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Electrical Switching and Memory Phenomena in Electrodeposited $[TBA]_x[Ni(DMID)_2]$ Thin Films

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This paper reports reproducible bistable electrical switching and memory phenomena observed in a lamellar structure with an amorphous film of $[TBA]_x[Ni(DMID)_2]$ between Pt and Al electrodes where the $[TBA]_x[Ni(DMID)_2]$ is electrically deposited on a Pt substrate with galvanostatic conditions (TBA = tetrabutylammonium, DMID = 1, 3-dithiole-2-one-4, 5-dithiolate). The switching effect is insensitive to air, moisture, light, and the polarity of the applied potentials. The device is stable over a long period of time and has a lifetime of roughly 20 switching cycles. The current-voltage characteristics reveal an abrupt increase in impedance from 300 Ω to about 100 kΩ at a field strength of about 2400 V/cm for a 10 μm film sample. Switching with high-power dissipation yields a high-impedance memory state which can be erased by the application of high voltage in either direction. The character of the switching from a low to a high impedance state in this organic charge transfer complex is in contrast to the organic charge transfer complexes of M-TCNQ type (TCNQ = tetracyanoquinodimethane). An interpretation of this behavior is presented.

Keywords: 1,2-dithiolene metal complex, charge-transfer complex, DMID, organic semiconductor, electrical switching

1. INTRODUCTION

The phenomena of threshold and memory switching in thin film devices have attracted a fair amount of attention since Ovshinsky's pioneering work on chalcogenide glasses in the late sixties.[1] A number of reports have since appeared that describe switching behavior in various organic,[2] metal oxide[3] and metal sulfide[4] materials. In the field of electrical switching, the use of organic thin films has been suggested by Elsharkawi *et al.*,[5] Stafeev *et al.*,[6] Carchano *et al.*,[7] Kevorkian *et al.*,[8] and Szymanski *et al.*[9] In 1979, Potember *et al.*, reported reproducible bistable electrical switching between resistance states in polycrystalline Cu-TCNQ (TCNQ = tetracyanoquinodimethane) films.[10] To date, three distinct classes of bistable devices have been demonstrated using organic materials based on charge transfer complexes of the TCNQ type;[10–12] these are optical, electrical, and optoelectronic switches.[13] All three classes of devices are activated by electric fields induced by applied potentials, optical beams, or various combinations of the two.

In this paper, we report a novel kind of bistable and reproducible electric field-induced switching and memory phenomenon observed in a lamellar structure with

an amorphous film of $[TBA]_x[Ni(DMID)_2]$ (TBA = tetrabutylammonium, DMID = 1,3-dithiole-2-one-4,5-dithiolate). We focused on these transition metal bisdithiolene complexes for the materials of molecular electronic devices based on the following thoughts: First, over the past decade, there has been renewed interest in metal complexes of multi-sulfur donor ligands for their unusual solid state properties (electrical,[14] magnetic,[15] and photoelectrical[16] properties). These acceptor complexes are of interest due not only to the potentially useful electronic, optical, or magnetic properties, but also to the many possibilities for chemical modification. Second, the amorphous thin film of the charge-transfer complex $D_2[Ni(DMIT)_2]$ (DMIT = 1,3-dithiole-2-thione-4,5-dithiolene) was reported to exhibit electric field-induced switching and memory phenomena.[17]

2. EXPERIMENTS AND RESULTS

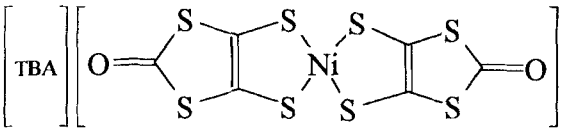
2.1 Synthesis

We have previously reported the synthesis of a series of multi-sulfur 1,2-dithiolene metal complexes of DMID ligand.[18] Some molecular structures studied here are shown in Figure 1.

