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Nanometer-scale recording with transition time at nanosecond

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Abstract

Recording at a nanometer-scale on 3-phenyl-1-ureidonitrile (CPU) thin films is successfully conducted using scanning tunneling microscopy (STM) in ambient conditions. Recorded marks are written when a series of voltage pulses are applied between the STM tip and the freshly cleaned highly ordered pyrolytic graphite (HOPG) substrates. STM current–voltage (*I*–*V*) curves of the films show that the electric resistance in the recorded regions is much lower than that in the unrecorded regions. Standard four-point probe measurements indicate that the transition time of the transient conductance is 6 ns. It is suggested that CPU organic thin films have potential in the application of future data storage.

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Keywords: Recording; Data storage; Transient conductance; Scanning tunneling microscopy

1. Introduction

Nanometer-scale data storage has stimulated much attention during the few past years because of its great technological interest. Much progress on this subject has been made recently [1–5]. Scanning probe microscopy (SPM), including scanning tunneling microscopy (STM) and atomic force microscopy (AFM), has been used increasingly to make surface modification for developing electronic devices for nanometer-scale data storage due to imaging and structuring down to the atomic scale [6–13]. Different materials have been used successfully for nanometer-scale data recording by SPM. Among them, organic molecules are paid much attention since molecular structures and thus the corresponding properties are controllable [14–22]. For example, Ma and his cooperators [17] have reported nanometer-scale recording on *m*-nitrobenzal malononitrile and diamine benzene (*m*-NBMN/DAB) complex thin films, and reached the data density of about 10^{13} bits/cm^2. It is well known that the films used for nanometer-scale storage must be very smooth and have a single-crystal region large enough for a larger-area recording in practical application. It is more convenient to meet the above demand in single organic thin films than in complex thin films [23]. So we pay attention to single organic materials. On the other hand, the fast transition between 0 and 1 state is also needed in nanometer-scale data storage for practical application.

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In this paper, we present the nanometer-scale data recording employing 3-phenyl-1-ureidonitrile (CPU) monomer thin films as media. The recording marks are performed in STM experiments through conductance transition when applying voltage pulses between the STM tip and the highly ordered pyrolytic graphite (HOPG) substrates. The transition time of transient conductance of the thin films is about 6 nm, which is ultrafast and adequate for practical application.

2. Experiment

The organic CPU material is deposited from powder materials on freshly cleaved HOPG substrates by vacuum evaporation. The base vacuum of the evaporation system is about 4×10^{-4} Pa. The organic powder material is heated to 80°C, in a crucible, in the vacuum chamber. The vacuum during deposition is about 7×10^{-4} Pa. The film thickness is about 20 nm.

The STM experiments are performed with a home-made CSTM-9100 in ambient conditions. A sharp Pt–Ir tip snipped with a wire cutter is used as the STM tip. The STM operation is in constant height mode. The recorded marks are obtained by applying voltage pulses between the STM tip and the HOPG substrates. STM current–voltage (*I–V*) curves are measured to indicate the change of electrical property of the unrecorded and recorded regions on the films. The STM tip is very stable; the HOPG atomic image could be clearly observed using the same STM tip before and after recording experiments.

3. Results and discussion

The STM images show that the CPU thin films have a uniform and rather planar surface, which is necessary for use in large-region data storage. The uniform, smooth film with a suitably large single-crystallized region is the basis for writing patterns.

Fig. 1 shows an STM image of a typically recorded pattern. The bright dots of 0.8 nm diameter in the STM images correspond to the recorded marks which are made by applying voltage pulses of 4.0 V for 10 ms, on the selected regions, one by one repeatedly. The scanning condition is $V_{\text{bias}} = 0.8$ V and $I_t = 0.3$ nA. The scanning mode is constant height. The recorded patterns are very stable during the scanning period for more than 2 h. In the data recording experiment, the ratio of successful recording is about 90%.

