Dielectric properties of (multilevel) switching devices based on ultrathin organic films

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Abstract

Dielectric properties of an organic material, which shows conductance switching with associated memory phenomenon, have been studied. The devices have been modeled as a parallel combination of a resistor and a capacitor. During conductance switching, devices’ resistive and capacitive properties have been found to change. Multilevel conductivity, which is due to different density of high-conducting reduced molecules in the devices, has also been manifested in dielectric measurements. We could induce ('write') a low-conducting state and three high-conducting states and probe ('read') them by measuring frequency dependence impedance characteristics without any dc bias for multilevel read-only and random access memory applications.

1. Introduction

Molecular electronics have been considered to be the one of the best solution to the scaling limit problem the semiconductor industry may have to face in the next decade. If specific electrical functions can be incorporated into a single molecule, it holds the promise of scaling integrated circuit down to nanometer dimensions. There are a number of organic molecules that exhibit electrical bistability and switch between strongly and weakly conducting states [1–9]. In memory switching, this high conducting state is retained without any bias. It has been suggested that this intriguing behavior may be due to reduction of the molecule [3,4] and/or conformational change [5]. These features of the organic molecules make them promising for random access memory (RAM) and read-only memory (ROM) applications.

Impedance or dielectric spectroscopy is a powerful tool to study relaxation and loss processes in organic and inorganic materials, both in solution and in the solid state [10–14]. It allows to study not only materials parameter like frequency dependent complex dielectric constants, but also the influences of interfaces between two different materials. Impedance characteristics in switching devices can enable one to study resistive and capacitive properties of the material and their change during the transition.

This work reports the dielectric properties of multi-level molecular memory devices based on ultrathin organic films. Multiple conducting states and memory levels have been achieved by varying the population density of high conducting molecules. Multilevel approaches can be used to increase the capacity with concomitant increase in data transfer rate. Storage of multiple bits on a single memory cell [6,7,15] increases the density of memory bits in the same space. Multilevel conductance and multibit memory are receiving more and more attention recently amongst researchers. In this Letter, we focused on studying the detailed impedance characteristics in all of the conducting states of the devices.
2. Experimental

The material chosen in this work is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), whose molecular structure is shown in the inset of Fig. 1. We have fabricated devices based on Langmuir–Blodgett (LB) films on indium tin oxide (ITO) coated glass substrate followed by aluminum (Al) evaporation. A mechanical shutter, which was operated from outside, was used to protect the LB films from excess heat before and after Al evaporation. Details of device fabrication have been described elsewhere [15]. Five and 10 LB layers of DDQ (mixed with Stearic Acid) were deposited at 25 mN/m to get molecular-level layers for the devices. UV–Vis absorption and photoluminescence spectra confirmed deposition of DDQ in the LB films. The thickness of DDQ film has been 12.5–25 nm and area of a device was 6 mm². The devices were kept in an evacuated chamber (10⁻³ Torr) which was kept in a shielded box. The measurements were carried out at room temperature and after a wait of 10 h. The impedance characteristics were measured in a parallel mode by Solartron 1260 Impedance Analyzer. The test voltage has been 100 mV rms. Open- and short-circuit compensations were performed with standard normalization procedure in order to minimize the effect of any stray and wire capacitances. The instruments were controlled with a personal computer via a general-purpose interface bus (GPIB). The measurements were carried out with SMArt software. Real and imaginary parts of impedance, Z' and Z", respectively, of the device were measured with and without dc bias.

3. Results and discussion

In memory-switching devices, two current–voltage (I–V) characteristics are observed at the two voltage-sweep directions showing presence of a high- and a low-conducting state. In DDQ, the high-conducting ‘On’ state is observed when the device is stressed at −2.5 V. It returns to the low-conducting ‘Off’ state after the application of a positive pulse of same or higher amplitude. Considering work-functions of the metal electrodes and electron affinity and ionization potential of DDQ, electron injection in ITO/DDQ/Al devices is favored in the reverse bias direction. The electrons eleetroreduce DDQ molecules to its anionic state, which has a higher level of conductivity than the neutral one. Such reduced species in the device result in high-conducting state. A positive bias oxidizes the molecules back to their neutral state. The density of high conducting reduced molecules determines the level of conductivity of the device. Higher amplitude of reverse bias would increase the density of such electromolecular reduced molecules with consequent higher level of conductance in the devices.