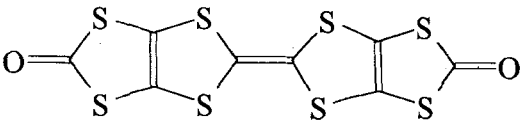
2.2 Film Preparation and Characterization

The basic configuration of the device is shown in Figure 2. Fabrication of the device consists of first removing any organic contaminants from a strip of Pt metal foil by means of immersing it in a 2 M NaOH aqueous solution, then rinsing with acid, water, and finally acetonitrile. The cleaned metal foil is immersed directly in a solution of dry, degassed, and freshly distilled acetonitrile which has been oversaturated with the precursor metal bisdithiolene complex of $[TBA][Ni(DMID)_2]$. The film was electrodeposited on the anodic Pt substrate under a constant current of 25 μA at room temperature. The cathode was graphite. Within hours, a black film was formed on the surface of the Pt substrate. This technique of forming semiconducting films by electrodeposition is used to grow films directly on the Pt substrate. These films can be grown to a thickness of 10 μm in a matter of hours. Once the film has been grown to the desired thickness, the growth process can be terminated by either simply removing the metal substrate containing the organic layer from the acetonitrile solution or cutting off the applied current. The two component structure is gently washed with additional acetonitrile to remove any excess precursor molecules and dried under vacuum to remove any traces of solvent. A three component structure is complete when a top metal electrode of aluminium is evaporated on the organic film under vacuum.

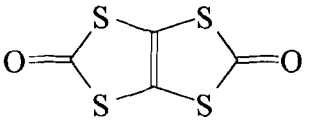
Scanning Electron Micrographs (SEM) showed it to be a net-like or dendritic structure (see Figure 3). This kind of structure formed may be the result of the high constant currents applied during the film growth. Typical film thicknesses were 10 μm, which were evaluated from the side view SEM of the same sample. The side view was obtained from a segment of the film peeled from the surface of the Pt substrate. X-ray powder diffraction of the film material showed it to be amorphous.



[TBA][Ni(DMID)$_2$]



Dithiapendione



Thiapendione

FIGURE 1 Molecular structures of [TBA][Ni(DMID)$_2$], dithiapendione, and thiapendione.

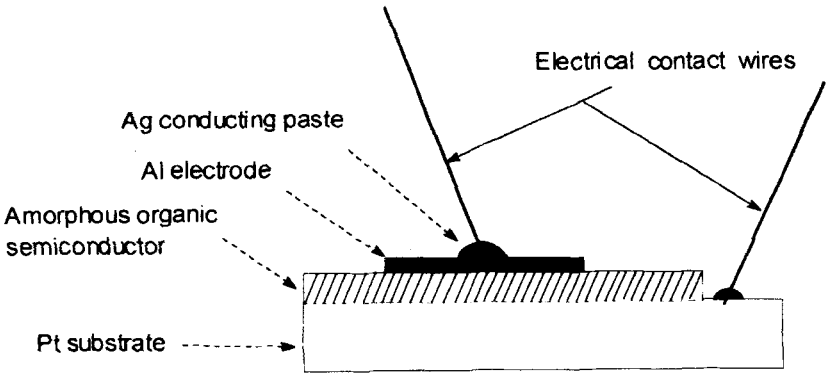


FIGURE 2 Schematic diagram of the organic switching device.

Elemental analysis performed on the bulk of the amorphous films of [TBA]$_x$ [Ni(DMID)$_2$] reveals that the value of x is about 0.9 within permitted experimental error. Infrared spectra were recorded on a Magna IR 750 (Nicolet) Fourier Transform Infrared (FT-IR) spectrophotometer in the region of 4000–400 cm^{-1} as KBr pellets

