Effects of different dopants on switching behavior of HfO_2-based resistive random access memory*

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(Received 4 July 2014; revised manuscript received 4 August 2014; published online 20 August 2014)

In this study the effects of doping atoms (Al, Cu, and N) with different electro-negativities and ionic radii on resistive switching of HfO_2-based resistive random access memory (RRAM) are systematically investigated. The results show that forming voltages and set voltages of Al/Cu-doped devices are reduced. Among all devices, Cu-doped device shows the narrowest device-to-device distributions of set voltage and low resistance. The effects of different dopants on switching behavior are explained with deferent types of CFs formed in HfO_2 depending on dopants: oxygen vacancy (Vo) filaments for Al-doped HfO_2 devices, hybrid filaments composed of oxygen vacancies and Cu atoms for Cu-doped HfO_2 devices, and nitrogen/oxygen vacancy filaments for N-doped HfO_2 devices. The results suggest that a metal dopant with a larger electro-negativity than host metal atom offers the best comprehensive performance.

Keywords: RRAM, conductive filament, doping

PACS: 73.40.Ns, 85.35.–p, 85.90.+h **DOI:** 10.1088/1674-1056/23/10/107306

1. Introduction

HfO_2-based resistive random access memory (RRAM) was recently intensively studied because it has a better switching performance than other transition metal–oxide (WO_x, ZnO_x, ZrO_2, TaO_x, CuO_x) based RRAMs.[1–3] The formation and rupture of conductive filaments (CFs), which may consist of oxygen vacancies or metallic atoms, are regarded as being the resistive switching mechanism in metal oxides. One critical issue for the large-scale manufacturing of RRAM is poor uniformity of both device-to-device and cycle-to-cycle, including the wide distributions of switching voltages and resistances of low resistance state (LRS). The decrease of forming voltage is another issue. Ion implantation is used as an effective approach to improve the performance of RRAM.[4–7] Zhao and Park[8] investigated the forming energy of oxygen vacancies and *I*–*V* characteristics by the first principles simulation, and gave some rules for dopants selection. Unfortunately, the resistive switching behavior is so complicated that simulation is far from the real case. In this paper, Al (Cu or N) ions are implanted into HfO_2 films to experimentally investigate the effects of different dopants on the resistance switching behavior. The experimental results are explained based on different types of conductive filaments. Finally, we propose a fundamental rule for selecting appropriate doping elements.

2. Experimental details

Both undoped and doped HfO_2-based RRAM devices were fabricated on thermally oxidized Si substrates. A 5-nm Ti adhesion layer and 50-nm Pt were deposited on an SiO_2/Si substrate with RF magnetron sputtering. Then, a 15-nm HfO_2 film was deposited on Pt with an atomic layer deposition (ALD) system under 250 °C, using tetrakis-ethylmethylamino hafnium (TEMAK) and H_2O as precursors. For doped devices, Al (Cu or N) ions were implanted into HfO_2 film with 1×10^{14} cm^{-2} dose under 30 keV. Finally, a 5-nm Ti layer and 70-nm Pt top electrode were deposited. *I*–*V* characteristics were measured with an Agilent B1500 semiconductor parameter analyzer at room temperature. The Pt bottom electrode was grounded and the bias voltage was applied to the Pt/Ti top electrodes. The compliance current of 100 μA was used for set operation of devices. Electro-negativities and ionic radii of relevant elements are shown in Table 1.

Table 1. Electro-negativities and ionic radii of relevant elements.

Element	N	O	Al	Cu	Hf
Electro-negativity	3.1	3.5	1.5	2.0	1.3
Ionic radius/Å	1.46	1.4	0.535	0.73	0.71

3. Results and discussion

3.1. Switching characteristics

The *I*–*V* characteristics of electroforming process are shown in Fig. 1. It is clear that the forming voltages are reduced by 2.2 V and 1.6 V for Al- and Cu-doped devices compared with for undoped devices, respectively. As for N-doped HfO_2 devices, the forming voltage is slightly larger than that for undoped devices.

*Project supported by the National High Technology Research and Development Program of China (Grant No. 2011AA010403).
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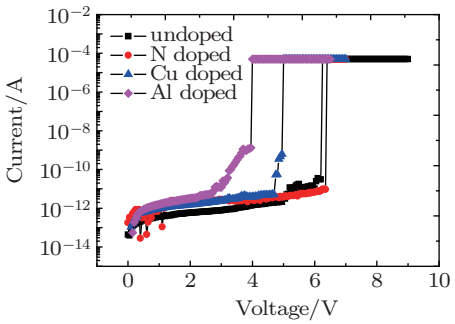


Fig. 1. (color online) Comparisons of electro-forming voltage among undoped and doped devices.

