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Resistive Switching Phenomena of HfO_2 Films Grown by MOCVD for Resistive Switching Memory Devices

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The resistive switching phenomena of HfO_2 films grown by using metal organic chemical vapor deposition (MOCVD) was studied for the application of resistive random access memory (ReRAM) devices. In the fabricated Pt/HfO_2/TiN memory cells, bipolar resistive switching characteristics were observed, and the set and reset states were measured to be as low as 7 μA and 4 μA, respectively, at V_{READ} = 1 V. Regarding the resistive switching performance, stable resistive switching (RS) performance was observed under 40 repetitive dc cycles with small variations of set/reset voltages and the currents and good retention characteristics of over 10^5 s in both the low-resistance state (LRS) and the high-resistance state (HRS). These results show the possibility of using MOCVD-grown HfO_2 films as a promising resistive switching materials for ReRAM applications.

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I. INTRODUCTION

The resistive random access memory (ReRAM) has recently attracted much attention as one of the most promising next-generation nonvolatile memory devices because of its useful properties such as its simple structure, low cost, and high density integration [1–4]. Because of these merits, various materials such as oxide-based materials [5–7] and nitride-based materials [8–11] have been investigated for their resistive switching (RS) characteristics. However, because RS materials have not yet been optimized for commercial applications of ReRAM devices, until now, various kinds of RS materials have been explored to improve their resistive switching characteristics and reliability. Among them, hafnium oxide (HfO_2) is suggested as one of the most promising candidates for ReRAM devices due to its excellent resistive performance and compatibility with silicon-based semiconductor fabrication processes [12, 13]. However, the HfO_2 films deposited by using physical deposition method, which were mainly investigated by many research groups for improving the RS performance, have faced limitations in the nanoscale fabrication process and low throughput manufacturing level of ReRAM devices. Therefore, if overcome these problems are to be overcome research on the RS characteristics of HfO_2 films grown by using chemical deposition is necessary.

In this work, we investigated HfO_2 films grown by using metal organic chemical vapor deposition (MOCVD) for application to ReRAM devices. In addition, to study the resistive switching phenomena of the HfO_2 films, we analyzed the properties of the HfO_2 films and investigated the current−voltage ($I - V$) and the reliability characteristics of the memory cells.

II. EXPERIMENTS AND DISCUSSION

For preparation of the samples, a Ti adhesion layer was deposited on a SiO_2/Si substrate, after which a TiN bottom electrode of 20-nm thickness was deposited by using a radio-frequency sputtering system. Subsequently, HfO_2 films with a 25-nm thickness were deposited by using MOCVD at a substrate temperature of 400 °C. Next, we deposited a 200-nm-thick Pt top electrode with a 50-μm diameter by using an electron-beam evaporation system. Finally, the sample was annealed in a nitrogen ambient at 400 °C for 30 min. Figure 1(a) shows a schematic drawing of the fabricated HfO_2-based memory cell with a simple metal insulator metal (MIM) structures, and the measurement configuration. We measured the electrical properties of the memory cells by using a Keithley 4200 semiconductor parameter analyzer.

First, in order to examine the structural property of the HfO_2 films, we used atomic force microscopy (AFM) in the non-contact mode at a scan rate of 0.4 Hz to investigate the surface of the HfO_2 films. As

