CONTRIBUTED PAPER

Fully Transparent Resistive Memory Employing Graphene Electrodes for Eliminating Undesired Surface Effects

In this paper, a ZnO-based transparent resistive random access memory that employs graphene as a transparent and stable resistive element with switching characteristics usable in memory applications is described.

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ABSTRACT | A ZnO-based transparent resistance random access memory (TRRAM) employs atomic layered graphene exhibiting not only excellent transparency (less than 2% absorptance by graphene) but also reversible resistive switching characteristics. The statistical analysis including cycle-to-cycle and cell-to-cell tests for almost 100 cells shows that graphene plays a significant role to suppress the surface effect, giving rise to the notable increase in the switching yield and the insensitivity to the environmental atmosphere. The resistance variation of high-resistance state of ZnO is greatly suppressed by covering graphene as well. The device reliability investigation, such as the endurance more than 10^2 cycles and the retention time longer than 10^4 s, reveals the robust passivation of graphene for TRRAM applications. The obtained insights show guidelines not only for TRRAM device design and optimization against the undesired switching parameter variations but also for developing practically useful applications of graphene.

KEYWORDS | Graphene; resistive switching; surface effect; transparent resistance random access memory (TRRAM)

I. INTRODUCTION

Two-dimensional materials, which possess atomic or molecular thickness and infinite planar lengths, are regarded as the thinnest functional nanomaterials and may serve as an attractive substitute to many traditional materials [1]–[12]. Among a variety of 2-D nanomaterials, graphene has motivated wide-ranging scientific and engineering studies because of its excellent mechanical, thermal, and electronic properties [3]–[12]. Due to low sheet resistance and high optical transparency [6], [8], one of interesting and promising applications is being a transparent electrode, making graphene as promising nanomaterials for the next generation of faster and smaller electronic devices, such as solar cells [7], [9], light emission diodes [10], and photodetectors [11]. The sheet resistance of the graphene film with ~90% optical transmittance is as low as ~30 $\Omega/\square$, which is superior to common transparent electrodes such as indium tin oxide (ITO) [12].

Transparent electronics is an emerging technology employing "invisible" electronic circuitry and optoelectronic devices, such as building-integrated photovoltaics

Manuscript received May 31, 2012; revised March 05, 2013; accepted April 14, 2013. Date of publication May 20, 2013; date of current version June 14, 2013. This work was supported by the National Science Council of Taiwan under Grants 99-2622-E-002-019-CC3, 99-2112-M-002-024-MY3, and 99-2120-M-007-011, and by the National Taiwan University under Grant 10R70823.

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Digital Object Identifier: 10.1109/JPROC.2013.2260112

and touch panel displays. In view of the integration toward see-through electronics, transparent nonvolatile memory devices are indispensable and still deficient. Several research groups have devoted their efforts in fabricating transparent resistance random access memory (TRRAM) devices consisting transparent electrodes and a resistive switching layer with a wide bandgap [13], [14]. ZnO as the candidates for a resistive switching layer holds great potential for TRRAM applications because of its high transparency in the visible region and excellent resistive switching characteristics [13]–[16]. However, most of devices based on metal oxide, such as resistive memory devices [17], gas sensors [18], and photodetectors [19], are influenced remarkably by the surface effect [20], including surface band bending [21], chemisorption/photodesorption at the surfaces [22], and surface roughness [23].

Taking metal–oxide-based resistive memory devices as an example, one of the widely believed switching mechanisms is the electrochemical redox process, which is associated with the formation/rupture of a conductive filament built by surface defects and oxygen vacancies (V_O) near the surface/interface between top electrodes and metal oxide [24]. Consequently, the resistive switching characteristics of metal oxide suffer from the surface effect [18]. One should note that the key development of resistive memory based on metal oxide for applying to large-scale manufacturing is the precise control of switching uniformity. Due to severe surface effects, significant parameter fluctuations exist in the resistance distributions, which include cycle-to-cycle and device-to-device fluctuations [18]. For example, noticeable tail bits in the resistance distribution observed in a large memory array remarkably reduce the resistance window and thus impede the realization of the multilevel capability of the resistive memory [25], [26]. In order to develop transparent metal oxide to practical TRRAM applications, developing an effective way to eliminate the surface effect for achieving the uniform switching behavior is indispensable.

