Resistive switching characteristics of a compact ZnO nanorod array grown directly on an Al-doped ZnO substrate

E J Yoo¹, J Y Shin¹, T S Yoon², C J Kang³ and Y J Choi¹

¹ Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Korea
² Department of Materials Science and Engineering, Myongji University, Gyeonggi 449-728, Korea
³ Department of Physics, Myongji University, Gyeonggi 449-728, Korea

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Abstract
ZnO’s resistive switching properties have drawn much attention because ZnO has a simple chemical composition and is easy to manipulate. The propulsion mechanism for resistive switching in ZnO is based on a conducting filament that consists of oxygen vacancies. In the case of film structure, the random formation of the conducting filaments occasionally leads to unstable switching characteristics. Limiting the direction in which the conducting filaments are formed is one way to solve this problem. In this study, we demonstrate reliable resistive switching behavior in a device with an Au/compact ZnO nanorod array/Al-doped ZnO structure with stable resistive switching over $10^5$ cycles and a long retention time of $10^4$ s by confining conducting filaments along the boundaries between ZnO nanorods. The restrictive formation of conducting filaments along the boundaries between ZnO nanorods is observed directly using conductive atomic force microscopy.

Keywords: resistive switching, conducting filament, ZnO nanorods, conductive atomic force microscopy

(Some figures may appear in colour only in the online journal)
on the bottom electrode [7, 17]. The ZnO seed layer also prevents an electrical short between the top and bottom electrodes during the top electrode deposition process. In some reports, the free space between individual ZnO NRs was filled with polymeric materials in order to avoid short circuits [37]. For easy fabrication of the device and clear interpretation of its operation, it is desirable to grow a ZnO NR layer compactly and directly on the bottom electrode; no additional seed layer or filler material is then required. By varying the temperature and pH level of the growth solution, or adding agents that control nucleation and crystal growth speed, we are able to grow compact ZnO NR arrays on Al-doped ZnO (AZO) bottom electrodes with various diameters and packing densities. In the ZnO-based RS memory device, CFs are mainly formed through defects such as oxygen vacancies and non-lattice oxygen ions in the ZnO layer, if there is no diffusion of metal ions from the electrodes [18, 19]. Not only can vertically oxygen ions in the ZnO layer, if there is no diffusion of metal through defects such as oxygen vacancies and non-lattice the ZnO-based RS memory device, CFs are mainly formed electrodes with various diameters and packing densities. In the ZnO-based RS memory device, CFs are mainly formed through defects such as oxygen vacancies and non-lattice oxygen ions in the ZnO layer, if there is no diffusion of metal ions from the electrodes [18, 19]. Not only can vertically grown ZnO NRs confine the CFs inside the NRs themselves [20], but the boundaries between the ZnO NRs may also limit the CFs’ path along them when the NRs are closely packed. However, it is difficult to visualize CFs along the boundaries between ZnO NRs, because a CF is only a few nanometers in diameter. Although Tour et al showed CF formation directly using in situ transmission electron microscopy (TEM) [20], it is very difficult to obtain reliable results. By contrast, because conducting atomic force microscopy (C-AFM) can provide information on the electric properties and topography of the surface simultaneously with nanometer scale resolution, we are able to point out where the CFs start to form by comparing the current image with the topographical image [21, 22].

In this study, we present the resistive switching property of a compact ZnO NR array grown vertically on an Al-doped ZnO (AZO) layer and visualize the starting position of CF formation using C-AFM. The possibility of confining CFs along the boundaries between ZnO nanorods is supported by the C-AFM current image and the suppression of the conductance in the samples with smaller boundary densities due to the reduced chance of forming CFs along the boundaries.

2. Sample fabrication and experimental details

A pre-cleaned SiO2/Si (1 0 0) substrate was coated with an AZO layer by RF magnetron sputtering. During the sputtering process, the chamber pressure was kept constant at 20 mTorr with the argon gas flow rate at 50 sccm. The 200 nm thick AZO was deposited for 2 h at 100 W RF power with a working temperature of 200 °C. Since the AZO has low resistivity, we can use it as the bottom electrode of the RS device and as a seed layer for vertical ZnO NR growth.

