

## Direct observation of a local structural transition for molecular recording with scanning tunneling microscopy

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We present a direct observation of a structural transition at molecular scale in an organic *p*-nitrobenzonitrile (PNBN) thin film using scanning tunneling microscopy (STM). STM images clearly show an ordered molecular structure of unrecorded regions in the films, while the PNBN molecular arrangements are disordered in the recorded regions. The current-voltage ( $I$ - $V$ ) measurements from the STM demonstrate a great increase of the conductance transition in the recorded regions after the voltage pulses. Those results suggest that the recording mechanism may be due to a crystalline structural transition, which is consistent with our previously proposed mechanism in another organic system for ultrahigh density data storage. © 2000 American Institute of Physics. [S0003-6951(00)04746-X]

Nanofabrication and nanometer scale data recording have stimulated much interest in the last two decades.<sup>1-14</sup> Scanning probe microscopes (SPM) including scanning tunneling microscope (STM), atomic force microscope (AFM), and scanning near-field optical microscope have proven powerful for conducting data storage at nanometer scale or molecular scale. Kolb and co-workers<sup>3</sup> reported a nanofabrication of small copper clusters on the Au (111) surface of a gold electrode using a STM. Modification on Ge (111) surface at an atomic scale was also investigated by Dujardin and co-workers.<sup>8,9</sup> Mirlin and co-workers performed direct-write dip-pen nanolithography on a gold thin film using an AFM.<sup>10</sup> Because of a few advantages of organic materials, such as lower cost, easy synthesis, and controllable properties, people tried to employ organic molecules as recording media to carry out the data storage with SPM. Yano and co-workers<sup>15</sup> reported the data storage on a Langmuir-Blodgett (LB) film using the conductance transition. In our previous studies, we have systematically investigated the properties of various kinds of organic thin films and the applications in the ultrahigh density data storage by STM.<sup>11-14,16-23</sup> Charge-transfer organic complex thin films consisting of an electron donor and an electron acceptor were first employed. Then, for exploring higher density data storage and studying the recording mechanism, smaller molecules without the charge transfer in the systems were tried. The data density achieved was approximately  $10^{13}$  bits/cm<sup>2</sup> with recorded marks  $\sim 1.0$  nm in diameter. However, the recording mechanisms are still questionable. Further experimental work and some theoretical calculations are needed to

understand the recording mechanisms. Though Gao and co-workers<sup>24</sup> investigated a molecular recording and did theoretical calculations on a NBMN-pDA organic thin film, and attributed the recording mechanism to the local crystalline structural change, direct observation of the structural change at molecular scale around the recorded marks are still needed to demonstrate the mechanism. In this letter, we will present the direct observation of a crystalline structural change in a *p*-nitrobenzonitrile (PNBN) thin film with a STM. STM current-voltage ( $I$ - $V$ ) measurement of the local region in the film indicates that the conductance transition or the data storage is due to the crystalline structural change.

The organic PNBN material was synthesized in our group. The detailed information can be found in Ref. 25. To prepare PNBN thin films, the organic PNBN was put in a crucible and heated to 70 °C in the vacuum chamber. For the STM experiments, PNBN films of 20 nm thickness with high resistance were prepared by vacuum evaporation ( $10^{-4}$  Pa) on freshly cleaved highly ordered pyrolytic graphite (HOPG) substrates at room temperature. Local conductance transitions were induced in high-resistance films with a STM (model: C-STM 9100) in ambient conditions. The STM tips were Pt/Ir (80/20) wires of 0.25 mm in diameter that were snipped with a wire cutter. During the STM experiments, the distance between the STM tip and the film surface is about several angstroms, which is very short compared with the thickness of the film, so the applied voltage is mainly acted on the film. Actually, a very small voltage bias can cause a high electric field, which allows tunneling current large enough for the STM. The STM operation was in a constant height mode. For checking the reliability of the experiments, different tips and samples were employed. The recorded marks were obtained when a series of voltage pulses were

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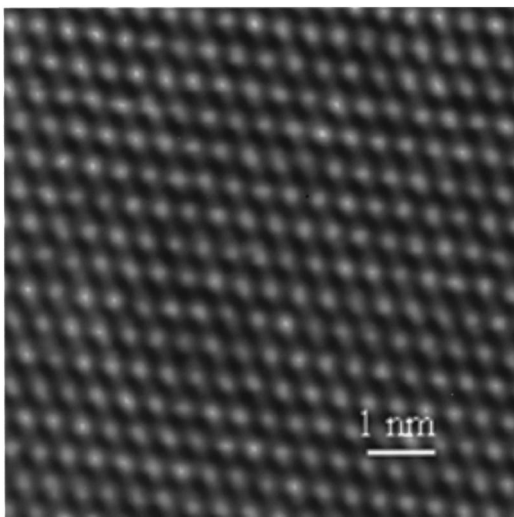


