Multimode Resistive Switching in Single ZnO Nanoisland System

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Resistive memory has attracted a great deal of attention as an alternative to contemporary flash memory. Here we demonstrate an interesting phenomenon that multimode resistive switching, i.e. threshold-like, self-rectifying and ordinary bipolar switching, can be observed in one self-assembled single-crystalline ZnO nanoisland with base diameter and height ranging around 30 and 40 nm on Si at different levels of current compliance. Current-voltage characteristics, conductive atomic force microscopy (C-AFM), and piezoresponse force microscopy results show that the threshold-like and self-rectifying types of switching are controlled by the movement of oxygen vacancies in ZnO nanoisland between the C-AFM tip and Si substrate while ordinary bipolar switching is controlled by formation and rupture of conducting nano-filaments. Threshold-like switching leads to a very small switching power density of $1 \times 10^3$ W/cm$^2$. Multimode switching with threshold-like, self-rectifying, and ordinary bipolar characteristics is demonstrated in one single-crystalline ZnO nanoisland with diameter of about 30 nm and height of around 40 nm under different current compliance. These three types of resistive switching are controlled by different mechanisms. The threshold-like switching behavior in ZnO nanoisland case is a bistable resistive switching with switching surface power density of only $1 \times 10^3$ W/cm$^2$. A switching mechanism is proposed for threshold-like and self-rectifying bipolar resistive switching, which was proved by the observation of build-in electric field change of ZnO nanoisland during the switching. For ordinary bipolar resistive switching, the mechanism is controlled by the formation and rupture of conductive nano-filaments consisting of oxygen vacancies.

Received 22 April 2013
Accepted 18 July 2013
Published 12 August 2013

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Results

Fig. 1 (a) shows a three-dimensional (3D) AFM image of ZnO nanoislands. Fig. 1 (b) and (c) show the 3D AFM and transmission electron microscopy (TEM) images of one nanoisland, respectively. Although AFM characterization results show that the ZnO nanoislands are large and connected due to tip effect, the TEM image in Fig. 1 (c) indicates that the diameter of the nano-island is about 50 nm. Detailed analysis of cross sectional scanning electron microscopy (SEM) images also showed that the diameter of the ZnO nanoislands is between 10 nm and 60 nm and these islands are discrete. In this experiment, we selected nanoislands with a diameter of around 30 nm and a height of about 40 nm. Fig. 1 (d) shows the schematic of ZnO nanoislands on Si and a C-AFM tip used for measurements.

Fig. 2 (a) shows the threshold-like I–V characteristics when the current compliance was set at 10 nA. During measurement, the voltage was swept according to the process as follows: (0) 0 ~ 10 V, (1) 5 ~ 0 V, (2) 0 ~ −5 V, (3) −5 V ~ 0 V, (4) 0 ~ 5 V. The current compliance was set at 5 nA for process (0), and 10 nA for process (1) ~ (4), respectively. During process (0), the ZnO nanoisland system was switched from high resistive state (HRS) to low resistive state (LRS) when the voltage reached 9 V. In process (1) and (2), the nanoisland was at LRS until −2.6 V where it was switched to HRS, which is corresponding to a LRS for negative reading bias. In process (3) and (4), the switching behavior is similar to that in process (1) and (2), while the switching point is 2.6 V. The switching power is lower than 25 nW, corresponding to the switching surface power density of only $1 \times 10^4$ W/cm$^2$ as the active cell area is considered. This is the lowest switching surface power density compared to that of any nanoscale resistive memory system reported to date.

When the current compliance was set at 100 nA, 100 μA–1 mA, the voltage sweep processes resulted in three types of resistive switching (threshold-like, self-rectifying bipolar and ordinary bipolar) in (a), (b) and (c), respectively.

To further understand the threshold-like I–V characteristics, a voltage pulse of $\frac{1}{2}$ V and $\frac{2}{2}$ V was utilized to read the current of the ZnO nanoisland after process (1) to (4), respectively. The statistical results are shown in Fig. 3. When a pulse of $\frac{1}{2}$ V was applied, the ZnO nanoisland kept at LRS after process (2) and (3). On the contrary, when a pulse of −$\frac{2}{2}$ V was applied, the ZnO nanoisland kept at HRS when the voltage swept from −10 V to 10 V before the voltage reached 6 V or 9 V, where the system was switched to LRS. Further increase of current compliance to be equal to or larger than 50 μA led to ordinary bipolar resistive switching phenomenon, as shown in Fig. 2 (c).

