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Resistive Switching and Nonvolatile Memory in TiO_2/CuPc Nanocomposite Devices

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An organic–inorganic nanocomposite has been prepared as a hybrid memory element, and a bistable data storage device has been fabricated. The composite device, consisting of a spin casted thin film of sol–gel derived titanium dioxide (TiO_2) nanoparticles followed by a vacuum evaporated thin film of copper phthalocyanine (CuPc), exhibits conductance switching and nonvolatile memory phenomenon. While the single layer device with TiO_2 nanoparticles showed unipolar switching characteristics, the composite device exhibited bipolar switching with highly improved performance. The erase/reset voltage for the single layer TiO_2 device is 4.5 V, which reduces to $|3|$ V for the composite device. The on/off current ratio of the composite device measured to be $> 10^4$, which is orders of magnitude higher in comparison to that in the single layer devices. The charge transport mechanism of the devices revealed that trap-related space charge limited conduction mechanism might be responsible for the composite device while it indicates possible formation of filamentary path in the single layer TiO_2 based devices leading to ohmic-like conduction. The ability of the composite device to write, erase, read, and refresh the electrical states fulfills the functionality of a dynamic random access memory having potential for next generation low cost memory applications.

Key words: Memory, bistability, nanocomposite, phthalocyanine, random access memory

INTRODUCTION

Present day semiconductor technology has witnessed remarkable development during the last two decades and has revolutionized electronics equipment. In spite of this, there is a long way to go to meet the challenges for low-cost, portable and miniaturized optoelectronic devices. Organic–inorganic hybrid nanocomposite materials have received recently growing research attention,[1–10] not only because these compounds offer designing of new materials for academic research, but their unique and improved mechanical, electrical and optical properties have encouraged researchers to develop smart functional materials for innovative industrial applications.[4–10] The reason for synthesizing organic–inorganic composite materials is that these hybrid materials exhibit properties of individual contributions of both phases, as well as some unusual characteristics that might result due to the predominant role of the organic–inorganic interfaces facilitating charge transfer from one component to other. The integration of dissimilar and useful characteristics of organic and inorganic components in a single molecular-scale composite is an obvious advantage of inorganic–organic hybrids and yet is a great challenge for materials design and processing.

The advantages offered by organic molecules, such as lightweight, cost-effective, easy fabrication, flexibility, scalability and large area production may open up possibilities for fabricating a large variety of optoelectronic devices at low cost, especially when combined with inorganic nanostructures. Charge

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transport through the inorganic–organic composite material has been studied as an attempt to design different optoelectronic devices, which includes photovoltaic cells,[4,5] light emitting diodes,[6] data storage and memory elements[7,8] and field effect transistors.[9,10] Additionally, the hybrid materials have been investigated by many researchers for biomimetic applications, such as dental fillings, scratch-resistant coatings and fire retardants.[11]

Organic–inorganic composite memory devices, where semiconducting nanoparticles have been incorporated in the organic matrix have been studied extensively in the recent past.[12–14] Based on the wide varieties of metallic/semiconducting nanoparticles, their synthetic tailor-ability with different particle sizes and concentrations, many composite devices can be fabricated with the knowledge of possible modulation factors controlling device performance. Titanium dioxide (TiO_2) nanoparticles modified with organic dyes facilitate electron transfer at the interfaces between the organic molecule and the nanoparticles. For this reason, the composite of TiO_2 nanoparticles and CuPc thin film have been studied earlier for photocatalytic application,[15,16] although not explored as memory elements. Furthermore, TiO_2 is one of the transition metal oxides that exhibit both unipolar and bipolar switching characteristics. TiO_2 nanoparticles embedded in polymer matrix exhibited unipolar switching.[17] On the other hand, changing of contact electrode or the increase of compliance currents was found to toggle from unipolar switching to bipolar switching in TiO_2 based memory device.[18,19]

In memory devices, the same voltage bias can produce two different conducting states, depending on the previous bias history of the device. The high resistance state is called the off-state, and the low resistance state is known as the on-state The high conducting on-state is retained in low bias, even without bias in nonvolatile memory, whereas, it is completely destroyed in volatile devices. Recently, there has been tremendous progress in both volatile (dynamic random access memory) and nonvolatile (flash) memory and switching devices.[20,21] As an alternative to flash memories, phase change memory (PCM) and resistive random access memory (RRAM) have been proposed. However, PCM lacks high switching speed and the material is observed to degrade due to heating effect. RRAM, on the other hand, offers the advantage of scalability, excellent device performance and high switching speed.[22] However, in spite of its promising performance, in-depth knowledge of the switching mechanism of RRAM is still lacking.

