

Calligraphy on Self-assembled Monolayer of Supramolecules

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Abstract— Information storage utilizing the bi-stable state of organic molecules has been a hot topic in molecular electronics, due to the promising future of single molecule devices. We demonstrated in this paper nanometer-scale pattern generation on the self-assembled monolayer of [2]rotaxane. The organic molecules are covalently bonded to the Au (111) surface of the substrate through the di-thiol groups at one end of the molecules. Electric bias was applied between the Au substrate and the conductive tip of a scanning probe microscope to stimulate the pattern generation. The line width and apparent height of the pattern is related to the bias voltage and there exists a threshold, below which no pattern can be generated.

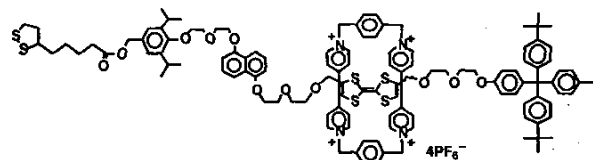
Keywords—molecular electronics; self-assembled monolayer; atomic force microscope

I. INTRODUCTION

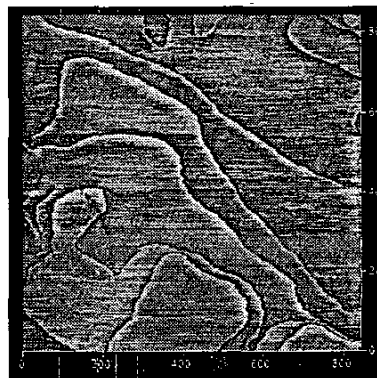
Information storage utilizing the bi-stable state of organic molecules has been a hot topic in molecular electronics [1], due to the promising future of single molecule devices. Nanometer scale, solid state devices have been fabricated and tested as switches, or memory cells [2-3]. Most of these devices use LB film or self-assembled monolayer of bi-stable organic molecules as the storage media. By applying external stimuli, which usually is electrical field, the physical properties of the unidirectional molecules adsorbed on the solid surface will change. Although the mechanism is still not clear, large conductance changes are observed in those devices and electrical signal can be read out directly. In this paper, we will demonstrate the nanometer scale information storage in a self-assembled monolayer of supramolecules by using a conductive atomic force microscope (AFM) tip. The supramolecule, [2]rotaxane, is chemisorbed on the Au surface through the di-thiol group at one end and form a densely packed monolayer. In our experiment, the Au substrate is used as one electrode, and the conductive AFM tip as counter electrode (which is grounded). By applying positive voltages on the Au substrate while scanning the tip on the monolayer surface, we can generate a height change at the scanned area. The height change will reserve even after the bias is retracted, which means the [2]rotaxane SAM can be used as a nonvolatile memory device.

II. SAMPLE PREPARATION

The supramolecule ([2]Rotaxane) we used contains a long carbon chain as the backbone. One end of the molecule is modified by a di-thiol group, which can form a covalent bond with gold atoms. The total length of the molecule is estimated to be 7 nm. The gold substrate was prepared using the method described in reference [4]. Briefly, gold thin film deposited onto the mica surface through thermal evaporation, and then annealed in hydrogen flame to form a (111)-orientated surface. Atomic level flat surface within 200-500 nm regions can be achieved using this method (Figure 1). The fresh prepared gold substrate was then dipped into the solution contains [2]rotaxane molecule for more than 24 hours. The sample was then rinsed thoroughly in acetone and dried in the nitrogen flow. A copper wire was connected to the gold substrate using the silver paste to form the bottom electrode. The quality of SAM was check using contact angle measurement.



(a) [2]Rotaxane



(b)

Figure 1. (a) the molecule structure of [2]rotaxane. (b) STM image of the Au (111) surface on mica.

III. EXPERIMENT

The SAM sample (1.2cm by 2.0cm) was mounted on a home designed sample holder, which have an electric connection to the Au substrate. The holder was then mounted onto the vacuum chuck of our AFM system (Dimension 3100 from Digital Instrument). The external voltage was applied to the Au substrate through the sample holder (Figure 2). The monolayer surface was then scanned by a conductive AFM tip in contact mode under constant force to image the surface. The etched silicon tip was coated with a 20-nm gold film on a 20-nm chrome adhesion layer. The gold coated tip was electrically connected to the tip holder, which was grounded. After the initial scanning, the tip was located to certain position and positive voltage was applied to the substrate to stimulate the molecules and generate patterns on the SAM surface. After the "writing" process, the pattern was imaged by the same tip using the same applied force, but without bias. A relatively fast scan speed ($\sim 0.5 \mu\text{m}/\text{sec}$) is used in imaging mode, and slow scan speed ($\sim 0.05 \mu\text{m}/\text{sec}$) in patterning mode.

