Modeling of conducting bridge evolution in bipolar vanadium oxide-based resistive switching memory*

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We investigate the resistive switching characteristics of a Cu/VO_x/W structure. The VO_x film is deposited by radio-frequency magnetron sputtering on the Cu electrode as a dielectric layer. The prepared VO_x sample structure shows reproducible bipolar resistive switching characteristics with ultra-low switching voltage and good cycling endurance. A modified physical model is proposed to elucidate the typical switching behavior of the vanadium oxide-based resistive switching memory with a sudden resistance transition, and the self-saturation of reset current as a function of compliance current is observed in the test, which is attributed to the growth pattern of the conducting filaments. Additionally, the related conducting mechanism is discussed in detail.

Keywords: resistive switching, vanadium oxide, conducting filament, magnetron sputtering

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1. Introduction

Electrochemical resistive switching memory, also named conducting-bridge random access memory (CBRAM), has been attracting much attention recently due to its low operation voltage, high programming speed, and simple fabrication.[1] The typical cell structure of CBRAM is a stack of active electrode/solid electrolyte/inert electrode. Resistive switching in simple binary metal oxide thin film, such as SiO_x,[2] TiO_x,[3] WO_x,[4] ZnO,[5] and MgO[6] has aroused great interest for possible applications in nonvolatile memory devices. Compared with other material systems, binary transition metal oxide (TMO) materials attract much attention for applications in RRAM devices since they have potential advantages such as simple structure, easy fabrication, and excellent compatibility with current complementary metal oxide semiconductor (CMOS) technology. Tran *et al.*[7] studied a unipolar RRAM based on NiSi/HfO_x/TiN structure, and observed well-behaved memory performance in terms of on/off resistance ratio, retention, and readout margin. The conducting filaments (CFs) have been proved to play a critical role in the resistance change process of the stacking structure.[8,9] Fast diffusion ions such as Ag or Cu in the active electrode are supplied into the solid electrolyte and reduced there, thus forming the conducting filaments. However, the formation and rupture dynamics of CFs are still unclear, which hinders the further application of RRAM devices. Therefore, it is required to modify the model and evaluation method for CBRAM.

Vanadium oxide has been known as a traditional binary compound with different polymorphs. The ability for VO_x (such as VO_2, V_2O_5, and V_2O_3) to switch its conductance between two distinct states (insulator and metal) provides the basis for electronic devices such as "smart windows" for energy saving, Mott field effect transistors, electrical–optical switching devices, and thermal sensors.[10–14] The relaxation time to the coexistence state of vanadium dioxide, compatible with non-volatile memory requirements, is longer than 10 years. That is, in 10 years the separation between the high and low resistance states will still be large enough for memory application.[15] The VO_x cell also exhibits self-selective performance and memory switching by electroforming method.[16,17] Vanadium oxide shows potentials in the next generation nonvolatile memory applications, and thus more research efforts should be focused on the effect of the vanadium oxide on the resistance switching (RS) properties.

In this paper, we demonstrate the resistive switching characteristics of Cu/VO_x/W devices. The fabricated cell shows ultra-low switching voltage and great cycling endurance. To determine the reaction related to resistive switching, we characterize the chemical bonding states of VO_x films and Cu electrode by focusing X-ray photoelectron spectroscopy (XPS). By investigating the experimental switching behavior, we develop a modified physics-based model to predict the unique

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switching behavior of the CBRAM. It is found that the comproportionation reactions of Cu account for the reversible and repeatable switching. The RS is also performed by scanning probes, and the dynamics of metallic filaments with RS is studied.