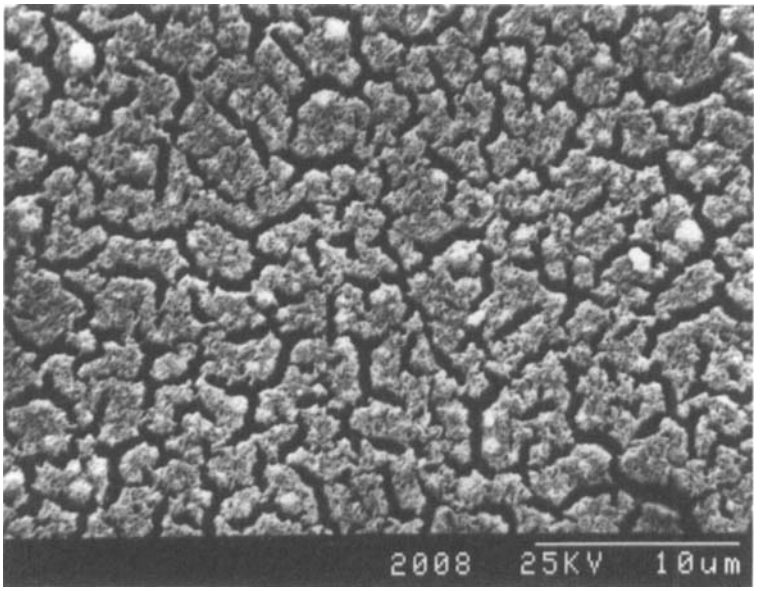


FIGURE 3 Scanning Electron Micrograph of the film electrically deposited on Pt substrate for 3 h.

with scans of 32 at room temperature. Micro Fourier Transform Infrared spectra were recorded on a Nic-Plan FT-IR Microscope and Magna IR 750 (Nicolet) Fourier Transform Infrared spectrophotometer in the region of 4000–650 cm^{-1} with 500 scans at room temperature. FT-Raman spectra were recorded on a Raman 910 (Nicolet) spectrophotometer in the region of 4000–100 cm^{-1} with 1000 scans and power less than 30 mW using a Nd: YV04 (1064 nm) laser. X-ray photoelectron spectra were recorded on a ES-300 (Kratos) photoelectron spectrometer with AlKα (1486.6 eV) X-radiation source under vacuum of $2 \sim 6 \times 10^{-6}$ Pa. The X-ray source was operated at 15 KV and 10 mA. Scanning electron microscopy (SEM) was done using a HITACHI S530 microscopy. The accelerator voltage was 25 keV with a working distance of about 10 mm.

2.3 Device Testing and Results

To prepare the samples for electrical characterization, metal electrodes (aluminium) were evaporated onto the surface of the films under vacuum forming $1 \times 1\,mm^2$ contacts. No further treatment was performed after a three component structure was complete and contact adherence was excellent.

The DC current-voltage characteristics were measured in the standard manner in air. The three component structure was connected through two external contact wires in series with a DC voltage source (voltage range 0–30 V) and a 510-Ω load resistor. The I–V curve was recorded on a X-Y recorder. In general, one contact wire was connected to the top electrode by silver conducting paste or by liquid metals of mercury, gallium, or gallium-indium eutectic and another one connected to the Pt substrate by silver

conducting paste or directly by pressure contacting so that the current flowed vertically through the film material.

Typical I–V behavior was as follows. At the outset, the device was in the "ON" state, i.e., for small applied voltage (of either polarity on the evaporated metal gate), the current was somewhat large, indicating a device resistance of about 1 kΩ. When the applied voltage exceeded a certain threshold (V_{th}), usually around 2.0 V, the device resistance abruptly increased to about 100 kΩ, thus putting the device into the "OFF" state. The ratio of R_{off}/R_{on} was generally 10^2–10^3. As the applied voltage was lowered (even to zero), the device impedance was unaltered so that true memory switching behavior was observed. If the device was continuously applied a higher voltage in the same potential direction in the "OFF" state rather than reduce the applied voltage, the device remained in the high resistance state until another certain voltage threshold was attained, typically about 14 V. At this point, the device conductance spontaneously increased and the low resistance state reappeared (see Figure 4). This does not mean that only in the same potential direction the low resistance "ON" state can reappear. In fact, the polarity of the applied potential is not important in the case studied here. Figure 4a shows the turn-off I–V characteristics and Figure 4b shows the turn-on I–V characteristics in the same potential direction.

