Resistive switching characteristics of Ni/HfO₂/Pt ReRAM

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Abstract: This study investigated the resistive switching characteristics of the Ni/HfO₂/Pt structure for nonvolatile memory application. The Ni/HfO₂/Pt device showed bipolar resistive switching (RS) without a forming process, and the formation and rupture of conducting filaments are responsible for the resistive switching phenomenon. In addition, the device showed some excellent memory performances, including a large on/off ratio (> 3 × 10⁵), very good data retention (> 10³ s @ 200 °C) and uniformity of switching parameters. Considering these results, the Ni/HfO₂/Pt device has the potential for nonvolatile memory applications.

Key words: resistive random access memory; programmable metallization cell; conductive filament; Ni electrode; HfO₂

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1. Introduction

Programmable metallization cell (PMC) technology has recently sparked scientific and commercial interest as a replacement for traditional charge-based memories. The structure of this new concept memory is typically solid-state electrolyte materials based on ionic transport composed between the oxidizable anode and inert cathode. Particularly, a PMC features a simple structure and superior performance, for example fast operation speed, high density, and great scale-down potential^[1,2]. However, several problems, such as undesirably low operation voltages, destructive readout under stress voltage, and especially poor retention of the low resistance state (LRS) at elevated temperatures must be resolved before commercial applications can be realized^[1,3]. To solve these issues, some new electrolyte materials (such as $CuC^{[4]}$ and $SiC^{[5]}$) were applied or a buffer layer was inserted between electrolyte and active electrode. However, these new electrolytes increase the complexity of device fabrication procedures, which can impede the mass production of PMC devices.

Recently, Lin *et al.*^[6] fabricated a Ni/HfO₂/Si device and demonstrated that its switching mechanism was similar to PMC devices. Because Ni atoms have a higher activation energy in oxide than Cu or Ag atoms, Ni might resolve the stability issues in PMC devices. In addition, Ni is already used in current CMOS technology as a favorable material and hence may be a potential candidate for PMC electrode material.

However, the deposition of Si film needs high temperature^[7], which is not advantageous for the integration of ReRAM both in 3D architecture and in back-end CMOS processes^[8]. In this study, the HfO₂ functional layer with a Ni top electrode (TE) was deposited on Pt substrates at room temperature (RT) conditions. We focus on investigating the switching parameters and retention property of the device by using direct current (DC) electrical measurement. The Ni/HfO₂/Pt device showed high temperature stability and uniform switching characteristics.

2. Experimental setup

The Ni/HfO₂/Pt device in this study was fabricated as follows. First, a 100 nm thick SiO₂ layer was thermally grown on an n-Si substrate by using a dry-oxygen oxidation method. In the next stage, 20 nm thick Ti and 80 nm thick Pt layers are sequentially deposited on the SiO₂/Si substrate by e-beam evaporation to form the bottom electrode. Subsequently, a 20 nm thick HfO₂ film was deposited on the Pt bottom electrode by ebeam evaporation using a HfO₂ target with a purity of 99.99%. After that, the top electrode layer consisting of Ni/Au (70/30 nm) was deposited by e-beam evaporation in succession without breaking the vacuum atmosphere. During e-beam evaporation, the chamber pressure was kept at 2.6×10^{-6} Torr. The Au layer was used to avoid the Ni electrode from being scratched by the probe tip during testing. The top electrodes (with an area ranging from $100 \times 100 \ \mu m^2$ to $1000 \times 1000 \ \mu m^2$) were patterned as squares via photolithography and a lift-off process. All electrical characterization was performed under ambient conditions using a Keithley 4200 semiconductor characterization system by applying voltage to the TEs with reference to a Pt electrode, as shown in the inset of Fig. 1(a).

3. Results and discussion

Figure 1(a) shows the typical I-V characteristics of the Ni/HfO₂/Pt memory device under a DC sweeping mode. The device was initially in the high resistance (OFF) state (HRS). When a positive voltage was applied on the top electrode, the device switched from the off-state to the on-state (denoted as the set process) at ~5 V. In this process, a 1 mA compliance current was set to protect the device from permanent damage. Surprisingly, no forming process was observed in the Ni/HfO₂/Pt structure, though it is commonly reported in metal–oxide–metal (MOM) devices. Haemori *et al.*^[9] has reported a similar phenomena in a Cu/HfO₂/Pt device, which was proved due to columnar paths formed in a HfO₂ thin film. When we applied a negative voltage without current limitation,

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Fig. 1. Typical plots of the I-V characteristics of the device under a DC voltage sweep. (a) Semi-logarithmic scale. The inset of (a) shows a schematic diagram of the measurement setup. (b) Logarithmic scale. The inset of (b) shows the I-V curve at low voltages in the LRS branch. The arrows indicate the sweeping directions.

the device switched back to the off-state at ~ -1 V (denoted as the reset process). Herein, we define the transition voltages of the set and reset process as V_{set} and V_{reset} , and define the resistances of the off-state and on-state as R_{HRS} and R_{LRS} , respectively.