2. Experiment

Si/SiO_2/Ti/Cu/VO_x/W structure was fabricated as a functional device. Initially, a 5-nm-thick titanium layer was deposited on SiO_2/Si by ion beam sputtering as an adhesion layer. Cu film (100 nm) was deposited on Ti adhesion layer by direct current sputtering. The flow rate of Ar was 20 sccm, and the sputtering power was 30 W. The temperature and working pressure of the deposition process were 200 °C and 1.5 Pa, respectively. Then, VO_x thin film was sputtered on the Cu electrode with radio-frequency magnetron sputtering. The sputtering was carried out in Ar+O_2 mixed gas ambient, the flow ratio of Ar to O_2 was 4:1 with a total flow rate of 30 sccm, and the sputtering power was 200 W. The substrate temperature and working pressure of the deposition process were 350 °C and 1 Pa, respectively.

In order to perform the resistive switching of the Cu/VO_x structure, a tungsten probe was used as the top electrode applied with a negative bias, the diameter of the RS spots was 50 μm. To examine the switching behavior of the CFs, the *I*–*V* characteristics of the RS spots were analyzed using a semiconductor parameter analyzer (Agilent B1500).

3. Results and discussion

To understand the conducting mechanism of the CBRAM structure, the crystalline structure of VO_x is determined by XRD. Figure 1 shows the XRD patterns of VO_x thin films. The peaks at $2\theta = 21.4°$, 23.6°, and 26.5° correspond to reflections in the (101) plan of V_2O_5, and (201) and (211) plans of VO_2 phase, respectively.

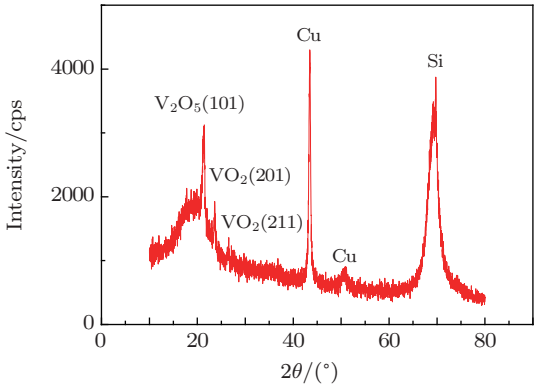


Fig. 1. (color online) XRD patterns of the Cu/VO_x/W thin film cell structure.

In order to further confirm the components of the film, the fabricated cell is analyzed with XPS. The spectra of V $2p_{1/2}$ and Cu $2p_{3/2}$ in the as-deposited film are shown in Fig. 2. It can be seen from the spectra that the main peaks of V $2p_{1/2}$ consist of components V^{3+}, V^{4+}, and V^{5+}. Therefore, we attribute this structure to the significant presence of V^{3+} (515.99 eV), V^{4+} (516.88 eV), and V^{5+} (517.62 eV) peaks in the V $2p_{1/2}$ envelope. One test of our interpretation of the deconvolution is to compare the estimated values of the average stoichiometry based on the ratios of these three components with values determined from the ratios of areas under V and O peaks. The areas under the V^{3+}, V^{4+}, and V^{5+} peaks in the deconvolution of Fig. 2(a) provide the ratios of ~17.96% (V_2O_3), ~37.56% (VO_2), and ~44.48% (V_2O_5).

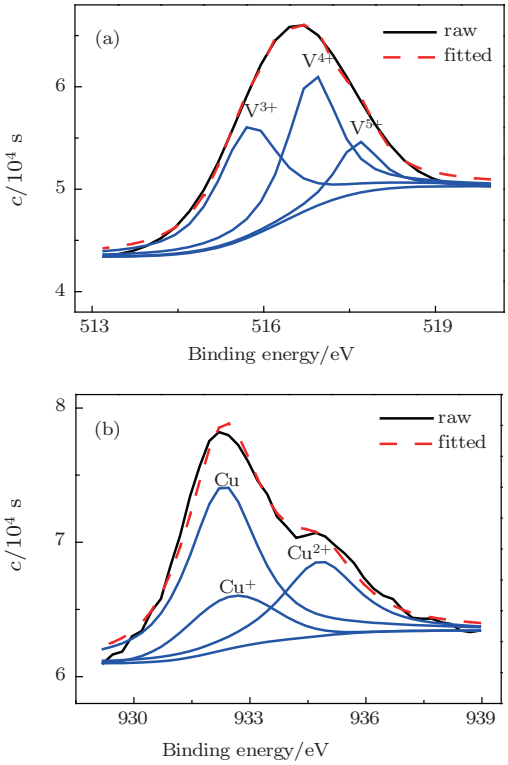


Fig. 2. (color online) XPS diagram of the (a) VO_x thin films and (b) spectrum of Cu electrode.