In this article, we report the synthesis of TiO_2-CuPc nanocomposite and its potential applications as memory and data storage element. A unipolar electrical switching has been observed in TiO_2 only device, whereas bipolar switching has been observed in TiO_2-CuPc composite based devices. Apart from the reduction in erasing voltage (by 1.5 V), the TiO_2-CuPc nanocomposite device exhibited on/off current ratio, which is orders of magnitude higher than that in single layer TiO_2 only devices. Both the devices were investigated for charge transport and switching mechanism and the conclusions were supported by earlier results. The composite device, in addition to bipolar switching behavior, showed improved retention ability and remarkable reproducibility. The TiO_2-CuPc composite device exhibited write-read-erase-read current cycles with high current difference between two successive read states and excellent reproducibility showing the potential for future miniaturized and cost effective plastic electronics and memory applications.

EXPERIMENTAL METHODS

Titanium dioxide (TiO_2) nanoparticles were synthesized via sol–gel method. For this, a solution consisting of 5 mL isopropanol and 5 mL titanium isopropoxide was prepared, into which 200 mL of de-ionized (DI) water was added gradually. The pH of the solution was kept fixed at pH = 5 by adding nitric acid. The mixture was stirred vigorously at room temperature (37°C) and kept under continuous stirring for 2 h until the completion of hydrolysis process. A transparent colloidal solution was obtained, which was left aging for 24 h. The solution was then filtered and dried at 100°C for 2 h to evaporate water and organic residue. Finally, sintering processes were carried out at 450°C for 4 h. By grounding the agglomeration, final product was obtained as fine powder. To fabricate devices, the powder sample was dissolved in ethanol (5 mg/mL) and then spin coated over cleaned ITO coated glass substrate at 1000 rpm. The deposited film was dried at 100°C in a vacuum chamber (10^{-3} torr). Thickness of the TiO_2 thin film was measured to be 100–120 nm. For the composite device, vacuum evaporated thin film (40 nm) of copper phthalocyanine (CuPc) was deposited over the TiO_2 film under high vacuum (10^{-6} torr). Finally, aluminium (Al) was thermally evaporated (50 nm) on top of the CuPc film (composite device) or over the TiO_2 film (single layer device) as the top electrode at a base pressure of 10^{-6} torr to complete the device fabrication. The current–voltage (I–V) characteristics of the devices were measured by HP4145B semiconductor parameter analyzer under ambient condition. X-ray diffraction characteristics of the synthesized powder sample was performed with an X'pert Pro (Pananalytical) x-ray diffractometer (with Cu-K_α radiation).

RESULTS AND DISCUSSION

The crystalline nature of prepared TiO_2 nanoparticles was confirmed by measuring the x-ray diffraction (XRD) spectra of the powder samples, the results of which are shown in Fig. 1. The diffraction peaks observed at 2θ values 25.3°, 38.3°, 48° and 54°

have been indexed to the crystal planes of (101), (004), (200), and (211) respectively and are in good agreement with literature values.[23] The XRD results also confirms that anatase phase of TiO_2 was formed.[23] The size of TiO_2 nanoparticles as measured from the scanning electron microscopy (SEM) images (not shown) were 15–25 nm. For thin film based electronic devices, it is desirable for nanoparticles to have smaller grain size. The larger the grain size, the higher the porosity in thin films, which consequently leads to greater leakage current or even electrical short in fabricated devices, resulting in inferior device performances.

The schematic of the device is presented in Fig. 2a. While the active memory element is TiO_2 nanoparticles-CuPc composite in the case of hybrid device, it is only TiO_2 nanoparticles in the case of a single layer device. The current–voltage (*I*–*V*) characteristics of TiO_2-only device is shown in Fig. 2b. For the single layer (TiO_2-only) device, switching to high-conducting (Set) state occurs at $\sim$ 1.5 V and the device remains in the high state even under reverse bias condition. The device again switched to a low-conducting off-state (Reset) at much higher positive bias voltage $\sim$ 4.5 V, leading to unipolar resistive switching characteristics. This shows that for this unipolar switching device, both Set and Reset occurs at same polarity (positive) of applied bias. The devices also exhibited reproducible switching behavior as depicted by three consecutive loops in Fig. 2b.