In this work, we fabricate ZnO TRRAM devices employing atomic layered graphene at the surface of ZnO exhibiting not only excellent transparency (less than 2% absorptance by graphene) but also stable resistive switching characteristics. The statistical analysis including cycle-to-cycle and device-to-device tests for almost 100 cells for evaluating the switching behaviors shows that graphene plays a significant role to suppress the surface effect, leading to the notable increase in the switching yield of ZnO from 58.3% to 75.0% in air ambience. As altering the surrounding atmosphere from O_2, air, N_2 at atmospheric pressure to vacuum, ZnO with graphene shows the suppressed switching yield variation (yield ranging from 66.7% to 75.0%) as compared to that of ZnO (yield ranging from 41.7% to 66.7%). It reveals that covering graphene shows a great improvement on the atmosphere tolerance of the ZnO memory devices. Moreover, the resistance variation of high-resistance state (HRS) of ZnO is greatly suppressed by covering graphene, showing the insensitivity to atmosphere conditions as well. The resistance ratio of HRS/low resistance state (LRS) is approximately 20 in air ambience. When it comes to the device reliability, there are no significant changes within 100 cycling test, and the retention time at room temperature is more than 10^4 s. The obtained insights provide guidelines for future TRRAM device design and optimization against the undesired switching parameter variations.

II. EXPERIMENT

A commercial ITO substrate was initially precleaned by alcohol and deionized water to avoid the contamination from the ambience. The ZnO thin films with 50 nm in thickness were deposited on ITO substrates by radio-frequency (RF)-sputtering technique. Graphene was grown by atmospheric pressure chemical vapor deposition (CVD) on polycrystalline Cu foils. Before putting into the CVD chamber, the Cu foils were cleaned by acetic acid for removing surface oxides. Then, the Cu foils were mounted in the CVD chamber with a steady 10-sccm flow of hydrogen and annealed at 1000 °C for over 40 min. In the CVD process, methane (20 sccm) mixed with argon (230 sccm) and hydrogen (10 sccm) was fed into the chamber for 2 min, during which graphene growth occurs. The Cu foils were then moved to the cooling zone where a cooling system is equipped. The self-limiting growth mechanism results in over 80% of single-layer graphene coverage. Clean transfer of graphene with surface cleanness onto the top of the ZnO thin film was employed. More details about growth and transfer of graphene can be obtained elsewhere [27]. ITO electrodes with 200 um in diameter were then deposited by RF-magnetron sputtering at 150 °C with a metal shadow mask. Finally, a transparent ITO/graphene/ZnO/ITO device can be achieved. For a comparison, a reference sample made without graphene layer was prepared under the same process.

The Raman spectroscopy for graphene layers was performed using a double-frequency He–Ne laser (633 nm) as the excitation source. Electrical properties were examined by Keithley 4200 semiconductor parameter analyzer. During the measurement in voltage sweeping mode, the positive bias is defined by the current flowing from top to bottom electrodes, and the negative bias was defined by the opposite direction.

III. RESULTS AND DISCUSSION

Fig. 1 shows the photograph displaying see-through areas of the ITO/graphene/ZnO/ITO device on the glass marked in a dashed-line rectangle in the inset of the figure. The "Small Lab" logo beneath the TRRAM device can be observed clearly without image blurring because of the excellent transparent characteristics of graphene, ZnO, and ITO materials. To quantitatively realize the transparency, the transmission

