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Reversible, electrical and optical switching on silver 3-phenyl-1-ureidonitrile complex thin films*

Zhang Hao-Xu(张昊旭)[a], Shi Dong-Xia(时东霞)[a], Song Yan-Lin(宋延林)[b], Liu Hong-Wen(刘虹雯)[a], Hou Shi-Min(侯士敏)[c], Xue Zeng-Quan(薛增泉)[c], and Gao Hong-Jun(高鸿钧)[a]

[a] *Nanoscale Physics & Devices Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing* 100080, *China*
[b] *Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing* 100080, *China*
[c] *Department of Electronics, Peking University, Beijing* 100871, *China*

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We report on the reversible, electrical and optical switching on silver 3-phenyl-1-ureidonitrile complex thin films. The films can switch from a high impedance state to a low impedance state with an applied electric field at the threshold of 3.5×10^7V/m. Furthermore, the films can be switched back to the original state by treating the samples at about 80 °C. The optical recording is fulfilled using a semiconductor laser with a wavelength of 780 nm. Erasure can be accomplished by bulk heating or by the laser working with the power beneath the threshold. No loss of the organic was found in the experiments. This material may have a potential application in ultrahigh data density storage.

Keywords: optical recording, thin film, electrical switching
PACC: 7130, 7360, 6470, 8560

1. Introduction

Organic complexes, with the advantage of small size, diversity of compositions and structures, ease of fabrication and ultrafast response over inorganic materials, have aroused much attention in the last decade. They will play a main role in nanoelectronics and molecular electronics in the near future. Among these organic complexes for data storage materials, the charge transfer complexes of metals with tetracyanoquinodimethane (TCNQ) have attracted considerable interest.[1−16] These complexes have shown promising properties for erasable optical data storage, though the loss of TCNQ in the process of write-in causes great problems.[3−6]

In our previous investigations, we have systematically studied the fabrication and properties of various kinds of organic materials.[17−24] One of the systems reported is of the electrical bistability of silver toluene 2,4-dicarbamidonitrile (TDCN) complex thin films.[24] And another similar organic molecule, 3-phenyl-1-ureidonitrile (PUN),[25−29] was designed to improve the stability of TDCN and the performance of the switching behaviour of the Ag–TDCN complex films. In this paper, we report on the reversible electrical and optical switching behaviour of Ag–PUN complex thin films.

2. Experiments

An ionized cluster beam (ICB) deposition method is employed to prepare the Ag–PUN complex thin films. The substrate is a silver film deposited on a glass plate. The silver film serves mainly as a reflection layer. The co-deposition of silver and PUN is carried out under the following conditions: substrate temperature 40 °C, ion acceleration voltage −600 V, ion current 5μA, and chamber pressure 1×10^{-3} Pa. After deposition, the samples are heated at 80 °C in vacuum for half an hour, so that the two kinds of raw materials can react completely. The Ag–PUN complex thin films are about 100 nm thick.

Optical recording experiments are conducted on a home-made apparatus.[30] The light source is a SLD201V-3 semiconductor laser made by the SONY company, with a wavelength of 780 nm. A JEM-200CX transmission electron microscope (TEM) and a Renishaw micro-Raman spectroscope with the laser

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wavelength of 632.8 nm are employed to characterize the films.

3. Results and discussion

Figure 1 shows the micrograph and transmission electron diffraction pattern of the film. From the electron diffraction pattern, it can be seen that the film is polycrystalline. However, due to the irradiation of the electron beam in the TEM, the rings in the diffraction pattern of the films disappeared quickly, and can only be maintained for a few seconds. So only the diffraction rings from the silver are found in the diffraction pattern. Further experimental results of the electron diffraction on a very small region indicate the existence of silver nanoparticles in the film. Also, the particles can be identified as the dark spots of about 2 nm in diameter appearing from the micrograph. Thus we can deduce that the film is composed of two phases: the organic medium phase and the silver nanoparticles.