On the contrary, the TiO_2-CuPc nanocomposite device exhibited bipolar switching, wherein Set-state occurs in the positive bias ($\sim$ 3 V) and Reset-state occurs almost at the same bias in opposite polarity ($\sim -$ 3 V). The typical *I*–*V* characteristics of TiO_2-CuPc nanocomposite device, which summarizes these results is shown in Fig. 3a. The nonlinear, asymmetric *I*–*V* characteristics of the devices indicate the possible formation of Schottky barrier at the CuPc/Al interface, which might help to induce the switching characteristics. In fact, it was shown earlier that the presence of a Schottky barrier at the metal/phthalocyanine interface is necessary in TiO_2 thin film for resistive switching and the control of switching properties was possible by modulating the barrier height.[24] Also, the presence of an interfacial oxide (Al_2O_3) layer might be helpful in obtaining switching characteristics.[25] The devices also exhibited reproducible characteristics as shown by multiple loops in the figure. The on/off current ratio, i.e., the ratio of the current in on-state and that in off state, for the composite device was measured to be $\sim 10^4$ or more, which is one order of magnitude higher than that of the TiO_2-only device. The result is depicted in Fig. 3b. It is worth mentioning that the increase in on/off ratio in the composite device is not due to the presence of CuPc/Al Schottky barrier nor due to the interfacial oxide layer. This is because the formation of an Al_2O_3 layer during top Al electrode deposition in both ITO/TiO_2/Al and ITO/TiO_2-CuPc/Al devices are the same and hence should produce a similar effect. Also, the effect of Schottky barrier should be the same in ITO/CuPc/Al (not shown here) and ITO/TiO_2-CuPc/Al devices.

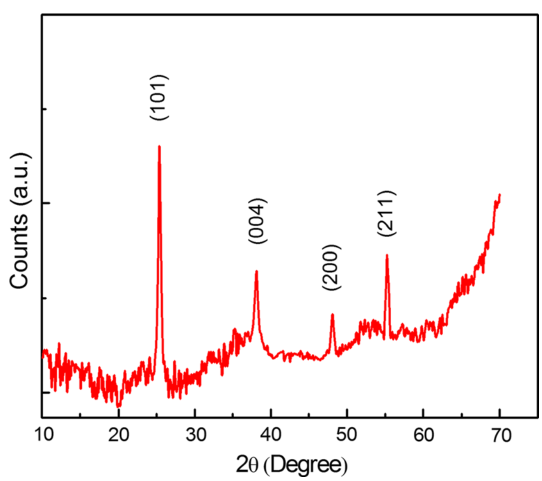

Fig. 1. (Colour online) XRD spectra of synthesized TiO_2 nanoparticles.

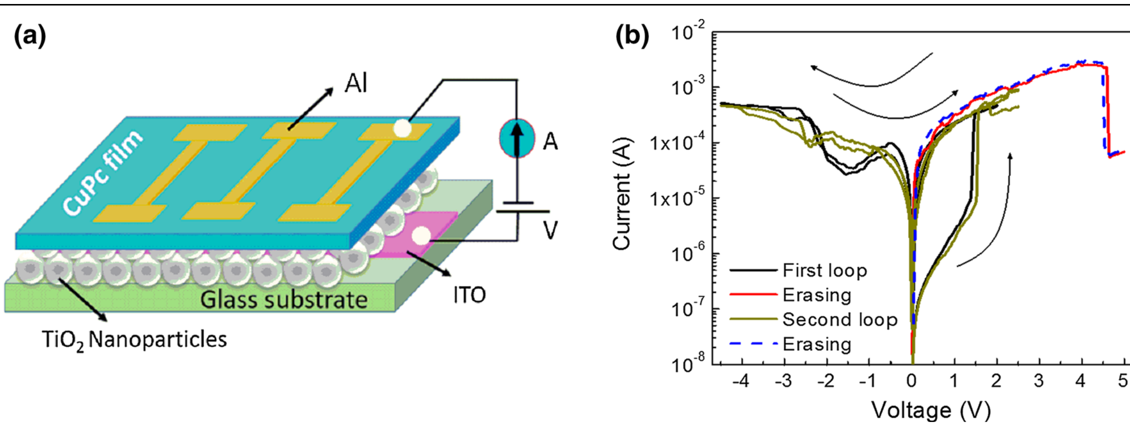

Fig. 2. (Colour online) **a** Schematic of the nonvolatile memory device. **b** Typical current–voltage (*I*–*V*) characteristics of ITO/TiO_2/Al device in semi log scale under three consecutive loops. Arrows indicate the direction of applied voltage bias.

