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To cite this article: Bo Chen et al 2018 Mater. Res. Express 5 066429

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Flexible one diode-one resistor composed of ZnO/poly (fluorene-alt-benzothiadiazole) (PFBT) heterojunction diode and TiO$_2$ resistive memory

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Keywords: resistive switching, finite element analysis, channel crack and interfacial delamination, flexible one diode-one resistor (1D1R)

Supplementary material for this article is available online

Abstract

One diode–one resistor (1D1R) memory is an effective structure to suppress sneak current and read interference of crossbar network. Organic–inorganic complex plays an important factor in the field of flexible microelectronic memory due to integrated flexibility and excellent electronic properties. Herein, we demonstrated a 1D1R based on the n–n heterojunction diode of ZnO/polymer and Al/TiO$_2$/Al resistor. The resistive switching performance of flexible 1D1R decreased with increase of bending times. Atomic force microscopy results show that the cracks on the ZnO film surface were related to the bending cycles. The scanning electron microscopy indicates crack growth path was along the grain boundaries. The finite element studies confirmed that channel crack of ZnO film and delamination between ZnO and polymethyl methacrylate interface are the main failure mode for the 1D1R under bending, which leads to a lower forward current in the low resistance state and weaken the ON/OFF ratio of 1D1R.

Introduction

Resistive random access memories, as one of the most promising next–generation non-volatile memory devices, are gaining much attraction due to their fast switching speed, simple crossbar architecture, high storage density and excellent stability [1]. Among all the switching matrix, the metal–insulator–metal configuration were widely studied because of easier fabrication process and lower process temperature in the past few years [2]. However, the sneak current will flow through neighbouring cells, leading to read disturbance when the crossbar array consists of a functional layer between two electrodes [3, 4]. To solve such issues, the one diode–one resistor (1D1R) cell consisting of one diode (1D) and one resistor (1 R) has been proposed because the diode can suppress sneak current and read interference by the rectifying characteristics.

Under read operation, the large ratio between forward and reverse current plays a key role on the performance of diode. There are several types of diode investigated in the past few years. Lin et al reported Ag/MgZnO/GaZnO/Au Schottky diode [5], which provides a high rectification ratio and convenient operation. The Ti/TiO$_2$/Pt diode was fabricated with rectification ratio up to 10$^6$@±5 V [6]. Besides, the P–type/N–type oxide diodes were investigated including NiO$_x$/n–Si and NiO/TiO$_2$ [7], which achieves high rectification ratio and single integration. However, traditional Si substrate and inorganic materials are incompatible with flexible applications.

Organic/inorganic plays a key role in the field of flexible memories due to excellent mechanical properties of organic compounds and established characters of inorganic materials [8]. Kastia et al show that the rectification ratio and current density of poly (3-hexylthiophene)/ZnO heterojunction can reach 10$^6$@±1 V and 10$^4$ A cm$^{-2}$ owing to the effective hole transport of organic compound [9]. Diode structure based on ZnO/PANI was studied for UV photodetectors because of excellent rectification ratio, ideal factors and mechanical characters [10]. The major benefits of organic/inorganic hybrid diode can retain high flexible process in the fabrication and
application [11]. For example, ZnO/graphene light-emitting diode was investigated by Liu et al under bending cycles of 100 times [12]. The perovskite–ZnO heterojunction shows stable current density under different bending radius [13]. However, few studies focus on the application of organic/inorganic heterojunction diode for flexible 1D1R and study switching performance under bending conditions.

In this article, we fabricated ZnO/poly (fluorene–alt–benzothiadiazole) (PFBT) n–n isotype heterojunction diode and integrated with Al/TiO$_2$/Al resistor [14]. A poly (methyl methacrylate) (PMMA) layer was inserted between the ZnO and PFBT to block electrons. Especially, the resistive switching of GaIn/ZnO/PMMA/PFBT/Al/TiO$_2$/Al 1D1R structure under bending conditions was systematically studied.

