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The characteristics of MIS BST thin film capacitor

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Abstract Electric and dielectric (Ba,Sr)TiO_3 [BST] thin films for Metal-Insulator-Semiconductor (MIS) capacitors have been studied. BST thin films were deposited on p-Si(100) substrates by the RF magnetron sputtering with temperature range of 500~600°C. The dielectric properties of MIS capacitors consisting of Al/BST/SiO_2/Si sandwich structure were evaluated to reduce the leakage current density. The charge state densities of the MIS capacitors were determined by high frequency (1 MHz) C-V measurement. In order to reduce the leakage current in MIS capacitor, high quality SiO_2 layer was deposited on bare p-Si substrate. Depending on the oxygen pressure and substrate temperature, both positive and negative polarities of effective oxide charge in the MIS capacitors were evaluated. It is considered that the density of electronic states, generated at the BST/SiO_2/p-Si interface due to the asymmetric structure within BST/SiO_2/Si structure, and the oxygen vacancy content has influence on the behavior of oxide charge.

1. Introduction

High dielectric constant materials, such as (Ba,Sr)TiO_3 [BST] and $SrTiO_3$, have attracted great interest for application to cell capacitors of dynamic random access memories (DRAM) which requires a very high density of stored charge [1-3]. Especially, BST thin films which have SiO_2 equivalent thickness less than 0.5 nm and low leakage current density is one of the most desirable material for DRAM capacitor. In DRAM capacitor a low leakage current, a high dielectric capacitor, and high breakdown strength are needed [4-5].

The paraelectric phase of BST thin film can be formed by controlling the Ba/Sr ratio. $BaTiO_3$ is a ferroelectric material with a Curie temperature of 120°C while $SrTiO_3$ is a paraelectric material without ferroelectric phase transition [6-7]. Therefore it is possible to change the characteristics of BST thin film from paraelectricity to ferroelectricity or vice versa by Ba/Sr ratio control. For $(Ba_x,Sr_{1-x})TiO_3$ system, the Curie temperature changes linearly with Ba concentration. The paraelectric phase at the operating temperature of DRAMs is also desirable to avoid fatigue due to ferroelectric domain switching [8]. Dielectric properties of BST thin film deposited by means of RF-sputtering technique have been reported [9].

In this study, (Ba,Sr)TiO_3 thin films were deposited on SiO_2/p-Si(100) substrate by using RF magnetron sputtering. In order to reduce the leakage current, SiO_2 layer was grown on Si substrate by thermal oxidation. By applying SiO_2 layer between BST thin films and Si substrate, low leakage current of 10^{-10} order was observed. Furthermore, the leakage current showed the dependence on the oxygen concentration in plasma gas and the (Ba + Sr)/Ti ratio. Also, the BST MIS structure showed relatively high capacitance even though it is the combination of high-dielectric BST thin films and SiO_2 layer. By C-V measurement, the polarity of effective oxide charge changed with the oxygen concentration in plasma gas and (Ba + Sr)/Ti ratio of sputtering target.

2. Experimental

High quality silicon oxide layer was grown on p-Si(100) substrate by thermal oxidation. (Ba,Sr)TiO_3 thin film was deposited on SiO_2/Si substrate by RF magnetron sputter using *in-situ* technique at temperature range of 500~600°C. The (Ba,Sr)TiO_3 ceramic powder targets were prepared for various (Ba + Sr)/Ti ratios of 1, 1.025 and 1.05 by mixing 99.98 % $BaTiO_3$ and 99.9 % $SrTiO_3$ powder and excess 99.5 % BaO,SrO powder. The sputtering gas flow ratio were O_2/Ar = 1/9, 3/7, 5/5. Total pressure was maintained at 1.0×10^{-2} Torr. Deposition rates, calculated by measuring film thickness with a surface profiler - Tencor a-step and scanning electron microscope (SEM), were 8~9 Å/min.

Crystallinity analysis of BST thin film was performed with X-ray diffraction (XRD) using Cu K_α radiation. The composition of BST thin films was confirmed by Rutherford Backscattering Spectroscopy (RBS) and showed almost same value with sputtering target. For electrical measurements, Al upper electrodes of 200 μm radius were fabricated by thermal evaporation. Capacitance vs. voltage characteristics were measured with HP 4280A 1 Mhz Cmeter/CV plotter. The leakage current was measured with a HP 4145B semiconductor parameter analyzer. The polarization versus voltage hysteresis loops were obtained by using the test system from radiant technology.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the BST films deposited on SiO_2/p-Si(100) substrate at various O_2/Ar ratio in plasma gas. The BST films were deposited at 550°C and the (Ba + Sr)/Ti ratio was 1.025.

As the O_2 content in the plasma gas increases, diffraction peaks of BST(100) and (200) were observed in addition to a weak diffraction peak of BST(110) when O_2/Ar = 5/5 while, at the O_2/Ar ratio of 1/9, 3/7, peaks of BST (110), (111) and (211) were observed. It showed the tendency of epitaxy as the oxygen pressure increased. X-ray diffraction patterns of BST peaks with (Ba + Sr)/Ti ratio in the films were shown in Fig. 2. When the (Ba + Sr)/Ti ratio was 1.025, the diffraction peaks from BST(100) and (200) showed strong intensity with negligible (110) peak. The (Ba + Sr)/Ti ratio in BST films was confirmed by RBS analysis (Fig. 3). When the (Ba + Sr)/Ti was 1.025 for sputtering target, the (Ba + Sr)/Ti ratio (1.03) in the BST films was almost same as the ratio for the target. Furthermore, the Ba : Sr ratio was 1 : 1. It is in the range of paraelectric region. Figure 4 shows the leakage current density of the films under various sputtering gas mixture. The leakage current density decreased with increasing O_2 ratio in plasma gas. Also the films deposited at O_2/Ar = 5/5 showed the lowest leakage current density of 10^{-9} order until higher electric field of 600