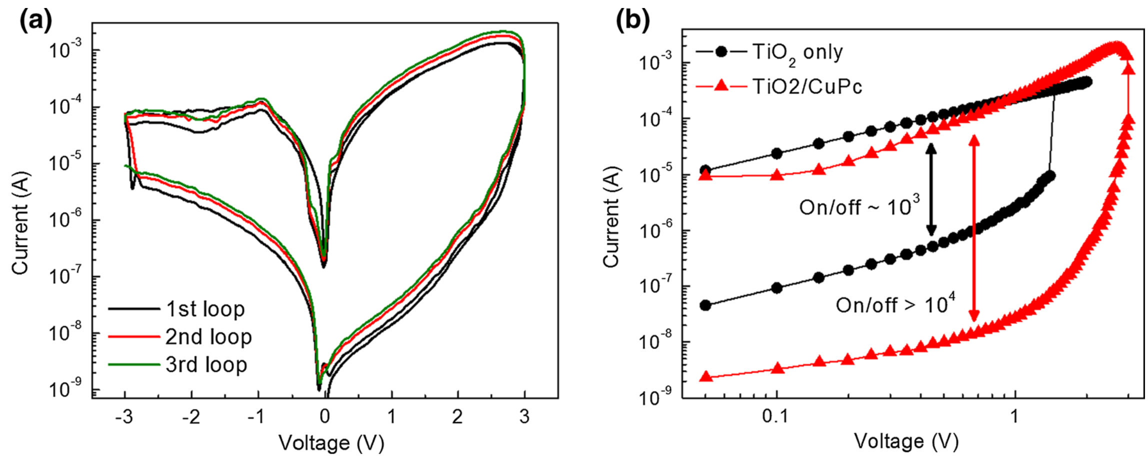

Fig. 3. (Colour online) Electrical performance of the composite device. **a** *I–V* characteristics of ITO/TiO_2-CuPc/Al composite device in three consecutive loops. **b** Log–log plot of the *I–V* characteristics for ITO/TiO_2/Al device and ITO/TiO_2-CuPc/Al composite device to measure the on/off current ratio.

The on/off ratio in the ITO/CuPc/Al device is much less compared to ITO/TiO_2-CuPc/Al device. In TiO_2-only single layer device, the off-state current is much higher (compared to the composite device), possibly due to the presence of oxygen vacancies,[26] yielding low on/off current ratio. On the other hand, the presence of the TiO_2/CuPc interface in the composite device produces higher resistance in the off-state and hence lower off-state current resulting in a much higher on/off ratio. During positive biasing of the device, prior to switching (< 1.5 V), the current was very low, presumably due to the presence of Schottky barrier. During the negative biasing, the positively charged mobile oxygen vacancies in TiO_2 film are possibly attracted towards the CuPc/Al interface, causing a partial decrease in the Schottky barrier height and making ease for charge conduction. In digital circuits, small current/voltage difference between high and low states may lead to confusion and error might occur at the output. Hence, for digital applications of electronic devices, it is desirable to have high on/off current or voltage ratio in order to avoid any low misreading rate.

