Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/S179-07
Chinese Physics
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ULTRAHIGH DATA DENSITY STORAGE WITH SCANNING TUNNELING MICROSCOPY*

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(Received 4 June 2001)

Ultrahigh density data storage devices made by scanning probe techniques based on various recording media and their corresponding recording mechanisms, have attracted much attention recently, since they ensure a high data density in a non-volatile, erasable form in some kinds of ways. It is of particular interest to employ organic polymers with novel functional properties within a single molecule (or a single molecular complex) for fabricating electronic devices on a single molecular scale. Here, it is reported that a new process for ultrahigh density and erasable data storage, namely, molecular bistability on an organic charge transfer complex of 3-nitrobenzal malononitrile and 1,4-phenylenediamine (NBMN-pDA) switched by a scanning tunneling microscope (STM). Data density exceeds 10^{13} bits/cm^2 with a writing time per bit of $\sim 1\mu$s. Current-voltage (I/V) measurements before and after the voltage pulse from the STM tip, together with optical absorption spectroscopy and macroscopic four-probe I/V measurements demonstrate that the writing mechanism is conductance transition in the organic complex. This mechanism offers an attractive combination of ultrahigh data density coupled with high speed. The ultimate bit density achievable appears to be limited only by the size of the organic complex, which is less than 1nm in our case, corresponding to 10^{14} bits/cm^2. We believe that provided the lifetime can be improved, molecular bistability may represent a practical route for ultrahigh density data storage devices.

Keywords: data storage, organic thin film, scanning tunneling microscopy
PACC: 7130, 7360, 0779, 8235

I. INTRODUCTION

There have been continuous efforts to find ways of modifying materials on ever decreasing length scales by improved recording methods, recording media, and recording mechanisms.[1−6] The scanning probe microscope has proven to be a promising tool for the manipulation of materials on the nanometer scale, and many different types of materials have been tested as substrates for data storage media, including metals, semiconductors, $Ge_2Sb_2Te_4$, and β-$Na_xV_2O_5$.[7−15] Recording mechanisms included the geometric change of surface morphology by electric field evaporation and deposition. Apart from such topographic methods, non-volatile, erasable writing has also been demonstrated using an amorphous-to-crystalline phase transition[13] and photoconductive materials.[14] Recently, using an epitaxial ferroelectric thin film,[15] a line of only 350nm width has been written. This paper covers an alternative approach to erasable data storage using the natural electrical bistability of an organic charge transfer molecular complex.

Such materials have aroused much attention due to their novel structures, properties, and potential application to electronic devices.[16−19] The switching, or conductance transition, in this kind of organic complex may be both reversible and fast, with transition times of less than 10ns, and non-volatile as well.[20] Here, we demonstrate that recording on such an organic complex system using the STM allows to achieve an extremely high data storage density in a non-volatile, erasable form. Indeed, the ultimate resolution appears to be controlled by the size of the organic molecule itself. In contrast, with a ferroelectric memory device the minimum bit size is limited by the finite size of a ferroelectric domain, of the order of 50nm,[21] thus giving an ultimate bit density of 4×10^{10}bits/cm^2.

II. EXPERIMENTS

Two conjugated compounds, 3-nitrobenzole malonitrile (NBMN) and 1,4-phenylenediamine (pDA) were selected to form the complex desired. The chemical structure of the NBMN-pDA complex can be seen in Fig.1. By x-ray diffraction the crystalline structure of NBMN-pDA was determined to be triclinic with the

*Project supported by the National Natural Science Foundation of China (Grant No. 69890223).

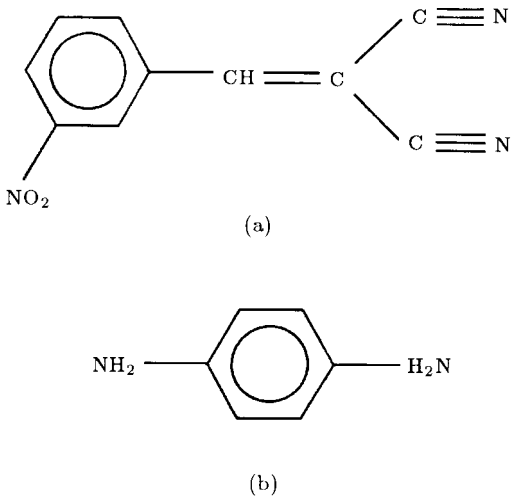


Fig.1. Structures of the molecules (a) NBMN and (b) pDA, forming the recording media.