From the above results, we can learn that the vanadium oxide deposited was in mixture phase. From a chemical viewpoint, VO_x is an excellent dielectric catalyst due to its rich and diverse chemical behaviors based on two factors: the variety of vanadium oxidation states ranging from 2^+ to 5^+, and the variability of oxygen coordination geometries. This structural richness is the source for the existence of differently coordinated oxygen ions which provide an important ingredient for controlling physical and chemical surface properties. Due to its layered structure, VO_x is a promising material for energy storage systems and has a high ionic storage capacity.[18]

It can be seen from Fig. 2(b) that the spectrum of Cu has components of Cu, Cu^+, and Cu^{2+}. It is hard to resolve Cu^+ from Cu because their binding energies are too close. The formation of copper oxide is possibly attributed to the diffusion

of copper atoms in the fabrication process. Several types of evidence, including experimental results and computational simulations indicate that the formation of Cu filament is attributed to the resistive switching behavior.[19] According to the XPS results of existence of CuO_x at the interface of Cu/VO_x structure, we suggest that CuO_xinstead of Cu atoms should be the supplying source for the conducting filament.

Typical bipolar switching characteristics of Cu/VO_x/Cu cell are presented. Figure 3(a) displays the well-behaved I–V curves of bipolar resistive switching, showing the set and reset processes occurring at 0.6 V and −0.35 V. It is worth noting that the forming voltage shows no difference in distribution between the set voltages, suggesting that the switching process does not take place. In order to compare with the Cu/VO_x/W structure, we fabricate VO_x cell with inert metal electrode (Pt/VO_x/W structure). In contrast to the Cu/VO_x/W sample, the inert electrode cell shows an unstable unipolar resistive switching phenomenon with a forming voltage of 5 V. The difference in the switching mode between samples with different electrodes can be only explained by the reaction at the interface in the electroforming process. First, the reaction only deals with the charged ion transfer between the electrode and the dielectric interface, and does not include the ion transport process in the dielectric layer, in which process the Cu ions have been proved to be dominative. Consequently, as the top active electrode is oxidized, fast metal ions drift toward the bottom electrode and are reduced to form the CF there. Thus, the CF vertically grows until it reaches the top electrode, at which time the set occurs. Therefore, we expect that a large number of cations can be supplied from the anode in order to form a filament, and hence, the dielectric layer is expected to have a high ionic storage capacity, and VO_x is proved to be a feasible option material in this process.

Figure 3(b) shows that $I_{\rm reset}$ is dependent on compliance current. An obvious increase trend of the reset current is observed with the increase in $I_{\rm cc}$. Two regimes can be observed in the figure. First, the reset current increases linearly with the compliance current. However, as $I_{\rm cc}$ further increases, the increasing trend of $I_{\rm reset}$ slows down and becomes saturated when $I_{\rm cc} = 9$ mA.

A modified physical model based on metal ion conducting filament is proposed to explain the above switching process of resistive switching in Cu/VO_x/W device. As has been proved, the set process is interpreted as a dielectric soft breakdown associated with the active electrode ions migrating toward the cathode. There has been experiments proving that varying the set compliance current $I_{\rm cc}$ at the set point could modulate the low resistance state (LRS) cell resistance $R_{\rm LRS}$ in the CBRAM.[20] A universal inversely proportional relationship exists between the cell resistance and the set compliance current

$$R_{\rm set} = \frac{C}{I_{\rm cc}}, \tag{1}$$

where C is a constant fitting parameter. As shown in Fig. 3(b), the data from Cu/VO_x/W CBRAM cells satisfy the inversely proportional relationship.

