

Deposition of Cr-doped SrZrO₃ thin films on Si substrates and their resistance switching characteristics

Min Kyu Yang^{a,b}, Jae-Wan Park^c, Sun Young Choi^a and Jeon-Kook Lee^{a,*}

^aOptoelectronic Materials Center, KIST, Seoul 136-791, Korea

^bDepartment of Electrical and Electronic Engineering, Yonsei Univ., Seoul 120-749, Korea

^cDepartment of Materials Science and Engineering, University of Wisconsin-Madison, Madison, WI 53705, USA

Cr-doped SrZrO₃ perovskite thin films were deposited on SrRuO₃ bottom electrode/SiO₂/Si(100) substrates by pulsed laser deposition. The SrZrO₃:Cr perovskite and SrRuO₃ bottom electrode showed a well controlled interface, as well as good resistive switching behavior with an ON/OFF ratio > 10³. Resistive switching memory devices made from Cr-doped SrZrO₃ thin films deposited on Si substrates are expected to be more compatible with conventional Si-based electronics.

Key words: Resistive switching, SrZrO₃, Non-volatility memory.

Introduction

Recently, oxide materials, such as Cr-doped SrTiO₃ [1], Cr-doped SrZrO₃(SZO) [2], Pr_{0.7}Ca_{0.3}MnO₃(PCMO) [3], PbZr_{0.52}Ti_{0.48}O₃(PZT) [4], and NiO [5] have attracted considerable attention owing to their resistive switching characteristics and possibility of random access memory (RAM) applications. The resistive RAM (ReRAM) is expected to have the advantages of non-volatility, simple device structure, high on/off resistance ratio, etc. The research trends of ReRAM materials have focused mainly on binary oxides (NiO) and PCMO perovskite [3, 5]. However, there are several disadvantages when a ReRAM device is fabricated using NiO and PCMO. The electrical currents of NiO- or PCMO-ReRAM devices are up to a few amperes, which is too high for high-density memory applications due to power consumption problems [5, 6]. In addition, the NiO-ReRAM, requirement of a current 'compliance' circuit is also a disadvantage [5]. In addition, repetitive turning on and off the compliance is needed in the read/write circuits of ReRAM memory devices, which will make the driving circuits more complicated. Cr-doped SZO is one possible solution to the above mentioned problems. Its electrical current is only a few milliamperes [2], which avoids power consumption problems. The resistive switching of Cr-doped SZO thin films is not controlled by the electric compliance but by the change in polarity in an external electric field [2]. However, turning on and off the compliance is not required in driving circuits. Accordingly, Cr-doped SZO is considered to be a suitable candidate for high-density ReRAM devices.

One of the weak points of the Cr-doped SZO is that until now, it has only been fabricated on perovskite substrates, whereas NiO-ReRAM devices have already been deposited on Si substrates [5]. The fabrication of RAM devices on Si substrates is important for commercialization because conventional electronics are based mainly on silicon materials. Cr-doped ReRAM will find a wide range of applications in embedded systems or conventional memory device manufacturing processes if it can be fabricated on Si substrates.

Therefore, this study examined how to deposit Cr-doped SZO thin films and whether resistive switching could be achieved on Si substrates. This short paper describes the elaborate deposition process and resistive switching behavior of an Au/Cr-doped SZO thin film/SrRuO₃(SRO)/SiO₂/Si(100) metal-insulator-metal(MIM) structure.

Experiments

Fig. 1 shows the MIM capacitor-like structure fabricated. Commercial Cr-doped (0.2 at%) SZO ceramics sintered by Praxair Technology Inc. were used as the target material. Before the pulsed laser deposition (PLD) process, the vacuum chamber was evacuated in < 133 μPa as well. P-type doped Si (100) substrates were used because a thin SiO₂ layer is naturally formed by the surface oxidation of silicon. SRO thin films, approximately 200 nm in thickness, were deposited on SiO₂/Si(100) substrates by PLD for the bottom electrodes. The PLD process was performed using a 248 nm-wavelength KrF excimer laser with an energy density of 2 J/cm² and a frequency of 5 Hz. The growth temperature and oxygen partial pressure were kept at 873 K and 13.3 μPa, respectively. The resistivity of the deposited SRO thin films was isotropic and 720 μΩ·cm at room temperature. Its temperature dependence reveals

*Corresponding author:
Tel : +82-2-958 5563
Fax: +82-2-958 6720
E-mail: jkleem@kist.re.kr

