

Enhanced resistive switching behaviors of HfO₂:Cu film with annealing process

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ABSTRACT

The effects of Cu doping and annealing process on crystal structure and resistive switching (RS) characteristics of HfO₂ films fabricated by RF magnetron sputtering were investigated. The chemical compositions of the films were characterized by X-ray photoelectron spectroscopy. The defects induced by Cu dopants played an important role on the RS characteristics. The enhanced ON/OFF ratio and reduced switch voltages were demonstrated for the doped film. The further annealing process for HfO₂:Cu film not only decreased the switch voltages but also improved the distribution of the switch voltages of the film. The RS behaviors of HfO₂:Cu films can be well explained by space charge limited current (SCLC) effect.

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1. Introduction

RRAM has attracted lots of interest as the next generation non-volatile memory due to its potential merits, including excellent scalability potential, fast operation speed, and low power consumption [1,2]. The resistive switching (RS) effects can be realized in various materials [2–4], especially in binary transition metal oxides (TMOs) for simply controllable composition and good compatibility with complementary metal oxide semiconductor (CMOS) process. The RS behaviors in binary TMO, such as CuO [5], TiO₂ [6], and HfO₂ [7,8] have been deeply studied in terms of device performance and RS mechanism. Although switching mechanisms are still under debate, the filamentary model is identified as a dominant one in binary TMO films. In practical applications, there are some open issues still remained to be solved. For example, how to improve the fluctuations of switching parameters and how to reduce the rather high operation current. Due to the random nature of electrical breakdown, the resistance states and related switching parameters usually vary in a large scale. Many methods have been proposed to modify the RS behaviors, such as inserting the buffer layer (metal or alloy) [9,10], annealing process [11,12] and doping technology [13,14] which is considered as one of the most effective ways to improving the RS performance. Cu is compatible with

CMOS technology and owns good mobility and conductivity, being used as a doping material to improve the RS properties [3,4]. Meanwhile, the proper thermal annealing process can improve device performance by affecting the crystal structure and electrical properties of the films [11].

In this paper, the doping technology and the annealing process are combined together to enhance the RS behaviors of HfO₂-based RRAM. The Cu/X/n⁺Si (X = HfO₂, HfO₂:Cu, AHfO₂:Cu. AHfO₂:Cu means the HfO₂:Cu film with annealing process) structures were fabricated to investigate the RS characteristics. The results show that all devices show the bipolar RS behaviors and an improvement of RS behavior was obtained by HfO₂:Cu film with annealing process.

2. Experiment

The Cu/X/n⁺Si (X = HfO₂, HfO₂:Cu, AHfO₂:Cu) structures were fabricated. After standard cleaning of Si wafers, the 20 nm thick HfO₂ film was grown on the Si wafer by RF magnetron sputtering at room temperature with a base vacuum of 7.8×10^{-5} Pa. The metal Hf target (99.995%) and highly pure O₂ (99.999%) were used as the source of Hf and reactive gas respectively. During the deposition process, the deposition rate was 1 nm/min, the flow rate ratio of Ar:O₂ was 12:3, the working pressure was 0.3 Pa, and the sputtering power was 80 W. Under the same deposition condition, HfO₂:Cu film (doped with 6% Cu) was fabricated by loading the copper uniformly on metal Hf target. Then using heat pulse AG610 atm

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controllable rapid annealing furnace, HfO_2 :Cu film underwent the rapid annealing process of 200 °C for 10 min in N_2 atmosphere, named AHfO_2 :Cu film. Finally, the Cu top electrodes were deposited on the film by evaporation using a shadow mask to pattern the size. The structure diagrams of three samples were shown in Fig. 1(a). The crystal structures of the films were characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM). The Cu element was verified to be present in HfO_2 :Cu film by X-ray photoelectron spectroscopy (XPS). The electrical testing was carried out by HP 4155C semiconductor characterization system at room temperature by applying the bias voltage to the top electrode while the bottom electrode was grounded.

3. Results and discussion

Fig. 1(a) shows the diagram of $\text{Cu}/\text{X}/\text{n}^+\text{Si}$ structure for I – V measurement. Fig. 1(b) displays the crystal structures of HfO_2 , HfO_2 :Cu, and AHfO_2 :Cu films. For HfO_2 film, no intense diffraction peaks was observed except a broad peak, which was the same for HfO_2 :Cu, and AHfO_2 :Cu films. It is found that the broad peak of HfO_2 :Cu film shifts slightly to higher diffraction angle, indicating the occurrence of shrinkage induced by Cu-doping [15]. It may be due to the replacement of the larger Hf^{4+} (0.071 nm) by the smaller Cu^{1+} (0.046 nm) or Cu^{2+} (0.062 nm). For AHfO_2 :Cu film, the broad peak can not be observed obviously which may be due to the diffusion of Cu in HfO_2 film. It is inferred that the main phase of the three films prepared is amorphous. The SEM surface images of

HfO_2 , HfO_2 :Cu, and AHfO_2 :Cu films are provided to prove the above results, as shown in Fig. 1(c) and (d). Fig. 1(d) indicates that doping Cu in HfO_2 film does not change the film structure significantly, which is consistent with Jia' study [3]. Also, the annealing process results in no crystallization of the film, as shown in the inset of Fig. 1(d).