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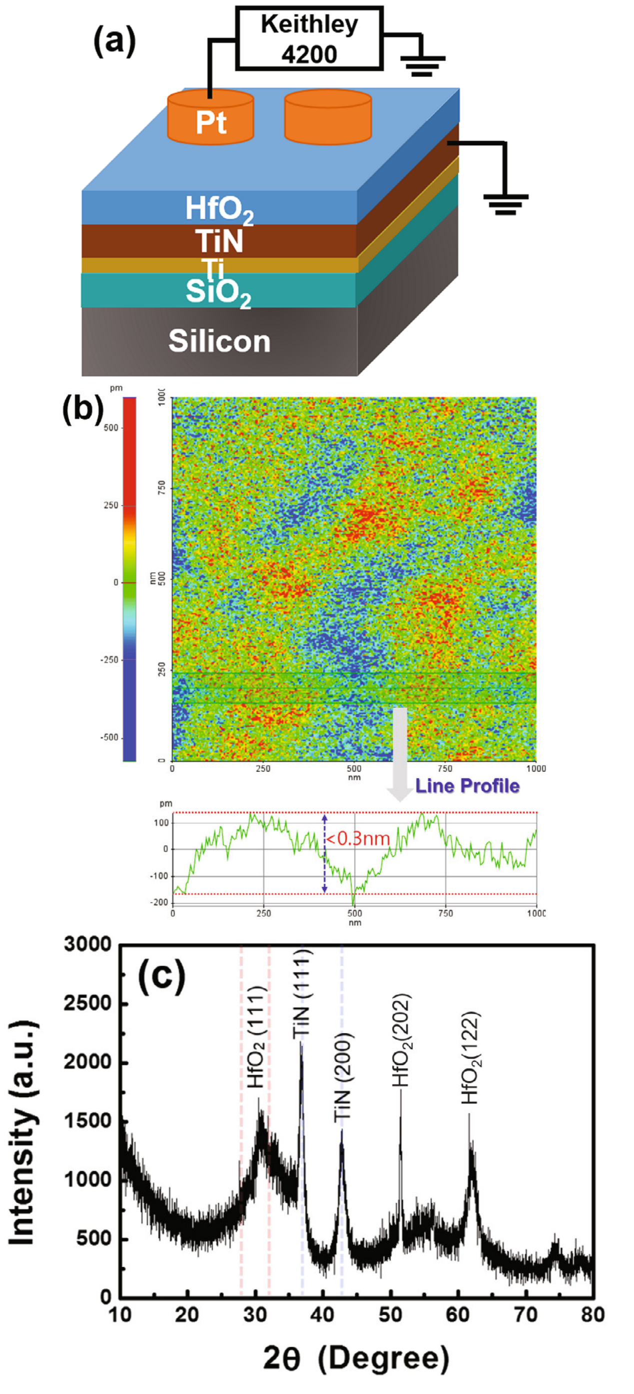

Fig. 1. (Color online) (a) Schematic drawing of the Pt/HfO_2/TiN memory cell and the measurement system. (b) Typical AFM image shown roughness of HfO_2 films (c) X-ray diffraction curve for the HfO_2 films.

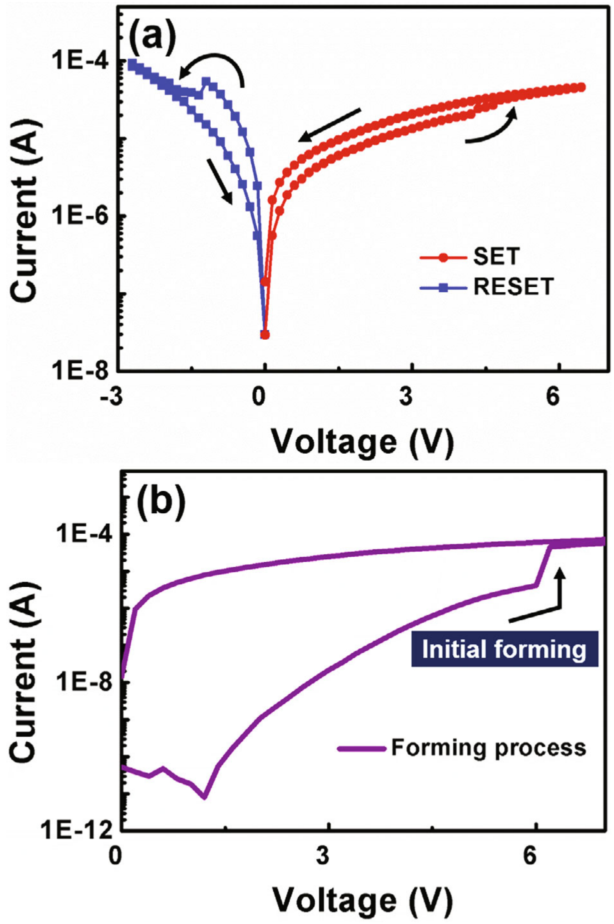

Fig. 2. (Color online) (a) Typical current-voltage ($I-V$) characteristics at room temperature for the Pt/HfO_2/TiN memory cells. (b) Forming process for the initial set operation.

shown in Fig. 1(b), we observed a number of small HfO_2 grains (*i.e.*, amorphous structures), and in this figure, the height difference between the lowest and the highest grain was < 1 nm when line profile was evaluated over the entire surface. Then, the roughness of the HfO_2 films was determined in a scanning range of 1000 × 1000 nm and the difference between the highest point and the lowest point was < 0.3 nm. These results mean that compared to physical vapor deposition, the MOCVD method can be used to deposit HfO_2 films uniformly for use as active layer.

