way for scientific research on nanosized molecular conductors. The fabrication methods are also useful for the preparation of devices such as sensors, for which the large surface/volume ratio of nanocrystals will be beneficial.

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Supporting Information Available: Hazard information, experimental details, and two-probe measurement results of $(DMe\text{-}DCNQ\text{-}d_7)_2Cu$. This material is available free of charge via the Internet at http://pubs.acs.org.

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