

# Nanometer-scale data storage on 3-phenyl-1-ureidonitrile thin film using scanning tunneling microscopy

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We present nanometer-scale data storage on 3-phenyl-1-ureidonitrile thin film using scanning tunneling microscopy (STM). This monomer film can become polymerized when a voltage pulse is applied between the STM tip and the substrate. The affected region changes from being electrically resistant to electrically conductive along the direction of the polymeric molecular chain. The recorded mark of the data occurs in the region, and is 0.8 nm. We have obtained recorded marks arranged regularly as  $6 \times 8$  arrays. A possible chemical mechanism of this data storage would be the phase transition from the monomer state to the polymeric state. The small marks are very stable.

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## I. INTRODUCTION

Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been used increasingly to make surface modifications on the nanometer scale to develop electronic devices for high-density data storage.<sup>1-12</sup> The main mechanism of data storage is phase transition from an amorphous state to a crystalline state.<sup>5</sup> Many kinds of organic functional complex materials have been used to prepare thin films as storage media, such as Cu-TCNQ (7, 7, 8, 8-tetracyanoquinodimethane),<sup>2</sup> Ag-TDCN (toluylene 2,4-dicarbamidoni-trite),<sup>6</sup> and m-NBMN/DAB (m-nitrobenzal malononitrile and diamine benzene).<sup>7</sup> The smaller data recorded marks can be acquired from these organic complex thin films, because the record does not need a relatively large region for phase transition from an amorphous state to a crystalline state.<sup>7</sup> In data storage recording, the region of the films used for storage must be very smooth and have a certain character. On the other hand, the films should have a large enough single-crystal region for larger-area recording for applications. It is very difficult to get a large enough single-crystal region in organic complex thin films. So we have turned our attention to single organic materials. It may be easier to get a large enough smooth single-crystal region for data storage in organic single thin film. Our research group made ultrahigh-density data storage using single thin films of *N*-(3-nitrobenzylidene)-*p*-phenylenediamine (NBPDA) and 3-phenyl-1-ureidonitrile (CPU), respectively.<sup>11,12</sup>

In this article, we used CPU as the data storage material. The purpose of our study was to arrange a number of recorded marks regularly in a relatively large area. We eventually acquired data recorded marks arranged regularly as  $6 \times 8$  arrays in a large region. The marks are about 0.8 nm.

## II. EXPERIMENT

The CPU monomer films were prepared from powdered materials by vacuum evaporating deposition. The base

vacuum of the evaporating system was  $5 \times 10^{-4}$  Pa. The vacuum level during deposition was about  $8 \times 10^{-4}$  Pa. The heating temperature was about 80 °C. The heating time was maintained at 5 min. The monomer CPU film was deposited on a freshly cleaned highly ordered pyrolytic graphite (HOPG) substrate. The thickness of the films was about 10 nm.

The experiments were performed with a homemade CSTM-9100 under ambient conditions. A sharp Pt-Ir tip snipped with a wire cutter was used as the STM tip. STM operation was in constant height mode. The recorded marks were obtained by applying voltage pulses between the tip and the HOPG substrate. Current-voltage (*I-V*) curves were measured by STM to determine the change in the electrical property of the region on the film before and after the voltage pulse. The STM tip was very stable. The HOPG atomic image could be clearly observed using the same STM tip before and after recording experiments.

## III. RESULTS AND DISCUSSION

The CPU molecular formula is  $C_8H_7N_3O$ . There is  $C \equiv N$  (cyan) in the CPU molecule,  $C_6H_6-NH-CO-NH-C \equiv N$ . There are two  $\pi$  bonds in  $C \equiv N$ , apart from one  $\sigma$  bond in  $C \equiv N$ . The  $\pi$  bonds are not strong and are easy to be broken under mechanical force. The CPU monomers will polymerize in the area of broken  $\pi$  bonds. The change from the monomer state to the polymeric state may occur when applying voltage pulses between the tip and the thin film. The CPU monomer is electrically resistant. Otherwise, the CPU polymeric state is electrically conductive along the polymeric molecular chain. The CPU films change from electrical resistance to electrical conductance can be used to make data storage recording in STM experiments.