The ZnO NRs were synthesized directly using the hydrothermal method. For the growth solution, we prepared a mixed solution of 15 mM zinc nitrate hexahydrate, 15 mM hexamethylenetetramine, and 5 mM polyethyleneimine, and this was stirred for 1 h. We also added some ammonium chloride to control the diameter and growth behavior of the ZnO NRs, because the ammonium chloride can change the nucleation and crystal growth speed of ZnO [19]. The substrate covered by the AZO layer was placed upside down in a beaker filled with 100 ml growth solution at 80 °C for 2 h. By varying the concentration of the ammonium chloride from 0.1 M–0.5 M, we were able to fabricate several kinds of compact ZnO NR arrays with different diameters but approximately the same height (~400 nm). (Index of the sample names—SA: 0.1 M, SB: 0.2 M, SC: 0.3 M, and SD: 0.5 M.) In order to compare the resistive switching characteristics of the ZnO NR array and film structures, a ZnO film layer with the same thickness as the compact ZnO NR array was also fabricated using RF magnetron sputtering. For the top electrode, we deposited 100 nm thick Au dots with a diameter of 100 μm on the ZnO NR array or the ZnO film through a metal shadow mask via the DC sputtering method at a power of 100 W for 1 h. During the sputtering process, the chamber pressure was kept at 20 mTorr with an argon gas flow rate of 50 sccm. The crystalline structure of the AZO layer was analyzed by x-ray diffraction (XRD, X’pert-Pro, PANalytical) using Cu radiation operated at 40 kV and 30 mA with a 2θ range from 20°–60°. The growth morphology of the ZnO NRs was characterized through field emission scanning electron microscopy (FE-SEM, S-4300SE, Hitachi). The existence and relative quantity of oxygen vacancies in the ZnO nanostructures was monitored by photoluminescence (PL, FLS 920, Edinburgh Instruments Ltd) with an excitation wavelength of 370 nm. The electrical properties of the Au/ZnO/AZO capacitor structure were measured using an Agilent 4156B semiconductor parameter analyzer. For the visualization of the starting points of CF formation in the compact ZnO NR array, we used C-AFM (Park systems, XE-100) with an Au-coated AFM tip, which replaced the Au top electrode in the Au/ZnO/AZO capacitor structure. We were also able to obtain the local I–V characteristics at the nanometer scale using C-AFM. During the I–V measurements, a bias voltage was applied to the bottom electrode with the top electrode grounded. Figure 1 shows a schematic of the device structure and electrical characterization process.

3. Results and discussion

The XRD patterns for the 200 nm thick AZO layer deposited on the SiO2 substrate at room temperature and 200 °C are shown in figure 2(a). It is well known that the growth
conditions of ZnO NRs are strongly influenced by the crystallography of the seed layer [23] and a seed layer with a c-axis oriented texture assists the vertical growth of ZnO NRs [24].

The AZO layer sputtered at room temperature gives a mixed pattern of (0 0 2), (1 0 1), and (1 0 0) peaks, whereas the AZO layer sputtered at 200 °C only shows a (0 0 2) reflection peak, which indicates complete c-axis texturing. So, we were able to fabricate vertically grown ZnO NR arrays on the AZO layer sputtered at 200 °C. The well-aligned boundaries between the ZnO NRs were confirmed by the cross-sectional SEM image (see figure 2(b)). In addition, the AZO layer was measured to have low sheet resistance of <100 Ω/□, enough to be used as a bottom electrode.

To investigate the resistive switching characteristics of the Au/compact ZnO NR array/AZO structure, the electrical properties were measured using a DC voltage sweep in the range −2 to +2 V. As shown in figure 3(a), typical bipolar resistive switching behavior was observed. When a positive voltage was applied, the resistance state of the device switched from the initial high-resistance state (HRS) to the low-resistance state (LRS); conversely, when a negative voltage was applied, the device switched from the LRS to the HRS. These bipolar switching behaviors were obtained without any forming process. In order to confirm the stability of the set/reset process, the DC voltage sweep from −2 to +2 V was carried out 300 times. The switching performance, including

Figure 2. (a) XRD data for AZO films deposited at RT (black line) and 200 °C (red line). (b) SEM image of the top view of the ZnO NR array. The inset shows the cross-sectional view.

