Extended Abstracts of the 2020 International Conference on Solid State Devices and Materials, VIRTUAL conference, 2020, pp125-126

Preparation of reactively sputtered ZrO_2 films at low temperatures

Masaru Sato and Mayumi B. Takeyama

School of Earth, Energy and Environmental Engineering, Faculty of Engineering, Kitami Institute of Technology
165, Koen-cho, Kitami 090-8507, Japan
Phone: +81-157-26-9282, E-mail: satomsr@mail.kitami-it.ac.jp

Abstract

In order to realize next-generation memory devices, we prepared ZrO_2 films at temperatures below 200 ℃ and investigated the fundamental properties of the ZrO_2 films. In this study, the ZrO_2 film without an interfacial layer observed on the Si substrate. The texture of the ZrO_2 film with dominant monoclinic phase showed fiber structure to the film thickness direction. The optical bandgap of ZrO_2 film using Ar+O_2 gas mixture (30%) was 4.47 eV. Furthermore, the ZrO_2 film indicated the relative excellent insulating property from results of C-V and I-V measurement. The ZrO_2 films with low temperature deposition will be needed next-generation memory devices in the future.

1. Introduction

The next-generation devices such as nonvolatile memory (NVM), resistive random-access memory (RRAM), and metal oxide-based electrochemical metallization memory (ECM) have attracted extensive attention due to the conventional memories approaching their scaling limits.[1-3] As one of the high dielectric materials, zirconium oxide (ZrO_2) thin film with relatively high dielectric constant (20~30) is an attractive metal oxide with wide band gap (5.8 eV) because of thermodynamic stability in contact with Si substrate.[4,5] The ZrO_2 film has many phases such as monoclinic phase (m-ZrO_2), tetragonal phase (t-ZrO_2), cubic phase (c-ZrO_2), and amorphous structure.[6] Since ZrO_2 film has many phases, it is necessary to form different phases depending on the intended use. However, the phase and structure of the ZrO_2 film depend on the deposition method and the condition.

In this study, we prepare ZrO_2 films at temperatures below 200 ℃ in order to suppress the diffusion and reaction with the underlying material and investigated the fundamental properties of the ZrO_2 films with different ratio of sputtering gas mixture. The ZrO_2 films have been characterized by FE-SEM, XRD, UV-vis NIR, C-V and I-V measurement.

2. Experimental Procedure

ZrO_2 films were deposited on a p-type Si(100) substrate that has been rinsed with hydrofluoric acid solution using a RF reactive sputtering system. A pure 99% ZrO_2 disk with a diameter of 50 mm was used as sputtering target. The sputtering mixture gas ratio of Ar + O_2 is used oxygen in the range of 20% to 40% to obtain the ZrO_2 film. The RF power and sputtering substrate temperature of the ZrO_2 films were 200W and 200 ºC, respectively. Feld emission scanning electron microscope (FE-SEM) and X-ray diffraction (XRD) were used to evaluate the cross-sectional structure, the crystallographic structure. The optical transmittance and optical bandgap of ZrO_2 films were measured by ultraviolet-visible-near infrared (UV-vis NIR) spectrophotometer (Shimadzu: UV-3600) in the wavelength range 200-800 nm. Fundamental electrical properties based on capacitance-voltage (C-V) and current-voltage (I-V) measurements of Cu/ZrO_2/Si specimen were performed by using HIOKI IM3536 LCR meter and Agilent 4155C semiconductor parameter analyzers. To form the Cu/ZrO_2/Si specimens for electrical measurement, Cu top electrode (Φ0.1mm) were prepared on the ZrO_2/Si specimens in the RF sputtering system using a Cu target with an Ar gas.

3. Results and Discussion

First, the structure/texture of the ZrO_2 film on the Si substrate was examined under the sputtering condition in which the gas mixture ratio of Ar + O_2 gas was changed. Figure 1 shows FE-SEM images of the ZrO_2 film deposited at 200 °C under different ratio in Ar + O_2 gas mixture. In Fig. 1(a), fiber structure to the film thickness direction obtained from the ZrO_2 film without an interfacial layer is observed. But, it seems that aggregation of ZrO_2 grains has occurred as seen in Fig. 1(b).

Figure 2 shows the XRD patterns of the ZrO_2 film at prepared at 200 ºC under different sputtering condition of Ar + O_2 gas mixture ratio. In Fig. 2(a), reflection lines corresponding to m-ZrO_2 and t-ZrO_2 are simultaneously observed.[7,8] But, the intensity of the peak from t-ZrO_2 is very weak. This indicates that the dominant phase of ZrO_2 film is the monoclinic phase. On the other hand, as shown in Fig. 2(b), the intensity of reflection line corresponding to m-ZrO_2 is slightly decreased. XRD results suggest that the obtained ZrO_2 film with monoclinic phase in normal direction is formed. Considering the results of FE-SEM and XRD, we decided to use ZrO_2 film using the sputtering condition of Ar + O_2(30%) gas mixture.

We performed UV-vis NIR measurement to the optical transmittance and optical bandgap of ZrO_2 films. Figure 3 shows the wavelength dependence of optical transmittance spectra of the ZrO_2 film using Ar + O_2(30%) gas mixture. A sharp absorption edge is observed at the wavelength of ~350 nm. The optical bandgap is determined from plot of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) as reported by Tauc.[9] The optical bandgap of the obtained ZrO_2 films is 4.47 eV as shown in Fig. 4.

