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Nitric Acid Oxidized ZrO₂ as the Tunneling Oxide of Cobalt Silicide Nanocrystal Memory Devices

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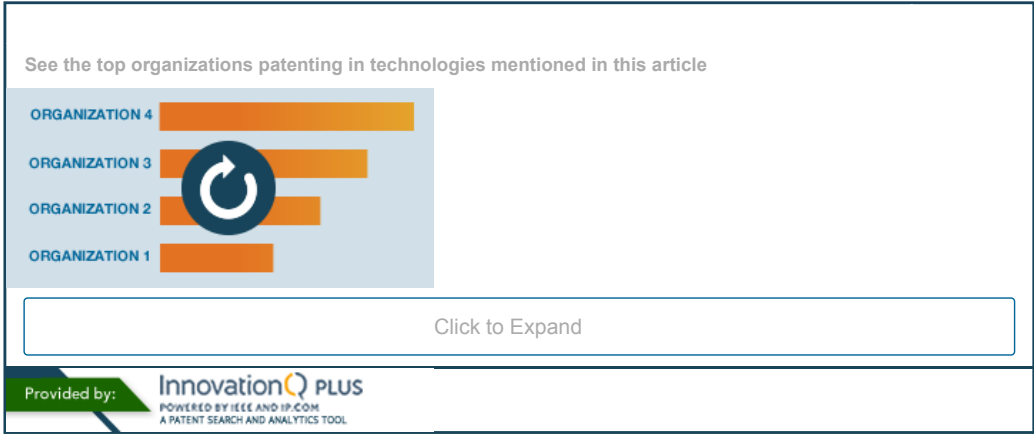
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Abstract:

In this study, ZrO₂ formed by the nitric acid oxidation method is proposed to be the tunneling oxide for nonvolatile memory device applications. The sputtered Zr thin film was oxidized by immersing in the nitric acid solution (HNO₃:H₂O = 1:10) for 60 s at room temperature. The quality of the formed ZrO₂ was also extracted by the capacitance-voltage and current density-voltage measurements. Then, X-ray photoelectron spectroscopy has been used to confirm that the deposited Zr can be oxidized completely after the oxidation process. Moreover, a CoSi₂ thin film was deposited on the nitric acid oxidized ZrO₂ as the self-assembled layer of the memory device. After the device fabrication, the electrical and material characteristics of the CoSi₂ nanocrystal memory devices have also been demonstrated and discussed.

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Contents

SECTION I.

Introduction

Today, nonvolatile memory (NVM) devices attract much attention as the requirements of portable products increase [1]. However, a dry oxidation process above 900 °C is the most common fabricating process to form the device tunneling oxide [2] [3]. Thermal budget issue limits the applications of the current NVM because the devices need a high-quality thermal oxide as the tunneling oxide to ensure the charge-storage ability. Therefore, low-temperature oxide deposited technology is critical for the next-generation NVM device. Several methods have been proposed to form a high-quality oxide at lower temperature such as the electron beam gun evaporation, atomic layer deposition, and supercritical fluid treatment [4]–[5][6]. Aforesaid methods need an expensive instrument or have a throughput issue. Recently, nitric acid oxidation has been confirmed as a novel and attractive method to form a thin and enough quality oxide at lower temperature [7]–[8][9]. However, it still needs more discussions about the nitric acid oxidation to support the feasibility for applying into the electrical devices.

In this study, the ZrO₂ film formed by the nitric acid oxidation method was prepared to be the tunneling oxide of CoSi₂ nanocrystal (NC) memory devices. First, metal–insulator–silicon (MIS) structure was fabricated to test the quality of the formed ZrO₂. Then, self-assembled CoSi₂ film was deposited to be the trapping layer of the memory device. After the fabrication of the metal-oxide-insulator-oxide-silicon (MOIOS) structure, the charge-storage ability of the NC memory devices using the

nitric acid oxidized ZrO₂ as the tunneling oxide has been discussed by the material and electrical analyses.