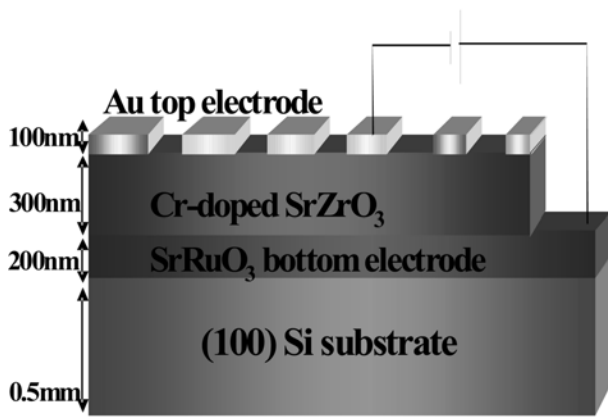


Fig. 1. MIM structure of Au/SrZrO₃:Cr/SrRuO₃ thin film deposited on a Si(100) substrate.

good metallic behavior, which is important for electrode applications [7]. Cr-doped SZO (SZO : Cr) thin films with a thickness of 300 nm were also deposited on the SRO/SiO₂/Si(100) structure using PLD under the same deposition conditions, except for an oxygen partial pressure of 33 μ Pa. The fabricated thin films were cooled to room temperature in vacuum at 288 K/min.

Results and Discussion

Fig. 2 shows the x-ray diffraction (XRD) pattern of a Cr-doped SZO/SRO/SiO₂/Si(100) thin film structures. The diffraction peaks corresponding to SZO and SRO were obviously observed. From the sharp and obvious XRD patterns, it is believed that Cr-doped SZO thin films and SRO bottom electrodes are well crystallized. XRD peaks corresponding to the (112), (004) and (132) planes of both SZO and SRO were observed (Fig. 2) with the highest intensity from the (112) planes.

Fig. 3 presents a cross-sectional transmission electron microscopy (TEM) image of the Cr-doped SZO/SRO/SiO₂/Si(100) structure. The thickness of the SZO thin film (\approx 300 nm)

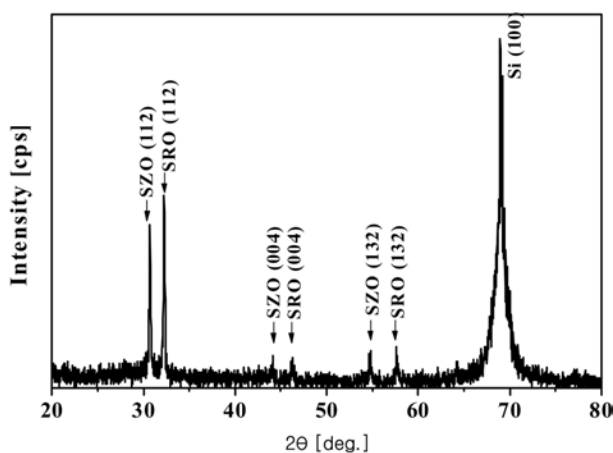


Fig. 2. XRD pattern of the Cr-doped SrZrO₃/SrRuO₃/SiO₂/Si(100) structure deposited at 600 °C.

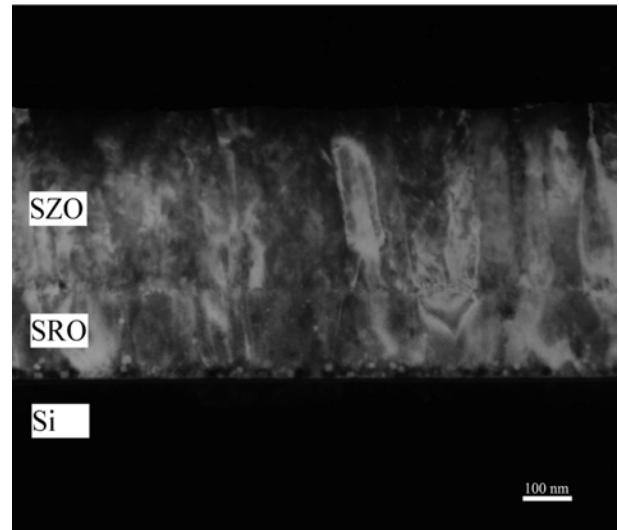


Fig. 3. A TEM image of the Cr-doped SrZrO₃/SrRuO₃/SiO₂/Si(100) structure.

and SRO electrode (\approx 200 nm) was determined from such cross-sectional TEM images. The SZO and SRO thin film layers were deposited in a form of columnar grains. The positions of the SZO grains matched to those of the SRO grains. From the XRD pattern in Fig. 2, the orientations of SZO and SRO thin films appear to coincide with each other (i.e. (112), (004) and (132) plane normals). It is believed that a well-controlled interface between the SZO and SRO thin films had been formed using the fabrication process described above.

