

Electrical Switching in Amorphous (NCTA)₂Ni(DMIT)₂ Thin Films

M.Y. Han, W. Huang,* D. Zhang,[†] and T.J. Li[†]

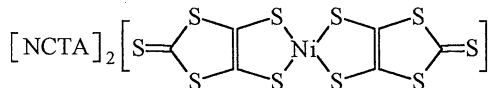
Department of Chemistry, National University of Singapore, Singapore 119260

[†]Department of Chemistry, Jilin University, Changchun 130023, China

(Received August 22, 1996)

Uniform amorphous thin films of molecular semiconductor (NCTA)₂Ni(DMIT)₂ were electrodeposited onto ITO glass. A reversible and reproducible bistable electrical memory switching was observed in an asymmetrical sandwich-type device upon applying a small voltage. More than 10⁶ cycles were repeated without failure.

Switching based on molecular semiconductors provides great opportunity to miniaturise the size of memory unit of electronic device.^{1,2} Switching phenomena have been reported originally in a few of inorganic thin films of metal oxides and amorphous chalcogenide glass alloys semiconductors,^{3,4} afterwards in organic semiconductor thin films.^{5,6} However, compared with organic molecular semiconductors, such as CuTCNQ (TCNQ denotes 7,7,8,8-tetracyanoquinodimethane), it has not been observed in an inorganic molecular semiconductor with organic counter cations incorporated by intermolecular weak covalent bonds instead of strong ionic bonds,⁷ although several inorganic molecular superconductors based on Ni(DMIT)₂ (DMIT denotes 1,2-dithiolene) anions *etc.*, have been reported.⁸



Scheme 1.

In the present work a switching phenomenon is observed in a new-type chalcogenic inorganic molecular semiconductor $[\text{CH}_3(\text{CH}_2)_{15}\text{N}^+(\text{CH}_3)_3]_2\text{Ni}(\text{DMIT})_2$ [*i.e.*, $(\text{NCTA})_2\text{Ni}(\text{DMIT})_2$, and denoted subsequently as CML, see Scheme 1] system which distinguishes itself from traditional chalcogenide glass alloys. Reversible memory switching effect is achieved simply by changing the polarity of the applied electric field across the device. It is unlike CuTCNQ system which switching can be erased by the application of a short current pulse.^{6,9}

An improved method according to the literature¹⁰ was used for the synthesis of CML. The basic configuration used to study the switching phenomenon was 0.2 μm amorphous CML thin films sandwiched between an indium tin oxide (ITO) glass bottom electrode and Al top electrode. A soft contacting electrical connection was adopted that a Ga-In liquid electrode was put directly on the Al top electrode surface. The thin films were prepared onto an ITO glass slide by potentiostatic electrodeposition (1.0 V, 20 min).

in 1.0 mmol dm^{-3} CML and 0.1 mol dm^{-3} acetonitrile solution of tetrabutylammonium perchlorate and the reference electrode used was SCE.

The characteristics of the amorphous thin films were tested and verified by XRD and SEM. XRD patterns show no diffraction peaks except a non-crystalline fringing peak in the small angle region. No microcrystals were observed by SEM. XPS results show that the composition of the thin films was nearly the same as the raw material since a large amount of the starting material can be embedded quite fast in the fractional oxidised (NCTA)_xNi(DMIT)₂ thin films in a high concentration of CML solution. The Ni 2p_{3/2} and the S 2p binding energies for the powdered sample and the thin films are (853.8 eV, 871.0 eV), (853.9 eV, 871.1 eV), and (162.2 eV, 162.3 eV), respectively.

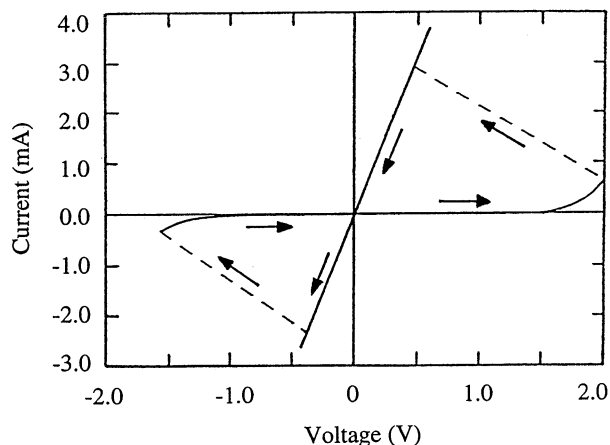


Figure 1. The I - V characteristics showing bistable switching in the sandwich structure Al/CML/ITO.

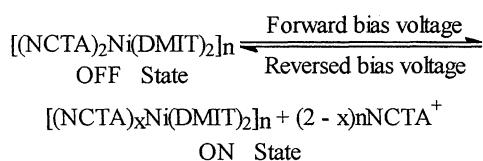
Figure 1 shows an oscilloscopic picture of the I - V characteristic curve which reveals electrical memory switching phenomenon. A 100 Hz pulse wave, which was generated from a full-wave rectification of a 50 Hz alternating current, was applied across the device. Initially, at a small applied forward bias voltage, the thin film was at high-impedance OFF state. When the forward bias voltage surpassed a threshold voltage (V_{th}), the resistance of the thin film dropped rapidly to a low-impedance ON state. The switching from the OFF to ON state occurred at an applied bias voltage of 2.0 V for the particular device which corresponding to an applied field strength of about 10^5 V/cm, and remained in this state without a holding voltage. Then it could be revert to the initial OFF state simply by a slightly smaller reversed bias voltage relative to the forward one applied across

the device. These results demonstrated that the relationship between the direction of the applied voltage and that of the switching is structurally determined, *viz.*, the asymmetry of I - V characteristic is mainly due to the asymmetrical structure of the device, not the different morphologies at both sides of the thin films.