With advancement of present day semiconductor technology, great improvements have been achieved in resistive RAM (RRAM) devices. In spite of this, the exact switching mechanisms of RRAM are not fully understood. To explain the unipolar and bipolar switching characteristics, a number of controlling parameters have been identified, such as device geometry, active materials used, the metallic electrodes deposited and accordingly different mechanisms have been proposed. These include anion migration,[27] nano-filament based conducting path formation,[28] amorphous to crystalline phase transition,[29] modification of Schottky barriers via bulk transport of oxygen,[30] and Joule heating causing lateral transport of conducting laments.[31]

To get insight about the conduction mechanism in present devices, we have plotted log (*I*) versus log (*V*) characteristics for both TiO_2-only and TiO_2-CuPc composite device (Fig. 4) and best linear fit has been obtained for on- and off-states. For TiO_2-only device with unipolar switching, the off- and on-state measured a slope of 1.215 and 0.995, respectively, indicating a good linear fit for both states. The results are presented in Fig. 4a. However, the slope of 0.995 in the low resistance on-state, which is nearly equal to 1, indicated the possible formation of conducting channels and dominance of ohmic conduction during switching from high resistance off-state to low resistance on-state.[28] A larger slope of 1.215 observed in the off-state indicated a more complicated conduction mechanism. On the contrary, in a composite device, a different conduction mechanism comes into play. For the composite device, deviation in slopes in different regions of high resistance off-state was observed (Fig. 4b). In the low voltage region, the slope was much less than 1 (0.65), while in the high bias region, it was much larger (3.01), suggesting a possible transition to trap-related space charge limited conduction (SCLC).[12,13] The conduction mechanism of this device can be explained by the injected charge carriers and are dependent on metal/TiO_2 interfaces traps that are exponentially distributed in energy. Hence, we conclude that the local establishment of trap sites at the set process and space charge limited conduction during high-conducting state might be the reason for the bipolar switching in the composite device.[32] The resistance of the TiO_2-CuPc composite device was significantly higher than the single layer TiO_2 device due to the presence of TiO_2/CuPc interface leading to larger turn-on voltages for the composite device. We, therefore, infer that among the two popular mechanisms for the resistive switching suggested in the literature, namely, the formation and breaking of filamentary path due to the oxygen vacancy and the effect due to barrier height at the metal/organic interface, one particular model is not sufficient to

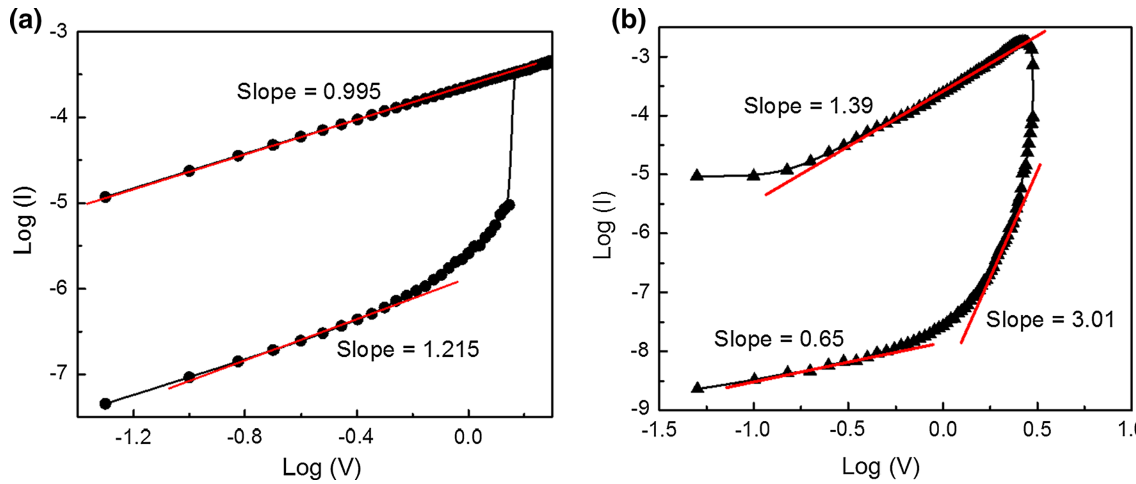

Fig. 4. (Colour online) Linear fitting of the *I–V* characteristics of **a** ITO/TiO_2/Al device and **b** ITO/TiO_2-CuPc/Al composite device.

