New organic bistable films for ultrafast electric memories

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Abstract

Thin films which have electrical bistable effects are mostly metal-organic complexes and/or organic-organic (all-organic) complexes. Very recently some simple (mono-molecular) organic materials have been discovered which have bistable states at room temperature, too. The threshold voltage across these organic films with a thickness of 60 nm is 4–6 V and the transition time is 5–10 ns. Therefore, they are suitable to make ultrafast, non-volatile, organic memories (WORM or EPROM). Another possible application for an STM type ultrahigh-capacity memory is also illustrated.

Keywords: Organic film; Electric bistable; Storage media; Memory

1. Introduction

A material which can transit from a highly resistive state to a conductive state by an electric field is called an electric bistable material. It can be used as a current switch, surge voltage protector, voltage sensor, etc., but the most important application is used for computer memories. For a bistable material used for the memories, we believe it should have the following features:

1. Transition under a suitable electric field can be performed at room temperature, and should have a sharp threshold.
2. The resistivity ratio before and after a transition should be >10⁵.
3. The transition time should be <100 ns.
4. No evaporation and/or change of composition are detectable at a temperature <100°C.

The most important electric bistable materials which can satisfy all these features are metal-organic complexes, such as stoichiometric Cu + TCNQ (7,7,8,8-tetracyanoquinodimethane) [1], Ag + TCNQ [1], and Ag + TDCN (toluylene 2,4-dicarbamidodinitrile) [2]. All of them can be prepared in the form of thin films by vacuum evaporation. The current I versus applied voltage U across the thin film (with a thickness of ca. 50–100 nm) curve gives a threshold value of several volts. The film resistivity transformed from high to low and the ratio can be 5–6 orders of magnitude. In principle, the transition time (Δt) at the threshold can be very fast due to the charge transfer process (our earlier report [3] gives Δt < 400 ns, but now it is <10 ns in most cases), and the effective volume can be very small (molecular dimension). It is proposed to make high-density memories, however, there will be difficulties where the line spacing is less than 0.1 μm (100 nm) because of the surface migration of metallic atoms. Hence, organic bistable materials without metallic elements are still being investigated.

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In 1995, two organic-organic complexes (or termed as “all-organic” complexes), MC (melamine cyanurate) + TCNQ and BBDN (bis(2-butene-2, 3-dithiolato(2−)-s,s’)-nickel) + TCNQ which have bistable behavior at room temperature had been discovered [4]. After that m-NBMN (m-nitrobenzal malononitrile) + DAB (diamine benzene) [5], TMB (3,3’,5,5’-tetramethylbenzidine) + CA (p-chloranil) [5], and TMB + TCNQ were found. Among them the all-organic complexes containing TCNQ keep the similar features as metal-TCNQ, i.e. the threshold voltage is 4–6 V; the transition time is a little longer, but still less than 100 ns.

Very recently we have discovered some simple organic substances (not complexes) also have electric bistable characteristics at room temperature. In this paper, some preliminary results of these materials will be given. Possible applications to non-volatile memory and STM-type ultrahigh-capacity memory will be described.

2. Materials and their main characteristics

Until now we have found three different simple organic materials with electric bistable characteristics under room temperature. They are as following (the structural formula are shown in Fig. 1):

1. 4-(2-pyridylazo)resorcinol, C_{11}H_{9}N_{3}O_{2}, abbr. as PAR.
2. 1-(2-pyridylazo)-2-naphthol, C_{13}H_{11}N_{3}O, abbr. as PAN.
3. Glyoxalbis-(2-hydroxyanil), C_{14}H_{12}N_{2}O_{2}, abbr. as GHA.

Their common specification is that they are used as reagents for the determination of metallic ions by spectrometry or liquid chromatography. No bistable phenomenon has been reported previously. All of them can be deposited to form thin films by vacuum evaporation.

The method for testing materials is as follows. On a flat glass plate or a polished Si wafer covered with SiO_{2}, a thin Al or Cr film was deposited as the base electrode, then a layer of organic material with a thickness 50–200 nm was deposited on it. Finally, a layer of Al in configuration of circular points or straight lines was deposited as top electrodes. Among any of the top electrodes and the base electrode, a ramp voltage was applied with a resistor R_{L} in series. The voltage drops across the organic film and R_{L} were feeding to a X-Y recorder (Sichuan Factory of Instruments Type 3036) as V_x and V_y, respectively. Since the current through the organic film and R_{L} are just same, then

\[ I = \frac{V_y}{R_L} \]  \hspace{1cm} (1)

A typical I–U curve of the organic film is shown (Fig. 2). From this curve we can see that, when U reaches a certain threshold value U_t, the high-resistivity state of the thin film will transform to the...
low-resistivity (conductive) state. The resistivity of all these four different films can be transformed to 6–7 orders of magnitude (from ca. \(10^{10}\) to \(10^{3–10^4}\) \(\Omega\) cm), hence they can be used for information storage where the high and low resistivity can be used as State “0” and State “1”, respectively. Moreover, once if the film is at “1” (after write-in), it cannot return to “0” when the applied voltage is switched off. Therefore, it can be used for non-volatile memories.

