Bipolar resistive switching with negative differential resistance effect in a Cu/BaTiO$_3$/Ag device†

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We demonstrate that a bipolar non-volatile resistive switching behaviour with negative differential resistance (NDR) effect is realized in a Cu/BaTiO$_3$/Ag device, which was deposited on a Si substrate via magnetron sputtering equipment. We suggest that the bipolar resistive switching is dominated by the trapping/detrapping of electrons at the BaTiO$_3$–Cu interface. In addition, we demonstrate that the device exhibits good performance, including a large on/off ratio, high reliability and long retention time. Therefore, BaTiO$_3$ may become a good candidate for application in resistive switching random access memory (RRAM) devices.

Introduction

As the fourth fundamental circuit element, the memristor device has attracted a lot of attention towards its applications and operating mechanism since it was discovered by the Hewlett-Packard laboratory in 2008. Resistive switching (RS) random access memory (RRAM), as one basic application of a memristor, is the most promising candidate to overcome the technological limitations and fulfill the essential requirements for 3-D integrated circuit architecture in the next generation of non-volatile memory. Based on the working principle of resistance change modulated by an electrical stimulus, RRAM has recently inspired scientific and commercial interests with its high operation speed, high scalability and multi-bit storage potential. Furthermore, a large variety of materials have been found to show these RS characteristics, particularly for metal oxides (NiO, TiO$_2$, TaO$_5$, HfO$_2$, ZnO, Al$_2$O$_3$, Cu$_2$O, Fe$_2$O$_3$, etc.) and the perovskites (SrTiO$_3$, BaTiO$_3$, BiFeO$_3$, etc.). To explain the RS phenomenon, researchers have proposed several theories, such as the formation and rupture of conductive filaments in the insulator, field-assisted drift/diffusion of charged ions, trap-controlled space-charge-limited current, Frenkel–Poole emission, and Schottky barriers. However, there exist too many controversies among them. Moreover, an interesting negative differential resistance (NDR) effect was observed in the RS devices. Although the NDR effect is certainly related to the bipolar RS phenomenon, its origin has not been clarified as yet. This effect will hopefully enable a number of very important applications in devices, such as high-frequency oscillators, memory devices, logic devices and fast switches. Hence, a considerable effort has been devoted towards discovering the inherent transport mechanism responsible for the NDR effect.

Barium titanate (BaTiO$_3$), which is well known for its high dielectric constant, stable ferroelectric properties and good chemical stability, has been widely used in microelectronic devices. Although numerous studies have been performed on the RS properties of BaTiO$_3$, the NDR effect has been rarely reported to date. Very recently, G. Yang et al. first demonstrated the NDR effect in F-doped SnO$_2$ polycrystalline BaTiO$_3$ thin films/Au devices. In this study, we have developed a new type of RRAM device consisting of Cu/BaTiO$_3$/Ag multi-layers, which can simultaneously show a significant NDR effect, high on/off ratio of 200, long retention time of more than 3000 minutes, good endurance, and high reliability at room temperature. In addition, with a different maximum voltage, the NDR phenomenon behaves quite differently. These bipolar RS behaviours, including the NDR effect, can be well understood by considering the trapping/detrapping of electrons in the BaTiO$_3$ layer when they pass through the Schottky barrier formed at the BaTiO$_3$–Cu interface under the different bias voltages.