Figure 3. (a) Bipolar I–V characteristics of the Au/compact ZnO NR array/AZO device. The numbered arrows indicate the switching direction. (b) Results for repeated I–V measurements under the same conditions. Results for (c) endurance and (d) retention tests at a voltage reading of 0.2 V. All data were taken at the SB sample.
the set/reset voltage and resistance value at HRS/LRS, was quite stable (figure 3(b)). The HRS and the LRS were well resolved after a pulse switching operation of more than 10⁵ cycles (figure 3(c)) and each state preserved its resistance value up to 10⁴ s (figure 3(d)). The resistance values in figures 3(c) and (d) were read at 0.2 V.

In our device, the RS behavior is associated with the formation and rupture of CFs via the redox reaction. As figure 4(a) shows, the negative oxygen ions start to migrate to the bottom electrode when the positive bias is applied to the bottom electrode. The oxygen vacancies, which are created by the removal of oxygen ions or exist naturally due to the crystallographic imperfections of the ZnO layer, form CFs at higher electric field. As a result, the resistance state of the device changes from HRS to LRS, which is called a ‘SET’ process. Since natural oxygen vacancies exist in abundance in the boundaries between vertically aligned ZnO NRs because of the relatively imperfect crystallography at the surface of ZnO NRs [25, 26], the CFs form easily along the boundaries, which implies a low set voltage. When a negative bias is applied to the bottom electrode, oxygen vacancies recombine with oxygen injected from the AZO bottom electrode and the CFs are ruptured. The device recovers its original high resistance state, which is called a ‘RESET’ process.

The $I-V$ curve of the HRS is replotted at a double-logarithmic scale in figure 4(b) to clarify the conduction mechanism of the device. The slope at the lower voltage region is 1, which exhibits ohmic conduction, and then the slope at
the higher voltage region is changed to 2. This result indicates that the conduction mechanism of our device is trap-controlled space-charge-limited conduction (SCLC) [27].

Ohmic behavior at a lower voltage corresponds to an unfilled trap region and the second order of the $I-V$ relationship at a higher voltage corresponds to a trap-filled region. The $J-E$ equation of trap-controlled SCLC can be described as equation (1) [28]

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \left( \frac{E^2}{L^3} \right),$$

where $J$ is the current density, $\varepsilon_0$ is the dielectric constant of vacuum, $\varepsilon_r$ is the dielectric constant of the film, $\mu$ is the electronic mobility, $E$ is the applied voltage, and $L$ is the thickness of the thin film. The inset of figure 4(b) shows the $I-V$ plot of the LRS in a double-logarithmic scale. The slope is measured to be 1 and this linear relation between the current and voltage implies that the conduction mechanism at the LRS is based on ohmic conduction [29].

In order to demonstrate the starting position of the conducting path, the AFM topography and the current image map were recorded simultaneously using C-AFM with a contact force of 10 nN and a scan rate of 0.3 Hz. The topography of the compact ZnO NR array surface is depicted in figure 5(a), and the corresponding current image at a sensing voltage of 3 V after the formation of CFs by scanning the same area at a bias of 5 V is shown in figure 5(b). Since the bright areas in the current image are highly conductive areas, they can be considered to be the starting positions of CFs. By overlapping the current image and the topography image, we find that the CFs mainly start to form at the boundaries between NRs, as shown in figure 5(c). In addition, $I-V$ measurements on the bright regions show bipolar resistive switching behavior that is similar to that of a capacitor-structured device, as illustrated in figure 5(d).

It is well known that hydrothermally synthesized ZnO nanostructures have defects such as oxygen vacancies, zinc vacancies, and zinc interstitials [30–32]. The existence of oxygen vacancies in ZnO nanostructures has been supported by PL measurements, where the green peak at around 500 nm in the PL spectra indicates the existence of oxygen vacancies [33, 34]. By comparing the relative intensity of the green peak and the UV peak (figure 6(a)), we can anticipate that there are more oxygen vacancies in the compact ZnO NRs than in a ZnO thin film with the same thickness. As shown in figure 6(b), the relatively abundant oxygen vacancies in compact ZnO NRs compared with ZnO film cause lower resistance in the HRS. The resistance value of the ZnO film is of the order of $10^5$Ω at a voltage reading of $-0.2$ V, which is $10^3$ times higher than the resistance value of the ZnO NR array. Previous reports support the contention that the electrical conductivity increases as the density of the oxygen vacancies increases [35, 36]. In addition, the quantity of oxygen vacancies could affect the HRS/LRS ratio. When a small quantity of oxygen vacancies exists in the switching layer, more oxygen vacancies are required to form the conducting filaments. In this case, a large bias voltage is needed to generate oxygen vacancies, through which large filaments can be formed instantaneously. As a result, the considerable change from HRS to LRS occurs, which leads to the high HRS/LRS ratio. By contrast, since many oxygen vacancies exist in a ZnO NR array—which are mainly distributed near the boundaries between ZnO NRs because of the crystallographic imperfections of the ZnO NR surface—the device with a ZnO NR array switching layer requires a smaller operating voltage to form CFs near the boundaries. The smaller operating voltage leads to narrowly formed small filaments along the boundaries, which contributes to the smallness of the change of the resistance from HRS to LRS. As a result, the HRS/LRS ratio is smaller in the compact ZnO NR array than in the ZnO film.

