Reversible and Reproducible Conductance Transition in a Polyimide Thin Film

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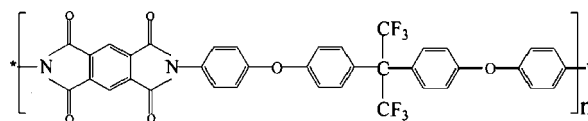*Received: July 16, 2008; Revised Manuscript Received: August 28, 2008*

A reversible and reproducible conductance transition is realized in the monolayer of polyimide (PI) Langmuir−Blodgett film on Au (111) substrate with a scanning tunneling microscopy (STM). The high-conductance state can be induced by applying a voltage pulse of about −2.7 V using the STM lithography method. The PI monolayer can spontaneously recover to its original low conductance state under a normal STM scanning condition. An electron trapping/detrapping process in the PI molecule can be responsible for its conductance transition. The reversible and highly reproducible conductance switching behavior in the PI film could provide its potential applications in the molecular logic and memory devices.

The conductance switching and memory phenomena in organic molecules are of great interest due to their potential applications in the molecular devices.[1–3] A significant amount of experimental and theoretical studies have been focused on addressing these novel phenomena and their mechanisms.[4–7] The scanning tunneling microscopy (STM) is one of the most powerful tools for these studies, having the advantage of the conductance characterizations and morphology observations done simultaneously.[8] During the past few years, our group has achieved STM-based ultrahigh density memories on a variety of donor−acceptor (D−A) type charge-transfer complex and compounds, which show very stable, reversible conductance switching attributed to the intermolecular charge transfer.[9–11] Our recent works demonstrated the first conductance transition in the solid state film of rotaxane-based molecules, which has been considered as a significantly potential memory material with structural bistablity in solution phase.[12]

Polyimide (PI) polymer material, which has been extensively applied as insulating or passivation layers in microelectronics industries, could be another promising candidate for future information storage due to its excellent thermal stabilities, chemical inertness, and producability. Yano et al. found that the local conductance of the Langmuir−Blodgett (LB) multilayer film of PI can increase by application of a voltage pulse with conductive atomic force microscope (AFM) probe and have stably fabricated 10^6 recording bits at nanometer scale in PI films.[13–15] However, erasing and rewriting the recording dots have not been realized on this system, and also the mechanism of conductance change is still kept unclear so far.

In this paper, we will present a reversible conductance switching behavior in the monolayer of polyimide LB film on Au (111) substrate observed directly with STM. The high-conductance state in the monolayer can be induced by applying

SCHEME 1: The Molecular Structure of the PI Polymer

a voltage pulse of about −2.7 V using the STM lithography method. What is interesting is that the polyimide monolayer will automatically recover to its original low conductance state from the high conductance state under the STM scanning. No surface modification in the film can be found in the low/high conductance transition processes up to hundreds of cycles. Our experimental and theoretical studies suggest that an electron trapping/detrapping process in the PI molecule is responsible for its conductance transition.

Scheme 1 shows the molecular structure of the PI molecule. The polyimide Langmuir−Blodgett (LB) films on Au(111) substrates were prepared using a precursor method via soluble polyamic acid alkylamine salts (PAAS).[16–18] The precursor LB films of the PAAS were immersed in a mixture of pyridine, acetic anhydride, and benzene (1:1:10 vol %) for 8 h and then were heated at 80 °C in vacuum. The conversion of the PAAS to polyimide was confirmed by Fourier transform infrared (FT-IR) spectra.[19]

STM experiments were performed using Solver P47 with a chemically etched tungsten tip. Before introducing the voltage pulse, the feedback loop was disabled and the probe was lifted 7 Å above the selected point of the film. Subsequently, a rectangle voltage pulse of 5 ms was applied between the tip and the PI monolayer/gold substrate (the probe is grounded). Then, the STM images were acquired continuously using the normal scanning STM mode. All the STM images were obtained with a constant current of 35 pA and a sample bias of 0.5 V in air at room temperature.