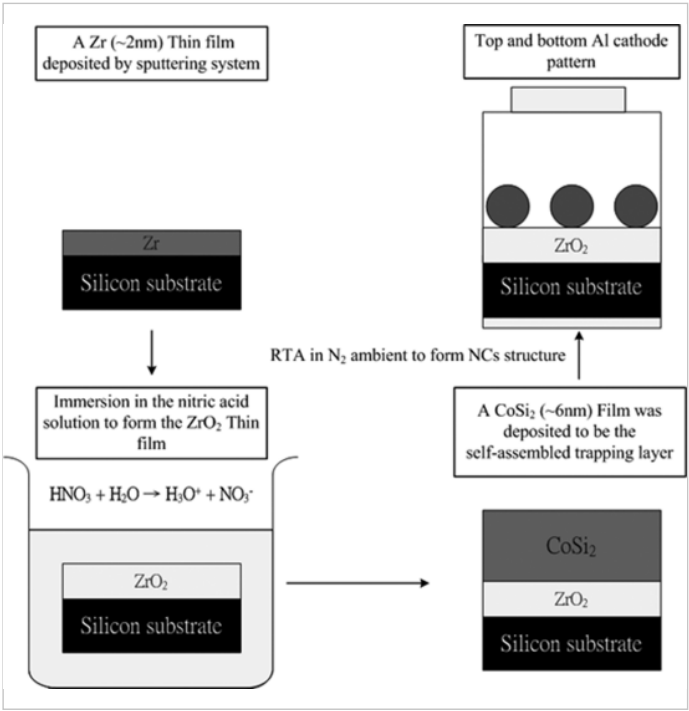


Fig. 1.
Process flow of this study.

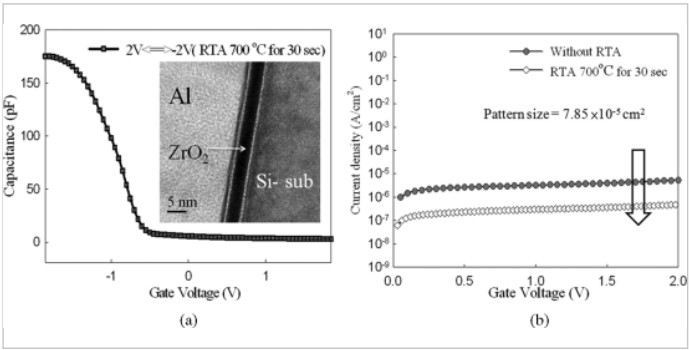


Fig. 2.
(a) C-V and (b) J-V results of the MIS structure.

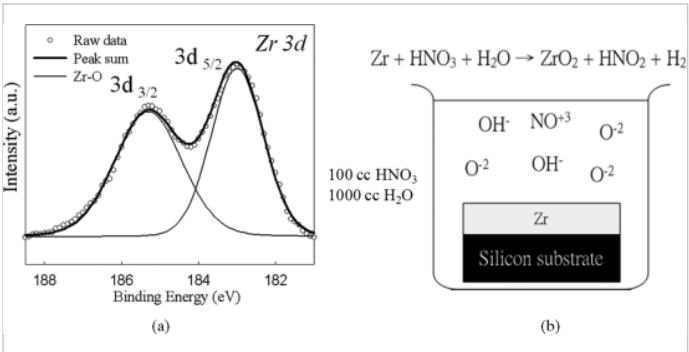


Fig. 3.
XPS and oxidation process of the ZrO₂ film.

SECTION II.

Experiment

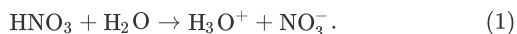
Fig. 1 demonstrates the process flow of this study. The experiment was started with a sputtering process to form about 2-nm-thick pure Zr film on p-type (100) Si wafer which had removed the native oxide and particles by the Radio Corporation of America (RCA) cleaning. Afterward, the deposited Zr film was immersed in the nitric acid solution ($\text{HNO}_3:\text{H}_2\text{O}=1:10$) for 60 s at room temperature to form the ZrO_2 film. Portion of the samples were fabricated to be the MIS structure to test the quality of the ZrO_2 film. Then, about 6-nm-thick CoSi_2 film was deposited as the self-assembled trapping layer by the sputtering system. In the sputtering process, the dc power and process pressure were set at about 50 W and 7.6 mTorr to yield a deposition rate of 0.01 nm/s. Subsequently, a rapid thermal annealing (RTA) set at 700 °C was performed in N_2 ambient for 30 s to enhance the CoSi_2 thin film to be aggregated and improve the quality of the ZrO_2 film. After the RTA process, a 50-nm-thick blocking oxide (SiO_2) was capped by a plasma-enhanced chemical vapor deposition system. Finally, top and bottom Al electrodes were patterned to form the MOIOS structure. After fabricating the NC memory devices, transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) analyses were used to study the compositions of the ZrO_2 and CoSi_2 NCs. Furthermore, the electrical measurements such as capacitance–voltage ($C-V$), current density–voltage ($J-V$), and retention and endurance were used to investigate the charge-storage ability of the formed NVM device.

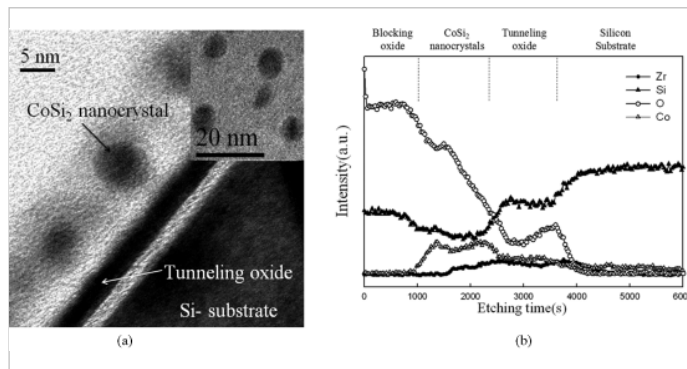
SECTION III.