Several important points should be noted. First of all, the device switched from low to high resistance only when the applied voltage exceeded a certain critical value. The polarity of the applied potential is unimportant. This is similar to the behavior of the memory switching elements reported, where polarity is unimportant,[3] but this is

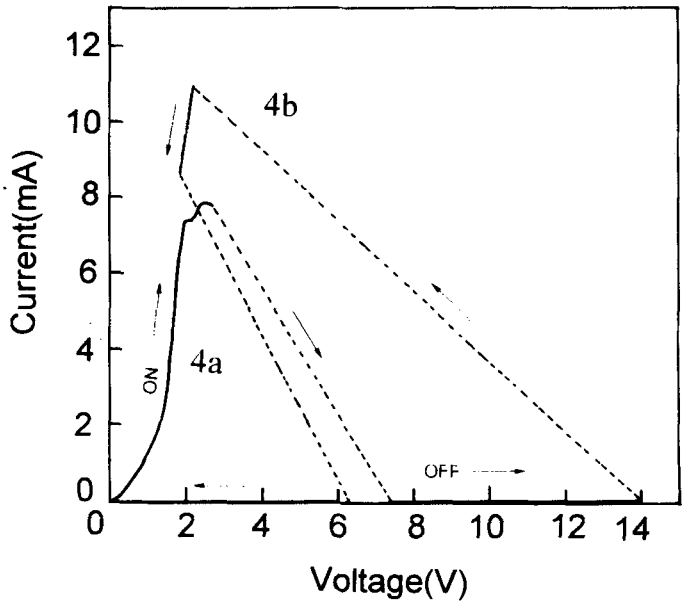


FIGURE 4 Typical DC current-voltage characteristic curve showing low- and high-impedance states for a 10 μm $[TBA]_x[Ni(DMID)_2]$ film sample. (4a) turn-off I–V characteristics; (4b) turn-on I–V characteristics with the same applied potential direction as that of turning off.

contrasted to the behavior of the memory switching elements reported elsewhere, in that only the application of a positive potential had effect on the device.[12] Second, the device could be switched "ON" by the application of high voltage in either direction.

Some preliminary results concerning device durability and stability are available. Several samples were subjected to repeated switching tests. The samples could be switched roughly 20 cycles before suffering catastrophic failure. The samples subjected to switching tests were stable over more than eight months.

3. DISCUSSION

3.1 Characterization of the Film Material

Elemental analyses are in agreement with the formula $[TBA]_{0.9}[Ni(DMID)_2]$. This may indicate that the integer oxidation state precursor compound [TBA] $[Ni(DMID)_2]$ was partially oxidised to the non-integer oxidation state or mixed valence species. This is consistent with the results of X-ray photoelectron spectroscopy (XPS).

It is known that XPS which measures the binding energy of core electrons in atoms and molecules has been successfully applied to the study of the oxidation states in mixed valence compounds.[19,20] Furthermore, XPS is well suited for the characterization of these devices.[13a] The interest in this study has sprung not only from the characterization of these film materials, but also from the difficulty to assign formal oxidation states to the transition metal according to the traditional rules of valence for those of non-stoichiometric complexes. To elucidate the oxidation states of Ni, S, N in the amorphous films of unswitched $[TBA]_x[Ni(DMID)_2]$ grown on Pt substrates, the solid-state photoelectron spectra of the films, $[TBA][Ni(DMID)_2]$ crystalline powder and some reference compounds: thiapendione (1, 3, 4, 6-tetrathiapentalene-2, 5-dione), dithiapendione, and TBABr (tetrabutylammonium bromide) were recorded. These spectra were then compared to one another and to the published spectra of metallic Ni, NiO.

For insulators or semiconductors, binding energy (B.E.) measurement usually requires the selection of an internal or external B.E. standard or calibration line in order to eliminate variable charging effects.[21] Without recourse to such standards, B.E.'s are generally unreproducible. In our experiments, C(1s) [B.E. = 285.0 eV] from pump oil contamination was used as a standard for charge correction. The B.E. data are summarized in Table 1. All the B.E.'s were reproducible to within $\pm$ 0.1 eV.

The Ni(2p3/2) B.E.'s of the film and $[TBA][Ni(DMID)_2]$ compound are almost the same. As a result of comparison of all the B.E. data, one can conclude that the oxidiation states of Ni in both the $[TBA]_x[Ni(DMID)_2]$ film and the precursor compound may be considered to have the formal valence states of + 3. The reasons for this assignment are as follows. First, the binding energies of Ni(2p3/2) in the film are higher than that of NiO. Second, the presence of Ni(II) in the $[TBA]_x[Ni(DMID)_2]$ film can be ruled out because no intense satellite features were observed in the spectra of Ni(2p3/2) in the films examined.