The resistive switching behavior of the MIM structure of SZO : Cr thin films was examined using a Keithley 237 source measure unit and gold (Au) electrodes deposited on the top of the thin films with a 100 nm thickness. The current-voltage (I - V) characteristics were recorded in the voltage control mode of the source measure unit. Fig. 4 shows the obvious linear I - V characteristics of the resistive

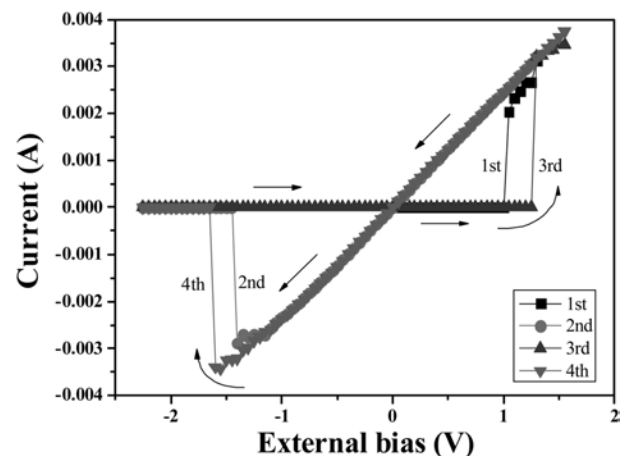


Fig. 4. The I - V characteristics of Cr-doped SrZrO₃/SrRuO₃/SiO₂/Si(100) structure at room temperature with arrows indicating the direction of the voltage sweep.

switching of the Cr-doped SZO thin films. When the external voltage was swept between -2 V and $+1.5$ V, the resistance of the thin films decreased suddenly by five orders of magnitude at approximately $+1.05$ - 1.3 V, whereas it increased suddenly to approximately -1.45 - 1.65 V. From the I - V characteristics, the typical resistance of the ON state (low resistance state) was 400 - 410 Ω . However, the resistance of the OFF state (high resistance state) was > 1 M Ω . This means that the ON/OFF resistance ratio $> 10^3$ (which is adequate for random access memory applications) can be achieved using Si substrates in resistive switching devices.

It was recently reported that the interface between the top electrodes and perovskite thin films plays an important role in resistive switching [6, 7], even though the microscopic mechanism of resistive switching is not completely understood. One of the most appropriate models for resistive switching is believed to be that reported by Rozenburg *et al.*, who assumed a large middle domain in the thin film with small top and bottom domains at the interfaces between the electrodes and perovskites [8]. The interfaces at the top and bottom electrodes strongly affect the switching behavior because the electrical properties of the small top and bottom domains are important factors in resistive switching. Therefore, the good linear I - V characteristics and switching behavior with a high ON/OFF ratio ($> 10^3$) could be obtained from the MIM structure on Si substrates, not only because of the top electrode effect but also because of the well-controlled interface between the SRO bottom electrode and SZO : Cr thin film, as shown in Fig. 3. The ReRAM devices made from the SZO : Cr thin films on Si substrates are expected to be more compatible with conventional Si-based electronics.

Conclusions

In conclusion, SZO : Cr resistive switching MIM structures

were fabricated on Si substrates, which is expected to make commercialization of SZO : Cr-ReRAM devices much easier. However, a more detailed investigation of the bottom electrode effects on the switching characteristics including an attempt to deposit SZO : Cr thin films on Pt/Ti/SiO₂/Si (100) substrates is currently underway.

Acknowledgements

This research was supported by “The National Research Program for the 0.1 Terabit Non Volatile Memory Development” Sponsored by Korea Ministry of Commerce, Industry and Energy.

References

1. Y. Watanabe, J.G. Bednorz, A. Bietsch, Ch. Gerber, D. Widmer, A. Beck and S.J. Wind, Appl. Phys. Lett. 78 (2000) 3738-3740.
2. A. Beck, J.G. Bednorz, Ch. Gerber, C. Rossel and D. Widmer, Appl. Phys. Lett. 77 (2000) 139-141.
3. S.Q. Liu, N.J. Wu and A. Ignatov, Appl. Phys. Lett. 76 (2000) 2749-2751.
4. J. Rodriguez Contreras, H. Kohlstedt, U. Poppe, R. Waser, C. Buchal and N.A. Pertsev, Appl. Phys. Lett. 83 (2003) 4595-4597.
5. S. Seo, M.J. Lee, D.H. Seo, E.J. Jeoung, D.-S. Suh, Y.S. Joung, I.K. Yoo, I.R. Hwang, S.H. Kim, I.S. Byun, J.-S. Kim, J.S. Choi and B.H. Park, Appl. Phys. Lett. 85 (2004) 5655-5657.
6. A. Sawa, T. Fujii, M. Kawasaki and Y. Tokura, Appl. Phys. Lett. 85 (2004) 4073-4075.
7. S. Tsui, A. Baikalov, J. Cmaidalka, Y.Y. Sun, Y.Q. Wang, Y.Y. Xue, C.W. Chu, L. Chen and A.J. Jacobson, Appl. Phys. Lett. 85 (2004) 317-319.
8. M.J. Rozenberg, I.H. Inoue and M.J. Sánchez, Phys. Rev. Lett. 92 (2004) 178302-178305.