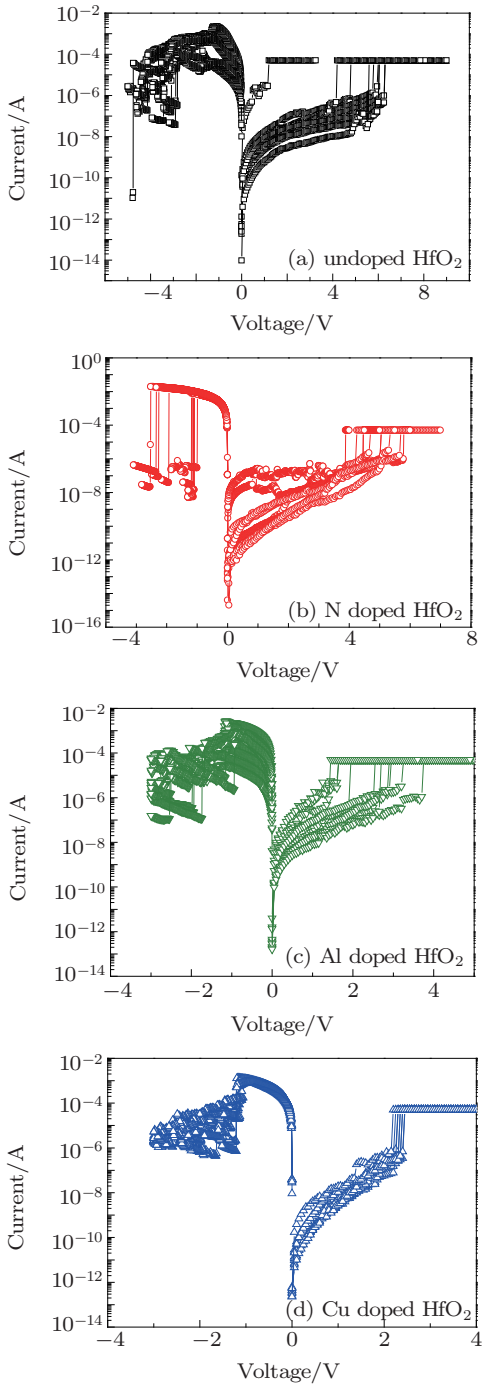


Fig. 2. (color online) *I*–*V* characteristics of (a) undoped, (b) N-doped, (c) Al-doped, and (d) Cu-doped devices.

The *I*–*V* characteristics of bipolar resistive switching behavior are shown in Fig. 2. We can find that the set voltages of Al- and Cu-doped devices are reduced by 2.4 V and 3.5 V, respectively. This is similar to the change of forming voltage after doping because the physical origins of electro-forming and set operation are basically the same. From Fig. 2 it can also be seen that only Cu-doped devices show a significantly improved cycle-to-cycle uniformity.

3.2. Device-to-device uniformity

Device-to-device uniformity is especially important for products. To study the effects of dopants on device-to-device uniformity, distributions of set/reset voltage and low resistance/high resistance of 100 devices are shown in Fig. 3. It is obvious that Cu-doped devices show the narrowest distributions of operation voltage and high/low resistance in all devices.

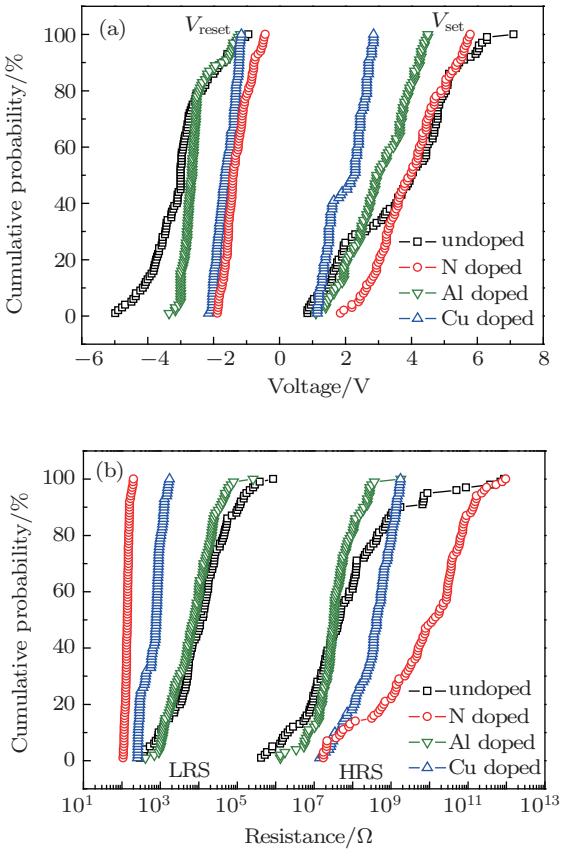


Fig. 3. (color online) (a) Distributions of (a) V_{set} and V_{reset} and (b) LRS and HRS of undoped, N-doped, Al-doped, Cu-doped HfO_2 devices.