**Experimental details**

The PFBT and PMMA were used as purchased from Xi’an Polymer Light Technology Group. The fabrication method of ZnO nanoparticles (NPs) can be seen elsewhere [15], while the TiO$_2$ nanoparticles were prepared by sol–gel hydrothermal method at 160 °C for 2 h [16]. To fabricate TiO$_2$–based memory device, Al was deposited onto polyethylene terephthalate (PET) as the bottom electrode. Then, TiO$_2$ nanoparticle film was spin–coated following by deposition of the Al top electrode. Third, the PFBT/PMMA/ZnO diode cell was stacked on the surface of the Al electrode. About 100 nm–thick PFBT was spin–coated on the clean Al electrode. Subsequently, 30 nm–thick PMMA layer was spin-coated onto the surface of PFBT [17]. Finally, about 200 nm ZnO nanoparticle film were spin-coated onto the PMMA surface. The spin-coating parameters are 800 rpm for 5 s followed by 2000 rpm for 30 s. All processes were completed under the ambient conditions.

The current–voltage (I–V) curves were recorded with a LK-2005Z potentiostat with the GaIn metal droplet as top electrode (see figure 1(a)). The device area is about 50 μm$^2$. For bending test, the device was bent with a homemade stage. The film morphologies were observed by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The thickness of the functional layers was observed by SEM cross–sectional image (see figure 1(b)).

**Results and discussion**

The typical I–V characteristics of isotype heterojunction diode and resistor were studied, respectively. As seen in the figure 2(a), the Al/PFBT/PMMA/ZnO/GaIn structure behaves obvious rectification properties due to the n–n heterojunction (see supporting information is available online at stacks.iop.org/MRX/5/066429/mmedia for details). The diode performs a rectification ratio of about 530 at ±1 V and an ideality factor of 1.7. Figure 2(b) presents the unipolar resistive switching for the Al/TiO$_2$/Al structure without any forming process [18]. The set voltage ($V_{set}$) and reset voltage ($V_{reset}$) are about 2 and 4.9 V, respectively, and ON/OFF ratio is about 580.

As given in figure 2(c), unipolar I–V curve can be observed in the GaIn/ZnO/PMMA/PFBT/Al/TiO$_2$/Al 1D1R structure, which only switches at the positive polarity. It is noteworthy that the $V_{set}$ and $V_{reset}$ increased from 2 and 4.9 V to 4.6 and 5.5 V, respectively, owing to the introduction of PFBT/PMMA/ZnO diode [19, 20].

To study the 1D1R flexible reliability, endurance and retention properties were investigated, respectively. As shown in the figure 3(a), reversible resistive switching can be observed over 30 times under multiple bias sweeping cycles, exhibiting that the Al/TiO$_2$/Al resistor is successively integrated with the Al/PFBT/PMMA/ZnO/GaIn heterojunction diode. The $V_{set}$ increased nearly 24.4% during sweeping cycles because of the Joule
heating under sweeping cycles oxidize oxygen-deficient defects in the TiO$_2$ film and weaken the conduction filaments (see inset of figure 3(a)) [21]. Figure 3(b) shows the ON/OFF ratio of unbent device with about 12.1% degradation over $\sim 10^7$ s at room temperature. These can be ascribed to the oxygen in the air reduces the density of oxygen vacancies and influences the carrier transport, which leads to a lower $I_{\text{LRS}}$ [22]. To investigate the effect of mechanical stress on the retention characteristic, we also did in-suit measurements on resistive switching of the 1D1R under bending condition. It is shown that the ON/OFF ratio reduced almost one tenth compared with

![Figure 2](image2.png)

Figure 2. (a) The I–V curve of Al/PFBT/PMMA/ZnO/GaIn 1D structure. (b) Typical unipolar I–V characteristics for the Al/TiO$_2$/Al 1 R structure. (c) The unipolar resistive switching behavior of the 1D1R device.