The ab initio calculations were performed using Gaussian 03 program to obtain the relaxed structures and the electronic properties of the PI monomers. A monomer (see Figure 4a) is

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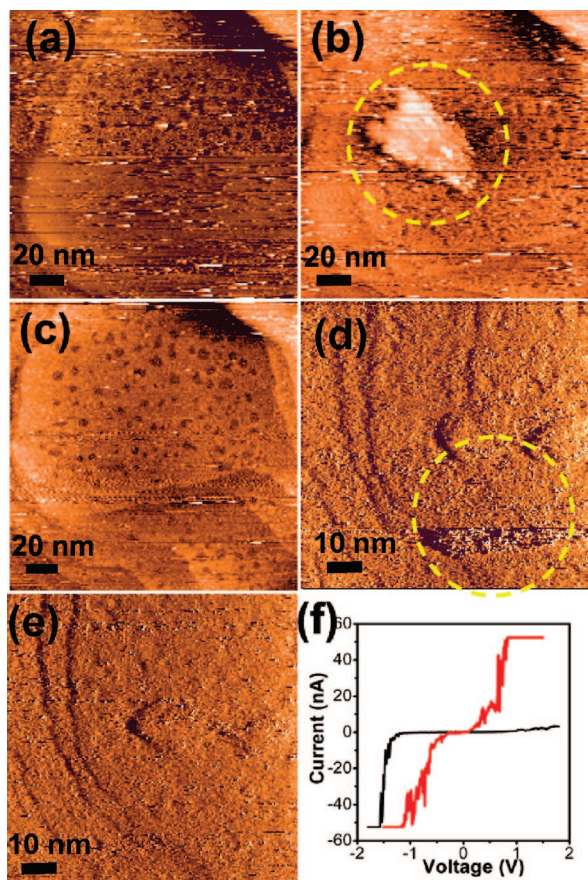[†] Chinese Academy of Science.
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Figure 1. STM images and spectra showing conductance transition in the PI monolayer. (a−c) STM height images, 200 nm × 200 nm. (a) The original film morphology. (b) The appearance of a bright spot (shown in the yellow circle) after applying a −2.7 V pulse on the PI film. (c) The subsequent disappearance of the bright spot in the next STM scanning. (d,e) STM current images, 90 nm × 90 nm. (d) A clear local high conductance state in the PI film (denoted in the yellow circle) induced by the −2.7 V pulse voltage. (e) The recovered original low conductance state on the next scanning. (f) Typical I−V characteristics measured using STM on the as-prepared film (the black curve) and on the voltage pulse-induced bright spot (the red curve) give further evidence of the high−low conductance switching phenomenon in the PI film. Note that the plateaus at ±50 nA are due to the saturation of current measurement.

constructed because the PI polymer molecule is too big for the ab initio calculations. Most of the useful properties of the polymers can be derived from the monomers. The constructed monomer is terminated with two methyl groups at both ends. All calculations were done at 6-31G** level using B3LYP exchange-correlation function.

Figure 1 shows the conductance transition of the PI monolayer triggered by the voltage pulses. STM height image (Figure 1a) reveals that the PI monolayer on Au substrate is not continuous but with a uniform height of about 0.45nm, which is consistent with the height of PI monolayer by AFM observations.[20] After applying a voltage pulse of about −2.7 V on the monolayer, a bright spot of about 50 nm in size with irregular shape appeared in the work zone, as marked in the yellow circle in Figure 1b. Interestingly, the next STM scanning showed that this bright spot disappeared completely (Figure 1c), while no obvious morphology change was found on the same position of the PI monolayer. The appearance of the bright spot corresponds to a conductance increase in the local region of the PI film. The irregular shape of the transition region may indicate that this conductance transition happens inside only one or several

neighboring polymer molecules with distinct boundary. Consequently, the size (∼50 nm) is usually much larger than the spatial resolution of STM, and also that of the recording dots (routinely one to approximately several nanometers) from other organic molecular systems.[9−12] The time for acquiring one STM image is about 4−5 min, indicating that the lasting time of the high conductance state is around 5 min.

Figure 1 panels d and e are the STM current images obtained by reducing the feedback gain from 1.5 to 0.2. The yellow circle in Figure 1d denotes a brighter region produced by a bias voltage of −2.7V. Similarly, the bright region disappeared in the subsequent scanning (Figure 1e). Since STM current images are obtained with a nearly constant distance between the tip and the sample, the difference in the brightness presents the changing in conductance in the film. This further confirms that the bright spot corresponds to a conductance increase in the corresponding region of the PI film. The appearance and disappearance of the bright spot represents a reversible local conductance transition. It was found that a positive voltage pulse up to +3.0 V could not introduce such conductance transition in the PI monolayer, indicating that the conductance transition of the PI molecules is highly sensitive to the polarity of the voltage pulses. Detailed experiments showed that negative voltage pulses less than −2.2 V cannot produce the conductance switching phenomena, and a voltage pulse with an absolute value exceeding 3 V usually causes an obvious destruction in the film.