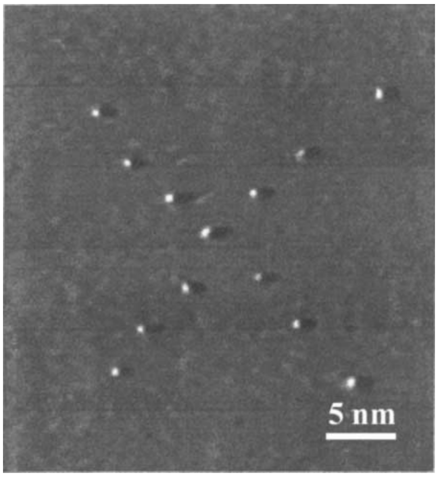

Fig. 1. STM image of a typically recorded pattern in CPU thin films. The recorded marks are obtained by applying a series of voltage pulses 4.0 V for 10 ms. Scanning condition: $V_{\text{bias}} = 0.8$ V, $I_t = 0.3$ nA; scan mode: constant height.

To understand the mechanism of the data recording, *I–V* curves of the unrecorded and recorded regions are measured by STM separately; the results are shown in Fig. 2. Curve a is the typical *I–V* character of the unrecorded regions, and curve b is the typical *I–V* character of the recorded regions. The unrecorded regions of the film before the voltage pulse are in a

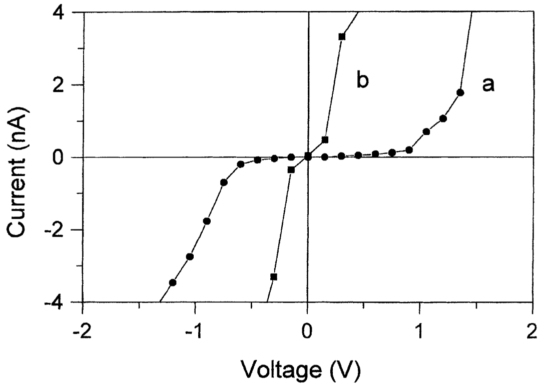

Fig. 2. Typical *I–V* curves of the recorded and unrecorded regions of the CPU thin films. Curve a is related to the unrecorded regions and curve b to recorded regions.

highly insulating state, which become conductive above a voltage threshold of about 1 V. In comparison, the recorded regions after the voltage pulse are electrically conductive indicating a transition to the conductive state.

From the above *I–V* curve measurement, it can be said that there is a conductance transition after the voltage pulse, but what is the cause of this transition. It is certain that the resistivity of the films is much higher than that of the HOPG substrate, and the electric field is mainly acted on the film. Probably, the high electrical field induces the field evaporation of the films, and then the conductive HOPG substrate may emerge which can cause the conductance transition, and thus a bright dot is observed. Otherwise, it can be suggested that the emergence of HOPG substrates after the damage of film by field evaporation is not the main cause of the conductance transition in the bright dots through the below experiment. At first, we scan the recorded region, but we cannot get the HOPG atomic image, then we apply a voltage pulse of 5 V for 20 ms and scan the recorded region at a high tunneling current to clean the region. Finally, we obtain the standard HOPG atomic image. We can also conclude that the mechanism of data recording is related to the conductance transition of CPU thin films.

The monomer state of CPU is electrically resistant, and the delocalized electrical system only exists in the single monomer CPU molecules [24]. There is a nitrile triple bond (C≡N) in the CPU molecule C_6H_6–NH–CO–NH–C≡N. There are two π bonds, apart from one σ bond in C≡N. The π bonds are not strong and may break under mechanical action, and the CPU monomers will polymerize in the area of broken π bonds, which is electrically conductive along the polymeric molecular chain direction. Fig. 3 is the diagram of CPU from monomer state to polymeric one. Before the voltage pulse in the STM operation and the monomer state films are 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 electrical 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 π bonds of C≡N in the affected region may break, 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 affected region becomes electrically conductive. A bright dot, which corresponds to the recorded mark, could be observed at the local region of the polymeric chain in the STM image. It is suggested that the data recording can be probably realized by the electrical conductance change between monomer state and polymeric state of CPU film.