![Figure 3](image3.png)

Figure 3. (a) The distribution of ON/OFF ratio under 32 sweeping cycles. The inset shows the threshold voltage for the 32 cycles. (b) Retention characteristics of the device under bent and unbent conditions.
that of the unbent one. As discussed later, the fatigue fracture induced by bending may weaken the resistive switching performance.

The stability of switching performance after dynamic mechanical stress is a key factor for flexible application. We thus study how the 1D1R behaves after repeated bending with the ON/OFF ratio and threshold voltage as functions. Figure 4(a) depicts the 1D1R structure bent continuously from flat to curving with a homemade translation stage. The bending distance is chosen to be about 25 mm. As given in the figure 4(b), the ON/OFF ratio decreases about 3% after bending 200 cycles. When the device was bent 400 cycles, the ON/OFF ratio decreases nearly 7% compared with the 200 cycle sample. Upon bending above 600 times, the ON/OFF ratio sharply reduces 14%, while the threshold voltage increases slightly with increase of bending cycles. As discussed later, these can be ascribed to the fatigue fracture hinder on the formation of conduction paths.

Compared with that of device applied constant strain, the cyclic strain may cause more severe degradation because of seriously fatigue failure induced by repeated bending [23].

To further investigate the effect of cyclic strain on the carrier transport in HRS, a log-log scale was fitted to obtain conduction mechanism (see figure 4(c)). Compared with the Ohmic conduction in LRS (see more details in supporting information), the slope of fitting line in HRS varies in a range of 1.6 to 2, which conforms to the space charge limited conduction (SCLC) mechanism. The results indicate that the bending cycle has no serious influence on the carrier transport.

Figure 5 shows the AFM micrographs of the fatigue fracture behavior for the 1D1R samples after different bending cycles. For device bent less than 200 times, there is no obvious fracture (see figures 5(a), (b)). With further fatigue fracture at 400 cycles, as given in the figure 5(c), linear cracks are vertical to the bending direction. Upon bending 600 cycles, the crack density increases obviously and cracks grow longer due to severe stress concentration exited at crack tip (see figure 5(d)). The inset shows that the depth of crack is about 150 nm. Moreover, the degree of fatigue deformation has a clear relation with the resistive switching (see figure 4(b)). Further cycling up to 800 times did not lead to a much higher crack density (see figure 5(e)).

The growth path of crack is a critical factor to influence the carrier transport. For better observing the surface morphology and growth path of fatigue crack, we performed SEM analysis. Figure 6(a) shows the surface of ZnO nanoparticle film with some voids detected [24]. Upon bending 600 cycles (see figure 6(b)), parallel crack separates the surface of ZnO film and propagates along the grain boundaries. The crack spacing is about 1 μm, which is consistent with the AFM observation. In the magnified view of the micro crack (see inset of figure 4(b)), the channel crack across the ZnO film can be clearly observed. This fatigue fracture could block the carrier

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Figure 4. (a) Schematic illustration for the 1D1R structure under bending tests. (b) Distribution of ON/OFF ratio and threshold voltage with different bending times. (c) The double log of HRS I-V of device under different bending cycles.
transport and the formation of conduction paths. The PMMA film with cycling strain exhibits no any fatigue fracture because of excellent flexibility [25]. Thus, the fatigue failure of PMMA under bending is not taken into consideration during the simulation process, as detailed later.

The mechanical property of oxide materials is significantly influenced by the grain size [26]. Compared with the highly crystalline ZnO nanoparticle [22], the state of TiO2 nanoparticle is amorphous with size of ∼10 nm [27]. The yield strength of TiO2 film is larger than that of the ZnO film based on the well-known Hall–Petch theory. Moreover, the top Al electrode of the resistor, has excellent ductility and flexibility, which could sever as a repairing layer to cover the surface defects of TiO2 film [28, 29]. In other words, the Al electrode may play an active layer role to boost the mechanical properties of resistor.

