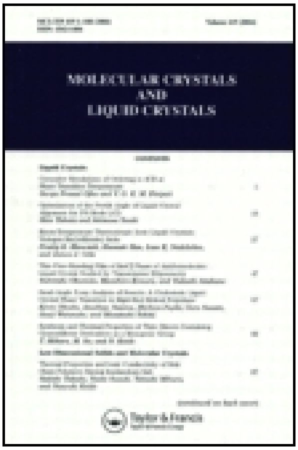

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Morphology and Electric Properties of Nonathiophene/Au Nano-Composite Thin Films Formed Between 1 μm Gapped Electrodes

Takuji Ogawa [a b], Wei Huang [a b] & Hirofumi Tanaka [a b]

[a] Research Center for Molecular Nanoscience, Institute for Molecular Science, National Institutes of Natural Sciences, Myodaiji-cho, Okazaki, Aichi, Japan

[b] Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan

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Takuji Ogawa
Wei Huang
Hirofumi Tanaka
Research Center for Molecular Nanoscience, Institute for Molecular Science, National Institutes of Natural Sciences, Myodaiji-cho, Okazaki, Aichi, Japan, and Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Agency (JST), Kawaguchi, Saitama, Japan

A nano-composite conductive film is formed between gold electrodes by immersion of the electrode pair in a chloroform solution of nonathiophenedithiol and gold nanoparticles. The homogeneous thin film is formed over an area of 3 mm × 3 mm surrounding the 1 μm-gapped electrodes. The thickness of the film (20 nm) corresponds to 2–3 layers of the dithiol-bridged Au nanoparticles. Temperature-dependent I-V curves reveal that a thermionic mechanism dominates in the high-temperature region (>80 K), while molecular tunneling is the main transport process at lower temperatures.

Keywords: conduction mechanism; dithiol Au nanoparticle composite; morphology

INTRODUCTION

Molecular electronics is a relatively new and fascinating area of research. However, as most single organic molecules are not conductive in a classical sense, long-range electronic transport

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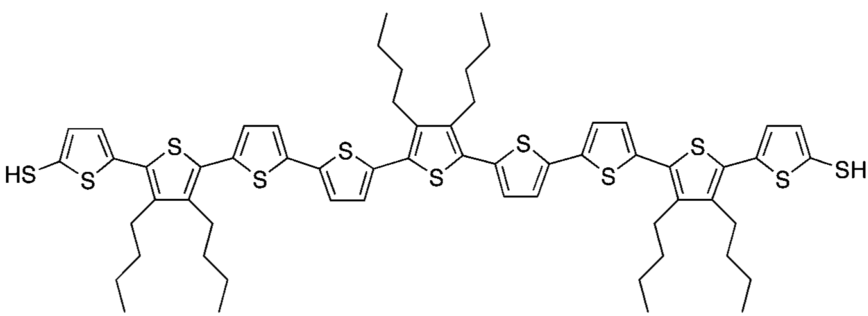
Address correspondence to Takuji Ogawa, Research Center for Molecular Nanoscience, Institute for Molecular Science, National Institutes of Natural Sciences, 5-1 Higashiyama, Myodaiji-cho, Okazaki, Aichi, 444-8787, Japan. E-mail: ogawat@ims.ac.jp

through single molecules is unlikely to be useful for practical electronic circuits. Our group is interested in composites of conductive nano-materials as attractive bases for molecular electronics. Structures such as carbon nanotubes, metal nanoparticles [1], and metal nanorods incorporating functional organic molecules have been shown to be possible. In a previous paper, homogeneous films formed by the simple mixing of organic dithiols with gold nanoparticles were shown to exhibit semi-conductor like electrical properties [2,3]. The present paper reports on the fabrication, morphology and electrical properties of films formed from nonathiophenedithiol and gold nanoparticles [4].

EXPERIMENTAL

The preparation of **1** has been reported previously [3]. Activated Au nanoparticles protected by *t*-dodecanthiol were prepared by a modified method of Brust [5].