following unit cell parameters: a=0.7823(2)nm, b= 0.8730(2)nm, c=0.7286(1)nm, α=105.90(3)°, β= 101.49(3)°, γ=78.75 (3)°. In this organic complex, the NBMN is an acceptor and pDA a donor. NBMN was prepared according to literature,[22] and the two materials were mixed with a nominal composition of 1:1 and deposited in vacuum on freshly-cleaved, highly oriented pyrolytic graphite (HOPG) substrates. Under particular deposition conditions (substrate: room temperature and evaporation rate: <5nm/min), insulating NBMN-pDA films can be prepared. The deposited films were identified to be polycrystalline by X-ray diffraction. However, when the substrate was put at room temperature and the evaporation rate exceeded 6nm/min, the deposited complex films became conductive. The base vacuum of the deposition system is in the order of 2×10^{-6}Torr, rising to about 2×10^{-5}Torr during film deposition. The thickness of the insulating film on the HOPG substrate was about 20nm. For the macroscopic four-probe I/V measurements, the complex thin films of 200nm were deposited on conductive ITO film-coated glass wafers. Films were simultaneously deposited on amorphous carbon films coated on TEM copper grids. Subsequent examination using a JEOL 200CX indicated that the coverage was very uniform. Data storage experiments were conducted using a commercial CSTM-930 under ambient conditions and operated in constant height mode. The STM tip was fabricated from 0.25mm diameter Pt/Ir (80/20) wire snipped with a wire cutter. Different tips and samples were employed to check the reliability of the experimental results. I-V relations were obtained by scanning tunneling spectroscopy.

Ⅲ. RESULTS AND DISCUSSION

Samples were strictly selected for the data storage by STM. In our case, only those possessing high-impedance were employed to conduct the data storage experiment. In fact, in our STM data storage experiments we never succeeded in making data storage by employing samples with a low impedance in the initial stage. Figure 2 shows typical images of the NBMN-pDA media of high impedance (which we refer to as the insulating state) including recorded marks. Figure 2 is a 3×3 array and an "A" pattern formed by the recorded marks, respectively. In order to demonstrate the reversibility of the recording process, we apply voltage with reverse polarity to the recorded mark according to the charge transfer mechanism as described by the equation below. As a result, by applying a voltage of −4.5V and 50μs, we successfully erased the recorded mark. As shown in Figs.2(d) and (e), two marks were erased one by one. This reversible transformation was repeated more than 10 times. It became impossible to erase the recording marks if a mark subjected to this writing and erasing process for more than 10 times. Figure 2(b) shows a resolution test results demonstrating that the distance between neighboring marks can be as low as 1.7nm. This result corresponds to a data storage density exceeding 10^{13}bits/cm^2. The tunneling conditions for these images were a bias voltage of V_b=0.19V, a tunneling current of I_t=0.19nA, and a scanning rate of 0.3 Hz/image. Particularly interesting are the lower two marks recorded, which provide evidence of quantization on the molecular level. Each of these write pulses have resulted in two recorded marks which were probably introduced by a two-tip effect at the STM tip and separated by 0.93nm, only a distance comparable to the size of the molecular complex. This indicates that the ultimate bit density could be achieved for this material, which is greater than 10^{14}bits/cm^2. In these STM images, the marks look bipolar. When the STM tip scanned the samples in the constant height mode, the feedback circuits actually were not completely turned off. So, behind a brighter recorded spot of high-current features, there is a low-current feature adjacent to it.