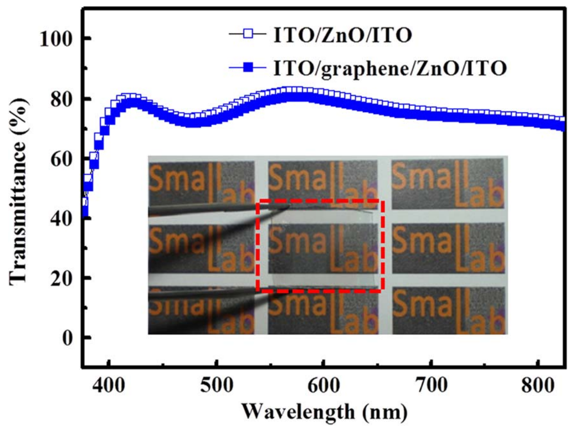

Fig. 1. ***The transmittance of ITO/ZnO/ITO/glass (open squares) and ITO/graphene/ZnO/ITO/glass (solid squares) devices within the visible region from 400 to 800 nm. The inset shows the fabricated ITO/graphene/ZnO/ITO TRRAM device. The background can be observed through the device without any refraction or distortion.***

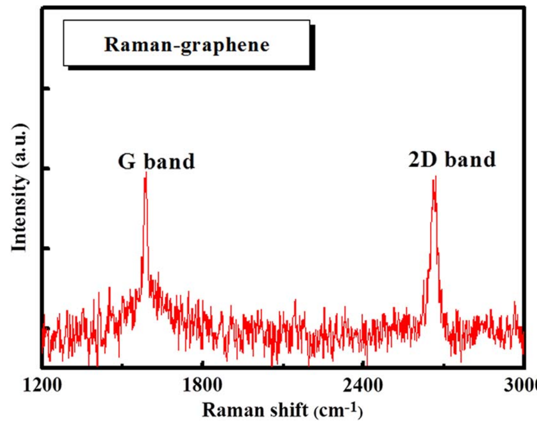

Fig. 2. ***Raman spectrum of pristine graphene using 633-nm He–Ne laser.***

spectra of the ITO/graphene/ZnO/ITO/glass and the ITO/ZnO/ITO/glass were investigated, as shown in Fig. 1. The average transmittance of the ITO/graphene/ZnO/ITO/glass is up to 75.6% within the visible wavelength region from 400 to 800 nm, which is slightly smaller than that of the ITO/ZnO/ITO/glass since graphene only absorbs ~2% of incident light over a broad wavelength range [28]. The results reveal that the graphene/ZnO device is suitable for transparent electronics applications. We do note that carbon nanotubes (CNTs), one of promising carbon-based nanomaterials, have been used as the electrode to scale down the memory device to the nanometer size for developing an ultradense and low-power nonvolatile memory technology [29], [30]. However, CNTs as a black body absorber are not suitable for transparent electronics [31].

Fig. 2 shows the Raman spectra of the graphene under the excitation of a 633-nm laser. For bulk graphite and graphene, two most intense features are G-band (~1583.5 cm^{-1}) and 2-D band (~2655 cm^{-1}) [32]. The former originates from the in-plane vibration of sp^2 carbon atoms, while the latter can be attributed to the two-phonon double resonance, which is closely related to the band structure of graphene layers [32], [33]. The comparable integrated intensity ratio of G-band and 2-D band, shown in Raman spectra, further indicates the nature of graphene used in this study [32].

Fig. 3 shows the typical resistive switching behaviors of the ZnO TRRAM device with and without graphene electrodes. An electrical stress with a high current compliance of 5 mA is required to initiate the switching property of the device, which is known as the forming process. The forming voltage is approximately 4 V. After the forming process, the device is in the LRS. By sweeping the voltage to the negative voltage above a certain value, a sudden drop of leakage current is observed (as denoted by the arrow of reset). The resistance of devices switching to the HRS is lower than the resistance of fresh sample before forming. While sweeping to the positive bias, an abrupt jump of leakage current reaches to current compliance (as denoted by the arrow of set), which means that the device switches to the LRS again. The graphene/ZnO device shows reversible and steady bipolar switching characteristics; the positive bias induces the LRS and the negative bias resets the HRS.

