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Switching and Memory Phenomena of Cu-TCNQ Thin Films Triggered by a Stimulus with an STM Tip

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Switching and memory phenomena were observed of Cu-TCNQ films, triggered by a stimulus with an STM tip. When a 1.5-volt stimulus was given to the film surface for 1 min, a convex image (120 nm in diameter) appeared in the STM image. This image, stable for at least 20 hours at room temperature, was deleted by a heat treatment.

Switching and memory phenomena have been observed by Potember et al.[1-4] using thin films of either copper or silver complex with an organic electron acceptor, TCNQ (7,7,8,8-tetracyanoquinodimethane). The conductivities of these films change reversibly by applying electric fields or laser irradiation. The high-conductive state reverts spontaneously to the low-conductive state when electric fields or laser irradiation is removed. Scanning Tunneling Microscope (STM) is a powerful tool in examining surface structures of solids. Recent progress in the utilization of STM has made it feasible to use STM for surface modifications of nanometer scale such as nanolithography[5] and atomic or molecular manipulation[6-8] as well as for the observation of structual images of the surfaces of various materials. It will open up a wide scope of applications of STM if switching phenomena are triggered by applying voltage with STM tips. In this study, we report the switching and memory effects of Cu-TCNQ thin films by applying voltage to the films with STM

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tips, examining structural changes of the surfaces of the films.

Cu-TCNQ films were prepared on HOPG (highly oriented pyrolitic graphite) by vapor deposition[9] for STM observations. First, 10 mg of TCNQ and 2 mg of Cu were vacuum-evaporated in this order. The complexation reaction proceeded by annealing this film in vacuum at 340-350 K for 15 min.[10] The resultant film was ca. 400 nm thick. A Nanoscope II (Digital Instruments Inc.) was used for all the STM measurements in this study with commercially available Pt-Ir tips in air at room temperature in the constant current mode.

Figure 1(a) shows a typical STM image of Cu-TCNQ film surface of an area 5.0 × 5.0 μm^2 with a tunneling current of 1.0 nA and a bias voltage of 600 mV. The maximum of the roughness was ca. 200 nm. A relatively planar surface of the size of 0.5 × 0.5 μm^2 as shown in Fig. 1(b) was chosen for the switching experiments.

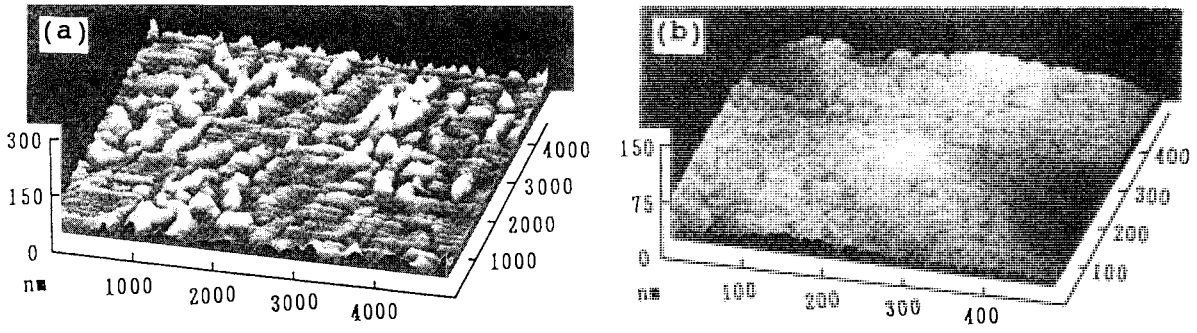

Fig. 1. The STM image of Cu-TCNQ films on HOPG: (a) a surface of 5.0 × 5.0 μm^2 and (b) an area of 0.5 × 0.5 μm^2.

Switching effect was examined as follows: (1) The STM image of the surface was observed with a bias voltage of 600 mV. (2) A stimulus was given to the surface by applying a constant bias voltage of 1 to 5 V for a given period with the tip held at the center position. (3) The STM image of the surface was observed with a bias voltage of 600 mV to examine the effect of the stimulus.

The switching and memory effects of the films were examined by changing the stimulus with the variation of the applied voltage and the duration period of the voltage. The initial surface of Cu-TCNQ film was almost planar with the roughness of ca. 20 nm.

First, the effect of the applied voltage was examined by changing the applied voltage from 1 to 5 V with a fixed duration period of 1 min. When a stimulus of 1.0 V was used, no change was observed in the structure of the film surface. In the case of a stimulus of 1.5 V, however, a convex image appeared as is shown in Fig. 2(a). This protuberance in the image, ca. 120 nm in diameter and ca. 40 nm in height, is probably due either to

the increased conductivity of the triggered portion of the film or to the rising of the particular portion of the surface. In contrast, a concave image of ca. 150 nm in diameter and of ca. 50 nm in depth was observed as is shown in Fig. 2(b) when a stimulus of 2.0 V was used. The hole in the STM image is formed probably due to destruction of the surface of the film. Similar results were obtained with a triggering voltage of 5.0 V.

