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# Flexible resistive switching bistable memory devices using ZnO nanoparticles embedded in polyvinyl alcohol (PVA) matrix and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)<sup>†</sup>

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The resistive switching memory effects in metal-insulator-metal devices with aluminium (Al) as top electrode (TE) and bottom electrode (BE). A solution processed active layer consisting of zinc oxide (ZnO) nanoparticles embedded in an insulating polyvinyl alcohol (PVA) matrix and polymer poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) has been studied by using flexible polyethylene terephthalate (PET) substrates. The current–voltage (*I*–*V*) measurements of hybrid Al/ZnO–PVA/PEDOT:PSS/Al/flexible PET substrate device exhibited a non-volatile bistable resistive switching behaviour, which is attributed to the trapping, storage and transport of charges in the electronic states of the ZnO nanoparticles. The performance of hybrid device is significantly enhanced over control Al/PEDOT:PSS/Al and Al/ZnO–PVA/Al devices due the presence of PEDOT:PSS polymer. This PEDOT:PSS improves the performance of oxygen ions (holes) migration toward BE and protect back oxygen vacancies (electrons) migrate toward BE from ZnO–PVA composites which may reduces the leakage current, as a result, increased the ‘ON state/OFF state’ current ratio of  $7.9 \times 10^3$  times. The fabricated hybrid device showed high ON/OFF switching current ratio larger than five orders of magnitude with low operating voltages. It is observed that, the existence of two conducting states, namely, low conductivity state (OFF state) and high conductivity state (ON state), exhibiting bistable behaviour. The state of the device was maintained even after removal of the applied bias, indicating the non-volatile memory. The observed current–time response showed good memory retention behaviour of the fabricated devices. The excellent stability and retention performances of hybrid device verify the reliability of this device and demonstrate their potential for application in non-volatile bistable memory device. The carrier transport mechanism of the bistable behaviour for the fabricated non-volatile organic bistable devices structures is described on the basis of the *I*–*V* experimental results by analyzing the effect of space charge and electronic structure. Interestingly, the device performance was not degraded and remains identical even after bending the device from 60–120° angles, which indicates high potential for flexible non-volatile bistable memory device applications. This demonstration provides a class of memory devices with the potential for future flexible electronics applications.

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## 1. Introduction

A mixture of semiconductor nanoparticles and polymers has been particularly interesting due to their potential applications in next-generation electronic and optoelectronic devices.<sup>1–4</sup> Nanocomposites containing semiconductor nanoparticles and polymer have promising potential applications in non-volatile memory

devices due to their high mechanical flexibility, low cost, and simple fabrication.<sup>5–8</sup> In memory devices based on nanocomposites, the electrical bistability is primarily determined by the semiconductor nanoparticles.<sup>9–11</sup> The prospect of applications of non-volatile memory devices utilizing nanocomposites has given rise to extensive research and efforts to develop semiconductor nanoparticles, serving as charging and discharging islands, embedded in a polymer matrix.<sup>12–18</sup> In the past decade, there are many kinds of advanced non-volatile memory devices have been generated.<sup>19,20</sup> Among the several types of non-volatile memory devices, the hybrid non-volatile bistable devices have been particularly attractive due to their easier fabrication, less expensive and high flexibility without additional sources and drains.<sup>21–23</sup> With the

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with  $\text{CuK}\alpha$  ( $\lambda = 0.15418$  nm) radiation operated at 45 kV and 40 mA. The surface morphology of PEDOT:PSS films and ZnO-PVA nanocomposite/PEDOT:PSS were carried out by atomic force microscopy (AFM) (Bruker, MultiMode-8) in tapping mode. The scanning electron micrographs (SEM) of the samples were taken using a Nova Nano (FEI, USA) Scanning Electron Microscope.