Meanwhile, the coexistence of bipolar and unipolar switching in resistive memory devices has been discussed extensively. In comparison with the bipolar operation, the unipolar operation cannot reveal stable switching behaviors on the as-fabricated device. The probabilities of switching yield of ZnO with graphene electrodes are shown in Fig. 4. One can see that within the fixed number of devices, which are chosen randomly, bipolar switching is much more

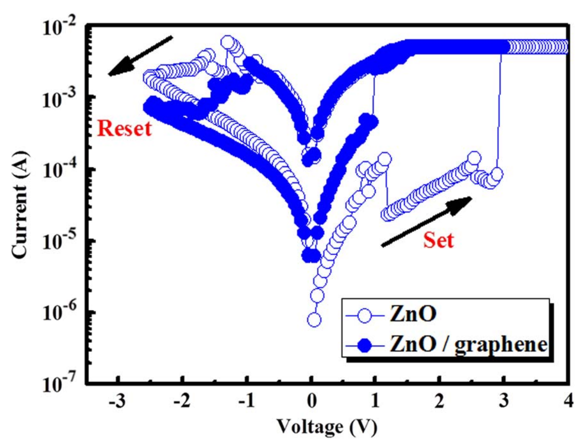

Fig. 3. ***Typical resistive switching behaviors of the ZnO TRRAM device with and without graphene electrodes. The positive bias induces the LRS and the negative bias resets the HRS.***

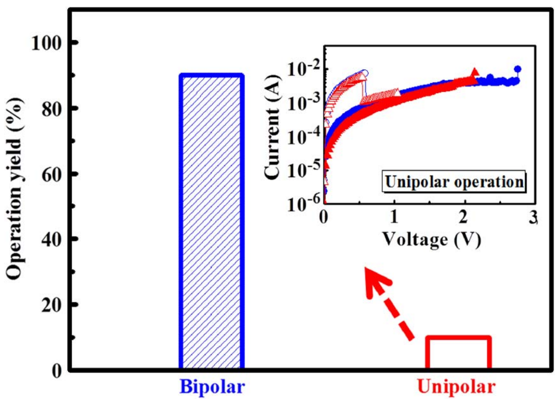

Fig. 4. ***Probabilities of switching modes of the ZnO memory with graphene electrodes, including both unipolar and bipolar operations. The devices are chosen randomly to conduct the statistics.***

preferred because of comparatively high yield. The typical I–V characteristic of unipolar operation is also shown in the inset. After two complete switching curves (set and reset), the cell reaches the current compliance, and fails in the end.

It has been known that the ambient oxygen partial pressure has a considerable influence on the electrical properties of metal oxide due to $O^{-}_{2(ad)}$ chemisorption [18], [34]–[36]. The O_2 molecules absorbing at surface defects of metal oxide, such as oxygen vacancies, act as electron acceptors to form chemisorbed $O^{-}_{2(ad)}$, leading to the decrease in the conductivity of metal oxide. As the oxygen partial pressure rises, more O_2 molecules chemisorbed at the metal oxide surface are expected. In order to access the importance of graphene on the resistive switching behavior of metal oxide, the switching yields of ZnO and graphene/ZnO devices are compared with different oxygen partial pressure by varying atmosphere conditions, as shown in Fig. 5(a). The percent yield is determined by the ratio of the amount of cells switching continually over 20 cycles without any set or reset failure to the amount of total cells within the measurement. The statistical analysis including cycle-to-cycle and cell-to-cell tests for 96 cells provides essential evidence for evaluating the resistive switching behaviors. Overall, the switching yield is greatly increased after introducing graphene at the top of ZnO under all atmosphere conditions; for example, the yield is increased from 58.3% to 75.0% in air ambience.