Figure 5 shows the relative dielectric constant of ZrO_2 film as a function of frequency from 1 to 8 MHz. The relative dielectric constant of ZrO_2 film of 1MHz is about 18. The relative dielectric constant decreases slightly as the frequency is increases.

The leak current density - voltage (J-V) characteristics of the $Cu/ZrO_2/Si$ specimen is shown in Fig. 1. The 50 nm thick ZrO_2 films was used for this measurement. the leak current density seen at 3V in the measurement is less than 1.0E-6A/cm^2.

We will elucidate the characteristics of ZrO_2 film after annealing treatment, and will report the details in conference.

4. Conclusions

We can prepare the ZrO_2 films sputter-deposited at 200 ℃ to fabricate next-generation memory and resistive switching devices. The obtained ZrO_2 film mainly shows the monoclinic phase with fiber structure even deposited at low temperature of 200 ℃. The optical bandgap, dielectric constant, and leak current of ZrO_2 films shows 4.47eV, 18 at 1MHz, 1.0E-6A/cm^2 at 3V. Despite the low temperature processing, relatively good characteristics were obtained.

Acknowledgements

The authors would like to thank Susumu Tokuda of Technical Division of Kitami Institute of Technology for FE-SEM observation.

References

[1] S. Yoneda, S. Ito, Y. Hayawaka, Z. Wei, S. Muraoka, R. Yasuhara, K. Kawashima, A. Himeno, and T. Mikawa, Jpn. J. Appl. Phys. **58**, SBBB06 (2019).
[2] D. Panda and T. -Y. Tseng, Thin Solid Films, **531**, 1 (2013).
[3] S. -Y. Wang, C. -H. Tsai, D. -Y. Lee, C. -Y. Lin, C. -C. Lin, and T. -Y. Tseng, Microelectron. Eng., **88**, 1628 (2011).
[4] M. Copel, M. Gribelyuk, and E. P. Gusev, Appl. Phys. Lett. **76**, 436 (2000).
[5] W. J. Qi, R. Nieh, B. H. Lee, L. Kang, Y. Jeon, and J. C. Lee, Appl. Phys. Lett. **77**, 3269 (2000).
[6] P. Gao, L.J. Meng, M. P. dos Santos, V. Teixeira, and M. Andritschky, Thin Solid Films, **377**, 557 (2000).
[7] JCPDS-ICDD card No. 37-1484.
[8] JCPDS-ICDD card No. 42-1164.
[9] J. Tauc, Mater. Res. Bull., **3**, 37 (1968).

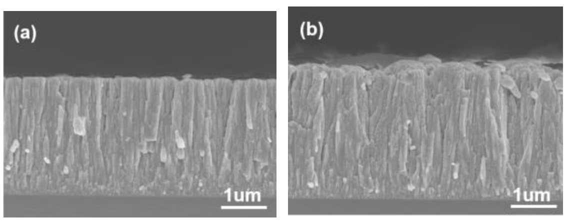

Fig. 1 FE-SEM image of ZrO_2 film prepared at 200 ºC under different $Ar+O_2$ gas mixture ratio: (a) $Ar:O_2$=70:30 and (b) $Ar:O_2$=60:40.

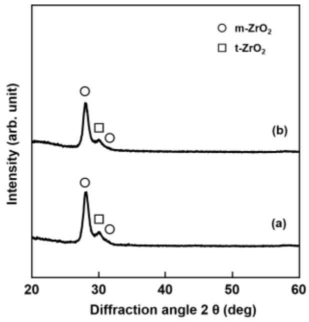

Fig. 2 XRD patterns of the ZrO_2 film prepared at 200 ºC under different $Ar+O_2$ gas mixture ratio: (a) $Ar:O_2$=70:30 and (b) $Ar:O_2$=60:40.

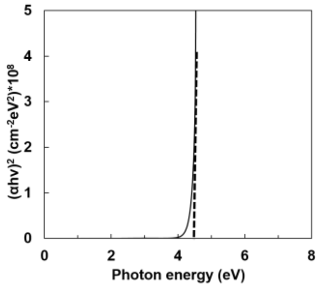

Fig. 3 $(\alpha h\nu)^2$ versus ($h\nu$) curves of ZrO_2 film prepared at 200 ºC using $Ar+O_2$ gas mixture (30%).

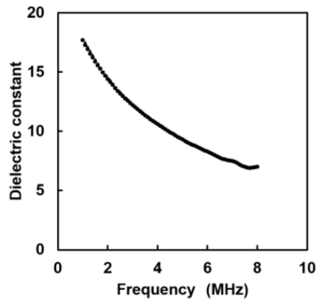

Fig. 4 Dielectric constant of ZrO_2 film prepared at 200 ºC using $Ar+O_2$ gas mixture (30%) as a function of frequencies.

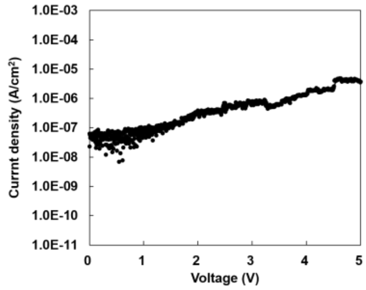

Fig.5 Current density-voltage curves of $Cu/ZrO_2/Si$ specimen.