### 3. Results and discussions

#### 3.1 Morphological characterization

The surface topography of PEDOT:PSS films were carried out (scan area  $1\text{ mm} \times 1\text{ mm}$ ) before and after spin coating of ZnO-PVA nanocomposite by atomic force microscopy (AFM) in tapping mode using phosphorous doped silicon cantilever. Fig. 1(a) and (b) show the plane view AFM micrographs of pristine PEDOT:PSS films and ZnO-PVA nanocomposite/PEDOT:PSS heterostructure sample formed on flexible Al coated PET substrates. The surface roughness of the nanocomposite films was determined from AFM topography in  $1\text{ mm} \times 1\text{ mm}$  area. The RMS surface roughness for pristine PEDOT:PSS films and ZnO-PVA/PEDOT:PSS films were estimated to be 33 nm and 85.3 nm, respectively. The higher surface roughness for ZnO-PVA/PEDOT:PSS film is attributed to the presence of ZnO-PVA nanocomposite. The micrograph

clearly indicates the formation of ZnO nanoparticles (NPs) uniformly distributed in large area. The particle size distribution is plotted at the inset of Fig. 1(b). From the histogram, the diameter of the nanoparticles variation can be estimated as 15–60 nm and the average diameter of the nanoparticles is found to be 35 nm. The average nanoparticle density has been estimated from  $1\text{ }\mu\text{m} \times 1\text{ }\mu\text{m}$  surface area and found to be  $\sim 3 \times 10^{13}$  NPs per  $\text{m}^2$ . Fig. 1(c) represents the typical SEM micrograph of ZnO nanosheets embedded in PVA matrix. It has been observed that ZnO NPs forms nanosheets-like structure inside the PVA matrix. The magnified SEM image of the ZnO nanosheets embedded in PVA matrix as depicted in the inset of Fig. 1(c). It is clearly seen that the SEM micrograph revealed the formation of ZnO nanosheets of thickness 20–40 nm with several micron lengths. Fig. 1(d) shows a cross-sectional view of the grown switching memory structure on flexible Al coated PET substrates. The FESEM micrograph clearly indicates ZnO-PVA nanocomposite, PEDOT:PSS film and Al electrode with sharp interfaces. The thicknesses of the ZnO-PVA nanocomposite and PEDOT:PSS films are estimated to be 100 nm and 180 nm, respectively. Fig. 2(a) represents the typical energy dispersive X-ray (EDX) spectrum of ZnO-PVA nanocomposites. The EDX spectrum confirms the presence of Zn and O elements in ZnO-PVA nanocomposites. The elemental analysis reveals the formation



Fig. 1 Plane view of AFM surface topography of (a) pristine PEDOT:PSS films. (b) ZnO-PVA nanocomposite/PEDOT:PSS heterostructure deposited on flexible Al coated PET substrates. The particle size distribution is plotted at the inset. (c) Plane view SEM image of ZnO-PVA nanocomposite deposited on the surface of PEDOT:PSS films. (d) The cross sectional SEM image of ZnO-PVA nanocomposite/PEDOT:PSS/Al heterostructure sample.



of stoichiometrically pure ZnO in PVA matrix. The additional elements Zn, O and C arise from carbon coated copper grids and PVA polymer.

### 3.2 Optical characterization

Fig. 2(b) shows the UV-visible absorption spectra of ZnO–PVA nanocomposite films with and without attachment of PEDOT:PSS in the range of 300–800 nm. The optical band gap ( $E_g$ ) of ZnO–PVA nanocomposite has been calculated using Tauc's formula.<sup>36</sup>

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (1)$$

where  $\alpha$  is the absorption coefficient,  $h\nu$  is the incident photon energy and  $A$  is a constant. Inset of Fig. 2(b) represents  $(\alpha h\nu)^2$  vs.  $h\nu$  plot for both samples. The optical band gap of ZnO–PVA nanocomposite and absorption edge of ZnO–PVA nanocomposite/PEDOT:PSS have been calculated by extrapolation at the linear region of  $(\alpha h\nu)^2$  vs.  $h\nu$  plot to the energy axis.

