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Preparation and electrical properties of high dielectric $(Ba_{1-x}Sr_x)(Ti_{1-x}Zr_x)O_3$ thin film capacitors by sputtering technique.

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Abstract

High dielectric $(Ba_{1-x}Sr_x)(Ti_{1-x}Zr_x)O_3$ (BZST) thin films were prepared on $Pt/Ti/SiO_2/Si$ substrates at 500℃ by rf magnetron sputtering technique. The dielectric constant and dissipation factor of a 100 ㎚ thick $(Ba_{0.65}Sr_{0.35})(Ti_{0.8}Zr_{0.2})O_3$ were 430 and 0.03 at an applied frequency of 100 ㎑, respectively. The dielectric films do not contain mobile ions and defects from the capacitance-voltage characteristics. The leakage current density was about 9.0×10^{-10} A/㎠ at 200 ㎸/㎝. The breakdown voltage of BZST films was about 600 ㎸/㎝.

Key Words(중요용어) : $(Ba_{1-x}Sr_x)(Ti_{1-x}Zr_x)O_3$ (BZST) thin film, Sputtering, Dynamic random access memories (DRAM), Breakdown voltage

Ⅰ. INTRODUCTION

Much attention has been paid to the application of ferroelectric thin films in dynamic random access memories (DRAM) and in nonvolatile ferroelectric memories (FeRAM)[1-3]. The application of thin films with high dielectric constant to DRAM capacitors would enable the realization of ultralarge-scale integrated-circuit DRAMs with simpler processes. Barium strontium titanate, $(Ba,Sr)TiO_3$ (BST), thin films have received a great deal of attention as a likely candidate for dynamic random access memory (DRAM) applications. However, even with BST films, which has high dielectric constant it is necessary to increase the electrode area of capacitor to obtain the required high capacitance. Therefore, new types of dielectric films with higher dielectric constant are necessary to be developed. The solid solution, $(1-x)BaTiO_3-xSrZrO_3$ (BZST[4-6]), exists in a single phase for a wide range of composition and for x value exceeding 0.2, it is a paraelectric phase within the operating temperature range of DRAM. When x was 0.35, dielectric constant of BZST was three times higher than that of BST and temperature coefficient of dielectric constant was very small. Therefore, it is considered that the BZST is one of the promising dielectric materials for DRAM capacitors. In this study, BZST films were prepared by conventional rf magnetron sputtering on Pt electrodes and the structural and electrical properties were evaluated.

Ⅱ. EXPERIMENTAL

The BZST target was processed by mixing BaO, $SrCO_3$, ZrO_2, and TiO_2 powders using a ball mill, then calcining the mixed powders at 1200℃, and pressing the calcined powders in a 2 inch diameter circular die. The pressed target was sintered for three hour at 1400℃ in the air ambient. The composition of the ceramic target was a $(Ba_{0.65}Sr_{0.35})(Ti_{0.65}Zr_{0.35})O_3$. Substrates used were p-type

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(100) Si wafers made by Silicon Quest International (USA), which had successive layers of SiO_2 (400 ㎚), Ti (150 ㎚), and Pt (200 ㎚) prepared by diffusion, evaporation, and sputtering, respectively. After pumping down the sputtering chamber to a base pressure of 5.0×10^{-6} torr, argon and oxygen mixtures were introduced into the sputtering chamber and controlled with a mass flow controller. The deposition pressure was changed by controlling the main valve between the pump and the deposition chamber. The detailed sputtering conditions of the BZST thin films are summarized in Table 1. The crystal structure of the films was characterized by an x-ray diffraction (XRD) employing Cu Kα radiation and an Ni filter. The morphology and the thickness of the deposited SBT films were determined with a scanning electron microscope (SEM).

Table 1. Sputtering conditions of BZST film preparation

Target material	Sintered $(Ba_{0.65}Sr_{0.35})(Ti_{0.65}Zr_{0.35})O_3$
Diameter of target	5.08 ㎝
Substrate	$Pt/Ti/SiO_2/Si$
Target-substrate distance	7 ㎝
Base pressure of system	5×10^{-6} torr
Working pressure	10 mtorr
RF sputtering power	100 W
Sputtering gas($Ar:O_2$)	1:1
Substrate temperature	500℃

The composition of SBT films was determined by Rutherford backscattering spectroscopy (RBS). For electrical measurements, top electrodes of platinum (80 ㎚ thickness and 100 ㎛ diameter) were deposited by dc sputtering using a shadow mask. The dielectric properties were measured as a function of frequency by using a Hewlett-Packard (4194A) impedance/gain phase analyzer. The capacitance-voltage characteristic was measured for a metal-insulator-metal (MIM) structure by measuring the capacitance at 100 ㎑, as a function of a swept positive-to-negative voltage bias (C-V curves). The leakage current measurements were performed with a Keithley 617 programmable electrometer under conditions of 0.05 V step and a delay time of 2 s.

