Investigation on the abnormal resistive switching induced by ultraviolet light exposure based on HfOx film

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ABSTRACT

Effect of ultraviolet (UV) light exposure on the resistive switching characteristics of a ITO/HfOx/TiN structure were investigated in this study. Samples exposed with and without ITO shield film exhibit distinct switching characteristics, including leakage current, I–V curves, set and reset voltage fluctuation. Based on random circuit network simulation by Liu et al., we suggest the distinction was attributed to the different filament shapes during forming process. Defects preexisted inside the HfOx film can cause large difference on the electrical properties. Therefore, the UV laser exposure is a critical issue on the electrical characteristics of RRAM devices.

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1. Introduction

The resistive switching (RS) phenomenon has attracted significant attention recently in view of its potential for nonvolatile memory application – resistive random access memory (RRAM). RRAM offers a possibility of high density integration, lower power operation, easier down-scaling and Si semiconductor compatibility [1]. This phenomenon has been demonstrated in different types of inorganic, organic, polymeric materials, and transition metal oxides. In recent research, several factors have been reported to influence the switching properties of RRAM strongly, such as operating type [2], current compliance [3], forming process [4], electrode materials [5,6], and treatment condition [7]. However, based on the proposed factors, the physical origin of the switching mechanism is still a subject of ongoing debate, though it is suggested to be closely related to the formation and rupture of conducting filamentary paths by an applied voltage. It is thus necessary to investigate other factors in order to determine a more reliable switching operation for a RRAM device.

Using transparent conductive oxides (TCO) as electrodes provide the possibility to broaden the scope to optoelectronics, such as organic light emitting diodes (OLED), transparent thin film transistors (T-TFT), and transparent resistive random access memory (T-RRAM). For these kinds of electronic devices, a high transmittance for the visible light and a good performance for stable reliability are critical issue to be sustained. However, for a highly degenerated n-type semiconductor ITO film, electrical conductivity was reported to be easily affected by ultraviolet (UV) light [8,9] and ozone oxidation [8]. Furthermore, laser-induced damage on oxide films has become more serious with the increase in the high quality demand for a lower leakage current during the past years. UV laser impact on the oxide film greatly depends on laser flux and pulse duration of the laser beam, as well as structural and compositional properties of oxide quality [10]. Because of highly correlation between the electrical properties and oxide quality, once the characteristic of ITO or oxide film has been influenced by UV laser, then the electrical properties will be altered simultaneously.

In this paper, we investigate the effect of laser effect on the electrical properties of a ITO/HfOx/TiN RRAM device. The UV light exposure on ITO/HfOx/TiN and HfOx/TiN structures was both experimented. The electrical characteristics of the ITO/HfOx/TiN devices show highly relationship on the exposure surface. Electrical properties such as I–V curves, endurance, devices yield, and switching mechanism was discussed in this paper. A probable switching mechanism was proposed based on the effect of the UV laser to explain the detail difference between these two device types.

2. Experiments

The device structure in this study is based on the ITO/HfOx/TiN/SiO2/Si structure. A 30 nm TiN bottom electrode (BE) was deposited on a 100 nm SiO2 layer by rf sputtering with the substrate at room temperature (RT). The nonstoichiometric HfOx film with a thickness of 20 nm was fabricated on TiN layer by atomic layer deposition (ALD) at 300 °C. Hafnium tetrachloride (HfCl4) and water (H2O) were used as reactants for HfOx deposition. Then, ITO top electrode (TE) of 100 nm was deposited by rf-magnetron sputtering system and here, a metal shadow mask with opening

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A B S T R A C T

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diameter of 200 µm was used. During the deposition of ITO films, working pressure, rf power and substrate temperature were maintained at 5 mtorr, 100 W and RT.

An average intensity of 80 mW/cm² at λ = 365 nm of UV light from a mercury lamp was used in the experiments. The UV light source was 8 cm away from the samples. UV light exposures on the HfOx/TiN sample with and without ITO shield film were both conducted, and denoted as S-samples (Shielded samples, the ITO top electrode was deposited before UV exposure) and U-samples (Unshielded samples, the ITO top electrode was deposited after UV exposure) in this study. Exposure times of 30, 60, 120, and 300 s were adopted to perform the experiments. Electrical characteristics were measured by precision semiconductor parameter analyzer (Agilent 4156C) in dc sweep mode at RT. All voltages were applied to the ITO TE, and the TiN BE were electrically grounded during all measurements.