The nano-composite film was formed between two gold electrodes as follows. The gold electrode pair (~1 μm width, ~1 μm gap) was cleaned and immediately immersed in a chloroform solution of nonathiophenedithiol **1** (0.1 mmol/L) for 30 min. To this solution was added a chloroform solution of *t*-dodecanethiol-protected active Au nanoparticles (0.1 mmol/L). This mixture was let stand for 30 h at room temperature in a glove box. The electrodes and surrounding film were then extracted, washed thoroughly with chloroform to remove excess unreacted Au nanoparticles and dithiols, and dried in a vacuum.



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SCHEME 1

RESULTS AND DISCUSSION

The scanning electron microscopy (SEM) image of the electrode pair (Fig. 1) reveals that a thin film with a rough surface formed around the Au electrodes in this procedure. A relatively smooth, dense and thick film also partially coated the electrodes, accompanied by sparse amorphous clusters. These amorphous clusters are postulated to have formed within the solution and adhered to the film surface during preparation, and the majority of these clusters can be removed by repeated washing with organic solvents. The roughness of the film between the electrodes was determined by AFM to be 7–10 nm, which approximately matches the size of the dithiol-bridged Au nanoparticles. From the depth of the cracks, the thickness of the film is estimated to be around 20 nm, corresponding to 2–3 layers of nanoparticles. This process could therefore be used to deposit a homogeneous thin film of 2–3 particle layers in thickness over an area of 3 mm × 3 mm on device chips. This can be achieved simple by mixing dithiol and Au nanoparticles in the presence of electrodes.

Arrhenius plots of the current vs. temperature characteristic at various voltages (0.2–3.8 V) are shown in Figure 2. At higher temperature (>80 K) the current was strongly dependent on the temperature

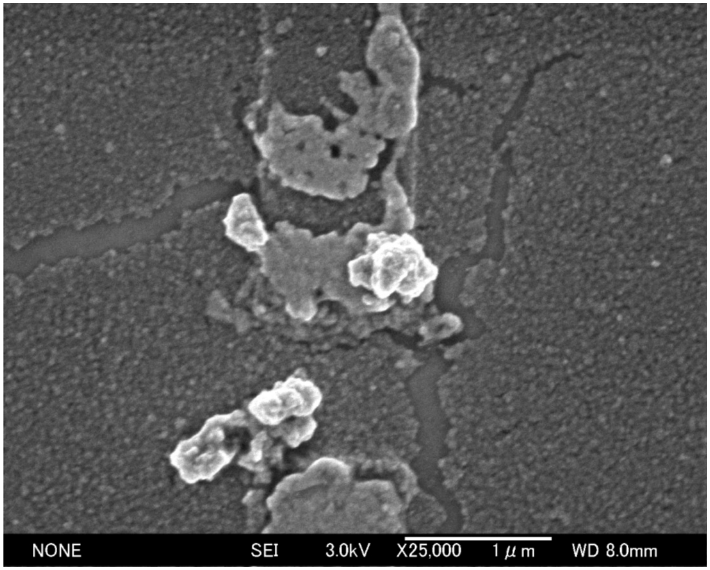

FIGURE 1 SEM image of film prepared from dithiol **1** and Au nanoparticles between 1 μm gapped Au electrodes.