Results and Discussion

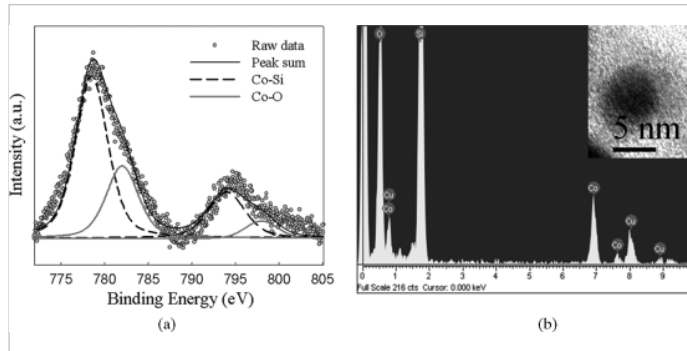
Fig. 2(a) and (b) shows the $C-V$ and $J-V$ results of the MIS structure. In Fig. 2(a), it is found that the nitric acid oxidized ZrO_2 shows an unobvious hysteresis phenomenon. The result indicates negligible oxide charges existed in the ZrO_2 film and even the oxide was formed by the brief nitric acid immersion and RTA processes. In addition, the interface characteristic was also tried by the conductance method [10]. The interface trap density of the formed ZrO_2 is about $7.27 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$, which is acceptable for the current electrical device. In the $J-V$ characteristic, the nitric acid oxidized ZrO_2 film before and after the annealing process was compared as shown in Fig. 2(b). It can be found that the gate current density of the ZrO_2 after the RTA process is about one order of magnitude smaller than that of the sample without RTA treatment. The results mean that the followed annealing treatment can bring an additional improvement in the oxide quality. The improved gate current is attributed to the reduced traps which exist in the ZrO_2 dielectric layer and the interface of Si/ ZrO_2 .

Fig. 3(a) and (b) shows the XPS and oxidation process of ZrO_2 in the MIS structure. It can be found that an obvious peak of the Zr–O binding energy at about 183 eV and no pure Zr signal at about 179 eV [11]. The results can confirm that the sputtered Zr film was oxidized completely. Following the results, the detailed oxidation process has been proposed in Fig. 3(b). The process of nitric acid oxidation depends on the fact that the nitric acid can be decomposed completely in aqueous solution according to the following chemical equation [12]:



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(a) TEM and (b) AES analyses of the CoSi₂ NC memory devices using the nitric acid oxidized ZrO₂ as the tunneling oxide.

**Fig. 5.**

(a) XPS and (b) EDS analyses of the NCs.

The decomposition of HNO₃ as a powerful oxidizing agent can provide a high concentration of atomic oxygen to oxidize the immersed metal layer. Therefore, the Zr thin film can be effectively oxidized after the brief nitric acid immersion. After the immersion, the followed annealing process is advantageous to improve the oxide quality further.

To study the feasibility for applying the nitric acid oxidation process into the tunneling oxide of memory devices, the CoSi₂ NCs have been formed as the charge-trapping centers. Fig. 4(a) shows the cross section and plane-view TEM images of the formed CoSi₂ NC memory devices. The ZrO₂ formation and CoSi₂ NCs aggregation are obvious after 700 °C RTA process. The thickness of the formed ZrO₂ film, the size and the density of the CoSi₂ NCs are about 4–5 nm, 5–6 nm, and $4.7 \times 10^{11} \text{ cm}^{-2}$, respectively. In addition, Auger Electron Spectroscopy (AES) analysis has also been proposed to eliminate the issue of Co contaminants as shown in Fig. 4(b). In Fig. 4(b), it is found that Co and Zr show an unobvious diffusion during the thermal annealing. Therefore, we believed that the formed ZrO₂ can restrain the Co diffusion even after an annealing process.

The composition of the NCs is confirmed by the Co 3d XPS in Fig. 5(a), which is extracted by analyzing the charge-trapping layer. The appearance of the peak at 778.3 eV fits in with the CoSi₂ phase of the reported literature [13]. Moreover, an EDS analysis of the NCs can be an additional tool for the composition of the NCs as shown in Fig. 5(b). During the EDS analysis, the electron beam was tried to focus at the NCs' region. The EDS result can support the XPS results because the NCs are composed of Co and Si elements obviously. The formation of

NCs is based on the self-assembled system that the deposited CoSi₂ thin film tends to be aggregated and form NCs' structure to minimize the surface energy and relax the interface stress when enough energy was provided by the RTA system [14]. Then, the CoSi₂ NCs can attribute the charge-storage sites for the memory application.