3. Results and discussion

Forming process was needed in the beginning to activate the resistive switching (RS) characteristics for all the devices and the data was shown in Fig. 1a. A positive voltage sweep from 0 to 5.5 V with a current compliance triggers the current value to a high level abruptly at the forming voltage (V_form), and the state switches from initial resistance state (IRS) to low resistance state (LRS). The U-samples exhibit much larger leakage current than of S-samples during the forming process, indicating that oxide quality of the U-sample was considerably deteriorated under direct UV light exposure. Several kinds of defects may be generated inside the bulk of the HfOx film after UV light exposure according to Druijf’s report [11], which can induce high leakage current on U-samples. Afterwards, a positive voltage swept again from 0 to 4 V causes the abrupt decrease of the conducting current at certain voltage value, which was named reset voltage (V_reset). Then, the state was switched from LRS to a high resistance state (HRS). Hereafter, the state could be switched to HRS and LRS repeatedly under positive bias. The state switched from HRS to LRS and from LRS to HRS was defined as SET and RESET process. Fig. 1b and c shows the unipolar I–V characteristics of ITO/HfOx/TiN devices that exposes under UV light for 120 s, the S- and the U-samples, respectively. The electrical properties of the S-samples show a typical I–V curves. Oppositely, the random occurrence of the abnormal resistance switching (ARS) behavior, where the current suddenly jumps to high current level at the end of the RESET process, is observed on the U-samples (indicated by arrows). The type of ARS was often observed on U-samples (about 70%), but is less on the S-ones. The U-samples using Pt as top electrode also demonstrating the ARS behavior shown in the inset of Fig. 1c, which confirms the influence of UV. We suggest that the distinction between the two types of the I–V curves was dominated by different switching mechanism, which was attributed to the effects of the UV light exposure.

To evaluate the reliability of the ITO/HfOx/TiN devices under UV light irradiation, endurance test was investigated. Resistance values with the switching cycles of S- and U-samples under UV light exposure for 120 s are presented in Fig. 2a. The resistance values were both read out at 0.1 V in each dc sweep. Although the resistance values of both HRS and LRS show some fluctuations, the on/off ratios are about seven without any obvious degradation within 100 cycles for S-samples, while on/off ratios with severe overlap within 30 cycles for U-samples. The distribution of the V_set and V_reset values versus switching cycles is shown in Fig. 2b and c for the S- and U-samples, respectively. V_set and V_reset are the two critical switching parameters to determine when the state is switched to another state, and the fluctuation on V_set and V_reset values has been considered to be an arduous issue to be ameliorated. V_set and V_reset distributes in a range of 4.2–5.8 V and 2.6–3.7 V on the S-samples (average V_set and V_reset is about 4.8 and 3.4), and in a range of 3.3–6.4 V and 2.3–4.0 V on the U-samples (average V_set and V_reset is about 4.6 and 3.1), respectively. As it can be clearly seen that the programming voltages of the U-samples are a little lower than that of S-samples under the same time of UV light
exposure. In addition, the dispersion of \( V_{\text{set}} \) and \( V_{\text{reset}} \) on the U-samples are worse than that of S-ones. Some factors have been reported to have a strong impact on the \( V_{\text{set}} \) and \( V_{\text{reset}} \) dispersion, such as electrode material [12], implanting dopants [13], interfacial defects [14], fabrication process [15], inserting an additional layer above the oxide film [16], etc. Because the same electrode materials and deposition process were adopted on all our samples, we suggest that the different electrical characteristics between the two types of samples may be attributed to the effect of UV light exposure. Since Druijf had claimed that some oxygen-related defects may be generated or induced inside the HfOx film under UV light exposure, a large amount of defects are existed inside the U-samples [11]. Furthermore, Choi et al. reported a Au/NiO/SiO\(_2\)/p+Si RRAM device with less \( V_{\text{set}} \), \( V_{\text{reset}} \), and less fluctuation in SET process with increasing SiO\(_2\) thickness (from 50 to 300 nm) due to reduction of localized state density inside thicker SiO\(_2\) layer [14]. Therefore, we rationally suspect that the oxygen-related defects preexisted inside HfOx film under UV light irradiation can be corresponding for the fluctuation degree of \( V_{\text{set}} \) and \( V_{\text{reset}} \).