Figure 1 shows a typical STM image of the monomer CPU thin film. The scanning mode was constant height. The scanning condition was  $V_{\text{bias}} = 0.8$  V and  $I_{\text{ref}} = 0.3$  nA. The scanning area was  $100 \text{ nm} \times 100 \text{ nm}$ . From Fig. 1, one notes a very uniform and rather planar surface. The uniform, smooth film with a suitably large single-crystalline region is the basis

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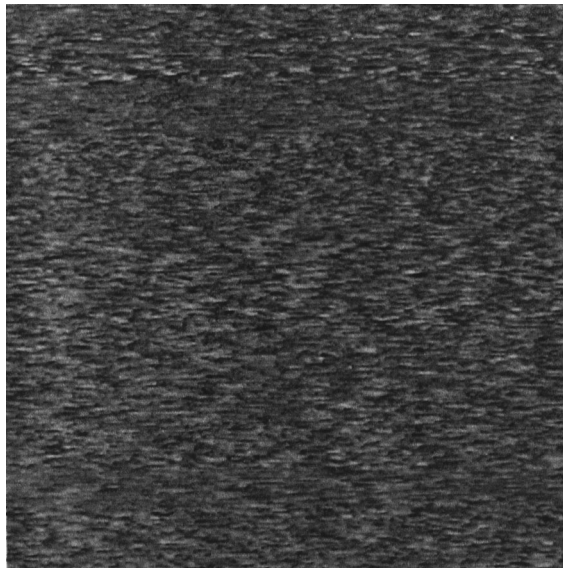


FIG. 1. Typical STM image of a monomer CPU thin film.  $V_{\text{bias}}=0.8$  V,  $I_{\text{ref}}=0.3$  nA. Scan area:  $100\text{ nm}\times 100\text{ nm}$ . Scan mode: Constant height.

for large-area data storage. This uniform, planar surface of the CPU thin film makes it possible for use in large-region data storage.

Figure 2 is a STM image of the CPU film with recorded marks arranged as  $6\times 8$  arrays. The scanning condition was  $V_{\text{bias}}=0.8$  V and  $I_{\text{ref}}=0.3$  nA. The scanning area was  $64\text{ nm}\times 64\text{ nm}$ . The scanning mode was constant height. The recorded marks were made by repeatedly applying voltage pulses of 4.0 V for 10 ms on the film one by one. One applied pulse voltage produced a bright dot in the region, with one bright dot corresponding to a recorded mark. A

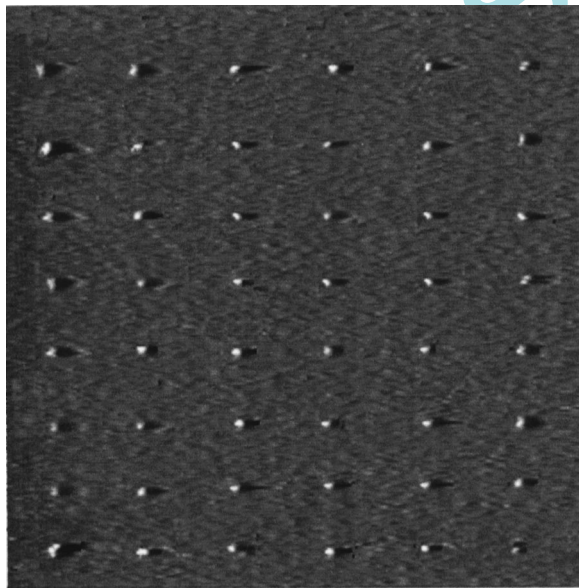


FIG. 2. STM image of CPU film with recorded marks arranged as  $6\times 8$  arrays. The recorded mark was obtained by applying a voltage pulse of 4.0 V for 10 ms.  $V_{\text{bias}}=0.8$  V,  $I_{\text{ref}}=0.3$  nA. Scan area:  $64\text{ nm}\times 64\text{ nm}$ . Scan mode: Constant height.

