Enhanced non-volatile resistive switching in suspended single-crystalline ZnO nanowire with controllable multiple states

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Abstract
Resistive switching nanostructures are a promising candidate for next-generation non-volatile memories. In this report, we investigate the switching behaviors of single-crystalline ZnO nanowires suspended in air. They exhibit significantly higher current density, lower switching voltage, and more pronounced multiple conductance states compared to nanowires in direct contact with substrate. We attribute the effect to enhanced Joule heating efficiency, reduced surface scattering, and more significantly, the positive feedback established between the current density and local temperature in the suspended nanowires. The proposed mechanism has been quantitatively examined by finite element simulations. We have also demonstrated an innovative approach to initiating the current–temperature mutual enhancement through illumination by ultraviolet light, which further confirmed our hypothesis and enabled even greater enhancement. Our work provides further insight into the resistive switching mechanism of single-crystalline one-dimensional nanostructures, and suggests an effective means of performance enhancement and device optimization.

Keywords: ZnO nanowire, resistive switching, suspended

(Some figures may appear in colour only in the online journal)

1. Introduction

The resistive switching (RS) properties of metal-insulator-metal nanostructures make them a promising candidate for next-generation non-volatile memories [1–20]. Their unique behaviors have attracted considerable interest from both academia and industry. Prototype devices have demonstrated extremely high stacking density, low power consumption, ultrafast switching speed [5, 6], and multistate operations [7–10, 21]. The devices are primarily based on two types of configurations. The first type (type I) consists of a layered hetero-structure with a thin insulating layer sandwiched between two metal electrodes, while the second type (type II) has both the electrodes and the switchable conduction channel built on the same surface, forming a co-planar structure.

Conduction channels of the type II devices are generally made of one-dimensional (1D) nanomaterials. A wide range of materials including NiO [6, 11], TiO2 [12], CoO [7, 13], ZnO [4, 14, 17] and CuO [15, 16] nanowires have been systematically studied. External electric fields drive the migration and redistribution of the internal ions (O2− or O3−).
vacancies) along the nanowire [10, 12, 16, 17], which in turn modify the spatially resolved energy bands and the overall conductance of the 1D channel. Unlike Type I devices, in which conduction filaments are formed at random locations, type II devices consist of well-defined conduction channels, enabling smaller device-to-device variation and better controllability during operations [8, 11].

Despite the above advantages, the performance of type II devices is greatly limited by a number of issues, mostly associated with the underlying substrate. First, ion mobility inside the 1D channel largely depends on temperature [18–22], whereas direct contact between the channel and the substrate (e.g. SiO₂) causes bad thermal isolation and low Joule heating efficiency [21, 22]. Insufficient thermal activation limits the ion mobility, thus resulting in large switching voltage during set/reset operations. Second, the nanowire–substrate interface creates traps for ambient molecular and ionic groups (e.g. hydroxyl), which form surface states and scattering sites for conduction electrons and give rise to a lower ‘on’-state current. Third, the surface of the substrate contains a large number of dangling bonds for charged species, which induce undesired electrostatic interaction with the nanowire and cause uncontrollable behaviors [23–25].

In this work, we have systematically investigated the switching behaviors of suspended ZnO nanowires. The setup removes the dielectric layer underneath the nanowire and isolates the conduction channel so as to allow us to probe its intrinsic transport properties. We have observed considerable reduction in switching voltage and considerable enhancement in ‘on’-state current by two orders of magnitude. The suspended devices also demonstrated multiple highly stable and distinguishable conductance states when configured by different ‘set’ voltages. We have carried out finite element simulations to understand the sharp contrast between the suspended and solidly mounted devices. It is suggested that the effect is associated with enhanced Joule heating and more importantly, a mutual enhancement mechanism between the local temperature and current density within the nanowire.

2. Experimental section

2.1. Materials and methods

Single-crystalline ZnO nanowires were synthesized via the vapor–liquid–solid deposition process. Details of the nanowire growth have been discussed in a previous report [26]. The typical length of the wires was 10 μm and the diameters ranged from 50 to 100 nm. RS devices were fabricated on highly doped silicon substrate, coated with 300 nm of thermal oxide. A 100 nm-thick AlN film was sputtered on the substrate as a sacrificial layer, followed by nanowire deposition on top of it. Electrode patterns were then defined via photolithography and electron-beam lithography on the substrate, followed by metal deposition of Ti/Au (100/50 nm) and lift-off. The channel lengths of the devices were typically 500 nm. To obtain suspended nanowire, the device was released by removing the sacrificial AlN layer with KOH solution (1 g/200 ml) for 5 min, rinsed in isopropyl alcohol for 30 s and then dried in N₂.

2.2. Characterization

Morphology and crystallinity of the ZnO nanowires were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A semiconductor parameter analyzer (Agilent B1500) was used to measure the electrical characteristics in voltage sweeping mode at room temperature. The ultraviolet (UV) illumination experiments were carried out with a hand-held UV lamp (LEAC-280L, 254 nm) placed 10 cm away from the device.