3.3. Analysis of switching mechanism

To clarify the switching mechanisms of the ion implanted devices, the *I*–*V* curves are replotted in double logarithmic scale in Fig. 4. For doped devices the low resistance curve exhibits a linear Ohmic behavior, which indicates the formation of conducting filaments in HfO_2 films during their setting. High resistance curve is composed of three regions: the Ohmic region ($I \propto V$), the Child's law region ($I \propto V^2$), and

the steep current increase region, which belong to the typical *I–V* characteristic of trap-controlled space charge limited current (SCLC). According to the above features, we can confirm that the switching mechanisms in all three kinds of devices are conductive filaments.

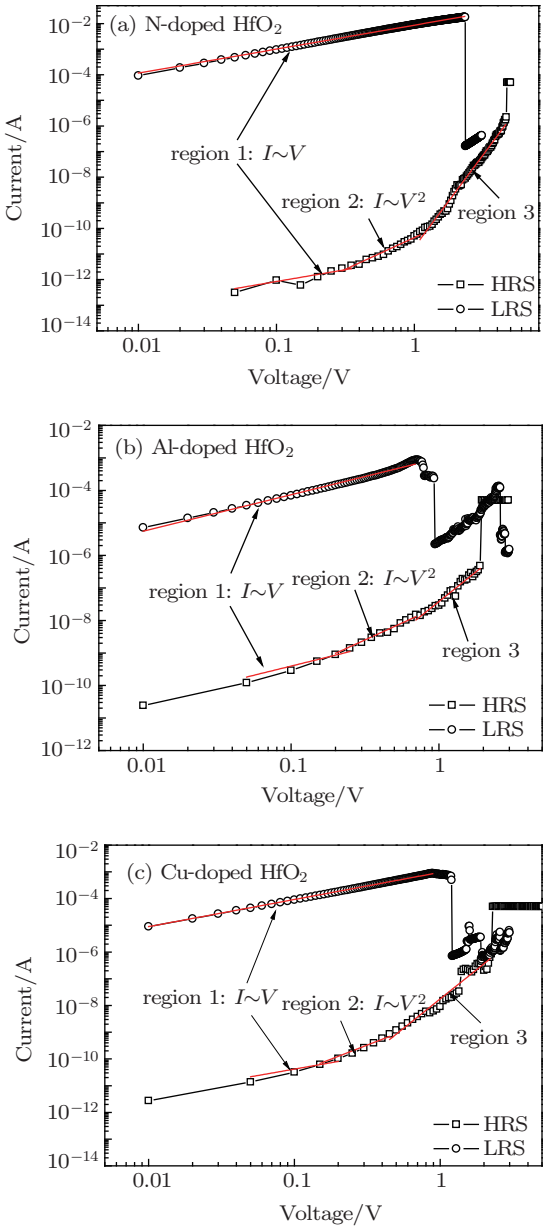


Fig. 4. (color online) Replots of the *I–V* characteristics of doped devices in log–log scale.

Among all of the devices we find that only the Cu-doped device shows both bipolar and unipolar switching behaviors. The *I–V* characteristics of unipolar behavior of Cu-doped device are shown in Fig. 5. This means that at least part of the filament in Cu-doped device consists of metal atoms according to our research.[9] While for the Al-doped device the filament consists of oxygen vacancies. This difference can be further verified by comparing with the Hf 4f XPSs in the regions near the interfaces of HfO_2/bottom electrode in Al- and Cu-doped devices (see Fig. 6). We can see from Fig. 6 that Hf^{4+} peaks in Al-doped devices are weaker than those in Cu-doped devices, while peaks of suboxide Hf in Al-doped devices are much stronger than those in Cu-doped devices. This implies that oxygen vacancies in Cu-doped devices are much less than those in Al-doped devices. In other words, at least part of the filament in Cu-doped device consists of Cu atoms.

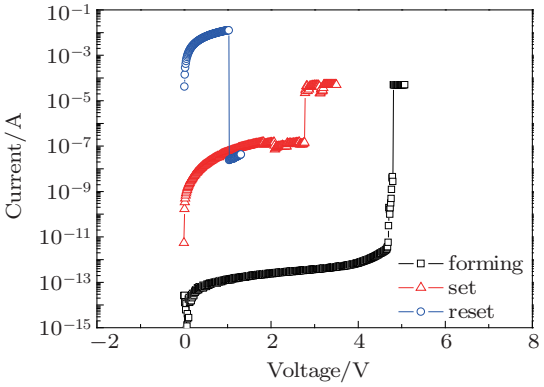


Fig. 5. (color online) Unipolar switching behaviors of Cu-doped device.