From the C-AFM and PL results, we suggest that the oxygen vacancies—especially those at the boundaries between ZnO NRs—make the main contribution to the resistive switching behavior. In order to further verify the influence of the oxygen vacancies at the boundaries on the resistive switching, samples with different boundary densities were investigated. Figure 7(a) shows the top-view SEM images of the samples. We changed the boundary densities by controlling the diameter of the ZnO NRs through varying the concentration of ammonium chloride in the growth solution. Figure 7(b) shows the $I-V$ characteristics of devices with different boundary densities. In spite of the different boundary
densities (depending on the size of the ZnO NRs), all the devices showed typical bipolar RS characteristics through the formation of CFs along the boundaries between ZnO NRs, as shown in the overlapped C-AFM topography and conductivity images. Figure 7(c) exhibits overlapped topography and current images. The current image in figure 7(c) was obtained at a sensing voltage of 3 V, where the bright region corresponds to the highly conductive region. From the current images, we can see that the CF paths primarily start at the boundary between ZnO NRs, regardless of the ZnO NR diameter.

Although typical bipolar RS characteristics were observed in each device, the resistance value in the HRS and the HRS/LRS ratio tends to increase as the density of the boundaries decreases. As we discussed in the comparison of the ZnO NRs and the ZnO film, the high resistance in the HRS and the large HRS/LRS ratio could be correlated to the existence of a small quantity of oxygen vacancies. Since the oxygen vacancies are mainly distributed between the ZnO NRs, the density of the oxygen vacancies will decrease as the diameter of the ZnO NRs increases. The PL measurement results shown in figure 7(d) support this assumption. From the calculation of the intensity ratio between the band edge UV peak ($I_{\text{UV}}$) and the defect peak near 550 nm ($I_{\text{defect}}$) from the PL measurement, the density of the oxygen vacancies decreases as the diameter of the ZnO NRs increases due to the decrease of the density of

|       | SA  | SB  | SC  | SD  |
|-------|-----|-----|-----|-----|
| Set voltage (V) | +1  | +1  | +3.5 | +5  |
| Reset voltage (V) | −1  | −0.8 | −3  | −3  |
| LRS/HRS ratio (read voltage: −0.2 V) | 1.30 | 1.90 | 2.46 | 4.91 |
| LRS (Ω) (read voltage: −0.2 V) | $3.94 \times 10^3$ | $4.11 \times 10^3$ | $1.01 \times 10^3$ | $1.19 \times 10^4$ |
| HRS (Ω) (read voltage: −0.2 V) | $5.15 \times 10^7$ | $7.84 \times 10^3$ | $2.30 \times 10^3$ | $5.88 \times 10^4$ |
the boundaries between the ZnO NRs. In this respect, it is reasonable to suggest that the SD device with the fewest ZnO NR boundaries, which implies the fewest original oxygen vacancies, has the largest operating voltage and HRS/LRS ratio among the four devices under measurement. In reverse, the SA device with the largest quantity of oxygen vacancies requires the smallest operating voltage for RS, resulting in the smallest HRS/LRS ratio. More detailed RS property values are summarized in Table 1.

4. Conclusion

Reliable resistive switching behavior is demonstrated in the Au/compact ZnO NR array/AZO structure device. The device exhibits stable resistive switching over 10^5 cycles and a long retention time of 10^4 s. From the C-AFM results, we suggest the possibility of the formation of CFs along the boundaries between vertically grown ZnO NRs. Furthermore, this is supported by an increased quantity of oxygen vacancies, which act as a source of CFs, in samples with higher boundary densities.

Our results will be helpful in developing more stable RS-based non-volatile memory devices by artificially restricting the CFs in a specific region.

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