Bipolar Resistive RAM Characteristics Induced by Nickel Incorporated Into Silicon Oxide Dielectrics for IC Applications

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***Abstract*—In this letter, we successfully produced resistive switching behaviors by nickel doped into silicon oxide at room temperature. The nickel element was doped into silicon oxide, which is a useful dielectric material in integrated circuit (IC) industries by cosputtering technology. Based on the proposed method, satisfactory reliability of the resistance switching device can be demonstrated by endurance and retention evaluation. We believe that the silicon oxide doped with nickel at room temperature is a promising method for resistive random access memory nonvolatile memory applications due to its compatibility with the IC processes.**

***Index Terms*—Nonvolatile memory (NVM), nickel, resistive switching, silicon oxide.**

I. Introduction

TO OVERCOME the technical and physical limitation issues of conventional charge storage-based memory devices [1]–[4], the resistive random access memory (RRAM) is one of the promising candidates for next-generation nonvolatile memory (NVM) devices, due to its simple cell structure, low power consumption, high operating speed, and nondestructive readout [5]–[11].

Although various materials have been reported to possess resistive switching behaviors, silicon-based oxide is a promising material for RRAM applications because of its great compatibility in integrated circuit (IC) processes. Therefore, the research using silicon-based oxide as the resistance switching layer was worthy of investigation.

In this letter, Ni metal doped into SiO_2 by cosputtering at room temperature was taken as the resistance switching layer of RRAM according to the previous study [12] to evaluate the availability for IC applications. To evaluate the resistive switching mechanism of a Ni-doped SiO_2 ($Ni : SiO_2$) layer dominated by the interface of a TiN electrode or a $Ni : SiO_2$ film, the $Pt/Ni : SiO_2/TiN$ device was fabricated in virtue of inertia of the Pt electrode as the reference electrode. In addition, the material and conduction mechanism analyses were discussed to explain the influence of Ni metal doped in SiO_2 on resistive switching behaviors.

II. Experimental Setup

The experimental samples were divided into two groups to verify the feasibility of RRAM properties by SiO_2 and Ni cosputtering technology. In the first group, the $Ni : SiO_2$ thin film (about 35 nm) was deposited on the $TiN/Ti/SiO_2/Si$ substrate by cosputtering with the pure SiO_2 and Ni targets. The sputtering power was fixed at RF power of 200 W and dc power of 10 W for SiO_2 and Ni targets, respectively. Subsequently, the Pt top electrode of 200-nm thickness was deposited on the $Ni : SiO_2$ film to form the $Pt/Ni : SiO_2/TiN$ sandwich structure by dc magnetron sputtering. On the other hand, the devices with the $Pt/SiO_2/TiN$ sandwich structure were made as control samples. The entire electrical measurements of devices with the Pt electrode of 4-μm diameter were performed using an Agilent B1500 semiconductor parameter analyzer.

III. Results and Discussion

Fig. 1(a) shows the electrical current–voltage $(I-V)$ properties of the control sample with the $Pt/SiO_2/TiN$ sandwich structure. The sputtered SiO_2 layer cannot exhibit the RRAM

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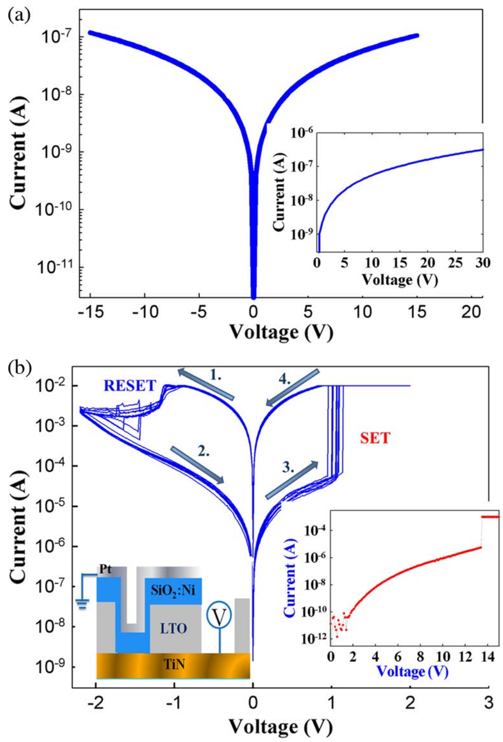