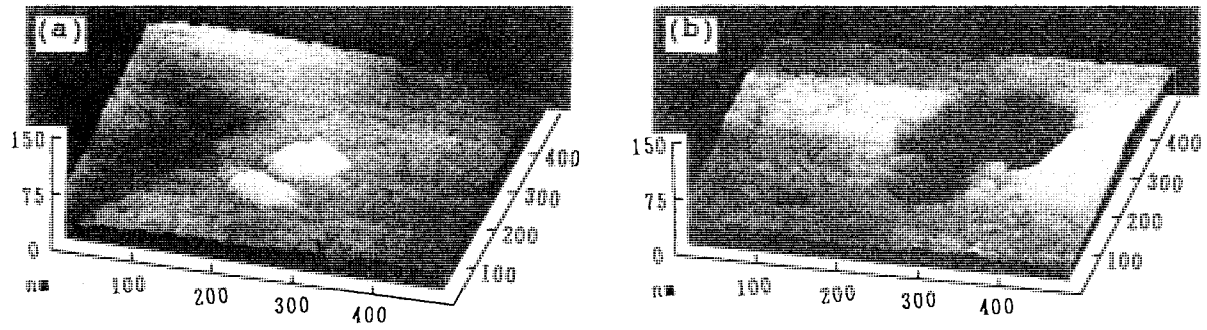

Fig. 2. The STM image of Cu-TCNQ films after applying a stimulus for 1 min: (a) a 1.5-volt and (b) a 2.0-volt stimulus.

Second, the effect of the duration period was studied by decreasing the duration period to 1 s. In this case, no change was observed in the STM image with an applied voltage below 2.0 V. A convex image was seen with a 3.0-volt stimulus, and a concave image appeared with a 5.0-volt stimulus. These phenomena seem to be similar to those for the cases with the duration period of 1 min. The main difference is that the threshold voltage of the formation of the convex image and the one from the convex to the concave image increased with a decrease in the duration period.

Third, the memory effect of the convex image was observed. Figure 3(a) shows a convex image triggered by a 1.5-volt stimulus for 1 min. No change was seen in 20 hours at room temperature after the stimulation (Fig. 3(b)).

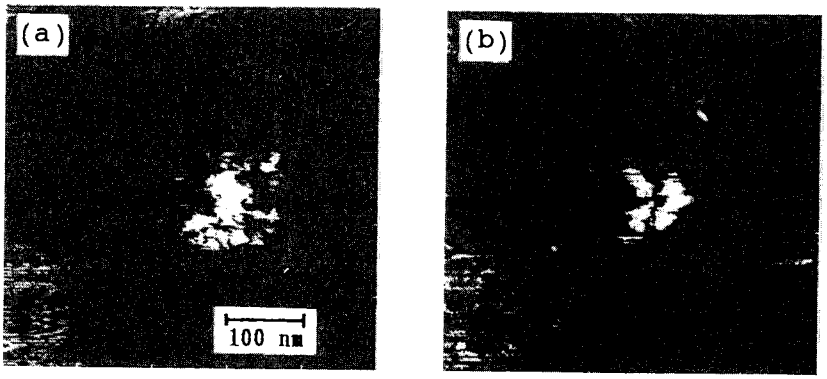

Fig. 3. The STM image of a triggered surface: (a) just after the triggering and (b) in 20 hours after the removal of the electric fields.

Last, the reversibility of the switching phenomena was confirmed. The convex image was formed on the surface by applying a 1.5-volt stimulus for 1 min (Fig. 4(a)). Then the image became planar by a heat treatment at 330 K for less than 1 min (Fig. 4(b)). Another stimulus of the same voltage and the same duration period to the same place restored another convex image as is shown in Fig. 4(c).

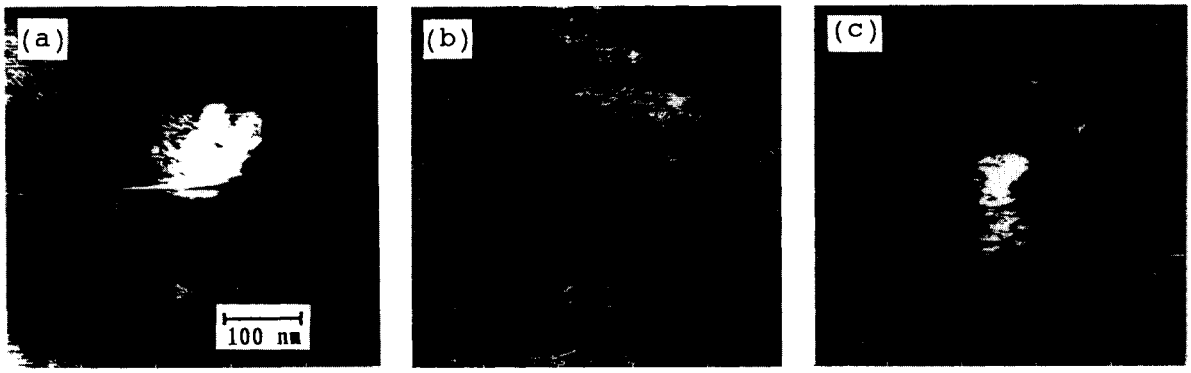

Fig. 4. The STM image in a cycle of the triggered, deleted, and retriggered surface: (a) triggered by a 1.5-volt stimulus for 1 min, (b) deleted by a heat treatment at 330 K for less than 1 min, (c) retriggered by a 1.5-volt stimulus for 1 min.

In conclusion, we have observed the switching and memory effects of Cu-TCNQ thin films triggered by a stimulus with an STM tip. The convex and concave images of 100 nm scale were drawn by using this technique. The threshold voltages of the trigger depend on the duration period of the stimulus with the STM tip. Among others, the convex image was deleted by a heat treatment and another image was restored by another stimulus. We have demonstrated that it is feasible to utilize Cu-TCNQ thin films as switching and memory devices and also to use an STM tip as a trigger.

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