The S(2p) spectra of the films prepared by electrodeposition for 180 minutes show, in addition to its primary feature centered at 163.0 eV, the characteristic "satellite" feature

TABLE I

Ni(2p3/2), S(2p) and N(1s) binding energies (eV) in (a) $[TBA]_x$ $[Ni(DMID)_2]$ thin film, (b) [TBA] [Ni $(DMID)_2$] polycrystalline powder, (c) dithiapendione, (d) thiapendione, (e) TBABr, (f) Ni and (g) NiO

compound	Ni(2p3/2)	S(2p)	N(1s)
a	854.8	168.4, 163.0	400.2
b	854.7	163.0	401.8
c		164.0	
d		164.8	
e			401.7
f*	852.3		
g*	853.3		

* from reference[22]

centered at 168.4 eV. But the precursor compound [TBA][Ni(DMID)$_2$] and the reference compounds do not show the feature. This characteristic "satellite" feature in the spectra of S(2p) in the film may be considered to be the result of the formation of partially oxidised species. This is in good accordance with the elemental analyses of the film. On the other hand, for both the precursor compound and the film, the main peak is found to be centered at about 163.0 eV.

Figure 5 shows the micro FT-IR reflectance spectrum performed on the surface of the film. It shows the characteristic bands of the metal bisdithiolene complexes of DMID ligand.

All the samples were freshly prepared. Wherever possible, elemental analysis was performed on the samples to verify their composition before measurement. We found that the C=O stretching peak in the reflectance band at 1620 and 1670 cm^{-1} for the film is consistent with the values measured for the precursor compound, and we can also notice that the C=O stretching mode in reflectance measurements shifted to a higher frequency by about 10 cm^{-1} from absorption measurements made on the same material, tabulated in Table II.

Raman spectrum performd on the film and the precursor material reveals that the film and the precursor compound exhibit almost the same characteristic scattering bands, shown in Figure 6. It should be noted that the strong Raman bands at 1147 and 1184 cm^{-1} for the precursor compound shifted to a higher frequency by about 7 cm^{-1} at 1154 and 1190 cm^{-1}, respectively, for the film.

As a whole, the evidence suggested by XPS, micro FT-IR reflectance and FT-Raman spectra measurements show that the basic molecular skeleton in the film and the precursor compound may be unchanged.

3.2 Electrical Behavior

Threshold and memory behavior is observed in these materials by examining current as a function of voltage across the two terminal structure. Figure 4a shows a typical ON-OFF dc current-voltage curve for a 10 μm thick film in Al/$[TBA]_x$ $[Ni(DMID]_2]$/Pt system. The trace in Figure 4a is made with 510-Ω load resistor in