Fig. 1. (a) Current–voltage $(I-V)$ curve of the Pt/SiO_2/TiN sandwich device at room temperature. (b) Bipolar resistance switching $I-V$ curves of the Pt/Ni : SiO_2/TiN device with compliance current of 10 mA. The bottom left inset shows the schematic measured with the grounded Pt electrode.

properties, although the applied voltage is biased to a maximum voltage of 30 V [see the bottom right inset in Fig. 1(a)]. Fig. 1(b) shows bipolar resistance switching characteristics of the Pt/Ni : SiO_2/TiN device for the initial 100 dc voltage sweep operations. The voltage sweep bias was applied on a TiN electrode with the grounded Pt electrode, as shown in the bottom left inset in Fig. 1(b). The forming process is required to activate the as-deposited samples using dc voltage sweeping with a compliance current of 1 mA [see the bottom right inset in Fig. 1(b)]. A sudden increase in current occurs at a voltage of 13.7 V, and the cell was translated from the high-resistance state (HRS) to the low-resistance state (LRS). In the Pt/Ni : SiO_2/TiN device, the resistance ratio of the HRS and the LRS is about 10^3 times at a reading voltage of 0.1 V, and there is no degradation after continuous $I-V$ sweep cycles.

In order to analyze the influence of the Ni element on resistance switching characteristics in the SiO_2 thin film, Fourier transform infrared (FTIR) spectroscopy was used to investigate the chemical bonding of the Ni : SiO_2 film in this study. Fig. 2(a) shows that Ni–O stretch bonding was found in the Ni : SiO_2 film at 585 cm^{-1} from Fourier transform middle-infrared (FT Mid-IR) spectroscopy. In addition, the antisymmetric and symmetric stretch modes of Si–O–Si bonds were discovered at 1060 and 835 cm^{-1}, respectively. The stretch mode of O–H bonding was also found between 3400 and 3600 cm^{-1} in the FT Mid-IR spectrum. Additionally, the Fourier transform far-infrared spectroscopy in Fig. 2(b) indicated that the absorption peaks at 620 cm^{-1} belonged to the Ni–O stretch mode bonding. The peak at 480 cm^{-1} belonged to the bending mode of Si–O–Si bonds. According to these absorption peaks expressed in FTIR spectra, we can confirm that

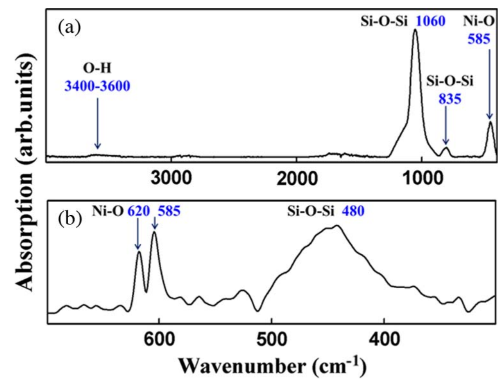

Fig. 2. FTIR spectra of the Ni : SiO_2 film measured in (a) middle-infrared and (b) far-infrared regions.

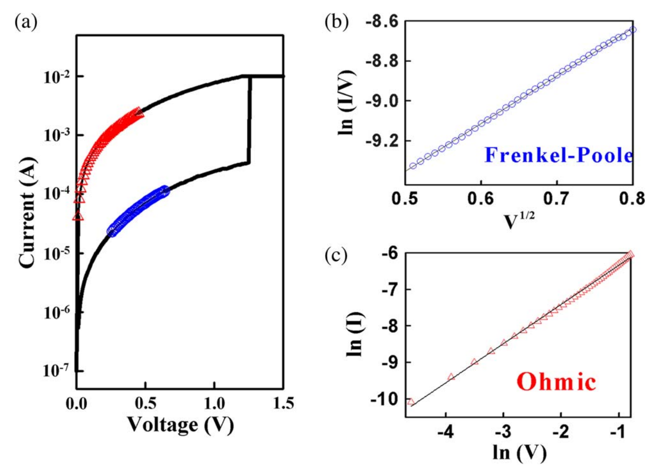

Fig. 3. Electrical characteristics of the Pt/Ni : SiO_2/TiN memory device with (a) typical $I-V$ curves, (b) a plot of $\ln(I/V)$ versus $V_{1/2}$ in HRS, and (c) a plot of $\ln(I)$ versus $\ln(V)$ in LRS.

the Ni element was bonded with the oxygen element in the SiO_2 film. To analyze the chemical composition of the Ni : SiO_2 film in this study, the mole fraction of Ni:Si:O in the cosputtered Ni : SiO_2 film was 2.4%:27.2%:70.4% by calculating from the peak areas of Ni, Si, and O X-ray photoelectron spectroscopy (XPS) spectra. The results of $I-V$ and XPS analyses demonstrated that the SiO_2 film can present the resistance switching property by doping with a small amount of Ni element.

