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Size-Independent Unipolar and Bipolar Resistive Switching Behaviors in ZnO Nanowires

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In this work, we report on the mixed bipolar and unipolar resistive switching behavior in ZnO nanowires observed through conductive atomic force microscopy measurements on an individual nanowire. Both bipolar and unipolar resistive switching in ZnO nanowires are size-independent, suggesting that the switching is due to conductive filaments with dimensions much smaller than the cross-section of the nanowire. During bipolar resistive switching, both the low resistance and the high resistance states exhibit ohmic conduction at low voltage, consistent with the filament-based model. During unipolar switching, the low-resistance state is a mix of defect-free ohmic conduction and defect-dominated space-charge-limited conduction, which may not be observed in larger devices. Defects also influence transport in the high resistance state, which exhibits trap-controlled space-charge-limited conduction. Our results clearly demonstrate the key role of defects on the resistive switching behavior of ZnO-nanowires, an important consideration for optimizing the material for nonvolatile memory applications.

Key words: Non-volatile memory, resistive switching, conductive atomic force microscopy, zinc oxide, zinc oxide nanowires

INTRODUCTION

If the electrical resistance of a device changes suddenly in response to an applied potential, then it is possible to switch between different electrical current states, and use this effect to store information. Such resistive switching (RS) phenomena have attracted great interest due to their potential applications in nonvolatile memory devices.[1–6] Among the materials that exhibit RS phenomena, zinc oxide (ZnO) based memory devices have several advantages, such as low cost and low synthesis temperature.[7] Moreover, due to its large direct band gap of 3.4 eV, ZnO has been considered for optical devices. Thus, it is possible to construct multifunctional devices, which employ both the memory and photonic properties of ZnO.[5] In addition, ZnO can be grown in various nanostructure forms, which is not only convenient for applications, but also enables the investigation of RS properties that are different from those in the bulk material.[8]

RS behavior can be categorized into two types: bipolar and unipolar.[4] For bipolar RS, the switching requires the application of voltage with both

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positive and negative polarities. For example, when one starts with zero voltage and ramps up a reverse bias $V < 0$, at a characteristic negative potential $V = -V_{SET}$, the current will suddenly increase as the system switches to the low-resistance state (LRS). If the potential is then increased, through zero and into forward bias, at a characteristic positive potential $V = V_{RESET}$, the current will suddenly decrease as the system switches to the high-resistance state (HRS). The *I–V* curve traces a butterfly hysteresis loop with two different slopes (a large slope for the LRS and smaller slope for the HRS) at the origin.

For unipolar RS, switching can be done using a single voltage polarity. For example, with the system in the HRS, one ramps the voltage up from zero, in the positive direction. Upon reaching $V = V_{SET}$ there is an increase in current as the system switches from the HRS to the LRS. If the device is disconnected and then a positive voltage ramped up once again, the current increases more rapidly with V (being in the LRS now) but at $V = V_{RESET}$, the system switches from the LRS to the HRS. If $V_{SET} > V_{RESET}$ then one may continue to increase the forward bias and see a second transition, from the HRS to the LRS at $V = V_{SET}$, within a single sweep.

ZnO memory devices have been found to exhibit both unipolar RS[9–12] and bipolar RS.[10–15] In some RS cases,[10–12] both types of RS are observed in the same devices. Below, we observe that certain ZnO nanowires exhibit unipolar RS while others display bipolar RS. We will consider possible mechanisms for both types.

Charge conduction inside ZnO-based RS devices, in which the electrical resistance can be changed between two stable states, is usually attributed to either the formation (disruption) of conductive filaments within the bulk or by the migration of carriers at the metal-ZnO interface.[16,17] The latter type of conduction often dominates in ZnO nanowires[14,18–21] but mixed conduction behaviors, in which both metallic filament-based conduction and homogenous carrier migration conduction play significant roles, are also observed.[11,12]

To understand the switching mechanism, it is important to determine if one or both of these conduction mechanisms are responsible for the RS switching of ZnO nanowires that we observe. When the conduction is due to the migration of carriers, and the switch occurs through a reversible change at the interface that blocks the current, the size of the ZnO nanostructure should have a significant effect on the RS properties. For surface charge carriers, the current in the LRS should scale with the nanowire radius. The size-dependence of metal-filament conduction is less clear. A large nanowire could accommodate a greater number of filaments, resulting in a current that increases with wire cross-sectional area. But if conduction through a small nanowire is due to only a few filaments, then RS properties may be size-independent. A study of the size-dependence of RS behavior is a simple, promising method to better understand the RS mechanism. However, few studies have addressed this issue.

In this work, we report on the coexistence of unipolar and bipolar RS behavior in ZnO nanowires grown by the hydrothermal method. By conducting measurements on an atomic force microscope (AFM) platform, we measured both topography and current–voltage (*I–V*) characteristics of individual nanowires. The size-dependence of the *I–V* characteristics could provide insights on the RS mechanisms inside nanowires.

EXPERIMENTAL DETAILS

ZnO nanowires were grown vertically on a (111) Ag/glass substrate using a seed-assisted hydrothermal process as described in Ref. 7. The (111) Ag film was sputtered on a commercial glass slide by gas-timing RF magnetron sputtering[22] with turn on/off gas-timing ratio of 50:15, RF power = 150 watts, and working pressure 0.5×10^{-3} mbar. The Ag substrate forms an ohmic contact with the nanowires.[23] The seeded Ag substrate was immersed in 40 mM $(Zn(NO_3)_2{\cdot}6H_2O$ growth solution for 6 h, which produced nanowires approximately 1 μm tall. The Ag substrate and the AFM probe serve as the bottom and the top electrodes for the *I–V* characteristic measurements. The measurements were carried out on an XE-120 Park AFM (Park Systems Corp, Korea). The measurement procedure starts with acquiring a 3 μm $\times$ 3 μm topography image of a randomly selected region of the sample using tapping mode AFM. Figure 1a shows an example topography image of the nanowire. The cross-section of the nanowires has a hexagonal shape. The average cross-section area of the nanowire is about 0.18 μm^2. The topography image was used as a reference for landing on top of each nanowire for *I–V* characteristic measurements. To ensure good electrical connection, we used solid platinum AFM probes (spring constant 18 N/m, resonance frequency 20 kHz, 25PT300A, Rocky Mountain Nanotechnology, Salt Lake City, UT). Figure 1b (inset) shows the schematic of our setup. Voltage was applied from the tip, while the sample was grounded. The *I–V* characteristic measurement was carried out using a Keysight B2900 source/measure unit. The voltage sweep and data acquisition were performed using a custom LabVIEW program. Both the positive voltage sweep and positive–negative sweep were applied on each nanowire to identify if the nanowire has unipolar or bipolar RS. Curve-fitting was done using Origin software (Microcal Software, Northhampton, MA), and the nanowire cross-section areas were measured using ImageJ software.