In addition, we also measured the X-ray diffraction (XRD) spectra in order to examine the structural properties of the HfO_2 films within the angular range from 10° to 80°. To analyze the measured results, we used Joint Committee on Power Diffraction Standards (JCPDS) such as #34-104 for the HfO_2 films and #38-1420 for TiN films. As shown in Fig. 1(c), broad diffraction peaks are seen near 32° (111), 52° (202), and 62° (122) for the HfO_2 films, which have an amorphous structure. In this formulation, the atoms are arranged in random fashion.

In order to confirm the RS characteristics, we investigated the electrical properties of the HfO_2 films. Figure 2(a) shows a typical $I-V$ characteristic measured from the Pt/HfO_2/TiN memory cell with a 25-nm-thick HfO_2 layer, where bipolar resistive-switching behavior is observed when the voltage is swept in the sequence; 0 V →

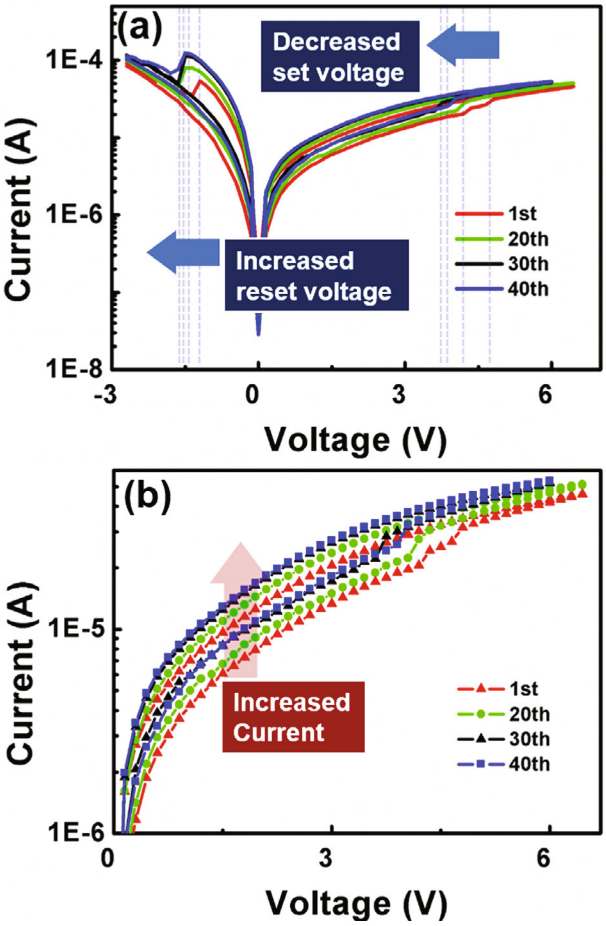

Fig. 3. (Color online) (a) DC cycling characteristics during 40 cycles. (b) Enlarged $I-V$ curves during dc cycling testing for positive polarity.