Ⅲ. RESULTS and DISCUSSION

Figure 1 shows SEM surface and cross-sectional images of BZST films deposited on $Pt/Ti/SiO_2/Si$ substrates at 500℃. The BZST films have the fine grain sizes and show the dense surface structure. From the cross-sectional images, BZST films have a thickness of 100 ㎚ which was also confirmed by RBS analysis. A typical RBS spectrum of the BZST films was shown in Fig. 2. The platinum peak existing at about 480 channels was due to the top electrode. From the compositional analysis, the atomic ratio of Ba, Sr, Ti, and Zr was about 0.65, 0.35, 0.80, and 0.20. According to RBS resolution, Ti content of BZST film is excessive compared with the stoichiometric target composition. This is due to the diffusion of Ti through the Pt bottom electrodes into BZST films during the deposition at 500oC as shown in SEM cross-sectional images. When the Pt(200㎚)/Ti(150㎚)/SiO_2/Si substrates were also used to deposit the $SrBi_2Ta_2O_9$ (SBT) thin films, the diffusion of Ti through the Pt bottom electrodes into SBT films was also observed[7]. Figure 3 shows the variation of dielectric constant and dissipation factor (tanδ) as a function of frequency. The dielectric constant at 1 ㎒ shows only the decrease of 10 % for the initial value. The dielectric constant and loss factor for a 100 ㎚ film at a frequency of 100 ㎑ were 430 and 0.03, respectively. The dielectric constant of BZST films was superior to that of a 200 ㎚ thick epitaxial BST film deposited on YBCO/MgO substrates[8].

Figure 4 shows the C-V characteristics of the films measured at 100 ㎑ in a MIM capacitor configuration. It may be seen that the capacitance was not affected significantly by the electric field within the region of applied voltage ±5 V. The voltage of maximum capacitance does not shift both for increasing and decreasing bias voltage. This indicates that the dielectric films do not contain mobile ions and defects. Figure 5 shows the leakage current characteristics of the Pt/BZST/Pt capacitors prepared at 500 ℃. The capacitor shows a very symmetrical I-V characteristics with respect to the bias polarity. The breakdown voltage of BZST films was about 600 ㎸/㎝. The leakage cur-

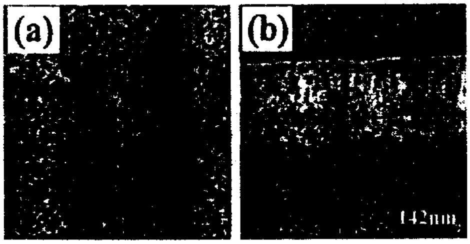

Fig. 1. SEM surface (a) and cross-sectional (b) images of the BZST films deposited at 500℃.

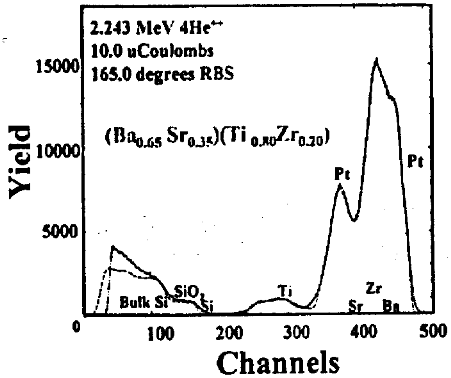

Fig. 2. Rutherford backscattering spectrum of the BZST films deposited at 500 ℃ : (----) theoretical ; (——) experimental.

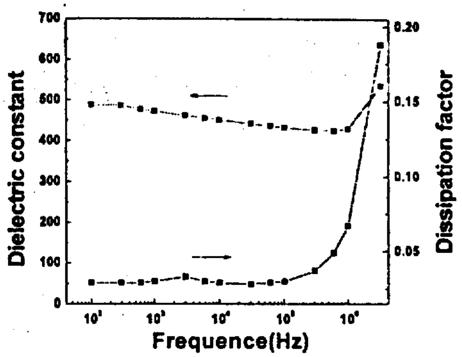

Fig. 3. Dielectric constant and dissipation factor of BZST film as a function of frequency.

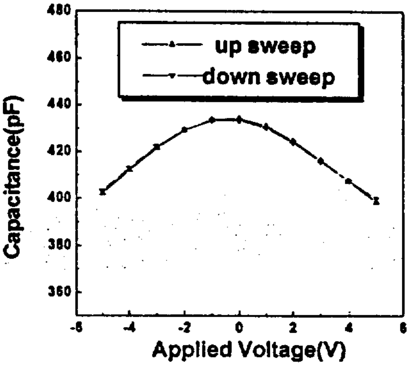

Fig. 4. Capacitance-voltage characteristics of thin films at the frequency of 100 ㎑ in MIM configurations.

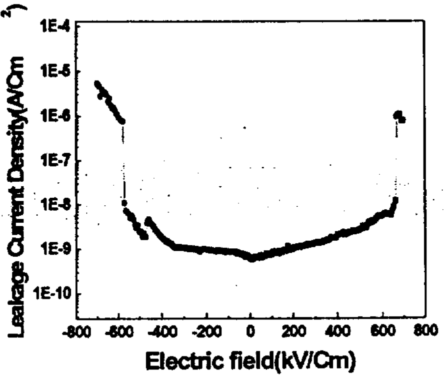

Fig. 5. Leakage current density as a function of applied field of BZST film deposited at 500℃.

rent density of the films was about 9.0×10^{-10} A/㎠ at 200 ㎸/㎝ and was superior to that of BST films reported by many researchers[9~11].

Ⅳ. CONCLUSIONS

The high dielectric BZST films were prepared on $Pt/Ti/SiO_2/Si$ substrates at 500℃ by rf magnetron sputtering technique. The dielectric films showed a dense and fine grain size. The dielectric constant and dissipation factor of a 100 ㎚ thick $(Ba_{0.65}Sr_{0.35})(Ti_{0.8}Zr_{0.2})O_3$ were 430 and 0.03 at an applied frequency of 100 ㎑, respectively. The dielectric films do not contain mobile ions and defects from the capacitance-voltage characteristics. The leakage current density was about 9.0×10^{-10} A/㎠ at 200 ㎸/㎝. High dielectric BZST films deposited at 500℃ were attractive for application to dynamic random access memory.

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