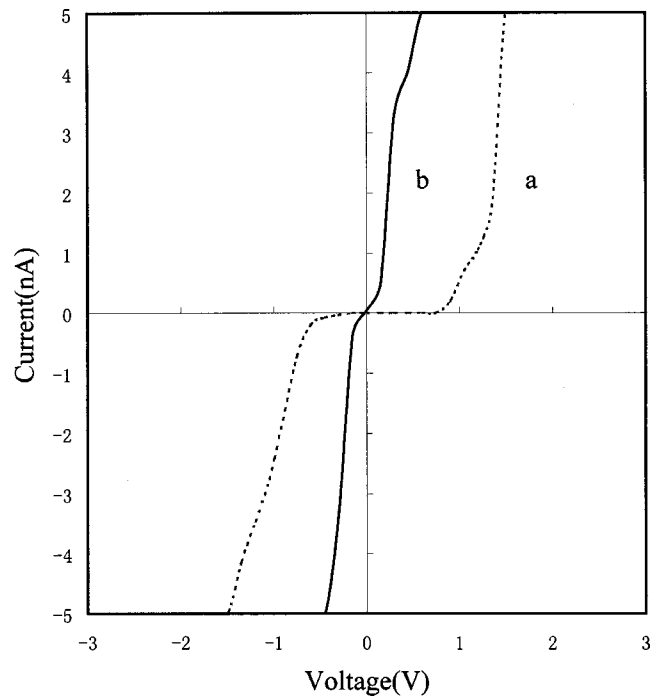


FIG. 3.  $I$ - $V$  curves of the region before and after the voltage pulse. Curve (a) shows region before the voltage pulse. Curve (b) is the region after the voltage pulse.

recorded pattern of  $6\times 8$  arrays was obtained by controlling regions of the recorded marks. The recorded marks were very stable during the scanning period, which lasted more than 2 h. In the data recording experiment, the percentage of successful recording was about 90%. It was known that numerous recorded marks could be obtained; however, it was very difficult to obtain numerous recorded marks arranged as uniform arrays in the STM experiment. Fortunately, we achieved a recorded pattern of uniform arrays, with 48 marks in the film.

To understand the mechanism of data recording,  $I$ - $V$  curves of the regions were measured by STM before and after the voltage pulse. The different  $I$ - $V$  curves of the region before and after the voltage pulse are shown in Fig. 3. Curve (a) is the  $I$ - $V$  character of the region before the voltage pulse. Curve (b) is the  $I$ - $V$  character after the voltage pulse. The region before the voltage pulse was electrically resistant, based on the  $I$ - $V$  characteristics of curve (a); on the other hand, the region after the voltage pulse was electrically conductive, as seen from the  $I$ - $V$  characteristics of curve (b). From the  $I$ - $V$  relations shown in Fig. 3, it is suggested that the recording mechanism is due to the conductance change in the thin film. There were delocalized electrons in the recorded regions. We attempt to explain the conductance change through the chemical structure of CPU molecules. Before the voltage pulse, the monomer state of CPU is electrically resistant, and the delocalized electrical system only exists in the single monomer CPU molecule. The film is highly electrically resistant at small voltage; however, the film allows tunneling current for STM experiments at small bias voltage that corresponds to a relatively high electric

field. When we apply a voltage pulse along the direction perpendicular to the film surface, a much higher electric field (over a critical value) is added to the monomer film, the  $\pi$  bonds in the affected region may be broken, and the monomer molecules polymerize. Finally, a conductive polymeric molecular chain may form in the affected region, a delocalized electronic system exists along the polymeric chain, and the region becomes electrically conductive. A bright dot could be observed at the local region of the polymeric chain in the STM image and the dot corresponds to the recorded mark. It is noted that some energy was needed to open the cyan bond. When applying a voltage pulse in the film between the tip and the HOPG substrate, the region in the film that is affected is very small. The cyan bonds in this small region may be broken, but the cyan bonds in the other region may not be broken. The recorded mark was very stable because it was caused by delocalized electrons in the polymeric chains. It is useful to characterize the polymer product by conventional spectroscopic methods, but it is not easy to find or locate every polymerized region in the characterization by spectroscopy under our present conditions.

The resistivity of the film is much higher than that of the HOPG substrate; the electric field mainly acts on the film. So the damaged HOPG substrate is not the main mechanism of data recording. Of course, a defect can be created in the damaged film by applying even higher voltage pulse, and the conductive HOPG substrate emerges which also causes a bright dot. In these STM experiments, we could not get a HOPG atomic image in the recorded regions, so we applied a voltage pulse of 5 V for 20 ms to a recorded dot and scanned the region at a high tunneling current to clean the region. Finally, we got a standard HOPG atomic image. It can be said that the defect in the film is not the mechanism of this data storage. It also confirms that deformation of the HOPG substrate is not the main mechanism of data recording.

#### IV. CONCLUSION

Uniform, regularly arranged data storage marks were obtained using a scanning tunneling microscope. An organic

monomer material was used as the data storage material. This monomer material might change to a polymeric state under a critical high electric field. Polymerization caused the change in the films' electrical property. The monomer state film was deposited by vacuum evaporation. The recorded marks were produced when voltage pulses were applied to the film in the STM experiments. The recorded marks were 0.8 nm and were very stable. A possible chemical mechanism of data storage could be polymerization of the monomer material, which may be a prospective technique in nanometer-scale data storage.

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