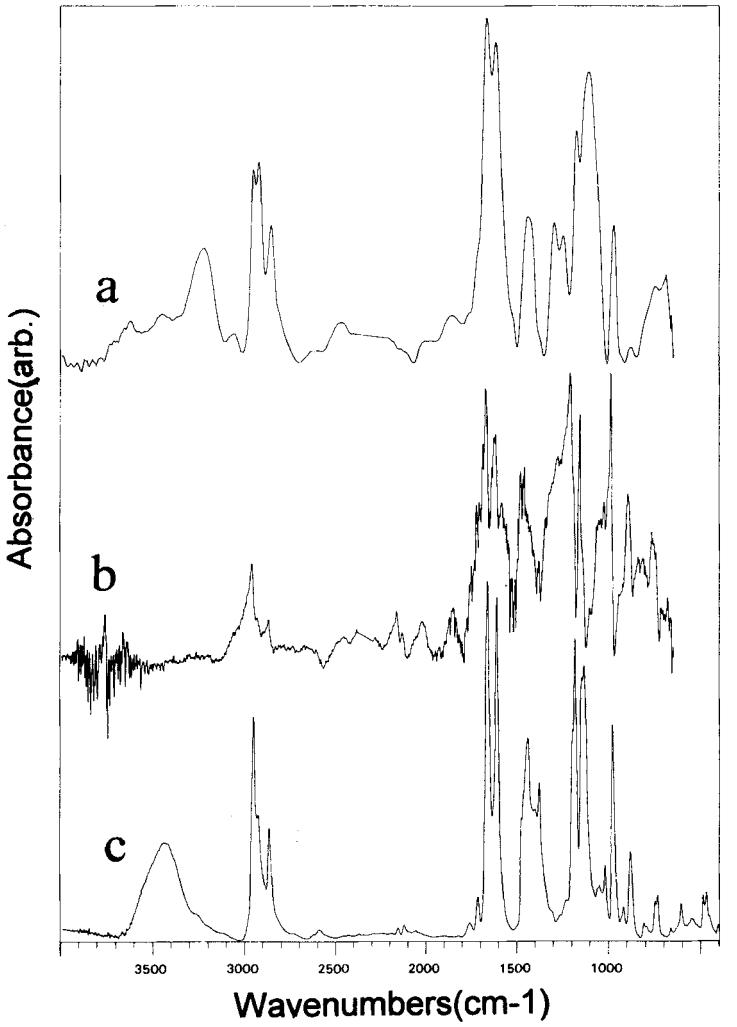


FIGURE 5 Micro FT-IR reflectance spectra of (a) $[TBA)_x[Ni(DMID)_2]$ thin film; (b) [TBA][Ni $(DMID)_2]$ precursor complex, and (c) FT-IR absorption spectra of $[TBA][Ni(DMID)_2]$.

series with the device. Figure 4a shows that there are one stable non-ohmic and one stable ohmic resistive states in the material. These two states, labeled "ON" state and "OFF"state, are essentially insensitive to air, moisture, light, and the polarity of the applied voltage. A rapid switching is observed from the "ON" to the "OFF" state along the load line when an applied field across the sample surpasses a threshold value (V_{th}) of 2.4 V. This corresponds to a field strength of approximately 2400 V/cm. At this field strength, the initial low impedance of the device (ca. 300 Ω) increases to a high impedance value of about 100 kΩ. A drop in current from about 8 mA to approximately 0.05 mA and a concurrent rise in the voltage to 7.3 V along the load line is observed in the $[TBA]_x[Ni(DMID)_2]$ system. The results in Figure 4a are contrasted to the

TABLE II

C=O stretching mode (cm^{-1}) in FT-IR absorption or micro reflectance measurements for $[TBA]_x[Ni(DMID)_2]$ thin film (a) and [TB A][$Ni(DMID)_2$] precursor compound (b)

a	1620	1670
b	1622	1678
b*	1614	1667

* Absorption measurements

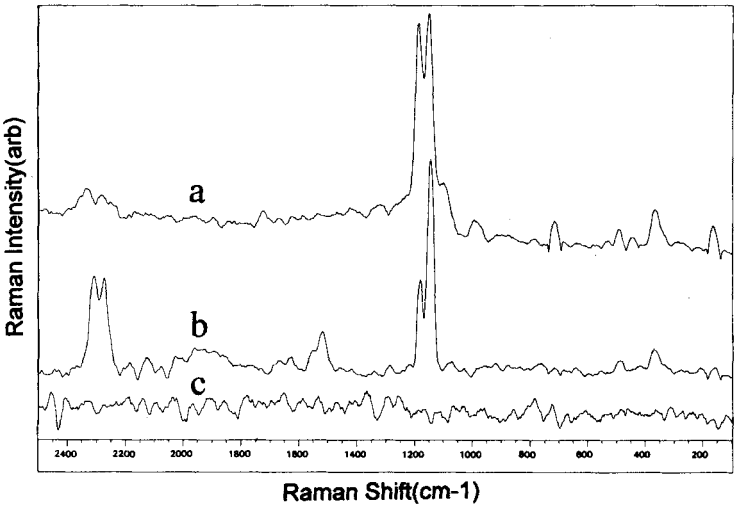


FIGURE 6 Raman spectra of (a) $[TBA]_x[Ni(DMID)_2]$ thin film; (b) [TBA][$Ni(DMID)_2$] precursor compound, and (c) metallic Pt substrate.

switching effects observed in the metal charge-transfer salts such as M-TCNQ, M-TNAP (tetracyanonaphthoquinodimethane) and so on, in which the switching effect can be observed from "OFF" state to "ON" state.[23] In addition, it has been observed that once the film is in the "OFF" state, it will remain in that state as long as an external field is applied. In every case studied, the film eventually returned to its initial low-impedance state after the applied field was removed, which is called a memory effect, i.e., memory state. This memory state can remain intact from a few minutes to several hours after the applied potential was removed and it can also be immediately removed by application of high voltage in either direction. The voltage required to switch back to the initial state appeared to be directly proportional to the film thickness, duration of the applied field, and the amount of power dissipated in the sample while in this state.