3. Results and discussion

Figure 1(a) shows the SEM image of ZnO nanowires grown on Si/SiO₂ substrate. The TEM images in figures 1(b) and (c) confirm the wurtzite structure of the nanowire with crystal orientation along the [0001] direction. The SEM image in figure 1(d) shows a typical device. The channel length is defined as the separation between two adjacent electrodes and is 500 nm in this case.

Typical switching behaviors of a solidly mounted device are characterized in figure 2. All measurements were carried out in air at room temperature. In the initial state, oxygen ions and intrinsic oxygen vacancies [6, 16–18] are uniformly distributed along the nanowire channel (figure 2(a), upper). Therefore, the I–V curve is symmetric and the wire behaves essentially like a resistor, as shown in the blue curve of figure 2(a). When we sweep the voltage on one electrode (defined as ‘anode’) from 0 to 30 volts while grounding the other one (defined as ‘cathode’), the electric force drives the oxygen ions to migrate towards the anode, leaving oxygen vacancies in the channel as n-type dopants. The oxygen ions accumulated near the anode form a large Schottky barrier (SB) near the electrode–nanowire interface [27, 28], leading to very low conductance under small voltage bias, as indicated by the red curve in figure 2(a) and the lower schematic. We define this low-conductance state as the ‘off’ state of the device. Compared with the initial state where oxygen ions are uniformly distributed, the resistance of the nanowire increases from 0.83 GΩ to 25 GΩ after the SB junction is formed.

When an even higher voltage bias is applied, more oxygen vacancies (O₂⁻) are generated. They drift towards the anode and reduce the width of the SB junction. At the moment when the junction is thinned to a threshold width, electron tunneling starts to dominate and leads to a dramatic increase in current density. The blue curve in figure 2(b) demonstrates this transition, which occurs at approximately 37 V. We define this transition as the ‘set’ process, and the resultant highly conductive state as the ‘On’ state. The conductance ratio between the on and off states (termed the ‘on/off ratio’) is nearly 2.5 orders of magnitude. The red curve in figure 2(b) illustrates the reverse process, defined as the ‘reset’ operation. When a sufficiently negative voltage bias is applied, the SB junction grows thicker and turns the device back to the off state. The device...
can be repeatedly and consistently switched between the on and off states for many cycles.

The experiment in figure 2(c) illustrates the switching under different Set biases. The voltage is double-swept across different ranges of 0–10 V, 0–20 V, 0–30 V and 0–40 V, respectively. A−40 V Reset voltage is applied after each Set operation. The data indicate that only the 0–40 V scan is sufficient to turn on the device, while a lower bias is unable to initiate any detectable transition. The threshold Set voltage is usually determined by the channel length [7, 15] and the original oxygen vacancy doping level in the nanowire [14, 16, 17]. Figure 2(d) shows the result of retention time measurement. Both the on and off states showed no trend of degradation during the entire measurement (2 × 10³ s).

As discussed above, the dielectric layer in direct contact with the nanowire can induce a number of negative effects that largely limit the device performance. Previous studies have primarily focused on the material and physical properties of the nanowires [5, 13, 29] and electrodes [9, 30, 31], while few have looked into the influence of the device substrates. In the following experiments, we remove the underlying dielectric layer to suspend the nanowire. This allows systematic comparisons between the cases with and without the supporting layer.

The SEM image of figure 3(a) shows a typical device after removal of the AlN dielectric by KOH etching. The nanowire is suspended 100 nm above the SiO₂ surface. Figure 3(b) plots the switching curves of the device. Four different Set voltages are used in the test, each configuring the device to a distinguishable conductance state. Figure 3(c) examines these states in more detail. The figure plots the device current (under 5 V reading bias) in different states, labeled as ‘0’ to ‘4’, respectively. We observe fairly large separation between adjacent states, ranging from half to one order of magnitude, which has rarely been achieved by other devices [8, 10, 21]. Each state corresponds to a specific oxygen ion/vacancy distribution profile, as illustrated in the schematics of figure 3(d). Retention time measurements demonstrated good stability of each individual state. In addition, the states are highly reproducible according to the small error bars in figure 3(c), indicating that the oxygen ion/vacancy distributions can be repeatedly and deterministically configured by voltage bias.
Besides the onset of multiple states, the suspended nanowire also distinguishes itself with a significantly higher current density and lower switching threshold compared to solidly mounted devices. Specifically, the device current in both the On and Off states went up by two orders of magnitude after removal of the supporting layer. At the same time, the threshold switching voltage dropped by more than 4 times from 40 V to <10 volts. The change can be attributed to improved thermal isolation between the nanowire and its surroundings, which helps retain the heat generated by Joule heating and results in higher local temperature. The thermal energy activates more conduction electrons and yields a higher current density [32, 33]. At the same time, the elevated temperature gives rise to a higher ion mobility; therefore, a lower electric field is required to relocate the oxygen ions/vacancies inside the nanowire, leading to a much lower switching voltage. More importantly, the increase in current density can, in turn, enhance Joule heating and magnify these effects through a positive feedback. It is the mutual enhancement between the current (or conductance) and the local temperature that enables these unique features. The optimization of thermal isolation, by itself, would possibly not achieve similar results. We have carried out finite element simulations for a more quantitative understanding of this mutual enhancement mechanism.