The pristine ZnO–PVA nanocomposite shows strong absorption in the UV region of wavelength threshold at 387 nm, corresponding to the energy band gap of 3.2 eV. Interestingly, the absorption edge has been slightly shifted to higher wavelength for ZnO–PVA nanocomposite deposited on PEDOT:PSS films ( $\sim 3.15$  eV), which is attributed to the strengthened photo-absorption in visible region. Moreover, the additional peak at 503 nm has been observed, which is attributed to the absorption edge of ZnO–PVA nanocomposite/PEDOT:PSS.<sup>37</sup> Fig. 2(c) shows the XRD spectra of the PEDOT:PSS film, ZnO–PVA nanocomposite films and ZnO–PVA nanocomposite/PEDOT:PSS heterostructure films deposited on Al coated flexible PET substrates. The XRD result clearly indicates that both ZnO–PVA nanocomposites and ZnO–PVA nanocomposite/PEDOT:PSS are highly crystalline. The strongest diffraction peaks observed at  $2\theta = 31.72^\circ$ ,  $34.40^\circ$ ,  $36.21^\circ$ ,  $47.49^\circ$ ,  $56.52^\circ$ ,  $62.80^\circ$ ,  $67.83^\circ$ , and  $68.97^\circ$  corresponding to the lattice planes (100), (002), (101), (102), (110), (103), (112), and (201) respectively, are attributed to the hexagonal wurtzite structure of ZnO.



Fig. 2 (a) Energy dispersive X-ray spectrum (EDX) of ZnO nanoparticles embedded in PVA matrix. (b) UV-visible absorption spectra of ZnO–PVA nanocomposite films and ZnO–PVA nanocomposite/PEDOT:PSS heterostructure films.  $(\alpha h\nu)^2$  vs.  $h\nu$  plot for ZnO–PVA nanocomposite and ZnO–PVA/PEDOT:PSS heterostructure (inset). (c) X-ray diffraction spectra of PEDOT:PSS, ZnO–PVA nanocomposite and ZnO–PVA nanocomposite/PEDOT:PSS heterostructure grown on PET substrates.



The data is in well agreement with the JCPDS card number 36-1451.<sup>38</sup> Interestingly, ZnO-PVA nanocomposites/PEDOT:PSS exhibits the same diffraction patterns with ZnO-PVA nanocomposites, and the additional diffraction peaks at 26° and 52.9° have been observed due to the diffraction from PET substrate.<sup>39</sup> However, no diffraction peak can be observed for the pure PEDOT:PSS film except two diffraction peaks at 26° and 52.9° due to the diffraction from PET substrate,<sup>39</sup> demonstrating its poor crystalline structure.

### 3.3 Electrical characterization

To study the resistive switching characteristics of ZnO-PVA nanocomposites [concentration ratio (ZnO : PVA) of 10 : 1]/conducting polymer heterostructure, the following three samples have been fabricated. The samples are (i) Al/PEDOT:PSS/Al/flexible PET substrate (denoted as S1), (ii) Al/ZnO-PVA/Al/flexible PET substrate (denoted as S2) and (iii) Al/ZnO-PVA/PEDOT:PSS/Al/flexible PET substrate (denoted as S3). In electrical measurements, Al top electrodes (TE) were connected to negative ('-') and Al bottom electrodes (BE) were connected to positive ('+') terminal to the source meter. Fig. 3(a) shows the schematic diagram of the S3 memory device and molecular structure of PEDOT:PSS film. Fig. 3(b) shows the current-voltage (*I*-*V*) switching characteristics of the S3 device.

The external electrical stimulation is supplied to the device in the form of an applied voltage in a sequence of 0 V → +4 V → 0 V → -4 V → 0 V, with a current compliance of  $5.1 \times 10^{-2}$  A to prevent the permanent dielectric breakdown of the device. The high-conductivity state (ON-state) was achieved by applying a forward voltage sweep on the device. With increasing positive voltage, the current starts increasing and jumps suddenly at +3.6 V, indicating the switching of the device from low conductivity state (OFF-state) to high-conductivity state (ON-state). This switching process from OFF state to ON state is referred to as the "writing" process, and which is known as the SET process. The ON state will remain in that state and will not return to the OFF state even after turning off the power supply (read process). The high conducting state (ON state) process is maintained from +4 V to -4 V, while reverse sweeping. Subsequently, the ON state switches to a low conducting state (OFF state) at a voltage of -3.6 V, as can be seen in the reverse bias voltage. This transition from ON state to OFF state is equivalent to the 'erasing' process in a digital memory cell,<sup>40</sup> which is also known as the RESET process. The low conductivity state (OFF-state) of the device can be read and reprogrammed to the high-conductivity state (ON-state) in the subsequent positive sweep, as a result, completing the "write → read → erase → read → rewrite" cycle for a non-volatile rewritable memory device.<sup>41</sup> It is observed that, the existence of two conducting