3.3 Mechanism

In inorganic switching devices, such as those amorphous alloy switches including chalcogenide glasses, which exhibit a current-controlled negative resistance, and those oxides of nickel, silicon, aluminium, titanium, zirconium, and tantalum, all of which exhibit a voltage-controlled negative resistance when arranged in a metal-oxide-metal sandwich structure, switching behavior has been attributed to the forming of filaments which are described by both thermal and electronic models. Each of these two models appears to have a range of applicability. The basis of the thermal model is the formation of highly conducting filaments. These filaments are formed by local joule heating which produces material rearrangement or even melting. Some consequences of this model include:[12] (1) incubation (delay) time that can be lengthy, on the order of 10 μs;[1] (2) insensitivity to the polarity of the applied field;[3] (3) some material rearrangement or damage;[4] and (4) the need for high applied power density. On the other hand, the postulated electronic models rely upon either a double injection model that effects a recombination instability or an electronic filament (as opposed to a material filament) or some type of redox mechanism.[10] Common features of all of these models are: (1) low power dissipation at threshold; (2) rapid and short-dealy switching; and (3) no visible material damage. The analysis of memory threshold switching in bistable systems further differentiates the thermal and electronic models. In the thermal model, the existence of two stable states corresponds to the production of two different structures or compositions.[24] On the other hand, the classical electronic model generally forbids memory switching since it demands a non-zero holding voltage to keep the structure in the high conductivity state, i.e., "ON" state. Nevertheless, it is known that the mechanism of switching in organic elements reported in the literature[5–9] are basically physical in nature. Impedance changes which accompany switching are asociated with molecular motion due to Joule heating which results in either crystallization phase transitions, metal filament formation, or elimination of compositional disorder, which could be basically described by the thermal model. But it is our feeling that the switching mechanism in the structure reported here is neither thermal nor electronic. It is possibly believed that the mechanism is a field-induced, solid-state, reversible electrochemical redox reaction which results in switching in the reported structure wherein integer oxidation state species or simple salts are in equilibrium with the initial high conductivity salt as exemplified by the following equation:

EQUATION 1

$$n\{[\mathrm{TBA}]_x[\mathrm{Ni(DMID)_2}]\} \xrightleftharpoons{\text{Electric field}} m\cdot x\{[\mathrm{TBA}][\mathrm{Ni(DMID)_2}]\} + (1-x)\cdot m\{[\mathrm{Ni(DMID)_2}]\} + (n-m)\{[\mathrm{TBA}]_x[\mathrm{Ni(DMID)_2}]\}$$

low impedance "ON" state — high impedance "OFF" state

Since non-integral oxidation states are common in solids, it's difficult to predict the exact stoichiometry in the equilibrium equation. The reaction shown in Equation (1) is reversible and the initial state can be readily reformed by the application of a high voltage in either direction. The observed changes in the electrical properties of devices fabricated from these organic materials is a direct consequence of the electric field induced reaction shown in Equation (1). The effect of the applied electric field on the film is to induce electrochemical redox reaction resulting the simple salts containing integral oxidation state complex [TBA][Ni(DMID)$_2$] and neutral [Ni(DMID)$_2$] compound. The integral oxidation state species and the neutral Ni-DMID complex formed as a result of this field induced redox reaction control the semiconducting behavior of these films.

