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Resistive switching properties of alkaline earth oxide-based memory devices

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ABSTRACT

A reduced high-resistance state (HRS) current assists in obtaining high ON/OFF ratio and is beneficial to operation flexibility. This study proposes that less difference in the atomic radius of alkaline earth oxide-based memory devices is beneficial to reduce the HRS current. Forming-free resistive-switching behavior in the alkaline earth oxide-based memory device using magnesium titanate (MTO), strontium titanate (STO), and barium titanate (BTO) thin films is fabricated by sol-gel method. The dependence of HRS current on the difference in atomic radius was predicted by the Hume–Rothery rule and confirmed experimentally. The hydrolyzed particles, surface roughness, and density of oxygen vacancy were decreased when the difference in atomic radius between the Ti element and alkaline earth metal was less. Compared with the BTO thin film, the MTO thin film has fewer particles, smoother surface, and less density of oxygen vacancy, resulting in lower HRS current. Thus, suitable element selection for the alkaline earth oxide-based memory devices can reduce the HRS current.

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1. Introduction

Resistive random access memories (RRAMs) are one of the most promising candidates for next-generation nonvolatile memories because of their low power operation, simple structure, high-density integration, and high speed operation [1]. Recently, many research groups have focused on finding the appropriate resistive switching materials and improving the device performances [2–4]. Among various materials, the titanate oxide plays an important role in memory applications owing to its wide applications and outstanding properties including good chemical stability, low thermal conductivity, and good compatibility with conventional semiconductor technology. The Hume–Rothery rules state that, considering that the atomic radius of the solute and solvent atoms differ by >15%, phase separation may occur. This phenomenon indicated that suitable element selection for the ATiOx-based (A = Mg, Sr, Ba) memory devices is beneficial to the surface morphology. Generally, the elements in the same period tend to have similar properties. To achieve a fair comparison, the selected elements prepared via a sol-gel method have to in the same period. Using the sol-gel method for the growth of oxide films can bring a lot of advantages, such as easy stoichiometric control, low fabricating temperature, compatible with flexible substrate, and roll-to-roll process. Compared with other periods, the more elements in the alkaline earth group can be used to prepare the ATiOx precursors. Using the alkaline earth group to investigate the surface morphologies and memory properties can offer versatile routes for varied metal oxide-based memory devices fabrication. In the BTO case, the existence of more amounts of particles and rougher surface morphologies result in the higher high resistance state (HRS) current. Relative higher HRS current was due to the more leaky paths occurred by the spacing between particles when the voltage was applied. Further, the retention ability in the low resistance state (LRS) of the MTO-based RRAM was more stable than that of the BTO-based RRAM. Thus, the smooth surface roughness may facilitate the stable resistive switching [5,6]. Hence, solution-processed materials that allow facile control of the chemical compositions and the suitable alkaline earth metal selection are required to synthesize the resistive layer of RRAM devices. The relationship between the difference in atomic radius and memory properties in the alkaline earth oxide-based memory devices has been investigated.

2. Experimental

In ΠIa group, the same sol-gel method cannot be applied to Be and Ra elements to prepare the sol precursor, and Ca (or calcium acetate) cannot be easily dissolved into glacial acetic acid. Thus, the alkaline earth metals selected were Mg, Sr, and Ba to prepare the MTO, STO, and BTO solutions, respectively. The MTO, STO, and BTO solutions were synthesized according to the flow chart shown in Fig. 1(a). First, an appropriate amount of material A (material A = magnesium acetate, strontium acetate, barium acetate) was added into glacial acetic acid at 100 °C and stirred. Second, Ti isopropoxide was mixed with acetylacetone and subsequently dissolved in 2-methoxyethyl. Then, the 0.5 M MTO, STO, and BTO solutions were prepared by adding 2-methoxythanol and stirred for 24 h. The MTO, STO, and BTO thin films were deposited by spin-coating on ITO/glass substrate followed by baking at 100 °C for

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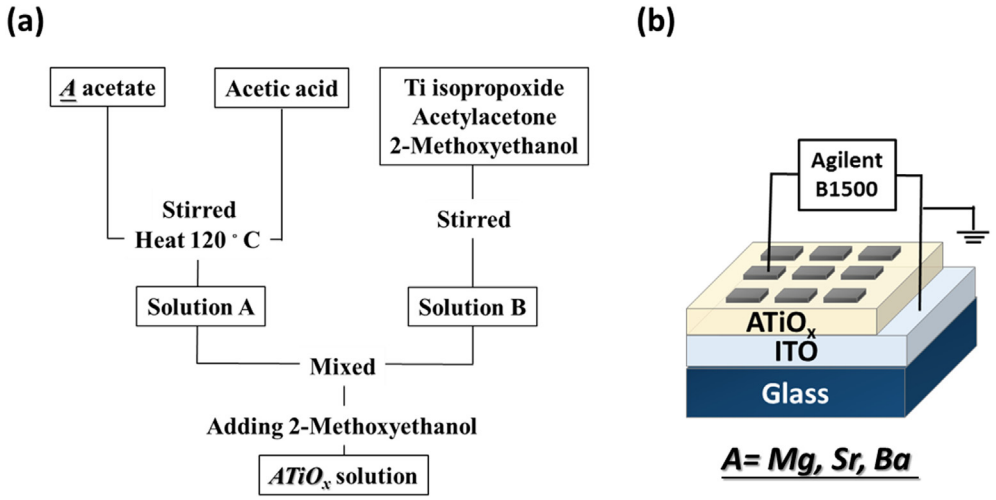

Fig. 1. (a) Flow chart of the preparation of the AZO_x sol precursor. (b) Schematic of the device with Al/AZO_x/ITO structure. (A = Mg, Ca, Sr).