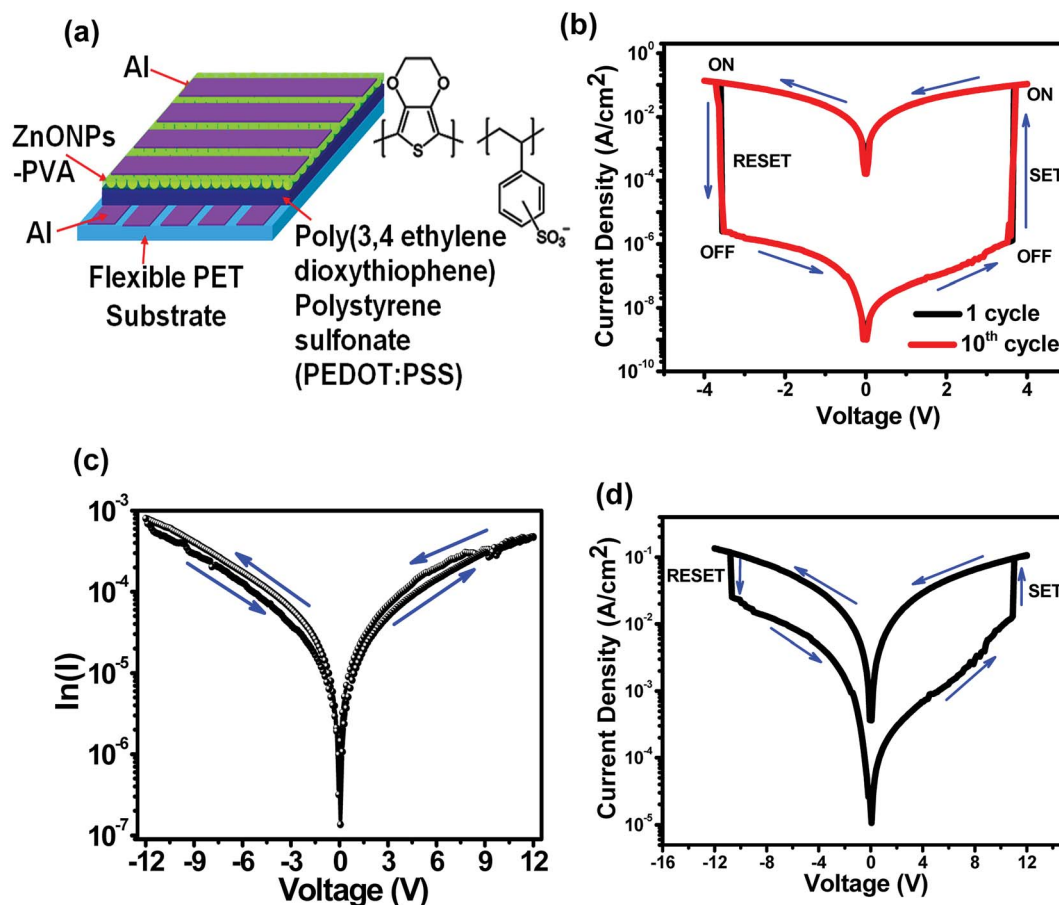


Fig. 3 (a) Schematic diagram of the S3 memory device and molecular structure of PEDOT:PSS films. Current-voltage (*I*-*V*) switching characteristics of the (b) S3 memory device, (c) S1 device and (d) S2 device.