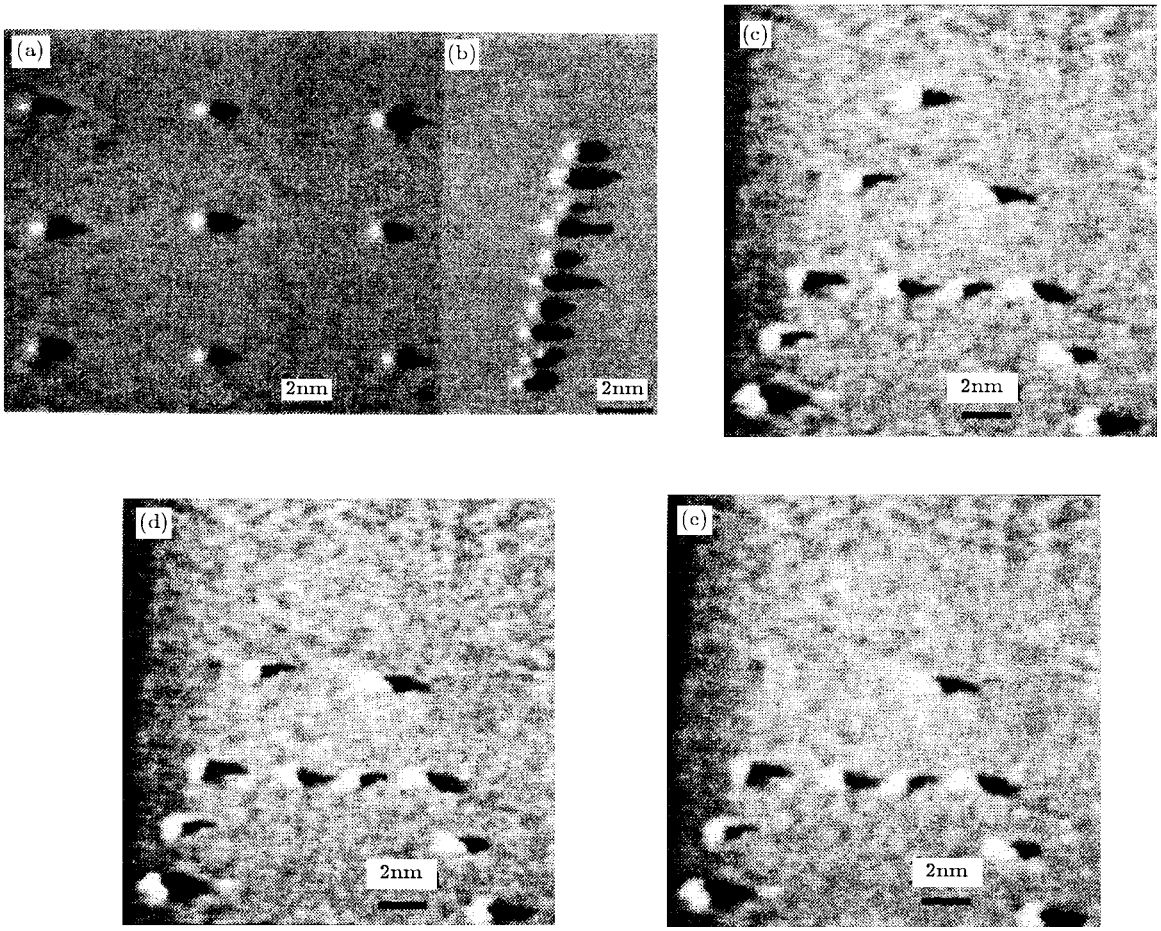


Fig.2. STM images of the NBMN-pDA film deposited on HOPG after application of voltage pulses between the STM tip and the sample; (a) a 3×3 array formed by voltage pulses of 4V and 1μs; (b) resolution test using voltage pulses of 4.2V and 10μs, the distance between neighboring marks being 1.5nm corresponding to a data storage density exceeding 10^{13}bits/cm^2. (c) an "A" pattern formed by voltage pulses of 3.5V and 2μs; (d) and (e) STM images after erasing the mark one by one by reverse-polarity voltage pulse of –4.5V and 50μs; scan conditions are V_b=0.19V, I_t=0.19nA, and a constant height scan mode.