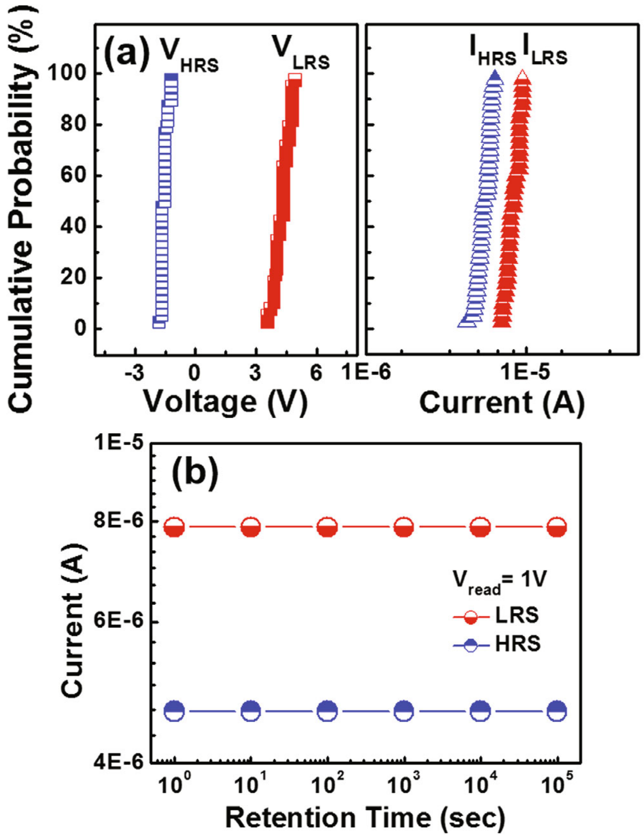

Fig. 4. (Color online) (a) Probability plots of the operating voltage and current at $V_{READ} = 1$ V in the LRS and the HRS. (b) Retention characteristics of the Pt/HfO_2/TiN memory cells.

+6.5 V → 0 V → −3 V → 0 V at room temperature. For the first set operation, an initial forming process of 6 V is required because of its own high resistance; conducting filaments can be formed by connecting oxygen vacancies between the top and the bottom electrodes in the forming process, as shown in Fig. 2(b). After that, by dc-sweeping the voltage from 0 V to +6.5 V, the current level abruptly increased and reached the low resistance state (LRS) with set operation, and the cell remained at the LRS during a sweep back to 0 V and below the reset voltage (< V_{RESET}). Subsequently, the current of the cell abruptly decreased at a negative voltage of −1.5 V (VRESET) under sweeping from 0 V to −3 V, which indicates that the cells change to the HRS with the reset operation. On the other hand, because we used materials with different work functions for the top and bottom electrodes, we could find a different current level for both bias polarities.

Then, in order to examine the RS performance as well as reliability of Pt/HfO_2/TiN memory cells, we investigated the dc cycling characteristics, and the results are shown in Fig. 3(a). During 40 repetitive positive and negative bias sweeping operations, stable RS characteristics maintaining stable $I-V$ curves were observed. On the other hand, with increasing number of dc cycles, the VRESET increased while the set voltage (VSET) decreased, because of the defects induced during the degradation of the HfO_2 films under repetitive biasing. During the set process, CFs can be more easily formed in the HfO_2 films through defects. On the other hand, during the reset process, rupturing the CFs as increasing the number and size of CFs caused by too many defects is difficult, which means difficulties in controlling the CFs in the HfO_2 films. Figure 3(b) shows enlarged $I-V$ curves under positive bias for a closer look at the increased current level under repetitive dc cycling.

Finally, we investigated the distribution of VSET/RESET and currents at the LRS and the HRS, as well as the retention characteristics, in order to examine the reliability of Pt/HfO_2/TiN memory cells. As shown in Fig. 4(a), stable RS performance with small variations of the voltages and currents was observed before and after programming. Especially, a large voltage window of > 4.5 V between V_{HRS} and V_{LRS} was obtained, which is enough to distinguish between the two operating voltages. In this cell, both the HRS and the LRS followed the model of CFs consisting of oxygen vacancies. We speculate that the basic switching mechanism of the HfO_2-based ReRAM might be closely related to the Hf^{n+}, O^{n-} and electron migrations in oxygen-related vacancies. When a positive bias over V_{SET} is applied, a conduction path can be formed across the bottom and top electrodes via the set process. Conversely, when a negative bias over V_{RESET} is applied, the conduction path can be ruptured via ionization of CFs in the reset process. The retention time for the LRS, on the other hand, is determined by using the thermal release time, which is exponentially proportional to ΔE_t as $\tau \propto \exp(\Delta E_t/kT)$. Accordingly, a long retention time is expected from materials having a high activation energy (E_t). In the retention test, we could not observe the failure phenomena for either the LRS or HRS. In other words, good retention characteristics for over 10^5 s have been identified without any degradation in both the LRS and the HRS for $Pt/HfO_2/TiN$ memory cells, as shown in the double logarithmic plot in Fig. 4(b).

III. CONCLUSION

HfO_2 films grown by using metalorganic chemical vapor deposition (MOCVD) for the application of ReRAM devices were investigated. As a result, we observed bipolar resistive switching characteristics in the 25-nm thickness of HfO_2 films with the amorphous structure. In the fabricated $Pt/HfO_2/TiN$ memory cells, the stable RS performance was observed under 40 repetitive dc cycles test with small variations of the set/reset voltages and the currents before and after programming. In addition, the good retention characteristics of over 10^5 s observed in this cell indicate that the HfO_2 films grown by using MOCVD are promising candidates for RS memory applications.

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