To further understand the threshold-like I–V characteristics, a voltage pulse of $+2$ V and $−2$ V was utilized to read the current of the ZnO nanoisland after process (1) to (4), respectively. The statistical results are shown in Fig. 3. When a pulse of $+2$ V was applied, the ZnO nanoisland was at LRS after process (1) and (4), while at HRS after process (2) and (3). On the contrary, when a pulse of $−2$ V was applied, the ZnO nanoisland stayed at HRS after process (1) and (4), while at LRS after process (2) and (3). These results indicate that both states can be kept after the power is shut down, which is bistable resistive switching behavior, while the resistance of the ZnO nanoisland depends on both the process that the nanoisland undergoes and the polarity of the reading voltage.
In order to study the threshold-like $I$–$V$ characteristics in detail, the zoomed-in plots are shown in Fig. 4 (a) for processes (1) and (2) with the current ranging between $-0.02$ nA and $0.04$ nA, and in Fig. 4 (b) for processes (3) and (4) with the current ranging between $-0.04$ nA and $0.04$ nA. As seen in Fig. 4 (a), the $I$–$V$ characteristics are the ordinary one for a forward-biased diode for process (1) and (2), while it is the ordinary one for the reversed diode for process (3) and (4), as shown in Fig. 4 (b). The $I$–$V$ characteristics of process (1) ~ (4) were repeatable only if the tip was kept on the ZnO nanoisland. Turn-on voltages of $V_1$ (1.1 V) and $V_2$ (0.9 V) are observed for the two diodes, respectively. Breakdown characteristics of the diodes are also observed, which may be due to tunneling effect.

To obtain the current distribution for the low resistive state of the ZnO nanoisland, C-AFM map measurements were performed. Fig. 5 (a) shows height image and Fig. 5 (b) and (c) show local current distribution images for LRS and HRS of ZnO nanoisland under the current compliance of 10 nA~10 $\mu$A, respectively. It is evident that the current at LRS is not distributed locally in the nanoisland in contrast to the conducting filament case.

**Discussion**

The $I$–$V$ characteristics shown in Fig. 4 can be explained by the schematic illustration shown in Fig. 7. In the initial state, the oxygen vacancies are uniformly distributed in the nanoisland. The nanoisland system can be modeled as being composed of one Schottky diode (between the C-AFM tip and nanoisland) and one $p^+$-n diode connected back to back, in series with the semiconducting ZnO nanoisland with a resistor as shown in Fig. 7 (a). During process (0), more oxygen vacancies are generated by the oxidation reaction of $O_O \rightarrow V^*_{O} + 2e^- + \frac{1}{2}O_2$. At the same time, both the original and generated oxygen vacancies move towards the cathode (the substrate). Finally, the portion of the ZnO nanoisland near the cathode side is heavily doped with oxygen vacancies, which act as donors in ZnO. Meanwhile, the portion of the ZnO nanoisland near the anode side (the C-AFM tip) becomes $n^-$-type. As a result, the diode between the ZnO nanoisland and heavily doped p-type Si substrate becomes a tunnel diode consisting of $p^+$-Si and $n^-$-ZnO, which can be treated as a resistor, as shown in Fig. 7 (a) and (b). During process (2), the tip is negatively biased. Oxygen vacancies move towards the C-AFM tip, converting ZnO near the C-AFM tip to be $n^+$. The barrier between the ZnO nanoisland and C-AFM tip is thinner, which results in significant electron tunneling. Therefore, the Schottky diode can be treated as a resistor in this case. At the
same time, the diode between the substrate and ZnO nanoisland turns into a p'-n hetero-junction, as shown in Fig. 7 (b) and (c). During process (4), similar reaction occurs as in process (2). The mechanism is confirmed by the results of C-AFM shown in Fig. 5 (b) and (c).

Under the current compliance of between 100 nA and 10 µA, the system can still be treated as a Schottky diode in series to one resistor, as shown in Fig. 7 (b), because oxygen vacancies move towards the substrate after operation of voltage sweeping from 0 to 10 V. The reason for the diode to be treated as a resistor is that heavily oxygen-vacancy-doped ZnO/p'-Si junction is a tunnel diode. After operation of voltage sweeping from 0 to −10 V, the diode between ZnO and p'-Si can now be treated as a regular heterojunction because oxygen vacancies move back to and gather around the C-AFM tip side again. In the meantime, the barrier between the C-AFM tip and heavily oxygen-vacancy-doped ZnO gives rise to Schottky characteristics because the C-AFM tip is mainly composed of Co, which has high work function of 5.0 eV\(^2\). In this case, the system can still be treated as an Ohmic junction or keeps as Schottky junction depending on the current compliance as a result of diffusion of oxygen vacancies after the voltage sweep from 0 to −5 V or −10 V. The Schottky junction can be treated as a resistor at current compliance of 10 nA because of current tunneling through the very thin barrier. Current self-rectifying resistive switching occurs when the Schottky diode can be treated as a rectifying diode rather than a resistor, as shown in the bracket in (c), in which tunneling current of 10 nA no longer represents RLS because of higher current value after the voltage sweeping from 0 to 10 V. At the same time, the p'-n tunneling diode between the substrate and ZnO nanoisland turns into a p'-n heterojunction. During the voltage sweep from 0 to 5 V or 10 V as indicated by an arrow pointing from (c) to (b), similar reaction occurs as in voltage sweep of 0 ~ −5 V or −10 V.