Experimental

The Cu/BaTiO$_3$/Ag film was deposited via magnetron sputtering at room temperature on an n-type Si(100) substrate with the...
native oxide. The sputtering targets of silver (Ag), copper (Cu) and BaTiO$_3$ were purchased commercially, and their purities were all higher than 99.99%. The base pressure was lower than $1.0 \times 10^{-4}$ Pa and the Ar pressure was maintained at 1.0 Pa during the film deposition process. A schematic of the sample’s stacked structure is shown in Fig. 1(a). The Cu layer was first deposited on the substrate as the bottom electrode, followed by the growth of the BaTiO$_3$ layer. Finally, to make the top electrode with a diameter of about 100 µm, a 100 ± 5 nm thick Ag layer was deposited onto the BaTiO$_3$ layer using a shadow mask. Scanning electron microscopy (SEM, JEM-2100) was utilized to measure the thickness of each layer by taking a cross-sectional image. As shown in Fig. 1(b), the thicknesses of the Cu and BaTiO$_3$ layers are 317 ± 2 nm and 74 ± 1.5 nm, respectively. Before the deposition of the top electrode, the BaTiO$_3$ surface morphology was characterized using atomic force microscopy (AFM, HITACHI Nanocute/E-SWEEP). As shown in Fig. 1(c), the AFM image reveals that the BaTiO$_3$ film consisted of grains with a maximum height difference of about 3.7 nm, and the rms roughness was calculated to be 0.59 nm, indicating that the surface of the BaTiO$_3$ film was flat. To our knowledge, for the fairly smooth surfaces of the BaTiO$_3$ films with the rms roughness varying from a fraction of one nanometer to tens of nanometers, the RS behaviour could be all observed clearly in the related BaTiO$_3$ film-based devices. For the same sample described in Fig. 1(c), the crystal structure was characterized by X-ray diffraction (XRD, Shimadzu XRD-7000) using Cu K$_\alpha$ radiation ($\lambda = 0.154$ nm). As shown in Fig. 1(d), the XRD pattern indicates that both the Cu and BaTiO$_3$ layers were polycrystalline and no impurity phases were detected. After deposition of the Ag top electrode, the current–voltage characteristics of the device were detected using a Keithley-2400 meter with the wires’ connection, as illustrated in Fig. 1(a). The positive bias was applied with the current flowing from the Ag top electrode to the BaTiO$_3$ layer and then to the Cu bottom electrode (i.e. Ag$\rightarrow$BaTiO$_3$$\rightarrow$Cu), and the negative bias was applied with the current flowing in the opposite direction (i.e. Cu$\rightarrow$BaTiO$_3$$\rightarrow$Ag). All characterization and measurements were performed in air and at room temperature.

Results and discussion

The current–voltage ($I$–$V$) loops of the Cu/BaTiO$_3$/Ag memory cells were studied using dc voltage sweep measurements at room temperature, and the results are illustrated in both linear (Fig. 2(a)) and semi-logarithmic scales (Fig. 2(b)). The voltage scan rate was 0.5 V $s^{-1}$ for all the $I$–$V$ measurements. During the $I$–$V$ loop measurements, the voltage bias was swept in a sequence of 0 V $\rightarrow$ 8 V $\rightarrow$ −8 V $\rightarrow$ 0 V, as indicated by the arrows in Fig. 2(a). A current compliance ($I_{cc}$) of 1 mA was applied to avoid the permanent dielectric breakdown of the device. The pristine device exhibits a low resistance state. When the applied voltage was increased from 0 V, a ‘reset’ or ‘off’ process occurred at 4.1 V, which is called the ‘reset voltage’. The process triggers a slow change instead of an abrupt change of the device from low resistance state (LRS) to high resistance state (HRS). This result cannot be explained by the conductive filament model, which is often utilized to describe the RS phenomenon in several oxides. According to this model, the device should be in a high resistance state originally and needs a ‘forming’ process to transfer into a low resistance state, which contradicts the present findings. When the applied voltage was increased from 4.1 V to about 7 V, the current decreased surprisingly, i.e., the NDR effect occurred. However, when the voltage was further increased from 7 V, but not exceeding 8 V, the current increased by only a small amount. The device was at HRS while decreasing the voltage from 8 V to 0 V. Subsequently, when sweeping the voltage in the reverse direction, a ‘set’ switching behaviour was observed, i.e., the transition from
HRS to LRS occurred. Fig. 2(c) shows the $I-V$ loops with the different voltage sweeping ranges. As shown in the inset of Fig. 2(c), the device was unable to show RS behaviour until the applied maximum voltage was equal to or higher than 4 V. Moreover, the NDR effect can only appear in the positive voltage region and the maximum applied voltage should be equal to or higher than 5 V. These results indicate that the NDR effect is closely related to the polarity and sweeping range of the applied voltage.