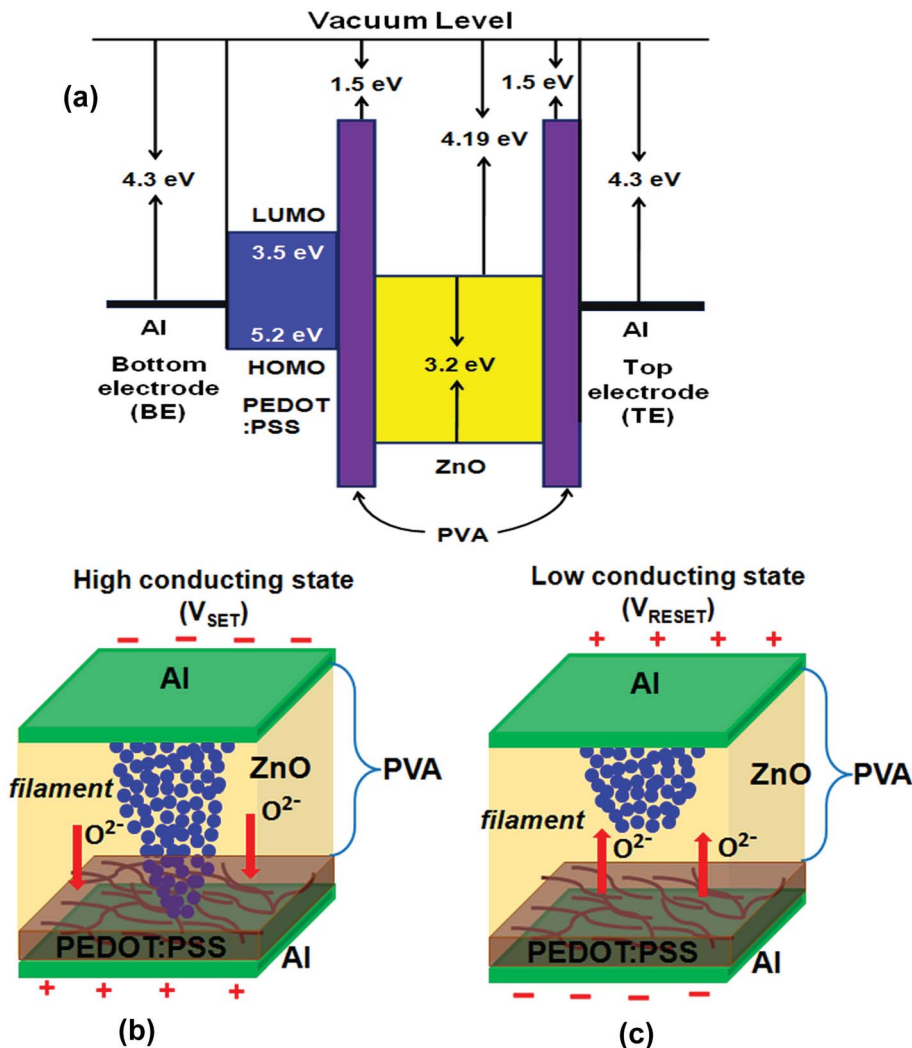


Fig. 5 Schematic diagrams of energy level corresponding to the operating mechanism for the S3 memory device. Schematic diagrams of the electronic structures corresponding to the operating mechanisms for S3 memory device with the (b) high conducting state (SET state) and the (c) low conducting state (RESET state).

state in terms of the cumulative distribution were examined. Fig. 4(b) shows the cumulative probability of switching resistance of the S3 device. The resistance values measured at a read voltage of 1 V is plotted as ON state and OFF state. The distribution of ON state is quite narrow for the device, while the distribution of OFF state is, relatively, broader. The average values of ON state and OFF state are found to be 9  $\Omega$  and 1.4 k $\Omega$ , respectively, with a high resistance ratio (ON state/OFF state) of more than  $3 \times 10^5$ . The presented S3 device provides an interesting candidate for high performance non-volatile flexible memory devices.