FIG. 1. Typical STM image of the PNB thin film showing the ordered molecular structure, scanning condition:  $V_{\text{bias}}=0.1$  V,  $I_{\text{ref}}=0.3$  nA.

applied to the STM tip. In order to know the electrical property of the organic film before and after the voltage pulse,  $I$ - $V$  curves of the unrecorded regions and the recorded regions were measured by the STM, respectively.

Figure 1 is a typical STM image of the PNB thin film. It can be seen that the molecules of PNB periodically arrange in two dimensions. The dimension of the observed periodic unit is  $0.427$  nm  $\times$   $0.518$  nm, which can also rule out the HOPG surface structure comparing with the crystalline HOPG parameters. So the ordered structure is from the crystalline PNB film. The recording experiment was performed by applying voltage pulse of  $4.4$  V for  $10$  ms to the STM tip, while the STM is in constant height mode at a defined bias voltage and tunneling current. The recorded pattern is shown in Fig. 2. We can see the brighter spots caused by the voltage pulse. The spot size is about  $1.4$  nm, which is at a molecular scale. It has been found that the threshold voltage of the recording can be influenced by the voltage bias and the tunneling current, which can affect the distance between the STM tip and the surface of the film, and also by the surrounding atmosphere.

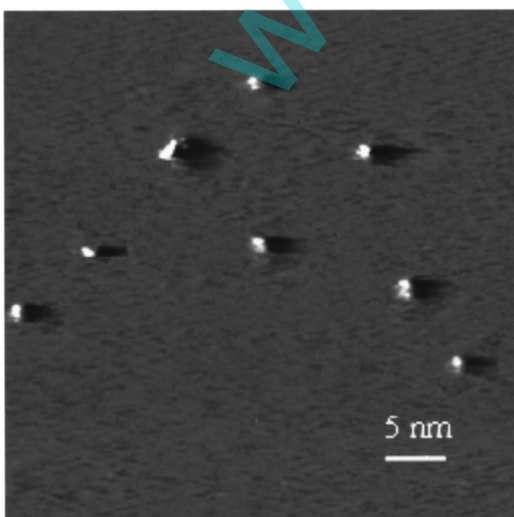


FIG. 2. STM image of a recorded pattern formed by voltage pulses  $4.4$  V for  $10$  ms, scanning condition  $V_{\text{bias}}=0.3$  V,  $I_{\text{ref}}=0.3$  nA.

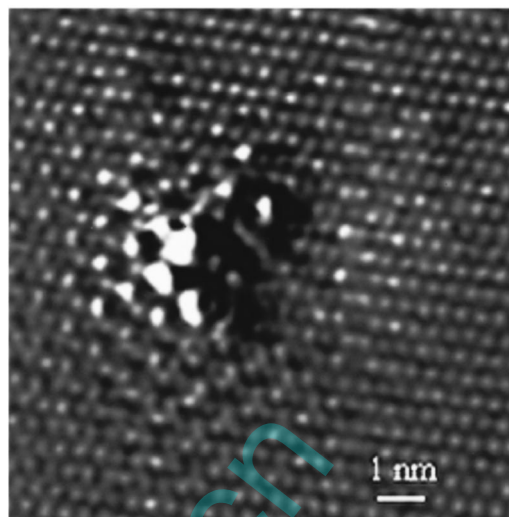


FIG. 3. STM image of a recorded mark showing the periodically arranged PNB molecules outside the mark and the disordered molecule inside the mark. The tunneling condition is  $V_{\text{bias}}=0.3$  V,  $I_{\text{ref}}=0.3$  nA.

In order to get the detailed structural information around the mark, we zoom in on one mark. As shown in Fig. 3, periodic molecular structure can be clearly seen. The brighter region in the middle of the image corresponds to the recorded mark with the size  $1.4$  nm in diameter. The PNB molecules arrange in a disordered manner in the recorded region, which is different from the images before the voltage pulse as shown in Fig. 1. On the other hand, the molecules in the unrecorded regions remain the periodic structure, as before. Subsequently, this experimental result directly shows the crystalline structure change at the surface of the films before and after the voltage pulse. However, another question may arise as to whether the ordered molecular structure of the mark inside of the film has also been changed after the voltage pulse. In order to understand the mechanism, STM  $I$ - $V$  measurements of the recorded marks before and after the voltage pulse were carried out.