The HRS and the LRS of $I-V$ curves were analyzed for the current conduction mechanisms in order to further discuss the resistance switching mechanisms in the Ni : SiO_2 thin film [see Fig. 3(a)]. The $I-V$ fitting exhibited that the current conduction in the HRS (0.26–0.6 V) was dominated by the Poole–Frenkel emission mechanism [see Fig. 3(b)]. According to the relationship of the Poole–Frenkel conduction, $I \propto V\,\exp[(q/kT)(2a\sqrt{V}-\phi_{Bt})]$, where a is $\sqrt{q/4\pi\varepsilon_i d}$, ϕ_{Bt} is the trap barrier height, and d is the insulator thickness. The Poole–Frenkel conduction is due to the emission of trapped electrons into the conduction band. The supply of electrons from the traps is through thermal excitation. Based on the material and electrical analyses, it could be inferred that doping Ni into SiO_2 may result in an increased amount of heterodefects in the film. When the voltage was applied to the film, the electrons were transferred through the heterodefects to make the current conduction dominated by the Poole–Frenkel

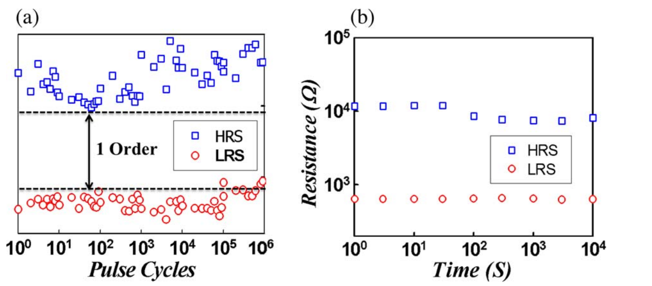

Fig. 4. (a) Endurance performance of the Pt/Ni : SiO_2/TiN memory device at room temperature. (b) Retention properties of the Pt/Ni : SiO_2/TiN memory device at 85 °C. Read voltage was 0.1 V.

conduction. On the other hand, the HRS will transform into the LRS when the applied voltage was higher than the set voltage. In this state, the result of the current fitting (0.01–0.45 V) revealed that the current conduction was dominated by the ohmic conduction mechanism [see Fig. 3(c)]. We believe that the conductive filament would be formed due to the current flowing through the Ni-induced defect in the Ni : SiO_2 film. The conductive filament results in low conduction resistance, leading to the current conduction mechanism dominated by ohmic conduction.

To further investigate the reliability properties of the NVM device, endurance and retention tests were measured. Fig. 4(a) shows the endurance characteristics during pulse cycling stress (the set and reset operation conditions were 1.5 V for 50 ns and −2 V for 70 ns). Both HRS and LRS resistance values were extracted at 0.1 V. The resistance ratio between the HRS and the LRS over one order can be obtained during the 10^6 cycling bias pulse operations. Fig. 4(b) shows that the retention performance and the resistive ratio of LRS/HRS remain almost one order of magnitude even after 10^4 s at 85 °C. These endurance and retention tests demonstrate that the device with the Pt/Ni : SiO_2/TiN structure has acceptable reliabilities. Therefore, the resistance switching performance of Ni : SiO_2 devices are more improved than NiO RRAM devices [13] because the Ni incorporated into the SiO_2 layer can effectively localize the conduction path.

IV. Conclusion

In conclusion, the reproducible bipolar resistance switching characteristics have been successfully achieved by doping 2.4% mole fraction of Ni metal into the SiO_2 film using the cosputtering technique at room temperature in this study. According to the analyses of current fitting, it is inferred that the current conduction was caused by the defects induced by doping Ni into SiO_2. In addition, the device has cycling endurance of greater than 10^6 and acceptable retention for 10^4 s at 85 °C. We believe that the resistance switching performance of a silicon oxide-based RRAM device can be improved in virtue of effectively localizing the conduction path by doping Ni into the SiO_2 film for IC applications in the future.

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