### 3.4 Conduction mechanism

To clarify the conduction mechanism of the S3 memory device, the  $I$ - $V$  characteristics were re-plotted in a log-log scale as shown in Fig. 4(c). From this plot, it is clearly seen that, the  $I$ - $V$  characteristics in OFF-state (low conductivity state) consist of three regions, namely, (a) ohmic region ( $I \propto V$ ) with a slope of  $\alpha_1 \sim 1$  at low voltages, (b) Child's square law region ( $I \propto V^2$ ) with

a slope of  $\alpha_2 \sim 2.03$  at higher voltages, and (c) steep increase in current region ( $I \propto V^m$ ) with a slope of  $\sim 20$ . Where  $V$  is the applied voltages between the two electrodes and  $m$  is a positive number. This kind of  $I$ - $V$  behavior is in good agreement with typical trap-controlled space charge limited conduction (SCLC) mechanism.<sup>44</sup> Whereas, the ON-state (high conductivity state) exhibits ohmic conduction behavior with a slope of  $\sim 1$ , which is attributed to the formation of conductive path between the top electrode (TE) and bottom electrode (BE) in the S3 device during the SET process.

Carrier transport in the resistive switching memory device based on ZnO-polymer composites had been explained mostly by SCLC<sup>45,46</sup> and Fowler-Nordheim (FN) tunneling.<sup>47</sup> Kim *et al.*<sup>45</sup> showed that the main conduction in Al/ZnO-PS composites/ITO followed SCLC by fitting the  $I$ - $V$  curves. However, the conduction mechanism in the cases of Al/ZnO-PMMA composites/ITO were unclear because it was just predicted as charge trapping without exact fitting of the log-log plot of the  $I$ - $V$  curves.<sup>11</sup> The conduction mechanism largely depends on the structure and



electrical properties of the polymer matrix. It is note-worthy that compared with the Al/ZnO–polymer/ITO device, our S3 device exhibits bipolar memory behavior. In addition, it has been previously reported that the heterojunctions and interface play important roles in the bipolar resistance switching memory.<sup>48,49</sup>

Based on the analysis above, it can be explained the conduction mechanism based on the formation and rupture of conduction filaments. In S3 device structure, the resistive switching is originated from the formation and rupture of the conduction filaments between two electrodes due to the migration of oxygen ions. The schematic diagrams of energy level corresponding to the operating mechanism for the S3 memory device as shown in Fig. 5(a). The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels for the PEDOT:PSS layer are 3.5 eV and 5.2 eV, respectively.<sup>50</sup> The reported values of work function for Al and ZnO have been utilized in the proposed model,<sup>51,52</sup> while the electron affinity of the PVA barrier is assumed to be  $\sim 1.5$  eV, similar to that of a non-conducting polymer. As shown in Fig. 5(b), when the positive voltage is applied to the device, some oxygen atoms are pulled out of the ZnO lattice, generating oxygen vacancies. These oxygen ions, act as p-type dopant, will move toward the PEDOT:PSS film and leave behind the tiny conducting filaments of oxygen vacancies in the ZnO–PVA composite layer. As a result, reducing the thickness of the depletion layer between p-type PEDOT:PSS and n-type ZnO. Subsequently, when the positive voltage reaches to SET voltage ( $V_{\text{SET}}$ ) of  $\sim +3.6$  V, those tiny conducting filaments gather speedily to form more conducting and stronger filaments leading to breakout the depletion layer of the ZnO/PEDOT:PSS interface and the conductive pathways connect from top electrode (TE) to bottom electrode (BE), which will convert to the ON state of the device, which is known as the SET process (read process). Then the charges can flow through the conductive filaments and sustain the device in an ON state (high conducting state). Conversely, as shown in Fig. 5(c), the oxygen ions in the PEDOT:PSS film might be pushed forward to ZnO composites under a negative voltage. When the conductive filaments path consisted of oxygen vacancies are neutralized by sufficient oxygen ions, conduct filaments rupture at the ZnO composites/PEDOT:PSS interface and device switches to the OFF state (low conducting state), which is also known as the RESET process (erase process). The PEDOT:PSS, acting as an oxygen ions supplier, can switch the device back to OFF state more efficiently and completely. In brief, the PEDOT:PSS in S3 device attributing to oxygen ions reservoir in SET process and acting as an oxygen ions supplier in RESET process. Additionally, PEDOT:PSS is a hole conducting polymer with high electrical conductivity up to  $200 \text{ S cm}^{-1}$  and often used in organic memory device.<sup>53</sup> The addition of a thin PEDOT:PSS layer with S2 device, improves the performance of oxygen ions (holes) transportation toward the bottom electrode (BE) and protect back oxygen vacancies (electrons) migrate toward the bottom electrode (BE) from ZnO–PVA composite which may reduces the leakage current. Consequently, increased the 'ON state/OFF state' current ratio of  $7.9 \times 10^3$  times. Hence, S3 device has superior resistive switching behavior compared to S2 device.