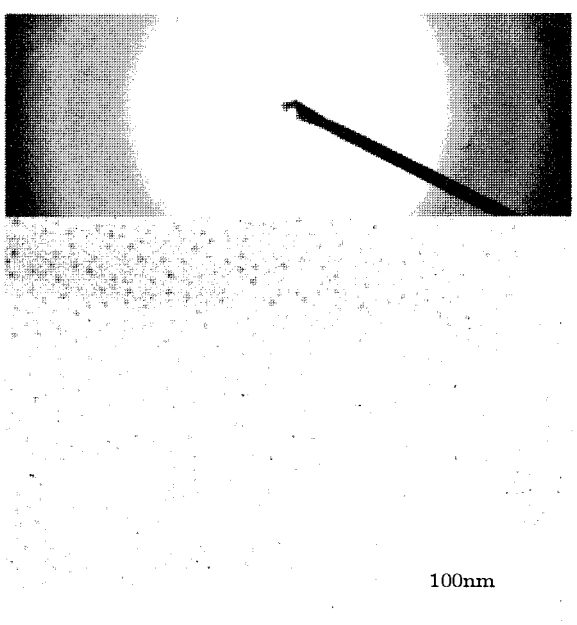

Fig.1. TEM micrograph (a) and the diffraction pattern (b) of the Ag–PUN complex thin film, indicating the polycrystalline thin film prepared.

The electrical bistability is found in our study on Ag–PUN complex thin films, as shown in Fig.2. When an external electric field exceeds a threshold of about 3.5×10^7 V/m, the conductance of the films can be enhanced by three to four orders of magnitude. Thereafter, the films will stay in the low-impedance state. If the films are heated to 80 °C, the conductance will return to its original high-impedance state. As is known, the degree of charge transfer between an electron acceptor and a donor is one of the most important factors that determine the electrical conductivity and the switching behaviour of the charge transfer complexes. So if the electrical bistability of Ag–PUN complex films is based on the charge transfer mechanism, the film is believed to be useful for optical recording.

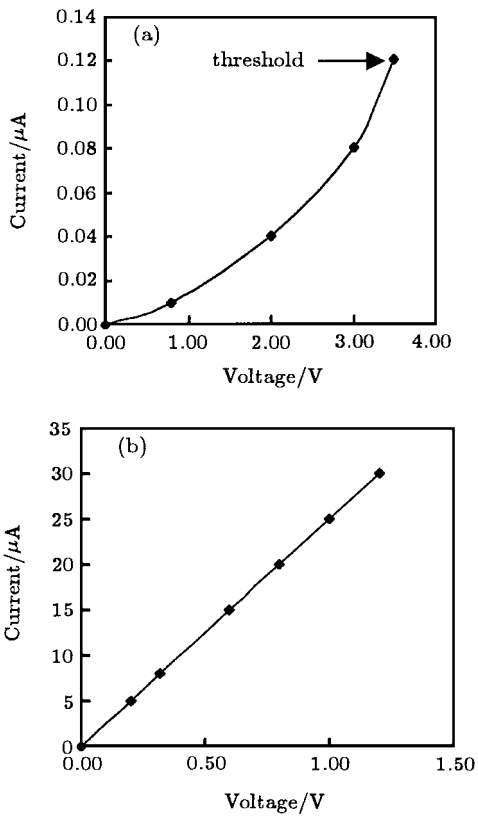

Fig.2. The dc $I-V$ curves of the Ag–PUN complex thin films: (a) before the transition; (b) after the transition.

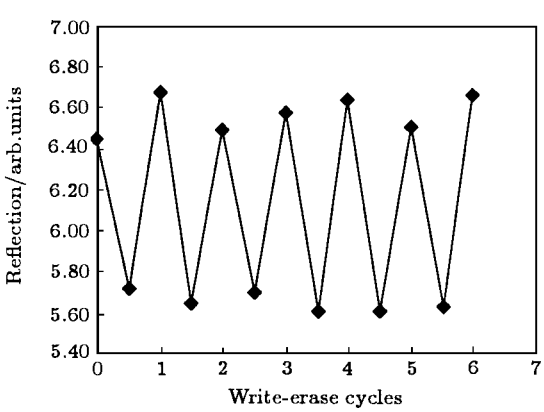

Fig.3. Typical results of reflection versus write–erase cycles. The write-in laser pulses are 10.4 mW for 10μs, and the erasure pulses are 7.0 mW for 1 ms.

The typical result of optical recording and erasing on using the sample is shown in Fig.3. The threshold

for the write-in pulses was 10.4 mW for 2μs. Here we use the pulses lasting for 10μs to complete the switching. The erasing pulses of 7.0 mW for 1 ms are used to heat the switched regions back to their original state. The recorded marks are found to be about 2μm in diameter under an optical microscope and remain stable for at least one week.