In the finite element model in figure 4, we couple the current density ($i$, in units of A m$^{-2}$) and local temperature ($T$, in unit of K) to each other through the following settings. On one hand, $T$ is determined by the power density ($p$) of Joule heating, which is proportional to $i$ in the form of

$$p = E \cdot i$$

where $E$ is the electric field across the nanowire (in V m$^{-1}$). On the other hand, the current density ($i$) is proportional to nanowire conductivity ($\sigma$, in units of S m$^{-1}$) at a fixed voltage bias, whereas $\sigma$ is a function of $T$ as in [34]:

$$\sigma = n(T) e \mu(T) = e G_C e \left( \frac{E_C - E_F}{kT} \right) \left( \frac{1}{\mu_l} + \frac{1}{\mu_i} \right)^{-1}$$

where $G_C$ is the effective density of states at the bottom of the conduction band, which is proportional to $T^{3/2}$, $E_C$ and $E_F$ are the energies of the conduction band and Fermi level respectively, $k$ is Boltzmann’s constant, $\mu_l$ is acoustic...
phonon-scattering-limited electron mobility ($\propto T^{-\frac{3}{2}}$), and $\mu_i$ is mobility related to ionized impurity ($\propto T^\frac{3}{2}$).

The equation takes into account the temperature dependence of both the carrier concentration ($n_i$ in m$^{-3}$) and electron mobility ($\mu_i$ in m$^2$V$^{-1}$s$^{-1}$). During the numerical simulation, the model iterates equations (1) and (2) to establish a positive feedback between the current density and local temperature in the nanowire.

Figure 4(a) plots the temperature profiles in a cross-sectional view. The left and right figures are for the same device before and after removal of the AlN layer. The red arrows indicate the directions of local heat flux. Under a voltage bias of 40 V, the average temperature on the nanowire is calculated to be 299 and 762 K for the left and right settings, respectively (the model sets the room temperature as 293 K). Figure 4(b) shows the calculated temperature as a function of voltage bias. It is interesting to note that the temperature of the suspended nanowire (red curve) increases exponentially with the voltage bias, which directly results from the two-way interaction between the temperature and current density. In contrast, if we intentionally turn off the mechanism by removing equation (2) from the simulation, the curve would follow a linear trend with a rather small slope (green dashed line in figure 4(b)), resulting in a much lower temperature ($\sim$442 K), even at $V = 40$ V. In addition, the temperature–current mutual enhancement also gives rise to an exponential increase in current, as shown in figure 4(c). The simulation results of the suspended nanowire (red curve) agree fairly well with our experimental data (blue dots).

Besides temperature and current, we are also able to calculate the mobility of oxygen ions inside the nanowire based on the Arrhenius law and the Einstein relation:

$$\mu_{\text{ion}} = \frac{qD_0}{kT} e^{\frac{E_A}{kT}}$$

The parameters are set to be $D_0 = 210^{-3}$ cm$^2$s$^{-1}$ (pre-exponential factor of diffusivity), $E_A = 1$ eV (direction-independent energy barrier), $k = 1.3810^{-23}$ JK$^{-1}$ (Boltzmann’s constant) and $q = 1.610^{-19}$ C (elementary charge) in our case [35]. Figure 4(d) plots the calculation results at different voltage biases. The ion mobility of the suspended nanowire (red curve) increases exponentially with voltage bias by several orders of magnitude. As the ion mobility
determines the difficulty of relocating and redistributing the oxygen ions/vacancies by electric fields \[35\], the simulation result perfectly explains the large reduction in switching voltage observed in our experiments.

Finally, we demonstrate an innovative approach to further enhancing the temperature–current positive feedback using photocarriers. We use UV light (254 nm) to illuminate the nanowire and pump the valence electrons to the...
conduction band. The illumination instantaneously raises carrier concentration and activates the temperature–current mutual enhancement even under very low voltage bias. This directly leads to a significant increase in On-state current, by more than three orders of magnitude, and a further reduction in switching voltage to less than 5 V (figure 5(a)). Furthermore, the UV illumination allows us to create multiple conduction states with a much lower bias of 10 V (figure 5(b)), as opposed to 40 V in the previous case. The experiments further confirm the ‘mutual enhancement’ model we proposed, and suggest an interesting and inspiring means by which to operate and optimize the RS device.

4. Conclusion

We have systematically investigated the resistive switching properties of single-crystalline ZnO nanowires. We observed a pronounced reduction in switching voltage and an increase in on-state current after removing the supporting layer to suspend the nanowire. FEM simulations suggest that the changes are primarily due to improved thermal isolation and, more importantly, a mutual enhancement mechanism between the local temperature and current density. We have also demonstrated an approach to further enhancing the mechanism by UV light illumination. Our work provides further insight into the switching behavior and mechanism in 1D metal oxide nanostructures, and suggests promising approaches for performance improvement and device optimization.

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