15 min. The top electrode contained an Al film with a diameter of 3 mm^2. Fig. 1(b) illustrates a schematic of the $ATiO_x$-based RRAMs (A = Mg, Sr, Ba).

3. Results and discussion

Figs. 2(a)–(i) show the X-ray photoelectron spectroscopy (XPS) patterns obtained after 90 s of Ar^+ ion sputtering, thereby representing the bulk layer of the MTO, STO, and BTO thin films. The atomic percentages of Mg, Ti, and O were obtained at 12%, 20%, and 68%, respectively. The peak in the energy of 50.3 and 458.3 eV represent MgO and TiO_2, respectively. For STO thin film, the atomic percentage of Sr, Ti, and O were obtained at 17%, 18%, and 65%, respectively. By fitting the peaks of Sr3d signal, two peaks at 132.9 eV and 135.2 eV are revealed to $SrCO_3$ and SrO, respectively. The binding energy of TiO_2 is approximately 458.2 eV. For BTO thin film, the atomic percentage of Ba, Ti, and O were obtained at 20%, 16%, and 64%, respectively. The binding energy of TiO_2 is approximately 458.1 eV. The energy peaks of 779.9 and 458.1 eV were obtained by BaO and TiO_2, respectively. The peaks for the O1s core level may be consistently fitted by two different near-Gaussian sub-peaks at 529.8 and 531.4 eV. The binding energy of the lattice oxygen is 529.5 eV, which is attributed to the bond between the O_2 ions and metal ions. The peak at 531.4 eV was associated with non-lattice oxygen ions, such as oxygen vacancies [7]. The positions of the peaks are obtained from the XPS database of NIST (Naumkin et al. 2012).

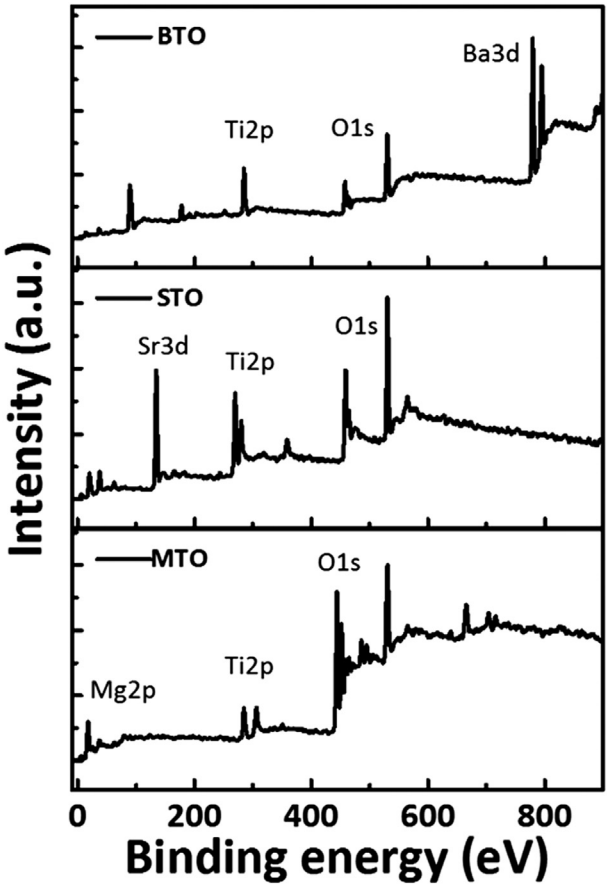

Fig. 2. XPS spectra of the MTO, STO, and BTO thin films.

Fig. 3(a)–(f) displays the AFM images of the surface morphologies and particles at MTO, STO, and BTO thin films. The corresponding root–mean–square roughness (R_{rms}) of MTO, STO, and BTO thin films were 0.5, 1.1, and 1.6 nm, respectively. More particles were observed from the surface of the STO and BTO thin films. The surfaces of the STO and BTO thin films were rough given the high density of particles, whereas the MTO thin film has nearly no particles in the surface.

The Hume–Rothery rules are a set of basic rules that describe the conditions under which an element could dissolve in a metal, forming a solid solution. The Hume–Rothery rule can be expressed as Eq. (1):

$$\%\text{difference} = ((r_A - r_B)/r_B) \times 100\% \leq 15\% \quad (1)$$

where, r_A is the radius of solute, and r_B is the radius of solvent. The differences in the atomic radius of Mg, Sr, and Ba between Ti atoms were 8%, 46%, and 51%, respectively. The electronegativity of Mg and Ti atoms on the Pauling scale is close (Mg: 1.3, Ti: 1.5). The Hume–Rothery rule states that if the % difference of atomic radii is <15% and the electronegativity of the elements is also similar, then a substitutional solid solution is most likely to be formed. These results revealed that the number of particles and R_{rms} value decreased with decreasing difference in atomic radius. Hence, the suitable element selection for the sol-gel $ATiO_x$ type material can obtain better surface morphology and smooth surface. Fig. 3(g)–(i) illustrate the scanning electron microscopy (SEM) cross-section of MTO, STO, and BTO thin films on the ITO substrate. The corresponding layer thickness is 70 to 75 nm.

The typical I—V curves of MTO, STO, and BTO memory devices are presented in Fig. 4(a). The devices showed the typical bipolar resistive switching behavior. The devices were operated without a forming

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