To testify this hypothesis, we investigated the electrical characteristics of the GaIn/ZnO/PMMA/PFBT/Al diode and Al/TiO2/Al resistor under cyclic strain, respectively. For the diode bent less than 1000 cycle, as given in figure 7(a), the rectification ratio shows no obvious degradation diode. However, the device rectification ratio decreases nearly 3 times upon bending 1500 cycles. It is noteworthy that forward current is significantly decreased, while the reverse current shows no change. As detailed later, these can be ascribed to that fatigue fracture destroyed the formation of n–n heterojunction. For the cyclic strain tests of resistor (see figure 7(b)), the ON/OFF ratio shows no noticeable degradation within 2000 cycles. After bending 3000 times, the ON/OFF
The rectification ratio decreases nearly 4%. The reason may be due to the development of cracks on the Al electrodes. As expected, the resistor shows more stable electrical performance than that of the diode under cycling strain.

Aiming to understand the stress distribution and structure failure under dynamic bending, we employed the finite element code ABAQUS. All the material parameters and thicknesses were listed in Table 1.

In building device model, the interfacial adhesion of different layers is also taken into consideration. Our studies show that the Al/TiO₂/Al resistor performs excellent flexural endurance under repeated bending. It is thus reasonable to assume that layers of resistor are perfectly bonded with each other. For inorganic–organic multilayer structure, typical failure modes under tensile stress include channel cracks in the top oxide film and interfacial delamination along the inorganic and organic interface. Cordero et al. studied the effect of critical strains on the channel cracks in the inorganic–organic–inorganic multilayer structure, where the inorganic–organic interface was assumed perfectly bonded. For our case, the Elastic modulus of ZnO and PMMA are $E_{\text{ZnO}} = 150$ GPa and $E_{\text{PMMA}} = 5.82$ GPa, respectively. The large difference in the material stiffness leads to incompatible failure behaviors. Meanwhile, the channel crack can be observed in the ZnO film, which plays a root role to cause interfacial crack. It is highly possible that the delamination exists along the inorganic–organic interface. However, the Elastic modulus and Poisson’s ratio of PFBT are $E_{\text{PFBT}} = 5.82$ GPa and $\nu_{\text{PFBT}} = 0.3$, respectively, which have a low mismatch level with the PMMA. There were hardly any micro cracks on the PMMA as detected by SEM, and consequently the interfacial delamination may not exist along the PMMA–PFBT interface. Based on above discussion, we build a tri–layer (ZnO–PMMA–PFBT) model perfectly bonded to the resistor to analyze the tensile failure.

As illustrated in the figure 8(a), we built a slice of material of two-dimensional module and set a pre-defined crack in the center of ZnO film. Meanwhile, we plotted 3 paths to compute the distribution of stress along different surfaces (path 1: along the ZnO surface between ZnO and PMMA, path 2: along the PMMA surface between PMMA and PFBT, path 3: along the PBET surface between PFBT and Al). Figure 8(a) shows that the stress counter of the path 2 and path 3 are less than that of the path 1, which indicates that interfacial stress is related to the Elastic modules of films. Further analysis exhibit that the stress along the path 2 is smaller than that of the path 3 due to a lower Elastic modules (see figures 8(e), (f)).

As a tensile stress is applied on the ZnO surface, the channel crack would initiate from the pre-defined crack and cross the ZnO film, causing further interfacial crack between ZnO and PMMA (see figure 8(c)). The growth of interfacial delamination is governed by the driving force and interfacial toughness between ZnO and PMMA. Jia et al. reported that the driving force is related to the delamination width (d) and film thickness (h) when the d is longer than the h, the driving force gradually reaches a plateau. Moreover, the value of driving force is equal to the interfacial toughness when the length of interfacial delamination is certain. For our case, the interfacial crack stops propagating at about 1.1 μm (see figure 8(d)). As detailed above, the interfacial

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Table 1. Material Properties of Layers Used in the FEA.