Figure 4 shows the Raman spectra of the Ag–PUN film before and after the switching, and also that of the PUN, as shown in curves (a), (b) and (c), respectively. The bands corresponding to the C≡N stretching modes of PUN molecules appear at 2249 and 2282 cm^{-1}. While in the Ag–PUN complex thin film they are greatly redshifted by the reaction between PUN and Ag, and thus they form two bands. The bands are at 2144 and 2217 cm^{-1} before the mark recording and at 2160 and 2206 cm^{-1} after the switching. The 2144 and 2160 cm^{-1} bands can be attributed to the PUN molecules connected with the Ag nanoparticles, and the 2217 and 2206 cm^{-1} bands to the PUN molecules in the organic medium phase. The dramatic difference between the spectra (a) and (b), especially the changes in the intensities of the two C≡N stretching bands, can be explained on the basis of the charge transfer mechanism of surface-enhanced Raman scattering.

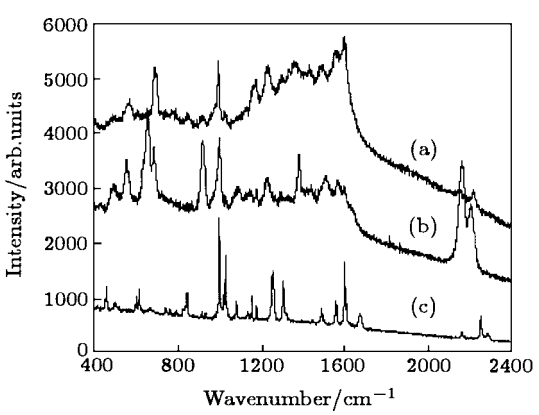

Fig.4. Raman spectra: (a) Ag–PUN film before recording; (b) Ag–PUN film after recording; (c) PUN.

It is noticed that no sign of PUN^0 molecules with the 2249 and 2282 cm^{-1} C≡N stretching bands can be found in spectrum (b). This phenomenon is important in considering the problem of the loss of materials from the film in the process of recording. The loss of materials may occur in PUN molecules. Since the bonding between Ag and PUN molecules in the medium phase is strengthened, the loss of materials does not occur in this phase. The bonding between PUN molecules and Ag nanoparticles is weakened. However, the film was very compact as shown in Fig.1. If the escape of the PUN molecules from the particles occurs, most of the molecules should still stay in the medium phase. Thus, they would either react with the Ag–PUN complex (which would weaken the bonding) or remain in a neutral state. But we can find no sign of either of these from curve (b) shown in Fig.4. So, based on our experimental results, the loss of organic materials TCNQ from the film does not occur during the optical recording.

There are three factors in the optical write-in process, i.e. the electric field, photons, and thermal effect. The thermal effect is in favour of erasure. The existence of the threshold for the power of the write-in pulses means that the electric field is essential. However, since the typical response time for the charge transfer in the complexes lies in the nanosecond timescale, i.e. much less than 2μs, it is necessary that the photons also play an important role in the write-in process. In Ref.[10] in order to elucidate the role of the photons, the authors compared the electric field of the laser in empty space for optical recording with the threshold for electric switching on Cu–TCNQ polycrystalline thin films; they found that it is 25 times weaker. Therefore, they considered that the photons seemed to assist the electric field effect by causing the electronic excitation of TCNQ. In our case, the electric field of the laser is at least five times weaker, but the existence of the Ag nanoparticles makes the situation complicated.

In order to elucidate the mechanism of the electrical bistability, we have examined the conductivity change activated by optical mark recording. The experiment is conducted in the following way. A region (about 2 mm^2) on the film is singled out at first. Then tens of marks are written within the region. Finally, a mask with holes is put on the sample, and a silver film is deposited on the film through the holes to form some top electrodes. By comparison of the conductance of the marked region with other parts of the film under the electrodes, the conductance enhancement caused by the mark recording is found to be by about four to five orders of magnitude. So the conductance enhancement in the electrical switching is one or two orders of magnitudes lower. However, we can explain it by taking into account the impedance (400 kΩ) put in series with the film to confine the current and protect the film. Once some high conducting paths emerge, the voltage across the film is lowered, so that other

parts of the film would remain in the low conductive state. Therefore, the enhancement of conductivity by optical mark recording is consistent with the case of electrical switching; and the electrical bistability can be attributed to the charge transfer mechanism.

4. Conclusion

We have found the reversible electrical switching behaviour of Ag–PUN complex thin films. Furthermore, we have realized optical mark recording, erasing, and reading on these films. The optical recording process involves charge transfer in both kinds of Ag–PUN complexes composing the film. According to this study, the electric field of the laser is essential for the recording, and the photons have also played an important role. To our surprise, no sign of loss of materials from the film has been found. This may be related to the unusual charge transfer phenomenon occurring in the film, which is different from the case of metal–TCNQ complexes. However, more work should be done on this kind of materials for a potential application in ultrahigh data density storage.

Acknowledgments

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