Among the many proposed models, the formation and rupture of the conducting filaments based on Joule heating effect inside the HfOx matrix may explain the switching mechanism observed in this study, due to abrupt switching of the conducing current from LRS to HRS [17,18]. Oxygen-related defects could play an important role on physical and chemical changes during switching, which is significantly correlated to the electronic properties of the HfOx film. Liu et al. utilized random circuit breaker (RCB) network to elucidate the observed random ARS behaviors on Pt/NiO/Pt structure, and well simulated the possible change on the microstructure during the RESET process [19]. According to their reports, we hypothesize that the shapes of the conducting filaments between S- and U-samples are different after forming process. The schematic diagram is shown in Fig. 3a–d for S- and U-samples to demonstrate the switching mechanism in each step. Fig 3a and c represents the structure of S- and U-samples after UV light exposure. The HfOx interface of U-samples is homogeneous damaged by direct UV light exposure and induced lots of defects on it (shown in Fig. 3c) [11], providing an isotropic formation of conducting channels during forming process (shown in Fig. 3d); while the S-samples, only about 50% intensity of the UV light at wavelength of 365 nm (not shown here) on the HfOx film does not large enough to cause severe damage to the oxide quality. Moreover, once the ITO films are under UV light, the UV light exposure will easily activate the oxygen ions inside the ITO film to the excited states [20]. Because of Hf metal has lower free energy to oxygen than In and Sn, the excited oxygen ions are more willing to oxidize with Hf metal and forms an oxygen-rich thin layer HfO\(_2\) at the M/O interface, as shown in Fig. 3a. Therefore, an anisotropic formation of conducting filaments during forming process makes the filaments more confined near the ITO/HfOx interface on S-samples, as illustrated in Fig. 3b. The filament types on U-samples easily

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**Fig. 2.** (a) Evolution of high and low resistance state during sequent voltage sweeping of Shielded UV-120 s and Unshielded UV-120 s samples. Distribution of SET and RESET voltages versus switching cycles of (b) the Shielded UV-120 s devices and (c) the Unshielded UV-120 s devices.

**Fig. 3.** Schematic diagrams show Shielded UV-120 s samples (a) after UV light exposure and (b) filament formation, and Unshielded UV-120 s samples (c) after UV light exposure and (d) filament formation.
cause formation and rupture at the same time during RESET process and lead to larger variation [19]. This different UV light exposure sequence causes a structural distinction at the HfOx film interface between the U- and S-samples, which reflects a variance on leakage current, $I-V$ curves, and fluctuation of $V_{\text{set}}$ and $V_{\text{reset}}$ values. The TE ITO with higher oxygen contents (oxygen partial pressure is about 33% during ITO deposition) was also experimented for verification. No ARS phenomenon and less voltage dispersion was observed on the oxygen-rich ITO samples. The results are similar to the reports that an additional oxide layer formed at the interface is efficient to suppress the fluctuation of $V_{\text{set}}$ and $V_{\text{reset}}$ [16]. It needs intensive investigation to explain the detailed physics of UV laser for reliable RRAM characteristics.

4. Conclusion

The electrical characteristics of an ITO/HfOx/TiN RRAM device under UV light exposure were investigated. When samples exposed under UV light with ITO top electrode (S-samples), the dispersion degree of set, reset voltage, high and low resistance values of ITO/HfOx/TiN RRAM was effectively reduced along with more stable electrical characteristics, which was attributed to an oxygen-rich HfO2 thin layer formed at the ITO/HfOx interface. Compared to the samples exposed without ITO Shield (U-samples), UV light exposure can cause the oxygen-related defects or oxygen vacancies inside HfOx film, which results in more random distribution on the conducting filaments. Based on our investigation, the effect of UV light exposure on our devices will cause the distinction on the conducting filaments, which may be the key issues for the reliability of transparent electronics.

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