As shown in Fig. 4, the  $I$ - $V$  curves of the film indicate the conductance transition. From  $I$ - $V$  curve a, we can see that the film is initially in a nonconductive state, and becomes conductive after the voltage threshold of about  $2$  V.

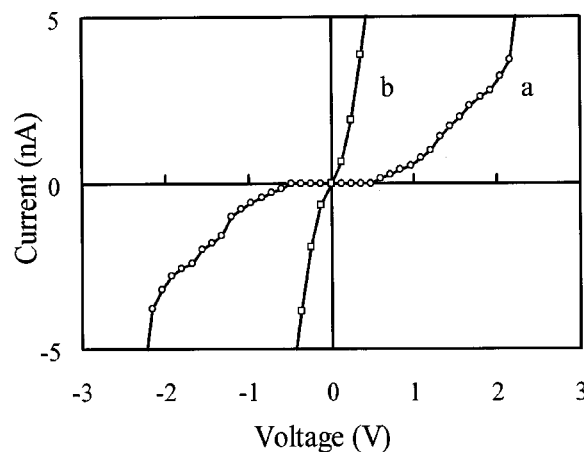


FIG. 4. Typical STM current-voltage relations of the PNB thin film. Curve (a) shows the nonconductive state of the local region of the film before the voltage pulse, and curve (b) a conductive state of the recorded region after the voltage pulse.

Curve b shows the  $I$ - $V$  relation of the recorded marks. It is clear that after the recording the recorded marks became conductive. So the  $I$ - $V$  measurements demonstrate the conductance transition in the local region of the film before and after the voltage pulse. Combining this  $I$ - $V$  result with the aforementioned STM images, we can conclude that the ordered molecular structure does also change inside of the film in the recorded marks. Since if the structural change only exists at the surface, the  $I$ - $V$  relations of the local region would not show much difference.

The recording mechanism is of importance for technological applications. Yano and co-workers<sup>15</sup> reported data storage on a LB film, and the recording mechanism was ascribed to the conductance transition without surface modification. But there were no further experimental demonstrations. In our previous studies, we attributed most of the recording mechanisms to the charge transfer and the polymerization. However, in the present case, there is no electron donor in the PNB molecule.  $\text{NO}_2$  and CN are all strong electron acceptor radicals. So the conductance transition in the recorded region is not because of the charge transfer from an electron donor to an electron acceptor in the PNB system. But the PNB is a polar molecule, and is not symmetric. So it might be reasonably torqued with a high electric field making the ordered molecules become disordered. In fact, the structural change in the PNB thin film in the recorded region reminds us of the recording mechanism proposed by Gao and co-workers<sup>24</sup> that the molecular recording was due to a crystalline structural change in the MBMN-pDA system based on experiments and *ab initio* calculations. But there was no direct observation of that structural change. The present results are just showing the crystalline change, which directly demonstrated the recording mechanism based on the local molecular structural transition.

Because the thickness of the electrically resistant thin film is less than one hundred nanometers, it can possibly be damaged when applying a higher voltage pulse. This is just what we want to show in this letter. Another possibility is that the brighter spot is the HOPG substrate, i.e., after the pulse, the film may go away and the HOPG may emerge. However, this is not the case when we compare the  $I$ - $V$  curve of PNB with that of the HOPG. The present result is consistent with our previous experimental results. Furthermore, in our STM experiments, we could not get the HOPG atomic image in the recorded region. On the contrary, in order to obtain the HOPG atomic image, we must clean out the organic molecules in the recorded region. Thereby, we applied a voltage pulse of 5 V for 20 ms and scanned the recorded region at a high tunneling current. And then, as a result, we can get the standard HOPG atomic image. So the emergence of the HOPG substrate is not the mechanism of this data storage.

It should be noted that the recorded marks are very stable and have no discernible change during scanning for 2 h. And after 2 weeks, the recorded marks can still be read by the STM. In our STM experiments, the probability for writ-

ing the marks is over 90%. When we accomplished a data recording and moved the STM tip to a new area, periodically arranged PNB molecules were still seen.

In summary, we have directly observed a local crystalline structural transition after the voltage pulse on the PNB films. The unrecorded region shows the periodically arranged PNB molecules, while the recorded area does not. Combined with the  $I$ - $V$  measurements, the STM results demonstrate that the recording mechanism in the PNB film is due to the crystalline structural transition.

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