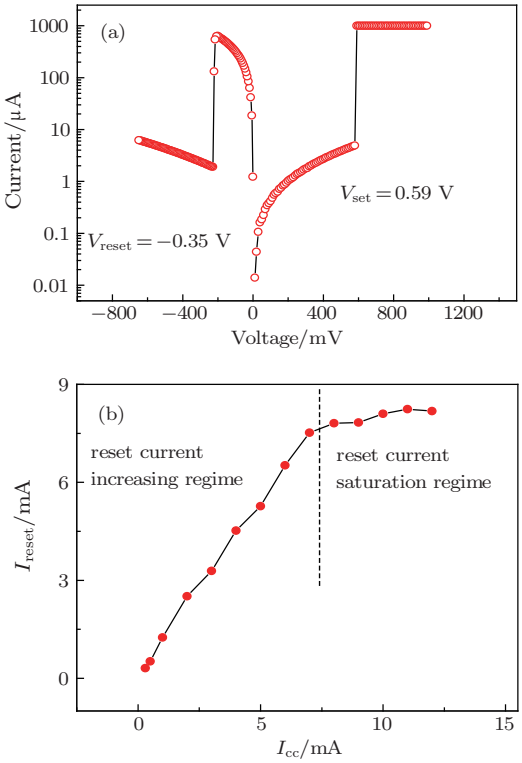


Fig. 3. (color online) (a) Set and reset I–V characteristics of Cu/VO_x/W cell; (b) trend of $I_{\rm reset}$ as a function of $I_{\rm cc}$. The sweep scope of $V_{\rm set}$ is set to 0–1.5 V.

The evolution of the CF height $h_{\rm CF}$ in a time interval dt can be expressed by the quantity of the charges in the reduction as

$$N_{\rm m} h_{\rm CF} = \frac{J}{Zq}\,{\rm d}t, \tag{2}$$

where $N_{\rm m}$ is the volume density of the metal (i.e., the number of metallic particles in unit volume), q is the charge, Z is the number of the ions charged, and J is the ion current density. The current density J can be described by the Mott–Gurney ionic hopping current in solid electrolytes as

$$J = 2ZqN_{\rm i}af \exp\left(-\frac{E_{\rm a}}{k}T\right)\sinh\left(\frac{ZqE_{\rm a}}{2kT}\right), \tag{3}$$

where $N_{\rm i}$ is the density of the metal ions in the solid electrolytes, f is the attempt-to-escape frequency, $E_{\rm a}$ is the activation energy, E is the electric field, kT is the thermal energy, and a is the effective hopping distance. This equation is used to account for the ion migration dependence on electric field. Combining Eqs. (2) and (3), we obtain the evolution rate of the filament height as

$${\rm d}h/{\rm d}t = v_{\rm h} \exp\left(-\frac{E_{\rm a}}{kT}\right)\sinh\left(\frac{ZqEa}{2kT}\right). \tag{4}$$

According to the above equation, larger set compliance would supply more metal ions to form a stronger CF when the set occurs. The increased volume of the CF in the vertical growth stage can be calculated by the accumulation of the metal atoms that discharge there. The above CF vertical/lateral evolution dynamics can be applied to both the set and reset processes, and this means that larger current and voltage need to be used to dissolve the stronger CF in the reset process.

The fast growth regime is due to the high local temperature after nucleation as a result of Eq. (4) and of the relatively large initial voltage V. The voltage across the fabricated device V is virtually equal to the applied bias V_{apply} during the initial stages of the set transition due to initial high resistance of the cell. As the resistance of the device R becomes comparable to the equivalent resistance of the testing circuit, the voltage across the cell also decreases according to the voltage partition formula

$$V \approx V_{\text{apply}} \frac{R}{R_{\text{SPA}} + R}. \tag{5}$$

As a result, T also decreases due to the quadratic relationship of Joule heating effect, thereby quenching the filament growth rate. The CF growth during set under a compliance system, consisting of a load resistance or transistor in series with the cell, can thus be viewed as a self-limiting process, where the increase in the filament diameter results in an exponential decrease in the driving force for ion migration, thus suppressing conducting path growth.