We measured the current−voltage (I−V) characteristics of the PI film using STM (Figure 1f). The black curve presents the I−V data measured from the as-produced film, showing an asymmetric characteristic. The PI film keeps at the low conductance state from +2 V to −1.5 V. A sudden current increase occurs at about −1.5 V, indicating that the molecules switch to the high conductance state. While the I−V curve measured on the bright region where it was pretreated by a negative voltage pulse of −2.7 V is symmetrical and exhibits a higher current compared to the black curve under the same bias (the red curve). This result is consistent with the observation that a negative voltage pulse can induce a high conductance region in the film.

By increasing the STM scanning speed, we imaged the detailed recovery process from the induced high conductance state to the original low conductance state in the PI film. Figure 2a−d shows the appearance, fading, and disappearance of the bright spot, respectively. The whole period takes about 5 min. This result shows that the decaying of the high conductance state in the PI monolayer is a continuous and gradual process.

The switching behavior of the conductance changes in the PI films is highly reproducible. Figure 3 shows the reproducible two-level conducting states of the PI films sequentially induced by repeatedly introducing the negative voltage pulse at the same position. We can find that the shape of the transition region is also reproducible on a given site though it is irregular. This conductance transition phenomenon can last up to hundreds of cycles, suggesting the switching behavior of the PI molecules can make them to work in the reliable molecule-based logic devices.

The above experiments describe a negative voltage pulse-induced, reproducible conductance state transition in the PI monolayer, which features an automatic recovery from the induced high conductance to the original low conductance state. Such a phenomenon possesses some similarities with that have been reported in the redox-active molecules, which characterize a controllable conductivity change at the reduced/oxidized
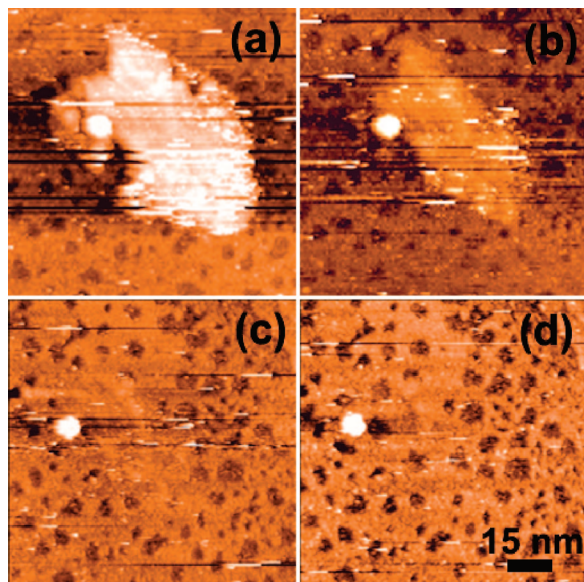
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Figure 2. STM images showing a gradual conductance state recovery process in PI film. (a) Appearance of a bright spot showing the induced local high conductance state in the monolayer after applying negative voltage pulse. (b,c) The fading process of the bright spot, indicating a gradual conductance decrease in the induced high conductance region. (d) After a long period, total disappearance of the bright spot showing that the PI molecules recover to their original low conductance state. The scanning area is 100 nm × 100 nm. The small cluster in the left of the transition area which may dropped from the STM tip can work as a mark.
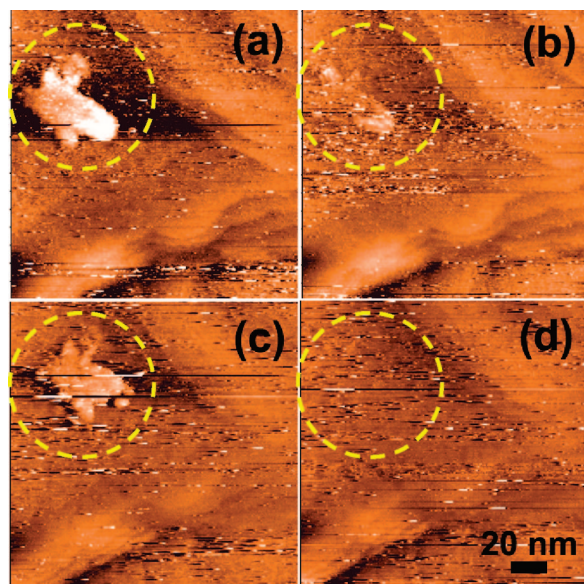