The concentration of chemisorbed $O^{-}_{2(ad)}$ at the ZnO surface in four measurement conditions at room temperature is vacuum $<$ N_2 $<$ air $<$ O_2, which has been widely confirmed by previous studies [18], [36]. Previously, we reported $O^{-}_{2(ad)}$ affects the formation/rupture of conductive filaments in ZnO near the top electrode, which is ascribed to the generation/annihilation of V_O at the electrode/ZnO interface, and further changes the switching functionality of resistive memory devices; i.e., the Set yield is decreased with the

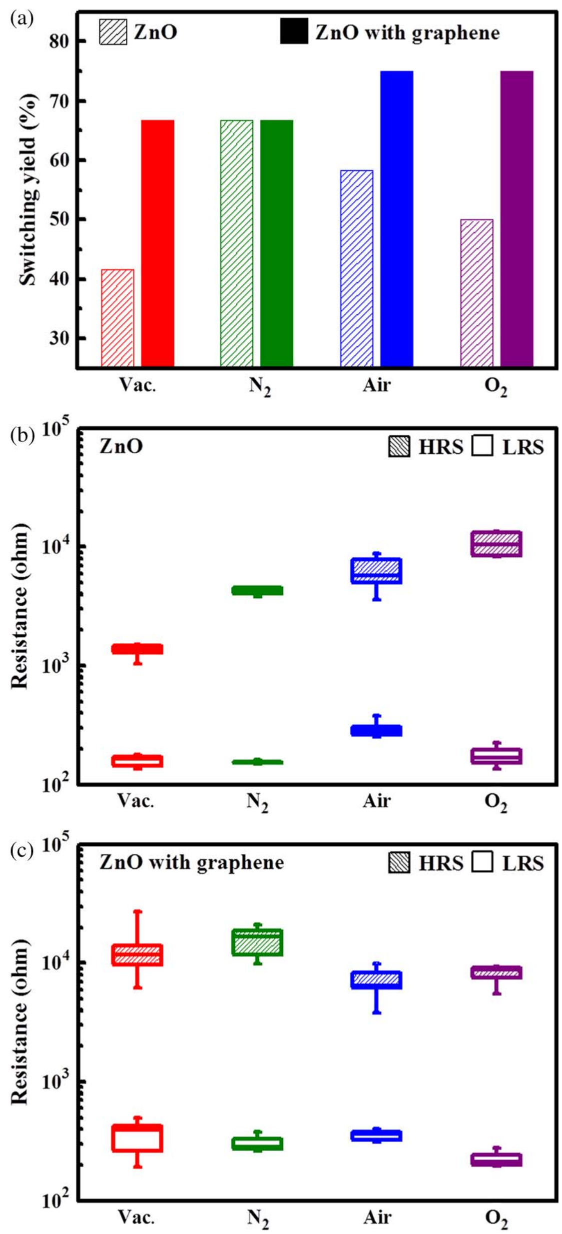

Fig. 5. ***(a) The switching yields of ZnO and graphene/ZnO devices obtained in vacuum (Vac.) and in the ambience of nitrogen (N_2), air, and oxygen (O_2) at atmospheric pressure. (b)–(c) Box and whisker plots for the atmosphere-dependent resistance in HRS and LRS of the ZnO TRRAM device with and without graphene electrodes. For box and whisker plots, the bottom and the top of the box are the 25th percentile and the 75th percentile, the band near the middle of the box is the 50th percentile, and the ends of the whiskers represent the 10th percentile and the 90th percentile.***

concentration of chemisorbed $O^{-}_{2(ad)}$, while the reset yield exhibits the opposite trend [18]. Accordingly, the ITO/ZnO/ITO device exhibits relatively low switching yield in vacuum and O_2 ambience (41.7% and 50.0%, respectively), as compared to the devices in the ambience of N_2 and air (66.7% and 58.3%, respectively). Surprisingly, the introduction of atomic layered graphene between ITO top electrodes and ZnO films, the switching yield of ZnO devices is greatly increased (to 66.7%, 66.7%, 75.0%, and 75.0% in vacuum, O_2, air, and N_2, respectively) and insensitive to the environmental atmosphere, which is beneficial for practical memory applications. The detrimental surface effect on the resistive switching behaviors can be improved by capping graphene layer, demonstrating that the graphene can be not only a transparent electrode material but also a passivation layer due to the weak chemisorption of O_2 molecules [37].