We then performed a number of experiments to demonstrate that the recording mechanism is the natural electrical bistability of this organic complex. Several other mechanisms could cause the formation of a mark, including a geometric change of surface morphology induced by an electric field, a thermal-effect-induced evaporation, and deposited charge.[23,24] First, we tried to reach data storage by employing STM tip voltages of different polarity voltage and found that both positive and negative voltage pulses led to the same kind of recording on the organic complex film. This suggests that material evaporation from the tip, as induced by the electric field, is not the main reason of mark formation. Secondly, we tried to make the data storage on the samples of low impedance with the same STM parameters at 4V and the voltage pulse time ranging from 1 to 10μs, and we all failed to make the marks. So, if the marks were made by thermally-induced evaporation, it would also have caused the marks in the low-impedance case according to the relation of V^2/R, where V is the applied voltage and the R represents electric resistance of the local area of the thin film. The last excludes deposited charge as the writing mechanism. By employing STM, we measured the I-V characteristics of the thin film before and after mark formation. Figure 3(a) compares the I-V relations obtained for the recorded and unrecorded areas. In curve a, the applied voltage is varied from 0 to 2.1V, but the tunneling current remains at ~0nA. This implies that the NBMN-pDA initially is a high-impedance thin film below an applied voltage of 2.1V. Beyond the voltage threshold, it changed from high impedance to low impedance. Curve b shows the I-V relation from a recorded mark,

which is significantly different from that of curve *a*. This suggests that the medium was now conductive. As the substrate of the recording medium is HOPG, it is impossible for the charges to be trapped in the local region. Therefore, it can be concluded clearly that the mark formation cannot attributed to the charge trap. Furthermore, to ensure that the mark is not simply a hole in the organic film, we also measured *I-V* curves of a graphite substrate, in a region in which the sample was not deposited and also on a freshly-cleaved piece of HOPG. In both cases, as shown in curve *c*, the *I-V* relation is a straight line, clearly different from curve *b*. Therefore, it can be deduced that the mark formed is not a hole in the organic film, but the film itself has locally been transformed into the conducting state as a result of the application of the voltage pulse. In addition, the field between the tip and the sample is estimated to be of the order of 0.1V/nm, which is two orders of magnitude smaller than the electrical field needed for field evaporation of Au or Pt.[12,25] These results indicate that recording originates neither from field-induced evaporation nor from charge trap and not from thermal-effect-induced evaporation either.

Standard four-point probe *I-V* measurements together with transient time measurements of the film conductance states were performed on the NBMN-pDA complex of 200nm.[26,27] As shown in Fig.3(b), electrical bistability was found in the film which showed a threshold voltage of 3.2V and a conductance difference between the two states in the order of about 4. The film was initially in the high-impedance state of $10^8\Omega\cdot$cm. When the applied voltage reached 3.17V, it was abruptly switched to the conductive state of $1530\Omega\cdot$cm. To measure the transition time of the two states, a 100M oscilloscope (HP54502) was employed. The transition time of the film was measured to be about 80ns. Based on this investigation, the transition threshold of the field was found to be of the order of 10^{-2}V/nm. Considering the difference in the spatial field distribution between the STM measurement (noncontact) and the four-point probe measurement (contact), it is reasonable to deduce that the field of 10^{-1}V/nm in the STM experiment is sufficient to induce the electrical transition of the organic complex. We expect that for thinner films the writing time by STM would be less than this value.