In order to more clearly observe the circumstances under which the NDR effect can occur, the forward (from negative to positive voltages) and reverse (from positive to negative voltages) $I-V$ curves were measured individually, as displayed in Fig. 3(a) and (b), respectively. The forward $I-V$ curves in Fig. 3(a) are in agreement with the $I-V$ loops shown in Fig. 2(c), indicating that the device can only exhibit the NDR effect in the positive voltage region when the maximum voltage is equal to or higher than 5 V. Moreover, as indicated by the red and green dotted lines in Fig. 3(a), the onset voltage for the appearance of the NDR effect varies between 3 V and 4.6 V as the voltage sweeping range is changed. On the other hand, the NDR effect was never observed in all the reverse $I-V$ curves with varied sweeping voltage ranges, as shown in Fig. 3(b).

To characterize the endurance performance of the Cu/BaTiO$_3$/Ag device, the $I-V$ loops were repeated for 1000 cycles with the applied voltage varying from –8 V to 8 V or from –9 V to 9 V, as shown in Fig. 4(a) and (b), respectively. It is clearly notable that the $I-V$ loops have a high degree of overlap under a maximum applied voltage of 8 V and 9 V, which hardly show any degradation even after 1000 cycles, indicating that the device has high stability and repeatability. Fig. 4(c) shows the cycle number dependence of the device’s resistance at LRS and HRS, respectively. During the measurements, the on/off ratio ($R_{\text{HRS}}/R_{\text{LRS}}$) was always kept at about 200 with the applied voltage fixed at 0.1 V. The retention time performance of the device has also been characterized at room temperature, as displayed in Fig. 4(d). One can see clearly that the resistances at both the LRS and HRS keep almost unchanged under a fixed applied voltage of 0.1 V even after 3000 minutes. All these measurements confirm that the switching between the LRS and HRS is highly controllable, reversible and reproducible, which is very helpful for information storage. It is worth mentioning that all the above results shown in Fig. 2–4 remain almost unchanged when the potential scan rate changes from 0.5 V s$^{-1}$ to 10 V s$^{-1}$.

To get a deeper understanding of the switching behaviours mentioned above, the conduction mechanism of the Cu/BaTiO$_3$/Ag device was investigated. To our knowledge, BaTiO$_3$ is often considered to be a typical n-type semiconductor. To verify this in our studies, a Ag/BaTiO$_3$/p-type Si device (Fig. 5(d)) was fabricated and the corresponding $I-V$ curve was obtained and is displayed in Fig. 5(a).

The rectifying characteristic of the $I-V$ curve demonstrates that a p–n junction was formed between the BaTiO$_3$ layer and the p-type Si substrate, proving that the BaTiO$_3$ is an n-type semiconductor. Usually, the n-type semiconductor BaTiO$_3$ contains a lot of oxygen vacancies, which can serve as trap states to capture electrons. In order to reveal the conduction mechanism of the Cu/BaTiO$_3$/Ag device, the type of the metal–semiconductor contact needs to be clarified at the Ag–BaTiO$_3$ and BaTiO$_3$–Cu interfaces. Therefore, the Ag/BaTiO$_3$/Ag and Cu/BaTiO$_3$/Cu devices were fabricated, as shown in Fig. 5(e) and (f), respectively. Likewise, the $I-V$ curves were measured for these two devices and are displayed in Fig. 5(b) and (c), respectively. The linear $I-V$ curve observed for the Ag/BaTiO$_3$/Ag device demonstrates that the Ag–BaTiO$_3$ interface belongs to an Ohmic contact, while non-linear one in the Cu/BaTiO$_3$/Cu device indicates that the BaTiO$_3$–Cu interface is a Schottky barrier contact. In order to further describe the non-linearity of the $I-V$ curve and quantify the Schottky barrier height, fitting

Fig. 3 The (a) forward and (b) reverse $I-V$ curves obtained for a Cu/BaTiO$_3$/Ag device with varied sweeping voltage ranges. The arrows indicate the voltage sweeping directions and the dotted lines are guides for the eyes.