To gain further insight into the effect of $O^-_{2(ad)}$ chemisorption on the switching behaviors of ZnO TRRAM devices, the resistance of HRS and LRS of ZnO with and without graphene electrodes under various ambient conditions was measured, as shown in Fig. 5(b) and (c). As for ZnO without graphene electrodes covered, the HRS shifts to a higher resistance value as the environment is altered from vacuum to O_2 ambience at atmospheric pressure [18]. This phenomenon can be understood by the $O^-_{2(ad)}$ chemisorptions induced conductivity lowering near the ZnO surface [35]. Once the O_2 molecules adsorb at the ZnO surface, the O_2 molecules capture the electron causing the surface band bending effect, which reduces the conductivity of ZnO near the surface [18]. The surface band bending effect is more pronounced as the $O^-_{2(ad)}$ concentration increases, resulting in the increase in the HRS resistance with the concentration of $O^-_{2(ad)}$. However, by the introduction of graphene at the surface of ZnO, resistance variations of HRS of ZnO are notably suppressed and average/variation of the HRS resistance shows little dependence on the environmental atmosphere, as shown in Fig. 5(c). Note that as the variations of HRS and LRS resistance are unacceptably too large, resistive memory devices would require an elimination method such as a bilayer oxide device structure, verify-programming and write-verify techniques that precisely control the resistance to enhance memory devices' endurance [25], [38]. Moreover, it has been reported that no obvious change in the LRS resistance of ZnO under different atmosphere conditions is obtained since the transport in the LRS is dominated by the metallic conductive filament in ZnO films, which is not influenced by the surface band bending [18]. Similar results are also observed in ZnO with graphene coating in this study.

To further evaluate the resistive switching characteristics of the graphene/ZnO TRRAM device, endurance and retention properties were measured. Fig. 6(a) shows the

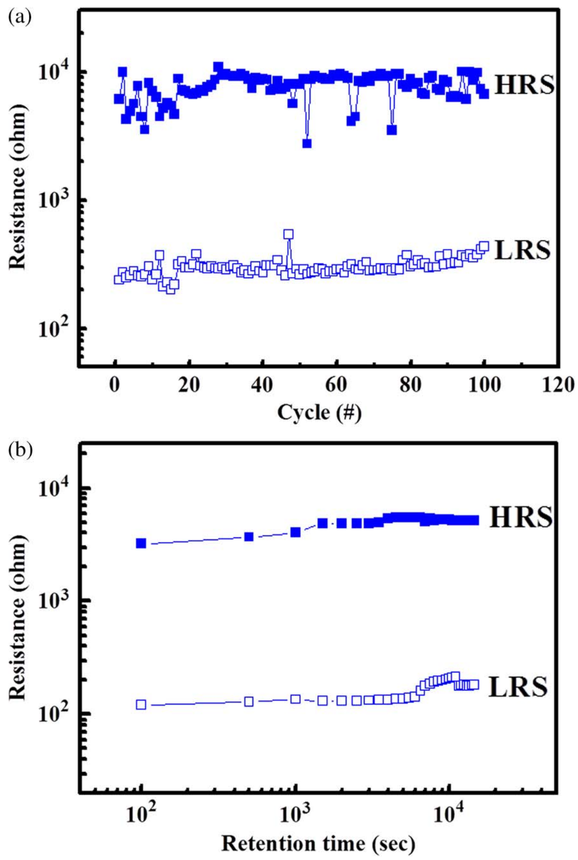

Fig. 6. ***(a) The evolution of resistance states of and graphene/ZnO device during the 100 resistive switching cycles. (b) The nonvolatile property of both HRS and LRS of graphene/ZnO devices at room temperature.***