Figure 4 shows the distribution of forming voltages. The dielectric breakdown has been proved to be a "weak link" event controlled by the first conductive filament between the electrodes; therefore it is expected to follow a Weibull statistics.[21] In our experiments, the distribution of forming voltages indeed follow a Weibull distribution, confirming that the mechanism of the Cu/VO_x /W cell is of filament type.

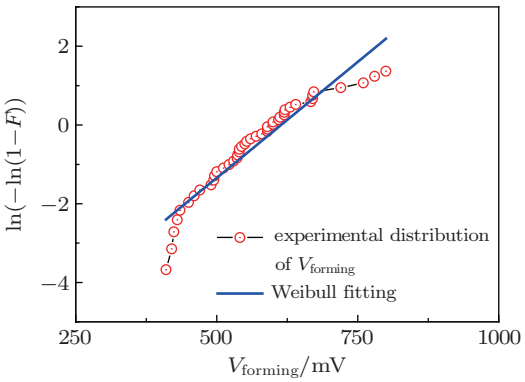


Fig. 4. (color online) Probability distribution of forming voltages. F is the accumulative probability.

Based on the XPS results and conducting filament model, a possible filament forming process based on electron trapping and de-trapping on the defects of nano-sized CuO_x is proposed to explain the mechanism of resistive switching in Cu/VO_x/W device as shown in Fig. 5. The copper atoms diffuse into surrounding VO_x grains to produce CuO_x. The migration of Cu ions is induced by the electric field and joule heating of the electric current. During the migration of Cu^+/Cu^{2+} ions, they are reduced to neutral Cu, thus forming a conductive filament. Positive bias induces the electron trapping on the defects, and the current transports along the occupied defects, which means that conducting filaments are formed and device switches to LRS. Negative bias triggers electron de-trapping on the defects, resulting in the device switching to HRS.

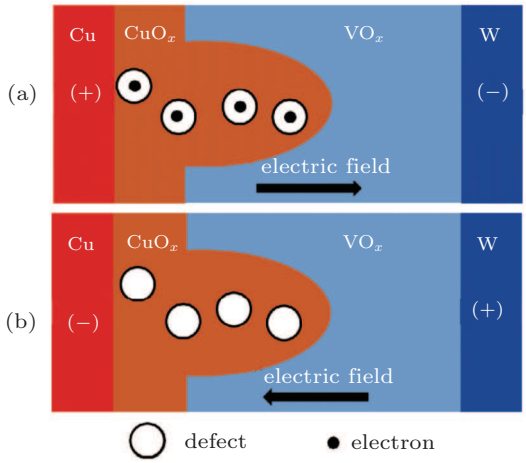


Fig. 5. (color online) Illustration of physical model based on electron trapping and de-trapping on the defects of nano-sized Cu_xO.

4. Conclusions

VO_x resistive switching on Cu electrode is demonstrated in this paper. The VO_x layer acts as the dielectric and the copper substrate acts as active metal electrode. XPS results suggest that Cu_xO might play a role in the formation of filament. The diffusion and oxidation of active metal electrode should be taken into consideration in the fabrication of cell devices. Additionally, self-saturation properties of the cell device are discussed. The dynamics of the metal conductive filaments accounts for the dependence of I_{reset} on the compliance current. A physics-based model is proposed to quantify the retention behavior of the bipolar vanadium oxide-based RRAM device. Due to the conduction and rupture of the filament in the oxide layer, a sharp resistance transition occurs during the retention process. The proposed model can accurately describe the resistive switching behavior of the oxide-based RRAM device as well as the dependence on applied voltage. Reproducible switching behaviors and the simple fabrication process of the VO_x film provide a path to optimizing device design and operation so as to maximize the RRAM performance.

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