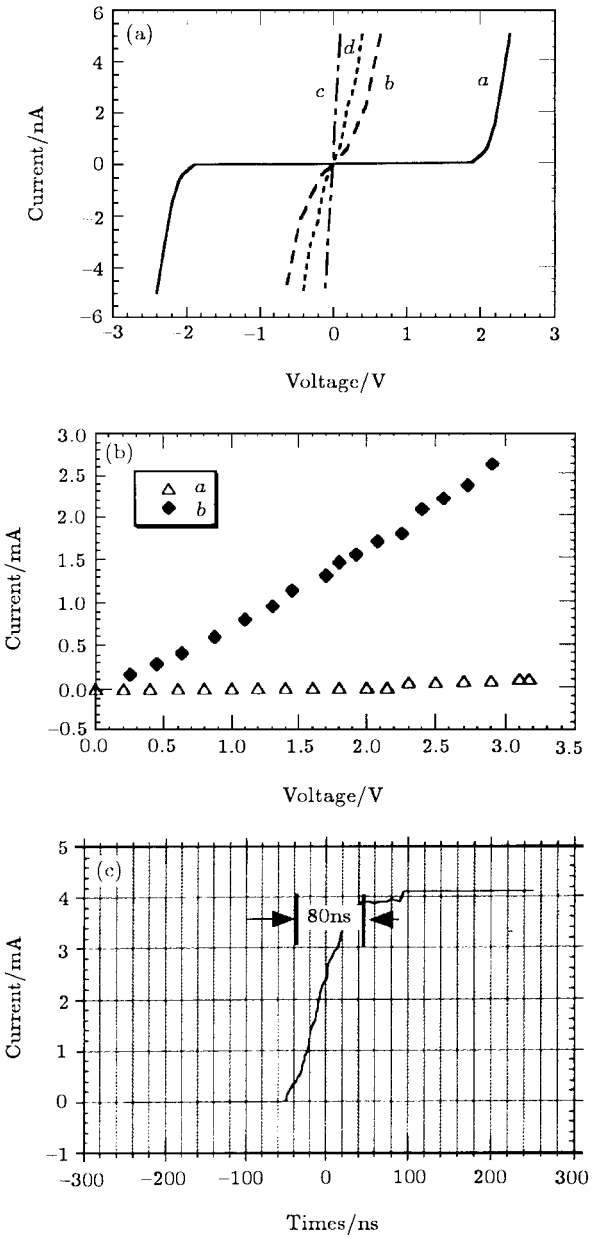


Fig.3. (a) Typical current-voltage relations of the regions unrecorded and recorded by STM. Curve *a* shows the *I-V* relation before the voltage pulse, indicating that the medium was initially nearly insulating below a voltage threshold of 2.1V and became conductive above 2.1V. Curve *b* shows the *I-V* relation after writing, indicating that the recorded region is conductive. Curve *c* is the *I-V* relation of the HOPG substrate, showing a linear behavior. Curve *d* is the *I-V* characteristic of a typical NBMN-pDA conducting film, exhibiting a behavior similar to curves *b* and *c*. (b) *I-V* relation of a 200nm film, showing the two "0" and "1" conductance states, voltage threshold: 3.2V. (c) Transition time curve of the two conductance states of the 200nm thick film, transient time: 80ns.

Definite evidence of the transfer of charge in the organic NBMN-pDA complex is provided by optical absorption spectroscopy. Figure 4 shows the UV-visible spectra of NBMN, pDA, and NBMN-pDA complex, respectively. From these spectra, it is clearly obvious that a new peak at ~385nm appears in the spectrum of the NBMN-pDA complex (Curve *c* of Fig.4). According to the results of Neta *et al.*,[28] this new peak can be attributed to the photoexcitation-induced electron transfer from pDA to the nitroaromatic radical anions of NBMN in the organic complex. NBMN is a strong electron acceptor and pDA is an electron donor. Based on the conductance change of the film by the application of the STM tip voltage and the electrical bistability of the complex film, the electrical transition is considered to be induced by the application of a voltage pulse,[26] and can be represented as follows,

$$[(\mathrm{NBMN})^- + (\mathrm{pDA})^+]_n \underset{\Delta}{\overset{E}{\rightleftarrows}} (\mathrm{NBMN})^0_x + (\mathrm{pDA})^0_x + [(\mathrm{NBMN})^-(\mathrm{pDA})^+]_{n-x}$$

"**0**" high – impedance state "**1**" low – impedance state

where the electric field (E) causes a transition from the high-impedance state ("**0**" state) to the low-impedance state ("**1**" state) by inducing pDA molecules to donate their electrons to NBMN molecules or a reverse transition. Why can the conductive NBMN-pDA be prepared with different deposition parameters? According to this equation if the deposited complex consists of neutral NBMN, neutral pDA, and $(\mathrm{NBMN})^-(\mathrm{pDA})^+$, it is likely that the complex is conductive ("1" low-impedance state). This can be done by increasing the evaporation temperature and, hence, the deposition rate, since the two molecules have different boiling points. However, the origin of the conductance transition still is questionable, since after the charge transfer the excited state cannot be stable. The lifetime is just in the order of a microsecond or nanosecond. In our experiments the "1" state can last some ten days. Thus, the charge transfer theory cannot satisfactorily explain of the conductance transition. We have proposed a model for the recording mechanism, which is a structural transition in the nanometer-scale molecules. Experiments and *ab-initio* calculations were conducted.[29] Results demonstrate that the recording mechanism is due to the molecular structural transition from the ordered to the disordered structure.