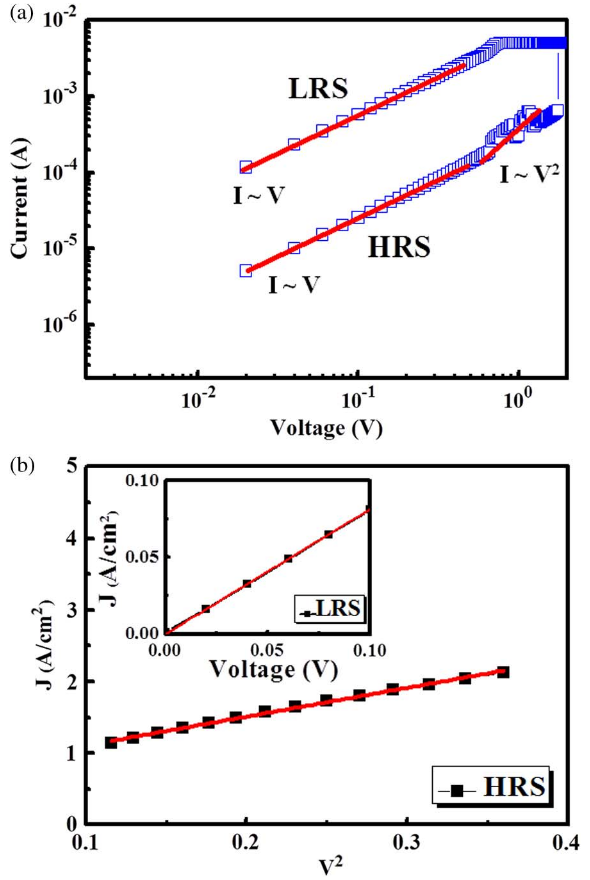

Fig. 7. ***(a) Conduction properties of the graphene/ZnO device. (b) Linear fitting of LRS and HRS in the graphene/ZnO device.***

endurance property during 100 successive resistive switching cycles. The resistance values were read at 100 mV in each direct current (dc) sweep. The ratio of HRS/LRS is approximately 20. Two well-resolved distributions of HRS and LRS provide a clear memory window. There is no conspicuous decay in both resistance states. The results indicate that the switching characteristics of the device are reproducible and stable. Fig. 6(b) shows the retention property of both HRS and LRS. The retention times with a sufficient memory window are obtained, although the LRS is somewhat fluctuant as the retention time is over 10^4 s, demonstrating the electrical reliability of the graphene/ZnO TRRAM device.

In order to understand switching mechanisms for the as-fabricated device, the original I–V curves are replotted. Fig. 7(a) and (b) shows the logarithmic plot and linear fitting of the previous I–V curve of ZnO with graphene electrodes (Fig. 3) for the positive voltage sweep region. The liner I–V relationship in LRS clearly exhibits an Ohmic conduction behavior, which can be regarded as the formation of conductive filaments in the device during the set process. Fitting results for HRS show that the charge transport of switching behavior is in good agreement with a model of space charge limited conduction, which consists of three portions: the ohmic region ($I \propto V$), the Child's law region ($I \propto V^2$), and the steep current increase region. Moreover, more details on the transport can be understood by employing the temperature-dependent I–V measurements, which is under investigation.

While the processes of the graphene electrodes are readily compatible with the existing processing technology in the memory industry, and highly applicable for various types of resistive memory, it is important to develop the techniques for patterning graphene electrodes for a high-density array of individually addressable cells/units in 3-D crossbar memory architecture. The techniques for patterning graphene electrodes are diverse. Demonstrating a reliable fabrication procedure of patterning graphene would pave the way for integrating graphene electrodes into future TRRAM fabrication processes.

IV. CONCLUSION

We demonstrated that graphene absorbing $\sim$2% of incident light sustains highly desirable transparent characteristics for TRRAM devices. More importantly, passivated ZnO TRRAM devices with graphene even exposing in different interface/surface chemistry environments exhibit better memory switching yield and performance uniformity than the unpassivated ones. The resistance variation of HRS of ZnO is significantly suppressed by covering graphene. Excellent endurance and retention characteristics of graphene/ZnO demonstrate the robust passivation of graphene for TRRAM application. These explorations give insights not only in understanding the surface effect for achieving the uniform switching behavior of TRRAM but also in developing practically useful applications of graphene. ■

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