An identical I - V characteristic curve of the switching was also measured using a DC voltage linear scanner instead of a 100 Hz full-wave rectification pulse in the same device.

The switching parameters appeared independent of the cross section of the Al top electrode. The threshold currents (I_{th}) were fairly constant over a wide variety of electrode sizes; The threshold voltage (V_{th}) was almost independent of electrode size, it was only a function of the thickness of the thin film. These indicate that conduction filaments were formed in the switching process.

The non-ohmic behaviour before switching and the ohmic behaviour after switching were noted. The non-ohmic behaviour in the OFF state can be explained by the initial formation of conduction filaments, whereas the ohmic behaviour in the ON state shows that the conduction filaments have been formed eventually. Therefore, the proposed switching transitions can be illustrated as Scheme 2:



Scheme 2.

where x stands for the fractional charge. It is believed that the mixed-valence species have higher conductivity than the original charge-transfer complexes.⁵ This is because that the $[\text{Ni(DMIT)}_2]^n$ ($n = 2, 1, 0$, and fractions) species can exist as dianionic, monoanionic, neutral and fractional charge complexes, of which the first three ones are semiconductors due to their filled HOMO orbitals or Peierls instability which usually show non-ohmic behaviour in switching devices. Non-integral charge species due to strong interactions between the molecule parts display high conductivity usually show ohmic behaviour after switching.

It is reported that some other switching processes can also be achieved reversibly by altering the polarity of the applied voltage pulse.¹¹ Most of the reversible recording and erasing mechanisms, such as those in vanadate glasses, have been explained on the basis of smaller ionised metallic ions migration possessing high mobility along the electric field.

In our experiment, there were no smaller ionised metals with high mobility in the thin films. In the process of the electrodeposition, only a few of lone pair electrons (not π electrons) in CML were first lost from the S atoms in the inner pentacycle containing Ni ion. In order that electrodeposition can be carried out continuously, there

must be some irregular conductive channels in the amorphous thin films because the long chain stackings are insulating. In addition, NCTA⁺ cation is so large that it can only move around its original position thermally.¹² Thus, the ON state must be generated from Ni(DMIT)₂ stackings instead of the long chain stackings.

Due to the strong S...S molecular interactions, the high conductive films in the ON state are so stable that they need not a holding voltage to keep the ON state of the memory switching.⁸ When the polarity of the applied field was reversed, the device switched to the OFF state because fractional negative charges were injected into the films along the filaments.

Compared with inorganic thin films, the unit number of the CML molecules with large volume in the thin films is greatly reduced. As the CML amorphous films with a long NCTA⁺ cationic chain are very stable,¹¹ it is difficult to separate out excess crystals which makes the switching become an irreversible process. Therefore, the irregular polymer-like aggregates based on Ni(DMIT)₂ stackings instead of the contribution of amorphous-crystalline conversion should be crucial to the ON state. If the chain length of the counter cation shorter, such as $(\text{CH}_3)_4\text{N}^+$ and $\text{CH}_3(\text{CH}_2)_4\text{N}^+(\text{CH}_3)_3$ cations, switching processes were broken after a few cycles. Perhaps it is because they are easily to separate out excess crystals, which hinders the reversible switching processes. These results demonstrate that long chain counter cations play an important role in the reversible and reproducible electrical memory switching.

In conclusion, the switching behaviour of the amorphous thin films, recorded on an oscilloscope, can be observed continuously for several hours without noticeable changes in their characteristics. The switching cycles can reach 10^6 without failure. This reveals the high reversibility of such devices based on Ni(DMIT)₂ amorphous thin films with long chain counter cations.

References

- 1 J. L. Fox, *C&EN*, **May 23**, 27 (1983).
- 2 M. C. Petty, M. R. Bryce, and D. Bloor, *An Introduction to Molecular Electronics*, Edward Arnold, London (1995).
- 3 S. R. Ovshinsky, *Phys. Rev. Lett.*, **21**, 1450 (1968).
- 4 T. W. Hickmott, *J. Appl. Phys.*, **35**, 2118 (1964).
- 5 A. R. Elsharkawi and R. C. Kao, *J. Phys. Chem.*, **38**, 95 (1977).
- 6 R. S. Potember, T. O. Poehler, and D. O. Cowan, *Appl. Phys. Lett.*, **34**, 405 (1979).
- 7 D. W. Bruce and D. O'Hare, *Inorganic Materials*, John Wiley & Sons, Chichester (1992).
- 8 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, and A. E. Underhill, *Coord. Chem. Rev.*, **110**, 115 (1991).
- 9 R. S. Potember, T. O. Poehler, and R. C. Benson, *Appl. Phys. Lett.*, **41**, 548 (1982).
- 10 G. Steimecke, H. J. Sieler, R. Kirmse, and E. Hoyer, *Phosphorus and Sulphur*, **7**, 49 (1979).
- 11 A. Sato and Y. Tsukamoto, *Nature*, **363**, 431 (1993).
- 12 O. Lindqvist, L. Sjölin, J. Sieler, G. Steimecke, and E. Hoyer, *Acta Chem. Scand. A*, **33**, 445 (1979).