\[
\tau = \frac{L}{\mu E_0 \sinh \left( \frac{V}{k_B T} \right)}
\]

where \(L\) is the height of the ZnO nanoisland. \(\mu = \frac{q a^2 e^{-\frac{q V}{k_B T}}}{k_B T}\) is the oxygen mobility, \(E_0 = \frac{2k_B T}{qa}\) is the characteristic field for oxygen vacancy in ZnO lattice, which is about 0.5 MV/cm at 300 K and 1.3 MV/cm at 800 K. \(E = \frac{V}{L}\) is the average electric field. \(k_B, T, q\) are the Boltzmann constant, temperature and charge of oxygen.
Self-assembled ZnO single-crystalline nanoislands were grown on pre-cleaned p-Si (100) substrates at 350 °C in a radio frequency plasma-assisted SVA/T MBE system. The growth details can be found elsewhere. Structural properties of ZnO nanoislands were characterized using TEM and AFM. The cross-sectional TEM specimens were prepared by a typical focus ion beam method, using FEI Quanta 3D FEG dual-beam instrument. The original sample surface was protected by a carbon layer and an electron beam-induced Pt layer formed by using Pt gas injection system and an electron beam. The TEM images were obtained using FEI CM-20 TEM operated at 200 kV with a LaB6 filament. FIB and TEM experiments were performed in the laboratory for Electron and X-ray instrumentation at UCI. Electrical characterizations of discrete ZnO nanoislands were carried out in air under controlled temperature (22 °C) and humidity (~12%) with an Agilent 4155C semiconductor parameter analyzer by applying sweeping voltages to obtain I-V characteristics at short integration time corresponding to the sweep rate of 6.4 ms/V for the nanoisland memory system, in which a Cr/Co coated C-AFM tip (MESP) with apex curvature of 20–50 nm was used as the top contact and the substrate as the bottom contact. The detail for equipment connection can be found elsewhere. AFM, C-AFM and PFM measurements were performed in air under controlled temperature (~22 °C) and humidity (~12%) using a Veeco Dimension Icon AFM equipment (Nanostrate v8.10) with C-AFM and PFM capabilities. The C-AFM images were measured under contact mode while AFM and PFM images were obtained under tapping mode. The amplitude and frequency of the ac voltage applied on the Cr/Co coated Si tip during PFM phase images measurements were −10 V − 10 V and 2 kHz, respectively. The hysteresis phase loop was acquired by scanning an axial dc bias from −10 to 10 V.

Methods

Self-assembled ZnO single-crystalline nanoislands were grown on pre-cleaned p-Si substrates at 350 °C in a radio frequency plasma-assisted SVA/T MBE system. The growth details can be found elsewhere. Structural properties of ZnO nanoislands were characterized using TEM and AFM. The cross-sectional TEM specimens were prepared by a typical focus ion beam method, using FEI Quanta 3D FEG dual-beam instrument. The original sample surface was protected by a carbon layer and an electron beam-induced Pt layer formed by using Pt gas injection system and an electron beam. The TEM images were obtained using FEI CM-20 TEM operated at 200 kV with a LaB6 filament. FIB and TEM experiments were performed in the laboratory for Electron and X-ray instrumentation at UCI. Electrical characterizations of discrete ZnO nanoislands were carried out in air under controlled temperature (~22 °C) and humidity (~12%) with an Agilent 4155C semiconductor parameter analyzer by applying sweeping voltages to obtain I-V characteristics at short integration time corresponding to the sweep rate of 6.4 ms/V for the nanoisland memory system, in which a Cr/Co coated C-AFM tip (MESP) with apex curvature of 20–50 nm was used as the top contact and the substrate as the bottom contact. The detail for equipment connection can be found elsewhere. AFM, C-AFM and PFM measurements were performed in air under controlled temperature (~22 °C) and humidity (~12%) using a Veeco Dimension Icon AFM equipment (Nanostrate v8.10) with C-AFM and PFM capabilities. The C-AFM images were measured under contact mode while AFM and PFM images were obtained under tapping mode. The amplitude and frequency of the ac voltage applied on the Cr/Co coated Si tip during PFM phase images measurements were −10 V − 10 V and 2 kHz, respectively. The hysteresis phase loop was acquired by scanning an axial dc bias from −10 to 10 V.

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Acknowledgements
The authors acknowledge the financial and program support of the DARPA/Defense Microelectronics Activity (DMEA) under agreement number H94003-10-2-1003 (3D Electronics), the Microelectronics Advanced Research Corporation (MARCO) and its Focus Center on Function Engineered Nano Architectonics (FENA), National Natural Science Foundation of China (No. 50902065), the Fundamental Research Funds for the Central Universities (No. Iuzhby-2013-33) and Open Project of Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University (No. LZUMMM2013008). We thank Applied Technology Training Center at San Bernardino Community College District for the AFM equipment.

Author contributions
J.Q. and J.L. conceived and designed the experiment. J.Q. and M.O. carried out the experiments. J.Z. performed the FIB and TEM experiment. J.Q. and J.L. wrote the manuscript and other co-authors commented the paper.

Additional information
Competing financial interests: The authors declare no competing financial interests.
How to cite this article: Qi, J., Olmedo, M., Zheng, J.G. & Liu, J.L. Multimode Resistive Switching in Single ZnO Nanoisland System. Sci. Rep. 3, 2405; DOI:10.1038/srep02405 (2013).

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