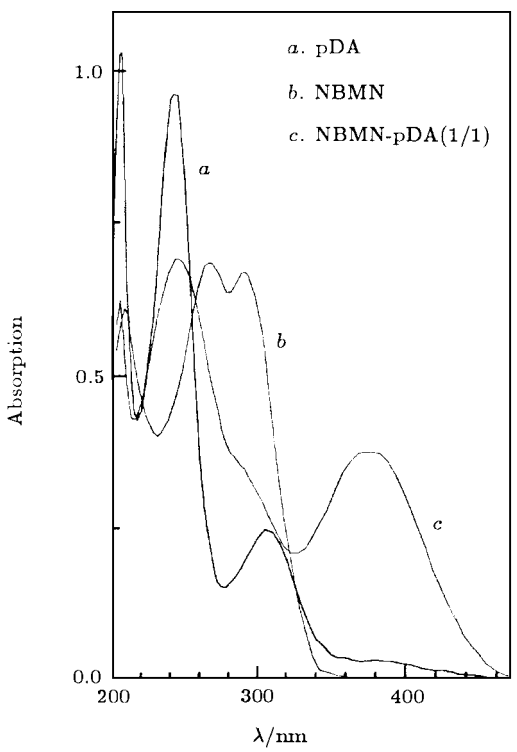


Fig.4. The UV-visible absorption spectra of the NBMN, pDA, and the NBMN-pDA complex, respectively. A new peak at ~385nm appears in the spectrum of the NBMN-pDA complex, indicating charge transfer from pDA to NBMN.

IV. CONCLUSION

Based on the results discussed above we believe that a significant potential exists for ultrahigh density data storage devices using the natural electrical bistability of organic charge transfer systems which need a much shorter transition time, principally less than a few nanoseconds and as in other cases, one microsecond. In our case, simple vacuum deposition method was employed only and the transition can be induced by an electric field and laser irradiation. Furthermore, molecular self-assembly techniques could be used to order the molecules vertically within a thin film, one component above the other (see Fig.5). As the charge transfer occurs within the molecular complex, the ultimate resolution would appear to be the diameter of the complex itself, less than 1nm, corresponding to a data storage density greater than 10^{14}bits/cm^2. In addition, chemical modifications of pDA or NBMN molecule could easily raise the energy barrier for the charge transfer process,[30] leading to reverse transition and commercially useful lifetimes with the STM tip. For such applications, further development of charge transfer systems is required.

ACKNOWLEDGEMENT

The author thanks Mr. and Ms. Y. L. Song, H. Y. Chen, W. J. Yang, L. D. Ma and S. J. Pang for experimental asistance and helpfal discussion.

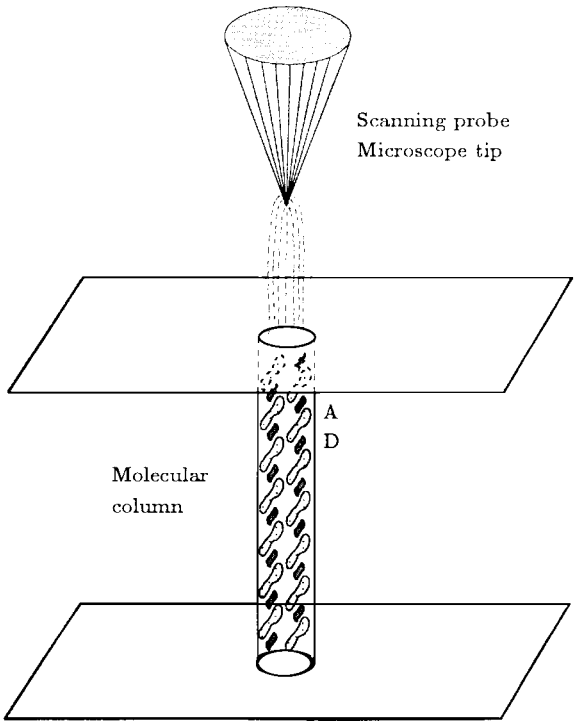


Fig.5. Schematic representation of a thin, self-assembled, organic data storage medium where individual aligned molecular columns act as bistable storage elements.

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