Figure 3. STM images showing the reproducible high-low conductance switching in the PI film, as denoted in the yellow circles. (a) A high conductance region in the PI film. (b) The high conductance state is degenerating spontaneously to a lower conductance state. (c) The reproducing of the high conductance state after applying a negative voltage pulse again on the same position in panel b. (d) The reproduced high conductance state has recovered to its original low conductance state in the PI film. The scanning area is 160 nm × 160 nm.

states.[5,21,22] It has been provided that the reduction/oxidation will change the electron conjugation in the redox-active molecules, and the change of electron conjugation can be realized through electron trapping/detrapping triggered by the external voltages. Though the trapping of the charges in the molecules is very fast (10^{-6} sec) under the applied potential, the gradual dissipation process of the trapped charges is much
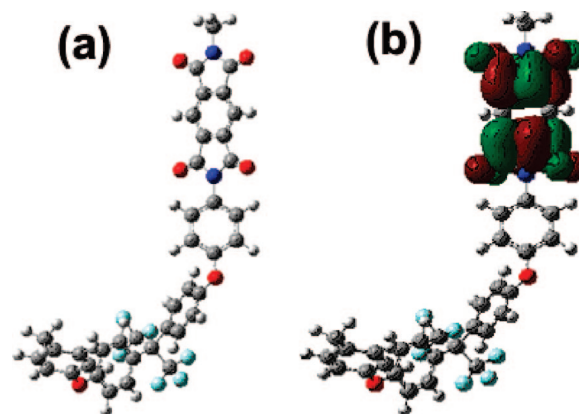

Figure 4. (a) The relaxed structure of a neutral PI monomer. (b) The relaxed structure of an anion (trapping an extra electron). The trapped electron distributes on the imide part.

slower (it can take as long as several hundreds of seconds).[23] The features shown in the conductance switching process in the PI monolayer, such as the voltage polarity dependence, the duration time, the gradual decay process, and the reversibility, and so forth, suggest that the reduction/oxidation of the PI molecules in response to the external voltage pulses might be responsible for its conductance switching behaviors. The similar conductance transitions induced by the electron conjugation were also found in other molecule systems.[3,6]

On the basis of the experimental results, we constructed a PI monomer (Figure 4) to investigate the origin of the conductance transition in the PI monolayer. We calculated the electronic properties of the anions of the monomer to verify the electron trapping/detrapping processes. The relaxed structures of the neutral molecule and the anion are shown in Figure 4, panels a and b, respectively. The configuration changes a little when the neutral molecule traps one or two electrons. From the total energies, we found that the anion with one trapped electron is the most stable state with a 2.0 eV less than that in the neutral molecule. The anions with two trapped electrons for the singlet and triplet states have the energies of 0.29 and 0.19 eV less than that in the neutral one, respectively. For the real system, the PI polymer, the energy differences will be different slightly from that in the monomer, but the stability should not be changed. In the anion with one trapped electron, the energy gap between the highest occupied orbital and the lowest unoccupied one is decreased, indicating a better conductance than that in the neutral state. We also found that the lowest unoccupied molecular orbital of the neutral molecule is mainly on the imide part, and when the molecule traps an electron, the extra electron also mainly distributes on the imide part (Figure 4b). When a negative voltage pulse is applied on the PI thin film, only one (or possibly several nearest neighboring) polymer molecule(s) are charged to form a high conductance state (anion state), so that the high conductance region have an irregular shape with the distinct boundary between PI molecules because of weak intermolecular interaction. This anion then decays back to the neutral state through the emission of the extra electrons into the gold substrate in several minutes. These results support our assumption that the reversible changes of the electron conjugation in the molecule during the electron trapping/detrapping (reduction/oxidation) processes will result in the reversible transitions of the molecular conductivity.

In summary, we have observed a reversible conductance transition in the PI monolayer on Au (111) substrate using STM. The high conductance state can be realized repeatedly by

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applying a critical negative voltage pulse onto the PI monolayer, and the high conductance state in the PI molecules will gradually switch back to its original low conductance state. Our experimental and theoretical studies suggest that the reversible conductance transition is related with the electron trapping/detrapping in the PI molecule. This conductance switching behavior is highly reproducible and controllable, suggesting that the PI polymer is a potential candidate in future molecule-based information storage applications.

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