Fig. 6 shows the $C-V$ and $J-V$ measurements for the CoSi₂ NC memory devices. The bidirectional $C-V$ sweeps were performed from deep inversion to deep accumulation and vice versa, which exhibited a flat-band voltage (V_{FB}) shift, indicating the charge-storage ability of the NCs. In Fig. 6(a), it is found that the CoSi₂ NCs' memory device shows an excellent memory window of 10 V under ± 10 -V gate voltage operation. The result also shows that the formed ZrO₂ can hold the charge in the NCs instead to lose into the Si substrate. The excellent charge-storage ability is enough to provide a judgment for the logic circuit design. In addition, the $J-V$ result of the MOIOS structure, as shown in Fig. 6(b), indicates that the nitric acid oxidized ZrO₂ without serious leakage current ($\sim 10^{-7}$ A/cm² at $V_G = 10$ V) has the potential for the application of the memory tunneling oxide.

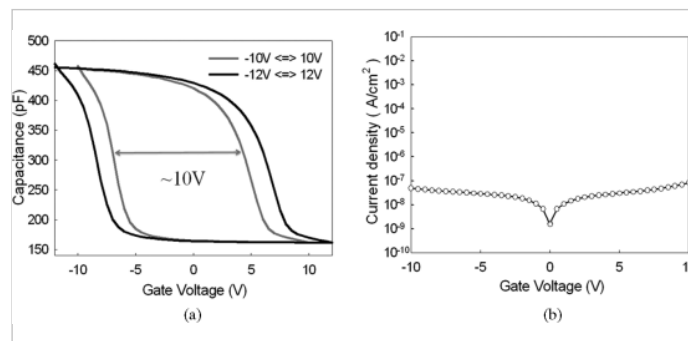


Fig. 6. (a) Memory effect obtained from $C-V$ characterization and (b) current density measurement of the formed CoSi₂ NC memory devices.

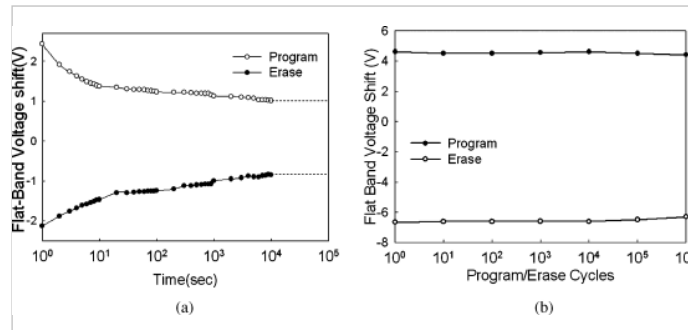


Fig. 7. (a) Retention and (b) endurance characteristics of the formed CoSi₂ NC memory devices.

Fig. 7(a) and (b) exhibits the retention measurement and the endurance characteristics of the CoSi₂ NC memory devices, respectively. The retention test was carried out by operating a ± 10 -V gate voltage stress for 10 s and measured up to 10⁴ s at 60 °C. It is found that the retention result of the device has an obvious memory window decay in the first 10 s. The decay is attributed to the stored charge in the shallow trap, is unsteady, and is easier to tunnel back to the substrate. After the fast degeneration of the memory window in the first 10 s, the formed memory device tends to maintain its charge-storage ability. The device can keep about 2-V memory window after 10⁴ retention test. In Fig. 7(b), the endurance characteristic of the device was extracted by the

continuous voltage pulse set at ± 10 V for 1 ms. About the $C-V$ curve, only slight memory window is degraded after a 10^6 program/erase cycle operation. The measurements show that the NCs' memory has enough reliability characteristics for the memory device application.

SECTION IV.
Conclusion

In conclusion, a ZrO_2 film formed by the nitric acid oxidation is proposed to be the tunneling oxide for the $CoSi_2$ NC memory devices in this study. Material and electrical results were used to ensure that the Zr thin film can be oxidized completely after immersing in the nitric acid solution. The result also indicates that the followed annealing process can improve the oxide quality further. In addition, the detailed oxidation process of the nitric acid solution has also been proposed in this study. By fabricating the MOIOS structure, the formed $CoSi_2$ NCs' memory reveals an obvious memory effect and good reliability characteristics. The nitric acid oxidized ZrO_2 film is advantageous to improve the thermal budget issue of the thermal oxide demand of the conventional NC memory devices because the higher fabrication temperature of the NVM devices is determined by the NCs. Moreover, the nitric acid oxidation method is inexpensive and easy to form the tunneling oxide of the current NVM devices.

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