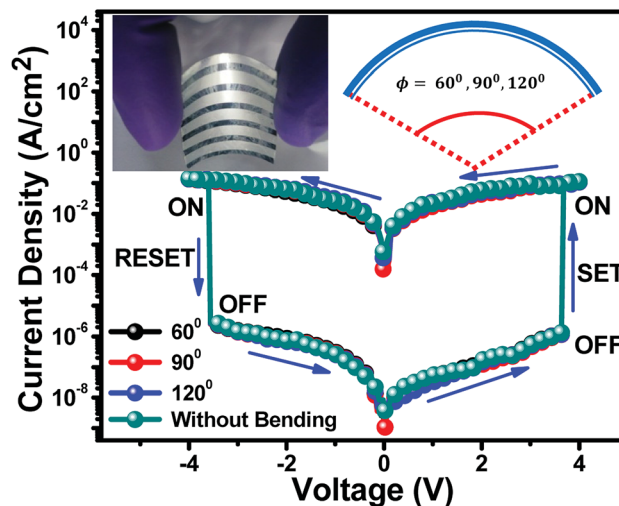


Fig. 6 Current–voltage ( $I$ – $V$ ) switching characteristic of the S3 memory device.  $I$ – $V$  switching characteristic were recorded at  $180^\circ$  (without bending),  $60^\circ$ ,  $90^\circ$  and  $120^\circ$  bending angles of the substrates. Photograph demonstrates the flexibility of a typical S3 memory device (inset).

### 3.5 Flexibility study

In this present study, it has been demonstrated that the potential use of S3 non-volatile bistable memory device in flexible electronic applications. Fig. 6 represents the  $I$ – $V$  switching characteristics of non-volatile bistable memory device without and with bending of angle  $60^\circ$ ,  $90^\circ$  and  $120^\circ$ . The photograph of organic bistable memory device with bending is presented at the inset of Fig. 6. Interestingly, the  $I$ – $V$  switching characteristics remained unchanged even after bending the device from  $60$ – $120^\circ$  angles, which is attractive for flexible electronic applications.

## 4. Conclusions

In conclusion, we have demonstrated the flexible non-volatile bistable resistive switching memory device using colloidal ZnO–PVA nanocomposites and PEDOT:PSS film deposited on Al coated flexible PET substrate. The surface roughness of the pristine PEDOT:PSS and ZnO–PVA/PEDOT:PSS was determined from AFM topography in  $1 \text{ mm} \times 1 \text{ mm}$  area. The RMS surface roughness for pristine PEDOT:PSS films and ZnO–PVA/PEDOT:PSS films were estimated to be 33 nm and 85.3 nm, respectively. The higher surface roughness for ZnO–PVA/PEDOT:PSS film which was due to the presence of ZnO–PVA nanocomposite. SEM micrograph clearly revealed the formation ZnO nanosheets of thickness 20–40 nm with several micron lengths. It was observed that, ZnO NPs forms nanosheets-like structure inside the PVA matrix. The EDX spectrum analysis confirms the presence of Zn and O elements in ZnO–PVA nanocomposites. The elemental analysis reveals the formation of stoichiometrically pure ZnO in PVA matrix. The additional elements Zn, O and C arise from carbon coated copper grids and PVA polymer.  $I$ – $V$  characteristic of the S3 device exhibited flexible non-volatile bistable resistive switching characteristics.









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