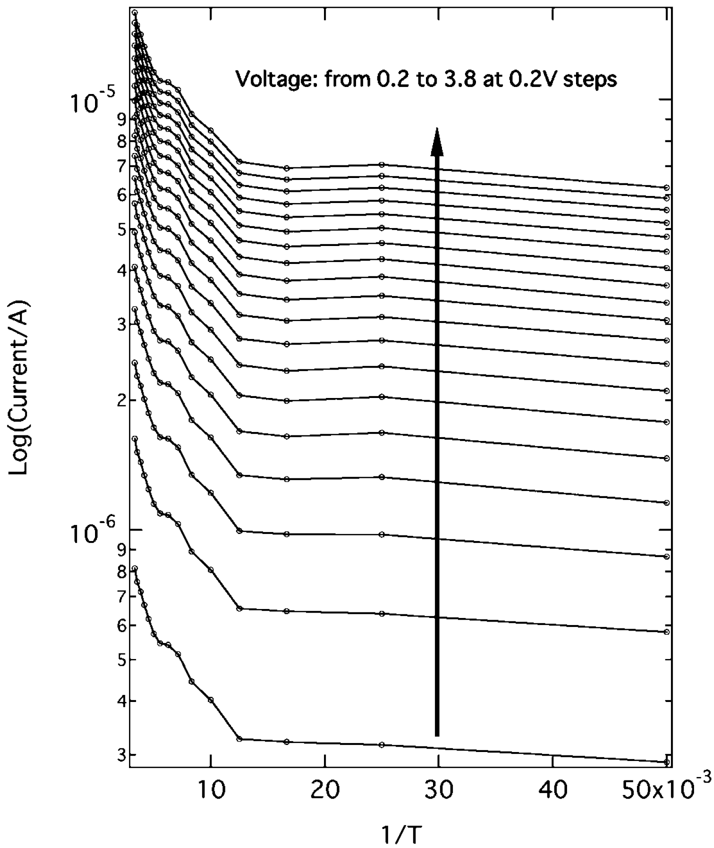

FIGURE 2 Arrhenius plots at voltages from 0.2 to 3.8 V.

showing that thermally excited conduction mechanism dominated. Detailed mechanistic discussion of this temperature range will be described elsewhere. Below 80 K, the current is almost independent of temperature, which is consistent with a tunneling conduction mechanism [6]. An interesting finding is the observation of characteristic structures in the d*I*/d*V*-*V* spectra for this film at low temperature (Fig. 3). These structures disappeared above 80 K, indicating that the structures reflect the density of state of the molecule. Tunneling conductance through the molecules therefore appears to be dominant at low temperature (< 80 K). These structures were not observed for all films prepared in this manner, probably due to the overlap of characteristics when a large number of conduction paths are present. These films also displayed cracks in the electrode span, which may have

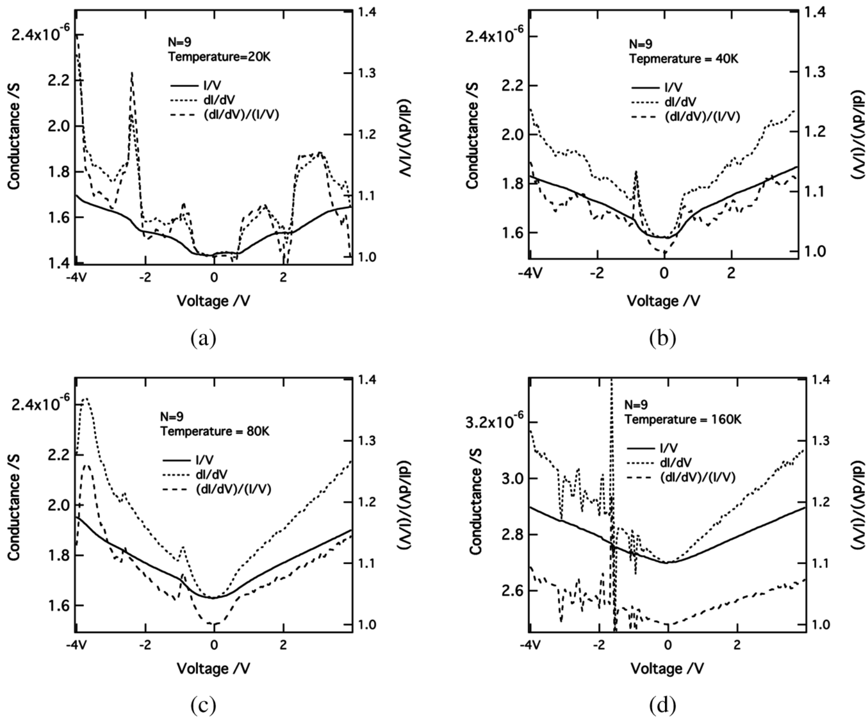

FIGURE 3 Conductance (solid line), differential conductance (dotted line), and $(dI/dV)/(I/V)$ (broken line) characteristics at (A) 20 K, (B) 40 K, (C) 80 K, and (D) 160 K.

obstructed the conduction path and affected the detailed structures observed in the dI/dV-V spectra.

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