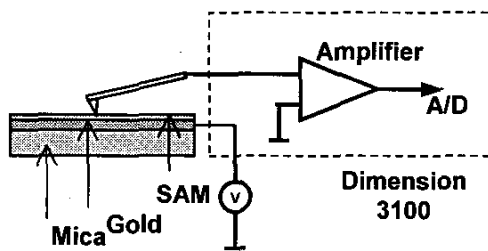


Figure 2. The configuration of the experimental set-up.

IV. DISCUSSION AND CONCLUSION

The line pattern in Figure 3 was generated under a positive 4.5V bias. From the AFM morphology imaging, the patterned area is about 1-2nm higher than the non-patterned area. Because the AFM can not distinguish the nature of the action force between tips and molecules, this height change does not necessary means real morphology change of the film. Electrostatic force from the dipole moment change in the film may contribute to the appeal height change of the AFM image. The width of the single line pattern is about 100nm, which is in the same range of the tip diameter (80-100nm). The pattern can only been generated under positive bias on substrate. The line width and height changes with the applied voltage and there exists a threshold value, below which no patterns can be written.

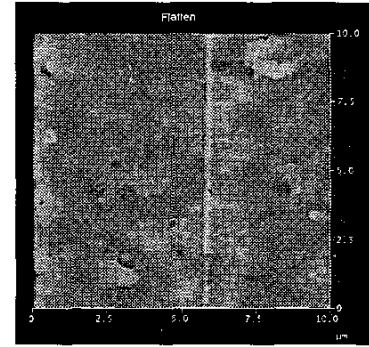


Figure 3. the AFM image of the line pattern written at +4.5V. The line width is about 100 nm.

We proposed that the reorganization of the molecules in SAM films as the mechanism of the pattern generation. Similar phenomena have been observed for spin-on thin films of [2]rotaxane molecules [1]. Those spin-on thin films undergoes a local phase change when stimulated mechanically by a SPM tip. The phase change can be monitored by the local height profile change. In our case, for self-assembled monolayer, the molecules may change their alignment angle on the Au (111) surface through the interaction between the applied electric field and the intrinsic dipole moment of the molecule. When the force is strong enough to overcome the free energy needed for the realignment, phase change will happen. This mechanism explains the existence of a bias threshold. Figure 4 shows a test pattern to study the relationship between tip bias and the line width and height. The threshold is between 3.0V to 3.5V (bias on substrate). The smallest line width we get was about 40nm (at 3.5V). The line width increases with the bias. At 5.0V, the width increased to 150nm. The height of the pattern also changes with the bias, but is much less sensitive as the width change. The tip scanning speed also affects the pattern generation. We use a very slow scan speed, $0.05 \mu\text{m}/\text{sec}$, when patterning the surface. When the speed was increased to $0.5 \mu\text{m}/\text{sec}$, no pattern can be generated, even at a high bias of 5.0V. This phenomenon indicates that it needs some time for the molecules to realign on the surface. One important factor need to mention is that the height profile monitored by the AFM tip may not be the real morphology of the film. Other factors, such as the electrical charge, may introduce some artifacts in the measurement.

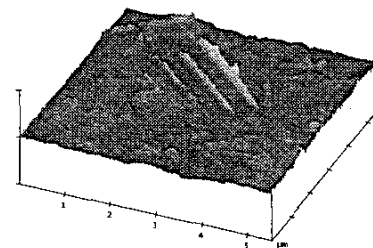


Figure 4. line pattern written with different voltage. Form left to right, the writing voltage changes from 3.0V to 4.5V, in 0.5V step.

TABLE 1. The Relationship Between Tip Bias and Pattern Height/Width

Tip bias (V)	3.0	3.5	4.0	4.5	5.0
Height (nm)	-	1.0	2.0	2.1	3.0
Width (nm)	-	40	80	100	150

V. SUMMARY

In this paper, we studied the nanometer scale patterning of organic molecular SAM using the conductive tip of a scanning probe microscope. The pattern was formed by the electrical stimulation of the [2]rotaxane SAM. A possible mechanism, the realignment of the molecules, is proposed to explain the electric field induced pattern formation. The line width and apparent height is related to the bias voltage and a threshold voltage is observed. Controlling the bias voltage, we can "write" patterns on the [2]rotaxen SAM surface with a

resolution of 40nm. This result demonstrated the nanometer scale patterning in self-assembled monolayer of [2]rotaxane, which has potential application in high density information storage technology.

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