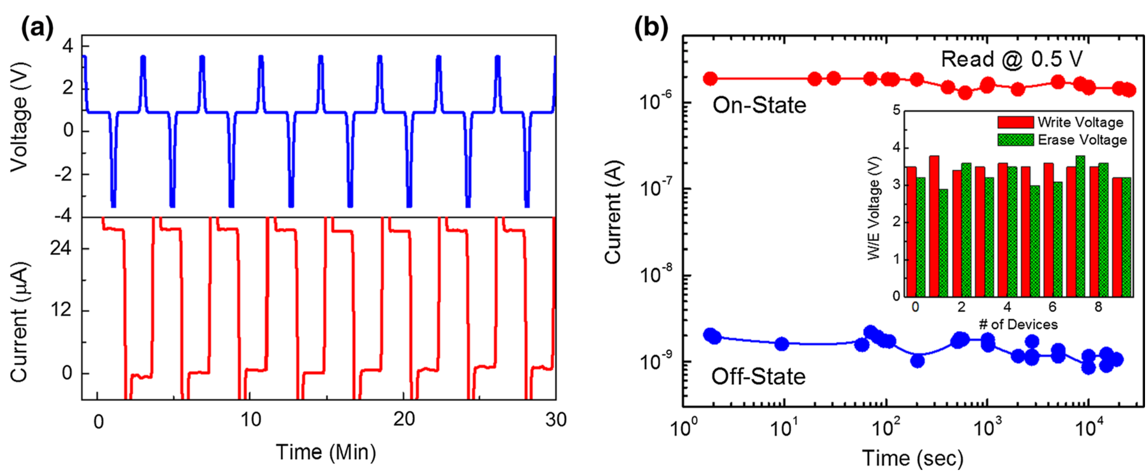

Fig. 5. (Colour online) **a** Voltage sequence and current response of the ITO/TiO_2-CuPc/Al composite device in write–read–erase–read switching cycle, where writing/erasing is done at ± 3 V and the corresponding states are probed/read at 0.7 V. **b** Endurance test of the composite device measured with time. The on- and off-states of the device are induced at ± 3 V and respective current values are read at 0.5 V (inset). Reproducibility test of the composite device by measuring write/erase voltage for 10 separate devices.

explain the experimental observations and both effect might be involved in the resistive switching process.

The composite devices were also investigated for RAM application. Figure 5a depicts a representative result of reproducibility measurement in terms of write-read-erase read (WRER) cycle performed on TiO_2-CuPc nanocomposite devices for hours. In each of the WRER cycles, writing (set) was done by applying a positive voltage pulse (3 V) and the erasing (reset) was realized by applying a negative voltage pulse (– 3 V). To probe the on- and off-states of the device a small read voltage (0.7 V) pulse was employed and the currents were measured in respective states. It is clear from the figure that the device switched to on- or off-states reproducibly under suitable voltage pulse and the probe current in the on (set) state is much higher than that in the off (reset) state ensuring that the device can be probed for RAM application for hours. The result also ensured that the two states of the devices can be flipped-flopped and probed for hours without any performance degradation.

The hybrid device comprising TiO_2-CuPc composite film was tested for retention characteristics. The device was set/reset at ± 3 V and the corresponding states were probed at read voltage of 0.5 V. Figure 5b shows the current variation of the device in the on- and off-state measured at room temperature under the read voltage (0.5 V). The result indicates that the two states are clearly separated in current magnitude by more than 10^3 even after a time span of 10^4 s. The stress test also indicates that there is not any significant current degradation in the on-state within the measured time, ensuring the nonvolatile memory and nondestructive readout property of the fabricated devices. Finally, to check the reproducibility in switching voltages of the composite device, a number of devices have been tested and switching voltages (both on and off) were recorded under identical conditions. The variation of write and erase voltages from device to device were seen to be negligible as indicated in the inset of Fig. 5b, thus supporting the reproducibility results obtained in Fig. 3a.

CONCLUSION

In conclusion, an organic–inorganic hybrid nanocomposite device comprising TiO_2 nanoparticles and thin film of copper phthalocyanine has been fabricated. The device exhibited electrical bistability and nonvolatile memory phenomenon with bipolar switching characteristics. In comparison to a TiO_2 nanoparticle-based single layer device, which showed unipolar switching characteristics, the composite device exhibited highly improved performances with reduced switching voltages, higher on/off ratio and greater retention characteristics. The fitting of the *I–V* curves revealed that space charge limited conduction mechanism might be responsible for the charge transport of composite device, while possible formation of filamentary path in the single layer TiO_2 devices leads to the ohmic-like conduction. The potential of the composite device for data storage, RAM and ROM applications fulfills the functionality for future low cost plastic electronic device applications.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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