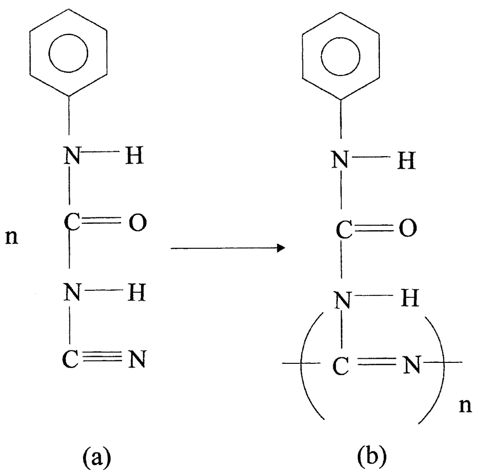

Fig. 3. Polymerization mechanism of data recording of CPU thin films related to: (a) the monomer state, which is in high electrical resistance; (b) the polymeric state, which is in low electrical resistance.

It is noted that opening π bond needs certain extent of energy. When applying a voltage pulse in the film between the tip and the HOPG substrate, the affected region in the film is very small. The π bonds in this small region may break, but the π bonds in the other region may not break. So the recorded marks are very small with the size 0.8 nm in diameter. Meanwhile, the recorded mark is very stable probably because it is caused by structural transition from a monomer state to polymeric one.

Of course, if we can observe the recorded regions using AFM before and after voltage pulses separately, the mechanism of data recording will be clearer. In addition, we try to know deeply the mechanism of data recording by other methods, for instance, conventional spectroscopic methods. Otherwise, every mark of data recording is too small to be found and located in our present condition.

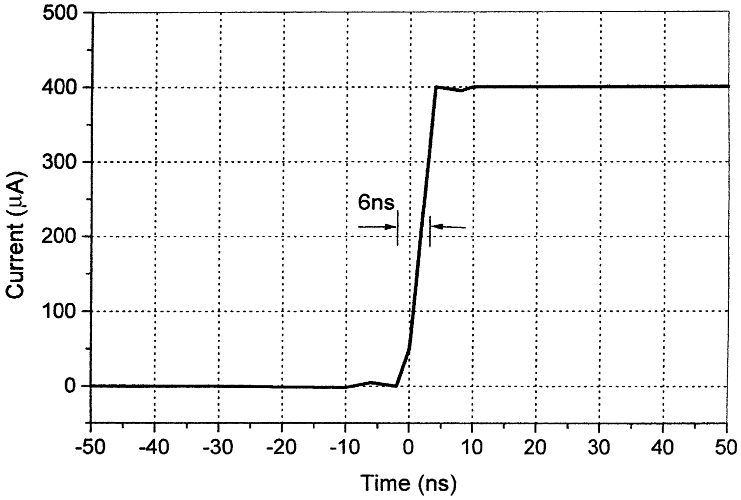

Fig. 4. Transient conductance measurement of 100 nm thick CPU films. The transition time is 6 ns between 0 and 1 state.

On the other hand, we use a standard four-point probe measurement to perform the *I–V* relationships and transition time of transient conductance on the 100 nm thin films. The *I–V* relationships also indicate that the films are electrically bistable. When increasing the voltage stepwise from zero, the current is about zero too at first stage, but when the voltage reaches to 9 V, the films abruptly switch to a conductive state. Fig. 4 shows the transient conductance of the films from high-resistant state to a conductive state, the transition time of the films is measured to be about 6 ns. It is obvious that the transition of transient conductance of the CPU thin films is in nanosecond, and the films have potential advantage in the application of ultrafast data storage.

In addition, the rate of data recording with one single STM tip is very slow, which is not adaptive to the actual application. The long-term perspectives are SPM multi-tips. For example, Binning and his cooperators [25] in IBM Research have performed AFM-based data storage using 32 × 32 probe arrays. Our next proposal is to develop multi-tips in the STM or AFM operation.

4. Conclusion

The organic monomer thin films CPU are used as data storage media prepared by vacuum evaporation. The recorded marks are obtained when applying a series of voltage pulses between the STM tip and the HOPG substrates in the STM experiments. The mechanism of data recording may be the polymerization of the monomer films in the local regions, which cause the conductance transition of the films from low state to high state. The transition time of transient conductance of 100 nm thick CPU thin films is about 6 ns. It is indicated that the CPU monomer thin films have potential in ultrahigh density data storage.

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