Fig. 4 The consecutive $I-V$ loops with a cycle number of 1000 measured for the Cu/BaTiO$_3$/Ag device under a maximum applied voltage of (a) 8 V and (b) 9 V. The cycle number (c) and retention time (d) dependences of the device’s resistance at LRS and HRS under an applied voltage of 0.1 V.
calculations were carried out for the $I$–$V$ curves at the HRS and LRS, respectively, which can be seen clearly in ‘ESI,† Fig. S1’.

Hence, the Cu/BaTiO$_3$/Ag device can be regarded as an equivalent circuit consisting of a Schottky-diode (Cu–BaTiO$_3$), an Ohmic resistance (BaTiO$_3$–Ag) and a bulk resistance of BaTiO$_3$ ($R_b$), as shown in Fig. 6(a). Similar to the In/Nb:Si:TiO$_3$/In devices, the conduction mechanism of the Cu/BaTiO$_3$/Ag device can be understood by consideration of trapping/detrapping electrons in the BaTiO$_3$ layer. As mentioned above, the BaTiO$_3$ layer is an n-type semiconductor and exhibits metal-like conduction behaviour, and thus the initial resistance of the Cu/BaTiO$_3$/Ag device is in the LRS. When positive bias was applied to the device, the Schottky-diode (Cu–BaTiO$_3$) was reversely biased. The Schottky barrier height near the Cu–BaTiO$_3$ interface increases upon increasing the applied voltage. Therefore, when the electrons are injected into BaTiO$_3$, they can hardly go through the barrier to reach the cathode. The injected electrons are captured by the trapping states near the cathode interface, as shown in Fig. 6(b). A built-in electric field is formed near the cathode interface, which has an opposite direction to the external electric field. The built-in electric field prevents the injection of electrons, resulting in a decrease in the conduction ability. When the built-in electric field is increased to a certain extent, the current will be reduced upon increasing the bias voltage, showing the negative differential resistance effect. Upon further increasing the bias voltage, the electrons are almost in the trapping state near the Cu–BaTiO$_3$ interface, thereby leading to an increase in the device resistance. However, if the voltage increases to a much bigger value, the electron will have enough energy to go through the barrier directly, leading to the current increasing again with an increase in the voltage, as shown in Fig. 2(c). The resulting HRS will be maintained when the positive bias voltage is reduced. When the negative bias is applied to the device, the Schottky barrier is forward biased. As the absolute value of the negative bias increases, the barrier height decreases and the electrons begin to be released from the trapping states, and thus the conduction ability of the device is enhanced. When a large enough negative bias voltage is applied on the device, most of electrons get away from the trapped states, leading to the device transferring into the LRS. Finally, it is notable that although the above charge trapping/detrapping mechanism can reasonably explain the observed RS behaviours, the redox reaction mechanism$^{31}$ cannot be excluded and further studies towards unravelling the inherent mechanism are necessary.

**Conclusions**

To summarise, we have reported a well-defined RS behaviour with significant NDR effect in the Cu/BaTiO$_3$/Ag device at room temperature. We also showed that this device possesses a high on/off ratio of about 200, long retention time of more than 3000 minutes, good endurance and high reliability. The bipolar RS behaviours were preliminarily considered to be dominated by the trapping/detrapping of electrons in the BaTiO$_3$ layer when they are passing through the Schottky barrier formed at the BaTiO$_3$–Cu interface under different bias voltages. Further studies towards unravelling the hidden physical mechanism are underway. The present studies demonstrate that BaTiO$_3$ may be a promising candidate for RRAM.

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References