Then the previously mentioned \(V_x\) and \(V_y\) are connected separately to the \(Y\)-axis of a digital sampling oscilloscope (Hewlett-Packard, type 54602) as \(Y_1\) and \(Y_2\), respectively. When the circuit is switched on, accompanying with the rise of ramp voltage applied, one can have the relationship of voltage \(U\) across the organic film varied with time \(t\) (\(U–t\) curve), as shown (Fig. 3). This oscilloscope can also measure the transition time \(\Delta t\) automatically at the threshold. The \(U_t\) and \(\Delta t\) values of these films are shown (Table 1).

It should be noticed that, unlike inorganic materials, both \(U_t\) and \(\Delta t\) are not single values. Sometimes they are changed on different sites of the surface even the uniformity of film thickness is good enough. It implies that, in case of an organic material, the electric properties are very dependent upon the microscopic parameters like crystal orientation, direction of molecular chains, etc. Further peering study will be needed.

<table>
<thead>
<tr>
<th>Material</th>
<th>(U_t) (V)</th>
<th>(\Delta t) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAR</td>
<td>5–6</td>
<td>4–8</td>
</tr>
<tr>
<td>PAN</td>
<td>4–6</td>
<td>&lt;8</td>
</tr>
<tr>
<td>GHA</td>
<td>4–5</td>
<td>&lt;10</td>
</tr>
</tbody>
</table>

The surfaces of organic films had been investigated by an atomic force microscope (AFM) from Park Scientific (Autoprobe CP type). The topographical micrograph of PAR is shown (Fig. 4). Most of the crystals have a sub-micron size. Surface microstructures of all other films are much alike and will not be described here.

3. Brief explanation of the phenomenon

Theoretical interpretation of the bistable characteristics of a simple organic substance is not yet available. The following is a very brief explanation [6].

Fig. 5 showed band structures of inorganic and organic semiconductors. In an organic semiconductor, the lowest unoccupied molecular orbit (LUMO) and the highest occupied molecular orbit (HOMO) are corresponding to the bottom of conductive band and the top of valence band, respectively, of an inorganic semiconductor. Since the chain structures in an organic molecule are easy to vary, then the enter of electrons may induce some structural distortions of surrounding molecular chains, and a composite particle, polaron [7], which is an electron surrounded by distorted molecular chains, will be formed. Such nonlinear excitations (polaron, soliton, domain wall) are commonly responsible for the transport phenomena and switching effect in low-dimensional organic...
compounds [8,9]. The energy level of the polaron is under LUMO (Fig. 5b), then, instead of LUMO, the electron can enter this level and, as a result, the potential barrier becomes lower. For a simple organic molecule, the separation between the polaron level and Fermi level is 0.1–0.5 eV (e.g. 0.4 eV in polythiophene [7]). If a material has a narrow gap, then it is easy to be injected with electrons or holes. Furthermore, the simple organic film is a molecular solid, and the interactions between molecules are only Van der Waals force. The coupling is so weak and the form of molecular arrangement is easy to be varied if an electric field is applied. Consequently, one state can be transformed to another.

Under a very intense electric field (e.g. the exertion of a STM tip), there will be another possible explanation. In an organic solid, polarons can be hopping between molecules, between molecular chains, and even between clusters. The potential barrier is about 0.1 eV. Since the distances between molecule to molecule, chain to cluster or cluster to cluster are about 1 nm, therefore, if the field intensity is $10^8$ V/m, then the voltage between neighboring molecules will reach 0.1 eV, and the polarons can be hopping into a conductive state.

4. Possible applications

4.1. Non-volatile write-once read-only memory

The basic structure of this memory is a matrix of metal-organic-metal switching elements, with a layer of amorphous Si to make Schottky contacts to avoid the “misread”, which is basically the same as described in ref. [3]. Now sets of parallel metallic lines with a period of 1 μm (0.4 μm for metal and 0.6 μm for spacing) can be manufactured in most laboratories, therefore, the storage density of this memory can be 100 MB/cm². Unfortunately until now we have not yet found the necessary conditions for erasing the storage made of the simple organic materials, hence they can only be used for non-volatile write-once memories (WORM or EPROM). Another problem of this memory structure is the RC delay of speed because the metallic lines used are very thin and the dielectric constant of the storage material is relatively high.

4.2. STM type ultrahigh-capacity memory

Data storage with a scanning tunneling microscope (STM) has been studied for a long time because this is the only way to get ultrahigh storage density. Many different methods and materials had been investigated [10–14]. However, most of these trials can not obtain both high storage density and capacity because of two reasons. First, the “write-in” time is too long. Most of the materials need a pulse-width of 10–500 ms. Obviously, they are not suitable for high-capacity memories. Second, the scanning area of a conventional STM is very small, then actually the maximal storage capacity (storage density × area) is only in the order of MB. In our case, the transition time of the organic materials is about 10 ns, and we [15] have proposed a mechanism to change the X-Y scanning
system into $\rho-\Theta$ scanning by a rotating cylinder, as shown (Fig. 6), which is mechanically more stable than a disc. This cylinder, what we termed as an “electric drum”, with a dimension of $\varnothing25\text{ mm}\times10\text{ mm}$, can have a storage capacity of 100 GB which is equivalent to a lot of red-light DVDs.

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