Fig. 2(a) and (b) presents the typical bipolar RS behaviors and distributions of switch parameters of HfO_2 , HfO_2 :Cu and AHfO_2 :Cu samples respectively. In Fig. 2(a), the current increases sharply at a positive voltage (V_{set}), indicating a switch from an initial state to a low resistance state (LRS). The LRS remains when the voltage sweeps back to 0 V. By applying the negative bias, the current decreases sharply at the reset voltage (V_{reset}), which is defined as the point where the current is the largest. After the reset process, the device switches back to the high resistance state (HRS) and remains. For HfO_2 sample, the ON/OFF ratio was smaller than 10^2 . Meanwhile, the V_{set} and V_{reset} were about 4 V and –6 V, as shown in Fig. 2(b) which was the statistical result of 50 switching cycles in three samples. While for HfO_2 :Cu and AHfO_2 :Cu samples, improvement in RS characteristics was observed, in terms of ON/OFF ratio larger than 10^3 (Fig. 2(a)) and switch voltages, which is consistent with the studies that doping can modify the RS performance [13,16]. Clearly seen, doping Cu in HfO_2 film decreased the switch voltages and the annealing process not only decreased the switch voltages further but also greatly improved the distribution of the switch voltages, as shown in Fig. 2(b). The AHfO_2 :Cu sample showed relatively low operating current during switching process.

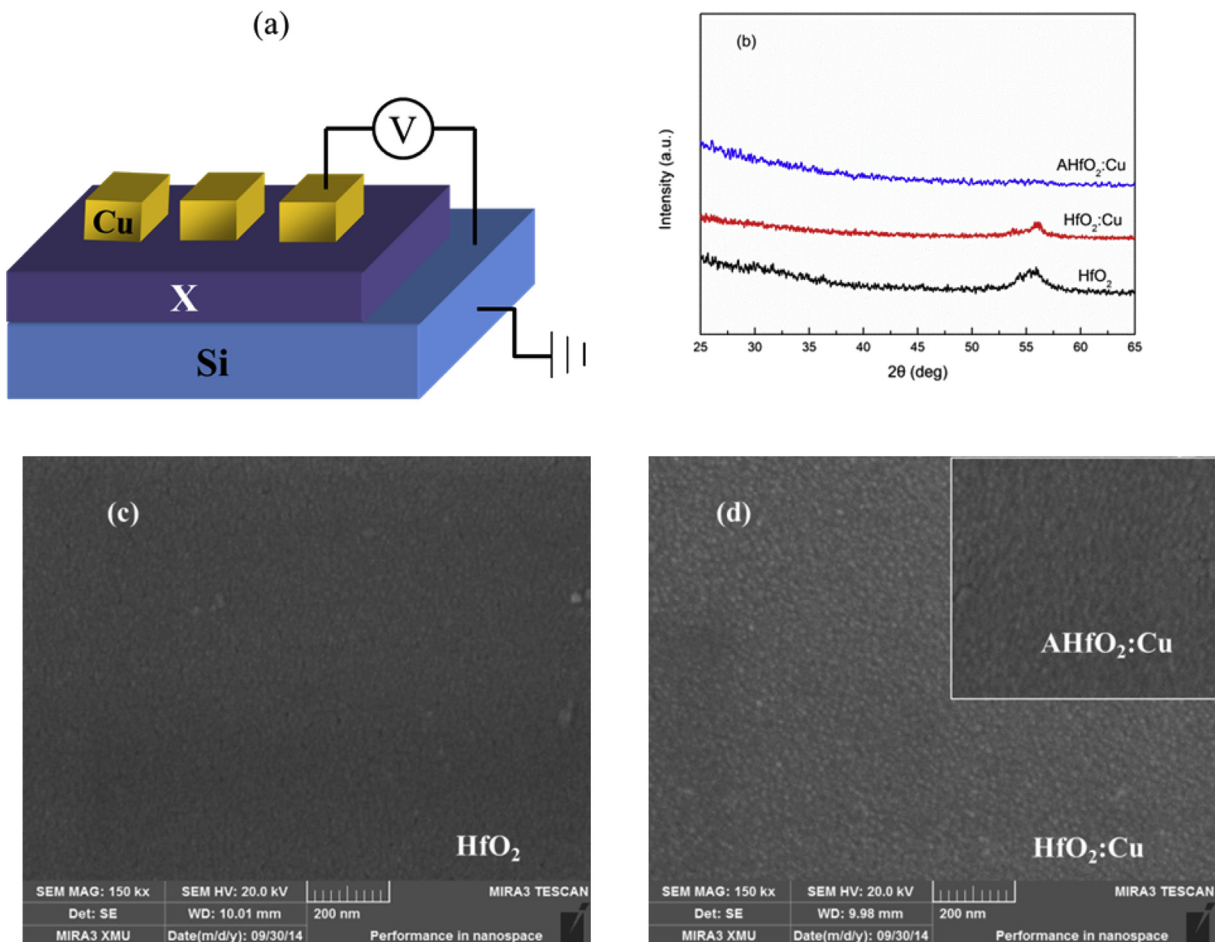


Fig. 1. (a) The structure diagram of $\text{Cu}/\text{X}/\text{n}^+\text{Si}$ ($\text{X} = \text{HfO}_2$, HfO_2 :Cu, AHfO_2 :Cu) cell. (b) The XRD patterns of three films. The SEM surface images of (c) HfO_2 and (d) HfO_2 :Cu films. The inset of (d) shows the SEM surface image of AHfO_2 :Cu film.

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