Impedance measurements in the frequency range at zero dc bias demonstrate semicircular arcs in Cole–Cole plots (Z’ vs. Z"), which reveal that the devices can be modeled as parallel combination of a resistor and a capacitor (C⁻¹–R⁻¹) networks. In Fig. 1, we have presented Z’" vs. Z’ plots of a five-LB layer device at 0 V dc bias. Either of +3.5, −2.5, −3.0, and −3.5 V pulses (width = 6 min) was applied initially. Frequency scans were carried out 12 min after the dc pulse. The dc voltages are known to induce an Off- and three On-states, respectively. To start from the same initial condition, i.e. to ‘erase’ any previous information, we have applied high positive voltage (+3.5 V) prior to the application of any negative ‘write’ voltage. The figure clearly reveals the distinction of the diameter of the semicircle, which corresponds to the bulk resistance of the device, between three ‘On’ states and one ‘Off’ state. Owing to the high impedance of the device in the ‘Off’ state (0 V after +3.5 V), full semicircle was not observed in the Z’"–Z’ plot. The three On-states have been termed as On1, On2 and On3-states or ‘01’, ‘10’, and ‘11’, respectively. The Off-state has been represented as ‘00’. Since the measurements were carried out without any dc bias and 12 min after a ‘write’ voltage pulse, the different conducting-states observed here implies an associated memory phenomenon.

To separate out the resistive and capacitive component of the device, we have calculated frequency response of R⁻¹ and C⁻¹ following a C⁻¹–R⁻¹ network. Fig. 2 shows a variation of R⁻¹ of the device as a function of frequency under null bias condition. The responses were taken 12 min after a voltage pulse of +3.5, −2.5, −3.0, and −3.5 V. The figure shows that with increase in reverse bias amplitude, the device turns to more and
more high conducting state as evidenced by gradual decrease in its bulk resistance. The impedance of the Off-state (0 V after +3.5 V pulse) has remained the highest. The capacitive properties of the devices in its Off- and three On-states have been shown in Figs. 3a,b. The frequency spectra of real and imaginary component of relative permittivity are shown in the figure. There is a large difference in the value of the dielectric constant ($\varepsilon'$) of the material and dielectric loss ($\varepsilon''$) between its Off-state and three On-states. Apart from the strong rise of $\varepsilon''$ at low frequencies, which is due to the onset of ionic dc conduction, the value of $\varepsilon''$ has been low showing absence of pinholes in the devices. At high frequencies, the peak in loss spectrum has corresponded with a decrease in dielectric constant suggesting a Debye-like thermally disordered system. The $\varepsilon'$ on the other hand

Fig. 2. Frequency response of resistance in parallel ($R_P$) at zero bias for the Off- and three On-states of the ITO/DDQ/Al device.

Fig. 3. Frequency response of real (a) and imaginary (b) part of dielectric function at zero dc bias for the four states of the ITO/DDQ/Al device.

Fig. 4. (a) Frequency response of resistance in parallel ($R_P$) at zero bias for the On3-state of an ITO/DDQ/Al device at different time after −3.5 V 'write' voltage pulse. (b) Time response of $R_P$ at 12 Hz (0 V dc) for the four states. The states have been induced following the same protocol as described in Fig. 1. (c) Long time response of the Off- and the On3-state.
did not show a variation in the three On-states of the device. The results therefore show that apart from resistive properties, the dielectric parameters of the material changes during conductance switching and hence can be used as a parameter to probe the state of the device.

The retention of memory in devices was characterized for nonvolatile applications. To investigate the stability of high conducting states of the devices, their time response has been studied. For the Off-state, impedance characteristics were recorded with 0 V dc bias continuously after a +3.5 V pulse (width = 6 min). For each of the three On-states, following an ‘erase’ voltage pulse of +3.5 V, a suitable voltage pulse (amplitude = −2.5, −3.0, −3.5 V; width = 6 min) was applied to ‘write’ an On-state. Impedance characteristics were recorded with 0 V dc bias at different time after the ‘write’ voltage pulse. Fig. 4a shows how the frequency response of $R_P$ changes with time after the On3 (‘11’) state was induced by −3.5 V. The time response of the Off- and three On-states has been summed up in Fig. 4b. All the four states showed clear separation from each other for more than 2 h. Extended stability test was carried out for the Off- and three On-states showing memory retention of more than 13 h. Fig. 4c shows such plots for $R_P$ at 12 Hz for the two states.

We have further carried out ‘write-read-erase-read’ sequence for RAM applications. While ‘erase’ meant the Off-state, either of the three On-states have been chosen to ‘write’ a state. The state previously written has been erased prior to writing any of the three On-states. Fig. 5 shows device resistance at 0 V dc bias calculated at 12 Hz under the sequence. The voltage sequence applied is also shown in the figure. We repeated ‘write–read–erase–read’ sequence for the three On-states eight times for an endurance test for memory operation and found that all the four levels were distinguishable during the tested cycles.

4. Conclusions
In conclusion, we have shown that multilevel conducting states can be created in sandwiched structure devices based on LB films of an organic semiconductor, DDQ. Multilevel conductivity, which has arisen due to different density of reduced DDQ molecules in the bulk of neutral molecules, has been observed in Cole–Cole plots. During conductance switching, devices’ resistive and capacitive properties have been found to change. The bulk resistances of four conducting-states have been found to be distinctly different over a period of time. Moreover, the Off- and three-On states have been written and read randomly for memory applications.

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References