Figure 1(b) shows the I-V curves of the Ni/HfO₂/Pt device redrawn on double-logarithmic scales. The fitting result of the I-V curve in the LRS follows a linear ohmic conduction, as can be seen from the inset of Fig. 1(b). This indicates that the current in the LRS can be explained by the formation and rupture of conductive filaments inside the HfO_2 film^[10]. For the HRS, the $I-V^2$ followed the trend of the I-V character as a positive voltage increase, indicating that the HRS is dominated by a trap-controlled SCLC conduction mechanism^[11]. Recently, Lin et al. demonstrated that the Ni element is the main component of the conductive filament inside the Ni/HfO₂/Si device by SIMS analysis. Hence, we have reason to believe that the conductive filaments comprise Ni atoms in our device, which is very similar to that of a solidelectrolyte-based ReRAM^[12-15], such as Cu/ZrO₂/Pt^[16] and Ag/ZrO₂/Pt^[17] devices.

We tested 15 cells each with an area of $100 \times 100 \ \mu m^2$ for 10 cycles, and we found that the average values of V_{set} and V_{reset} of the Ni/HfO₂/Pt device were relatively high. Figure 2 shows the distribution of V_{set} , V_{reset} and their average values



Fig. 2. (a) Distribution of V_{set} and V_{reset} during testing cycles. (b) Distribution of R_{HRS} and R_{LRS} during testing cycles.

and standard deviations. Mean values of V_{set} and V_{reset} achieved 5.12 V and -1.19 V, respectively. It is worth noting that even the minimum set voltage was larger than 2 V, which can be seen in Fig. 2(a), while the V_{set} of the undoped device with a Cu TE generally shows a wide dispersion^[16]. This indicates more energy is required to form Ni filaments. The increase of operation voltages may lead to a slight growth of power that the device may consume, but it also means the read voltage can be set higher to avoid outer electrical noise interference. Additionally, our device showed uniform switching parameters. As seen in Fig. 2, V_{set} varied from 2.03 to 6.46 V and more than 80% were greater than 4 V, while V_{reset} varied from -2.7 to -0.58 V. R_{LRS} ranged from 14.41 to 196.86 Ω and R_{HRS} ranged from 5.83 $\times 10^7$ to 1.61 $\times 10^{10} \Omega$. The storage window could achieve 3×10^5 .

Thermal stability is important for the purpose of memory applications. It has been reported that a PMC is stable in the HRS but lacks reliability in the LRS, especially in a high temperature environment^[12]. Usually, the variation is attributed to the percolation process at the LRS when different ruptured filaments are reconnected randomly at each switching cycle^[6]. However, as revealed in Fig. 3, our Ni/HfO₂/Pt device showed no degradation up to 200 °C both in the HRS and the LRS for a considerably long time, which is even ahead of the highly stable Cu/SiC/Pt device fabricated by Lee *et al.*^[5]. This improvement of reliability can be attributed to the composition of the conductive filaments. Specifically, the retention property is



Fig. 3. Retention characteristics of both the LRS and HRS, which are stable even under 200 $^{\circ}$ C.

determined by the energy required to disrupt conducting filaments or oxygen vacancies^[5, 6]. Since a Ni TE owns a larger activation energy, much greater power is needed to drive the Ni atoms in the Ni filaments and rupture the conductive paths. Under the condition that temperature is not very high, the insufficient thermal density would keep Ni filaments inactive at the LRS. Consequently, the reliability of the low resistance state is significantly improved. This result is also supported by the cluster-connected filament model proposed by Lee *et al.*^[18].

4. Conclusion

In summary, we fabricated the Ni/HfO₂/Pt structure and evaluated its potential for the nonvolatile memory application. Particularly, the ambient temperature fabricated device showed a long retention and forming free stable resistive switching, which are always pursued for the practical application of resistive random access memory. In addition, Ni is commonly used in microelectronics manufacturing technology with a simple fabricating process, while a HfO₂-based film is one of the most probable high-k dielectric gate materials. All of the above advantages make Ni/HfO₂/Pt cells highly promising for nonvolatile memory applications.

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