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>150</td>
<td>0.3</td>
<td>200</td>
</tr>
<tr>
<td>PMMA</td>
<td>5.8</td>
<td>0.33</td>
<td>30</td>
</tr>
<tr>
<td>PFBT</td>
<td>2</td>
<td>0.3</td>
<td>100</td>
</tr>
<tr>
<td>Al</td>
<td>71.7</td>
<td>0.27</td>
<td>100</td>
</tr>
<tr>
<td>TiO₂</td>
<td>200</td>
<td>0.33</td>
<td>200</td>
</tr>
</tbody>
</table>
delamination could block electron transport among the ZnO/PFBT heterojunction, which reduces the diode rectification ratio (see figure 7(b)).

In order to understand effect of fatigue fracture on the conduction mechanism, the schematic resistive switching mechanism and band diagrams of 1D1R were discussed under unbent and bent conditions. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of PFBT are calculated by the density and functional theory in previous studies [33]. The LUMO, as path of charge transfer, plays a key role in affecting the carrier transport [34]. For PFBT, the carrier transport can be attributed to the charge trapping/detrapping process owing to the defects in the polymer [33]. For metal oxide, it is known...
that the switching mechanism is related to conduction filaments [11, 14]. Previous studies of TiO$_2$ based memory films showed that the switching mechanism is dominated by oxygen ion and vacancies [34, 35]. Yeom et al reported that switching mechanism of the Al/TiO$_2$/Al can be attributed to the oxygen vacancies in the TiO$_2$ layer near the anode [36]. The switching mechanism of our 1D1R may be dominated by oxygen vacancy filaments. And When a positive voltage was applied to the GaIn electrode, the oxygen ions moved towards to the Al anode, more and more oxygen vacancies formed conduction filaments during the set process (see figure 9(a)). The bottom injected electron transferred through conduction band of TiO$_2$ and passed through the PFBT/ZnO n–n heterojunction to form a LRS current (see figure 9(c)) [4]. Under a higher reset bias, the accumulation of Joule heating near the anode exacerbating the diffusion of oxygen vaccines and oxygen ions migrated out of the anode [37], leading to the rupture of conduction filaments (see figure 9(b)). Meanwhile, the tunnel barrier with a higher conduction band (in contact with Al and TiO$_2$) broke the conduction path in LRS and fast recovered to HRS (see figure 9(d)). For the bent sample, the interfacial delamination between PMMA and ZnO may play a key role as blocking layer to hinder electron transfer from PFBT to ZnO (see figure 9(e)), leading to a lower forward current [38]. And there are fewer grain boundaries to sever as conduction paths because of large defects and micro crack among the ZnO nanoparticle film (see insert of figure 6(b)) [22]. Thus, under the same bias, the current of bent device in LRS is lower than that of the unbent sample, leading to the switching deterioration.

Figure 9. The diagrams of switching mechanism and corresponding energy band of 1D1R device before bending at set condition (a) and (c), reset condition (b) and (d), respectively. (e) The energy band of 1D1R device at set condition after bending.
Conclusion

In summary, we have successfully integrated n–n heterojunction of ZnO/PFBT diode and Al/TiO$_2$/Al resistor on the PET substrate. The 1D1R device behaved stable unipolar resistive switching behavior over 10 cycles and slightly decrease retention characteristics over $\sim 10^7$ s. The ON/OFF ratio decreased clearly with increase of bending times. Fatigue fracture analysis show that the crack density in ZnO nanoparticle film is related to the bending cycles. The growth path of crack is along the grain boundaries, which blocks the carrier transport and the formation of conduction paths. I–V measurements indicate that the forward current of diode decreased with increase of bending times. Further FEA show that interfacial delamination among the ZnO–PMMA interface acts a blocking layer to hinder tunneling effect and deteriorates the switching performance of 1D1R. Our studies may provide a reference for the future development in flexible 1D1R.

Acknowledgments

This research is supported financially by the Project of National Natural Science Foundation of China (Grant no. 51773030).

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