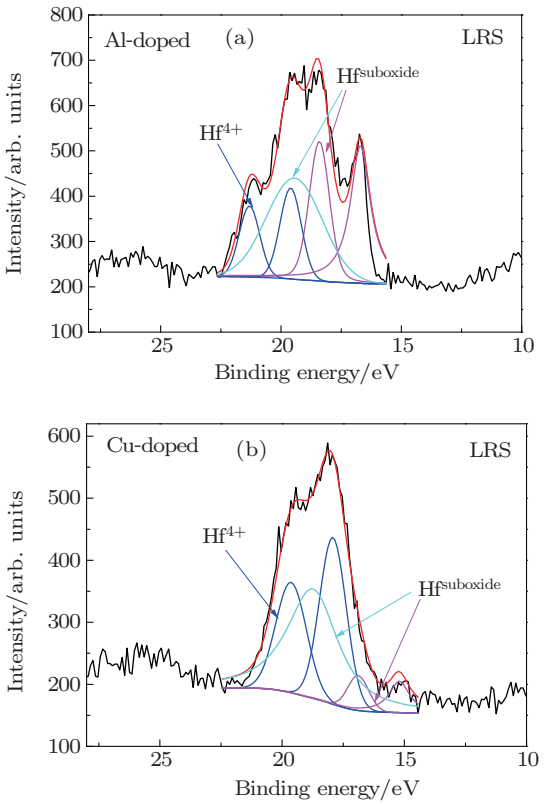


Fig. 6. (color online) Hf $^{4+}$ XPS spectra of Al- and Cu-doped devices at low resistance state: (a) Al-doped and (b) Cu-doped devices.

3.4. An explanation of the different effects of Al, Cu, and N

We can now establish the relationship between electronegativity and ionic radius of the dopant and investigate the corresponding doping effect. The electro-negativities of Al and Hf are 1.5 and 1.3, respectively. Hf atoms exist as substitutional impurities, which leads to lattice distortion and degrades

the local symmetry because of their smaller ionic radius. Al atoms induce more oxygen vacancies and non-lattice oxygen atoms, and make the formation of Vo filament easier. This is why the forming voltage of Al-doped devices is significantly reduced. On the other hand, the device-to-device uniformity is not remarkably improved because of the randomness of the position of substitutional Al atoms, which determines the number and size of filaments.

The Cu–O bond is weaker than Hf–O bond because its electro-negativity is higher than that of Hf. Then, Cu atoms exist in HfO_2 matrix as interstitial impurities. Besides a similar effect of degradation of local symmetry to the effect of Al atoms, interstitial Cu atoms in HfO_2 matrix will partly contribute to the formation of conductive filaments, as mentioned above. This twofold effect explains the reduction of forming/setting voltage and the improvement in device-to-device uniformity. Although the ionic radius of Cu is close to that of Al, the interstitial impurities Cu atoms induce local stress in the HfO_2 film and lower the formation energy of oxygen vacancies, as Al atoms do, resulting in the significant reduction of forming/setting voltage. The difference between Cu and Al lies in the fact that Cu atoms move under applied voltage and relatively high temperature is caused by current. This could explain the improvement in device-to-device uniformity for Cu-doped device.

N atoms with electro-negativity of 3.1 will occupy oxygen sites in a HfO_2 matrix when they are incorporated into the HfO_2 layer. Thus, the resistive switching behavior may be attributed to the formation and rupture of a hybrid filament, consisting of nitrogen and oxygen vacancies. On the one hand, N atoms will inhibit O diffusion and increase the formation energy of oxygen vacancies, which restricts the formation of oxygen vacancies. On the other hand, the electro-negativity difference between Hf and O is larger than that between Hf and N, indicating that the Hf–O bond is stronger than the Hf–N bond. In other words, Hf–N bond is easier to break than the Hf–O bond. As a result, the forming and setting voltages of N-doped devices are close to those of undoped devices and fluctuate depending on the competition between N and O vacancies.

4. Conclusion

We investigated the effects of different doping atoms (Al, Cu, and N) on resistive switching of HfO_2-based RRAM. The resistive switching characteristics in all devices are attributed to their conductive filaments. Our experimental results show that both Al and Cu doping can reduce the forming voltage and setting voltage. Only Cu-doped device improves the device-to-device uniformity remarkably. The above effects of dopants are found to be due to different compositions of filaments at a low resistance state. We find that a doping metal dopant with larger electro-negativity than the host metal atom is a good choice to achieve comprehensive switching performance.

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