In addition, an ionic or a molecular displacement associated with this equilibrium could explain the observed memory phenomena and the fact that all the devices show only two stable resistive states. Since conduction in these narrow band semiconducting metal complexes is believed to be limited by the motion of unpaired electrons along the stacks of planar [Ni(DMID)$_2$] anions, this interpretation is in accordance with the electrical behavior reported in these films when fabricated into switching devices.[25] The low conductivity in these integral oxidation state complexes such as the "switched" form of the film is due in part to an increase in the energy required to overcome the repulsive Coulomb forces that result when a conduction electron is removed from one anion and placed into a higher energy orbital of another anion, which is consistent with the analysis of the cyclic voltammogram of the integer oxidation state metal complex of [TBA][Ni(DMID)$_2$]. We can notice that the difference between the oxidation potential ($E1$) and the reduction potential ($E2$); i.e., the $\Delta E(=E1-E2)$ values of this compound are 0.8 V. This suggests that the intermolecular Coulomb repulsion energy in the conducting state may be large. Therefore, the powder conductivity of [TBA][Ni(DMID$_2$] at room temperature is about 3×10^{-11} S·cm^{-1}. However, in the case of a partially oxidised complex such as the "unswitched" form of the film, there are more anions than there are unpaired electrons and, therefore, electrostatic repulsion of charge carriers is kept at a minimum by allowing conduction electrons to occupy the empty molecular orbital of the anion. This is a lower energy pathway compared to putting more than one electron on the same anion site and it may explain how partially oxidised semiconducting complexes like the "unswitched" form of [TBA]$_x$[Ni(DMID)$_2$] can exhibit greater conductivity than similar complexes with integral oxidation state species like the "switched" form of [TBA][Ni(DMID)$_2$] or [Ni(DMID)$_2$].

Switching by means of electrochemical changes was not suggested until Potember *et al.*[26] reported the switching behavior in a metal complexed with TCNQ, TNAP, TCNE (tetracyanoethyene), DDQ (dichlororicyanobenzoquinone) or TCNQ derivatives. Futher work is required and various diagnostic techniques to validate the mechanism shown in Equation (1) must be applied to the specimens. For example, an experiment designed to measure the response to a very short pulse in order to determine values for the conventional delay time and rise time and an experiment designed to determine if the device generates an open-circuit voltage or electromotive force (emf) when returning from the high- to low-impedance mode are under way. If the open-circuit voltage is observed in the designed experiment, the voltage does show that

the mechanism by which the switching occurs is consistent with a field-induced solid-state reversible electrochemical reaction associated with the charge-transfer complex. In contrast to the prior work on switching devices, the present work is significant by exploring a new kind of material—organic charge transfer complex derived from bisdithiolene metal complex of DMID ligand for molecular electronic devices (MED) and furthermore by providing a method of fabricating an organic functional thin film device, solid-state semiconductor, field-induced, bistable switch comprised of the material. The present work produces a switch responsive to electrochemical changes in the thin film semiconductor, i.e., it is significant to fabricate a thin film to effect switching by means of a field induced redox reaction in the film wherein partially oxidised species or complex salts are in equilibrium with the simple, low conductivity salts. The significance of the work also lies in constructing an organic thin film device exhibiting reliable, high-speed, reproducible switching in a threshold memory mode and specifically in fabricating an organic, solid-state semiconductor device wich switches in response to very low voltage (about 2 V for a 10 μm film). In the "OFF" state studied here, the device will not break down with voltage applied in excess of 10 V and in the "ON" state, the device will not break down with currents applied in excess of 10 mA. These parameters render the work practical for conventional electronic switching applications.

4. SUMMARY

A novel charge-transfer complex thin film structure has been reported which demonstrates bistable memory switching behavior. The structure exhibits a rapid transition from a high conductance to a low conductance state with a conductivity ratio of approximately 10^2–10^3 at a field strength of about 2400 V/cm. The device is stable over more than eight months and has a lifetime of roughly 20 switching cycles. These chemical and physical properties of the particular class of charge transfer complex (organometallic solids) may be used in two terminal bistable threshold and memory logic elements. These materials may find application in both conventional and novel information processing and storage. In the two terminal bistable switches, the rapid resistance changes which accompany the field-induced solid state, reversible electrochemical redox reaction may be used in logic elements for associative memories. In the device and possible applications, the concept of molecular architecture is utilized in that chemical structure dictates the specific physical properties observed in the device. This research has established a foundation of materials, and fundamental scientific principles amenable to the design of organometallic molecular electronic devices.

Our current explorations have centered on designing and constructing bistable switching materials which can be used to store and process information. These organic-based switching materials are used in devices which rely on very fast reversible electron-transfer reactions to change the solid-state properties of the thin film structures. In these systems, the logic or memory operation is performed within the confines of the organic molecular structure of the device.

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