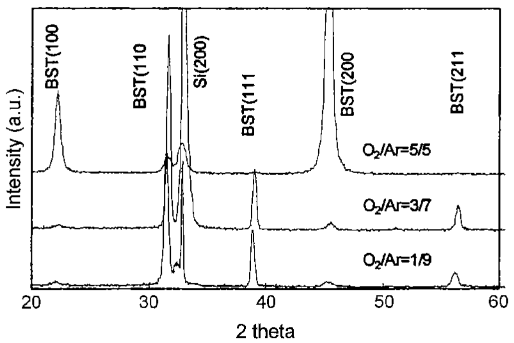

Fig. 1. XRD patterns of BST (1500 Å) films deposited on SiO_2/Si at 550 with various O_2/Ar ratio.

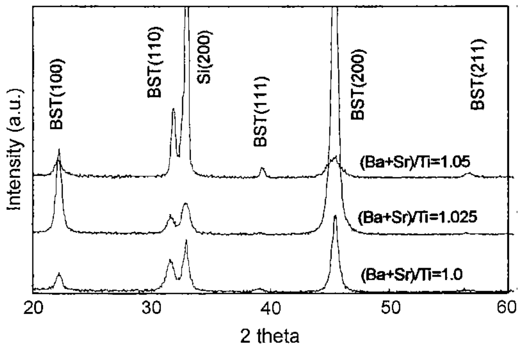

Fig. 2. XRD patterns of BST (1500 Å) films deposited on SiO_2/Si at 550°C with various (Ba + Sr)/Ti ratio.

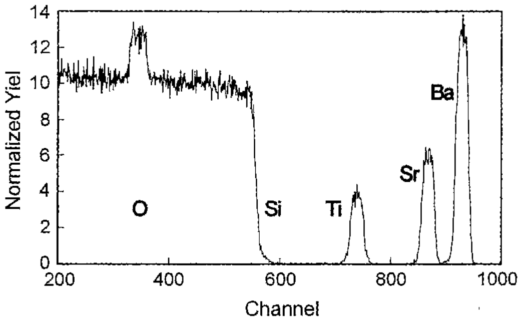

Fig. 3. RBS spectrum of 1500 Å thick BST film deposited on SiO_2/Si at 550°C with ratio of (Ba + Sr)/Ti = 1.025.

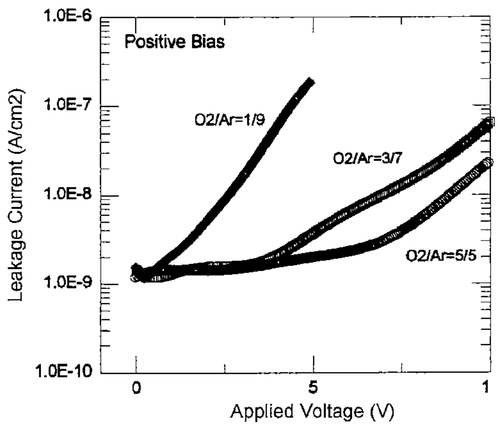

Fig. 4. Leakage current density of BST films with various O_2/Ar ratio.

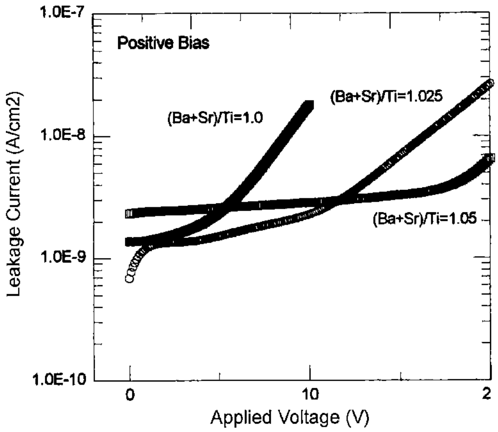

Fig. 5. Leakage current density of BST films with various (Ba + Sr)/Ti ratio.

kV/cm (9 V).

It is considered that the increase of O_2 ratio has the effect of decreasing the oxygen vacancy densities in the BST films and then decreasing the leakage current densities. The dependences of leakage current density as function of (Ba + Sr)/Ti ratio were shown in Fig. 5.

Leakage current densities for BST films with excess Ba,Sr (A/B ratio > 1) are lower than stoichiometric BST films for higher voltage. The leakage current density increases again for (Ba + Sr)/Ti = 1.05 in the range of 0~10 V.

Figure 6 shows the I-V characteristics for various deposition temperatures.

The film deposited at 550°C showed the lowest

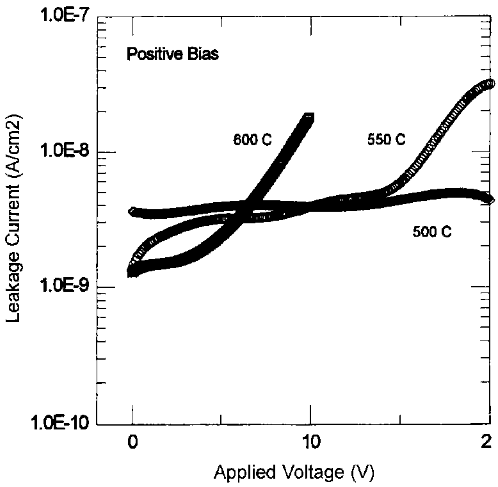

Fig. 6. Leakage current density of BST films with various deposition temperature.

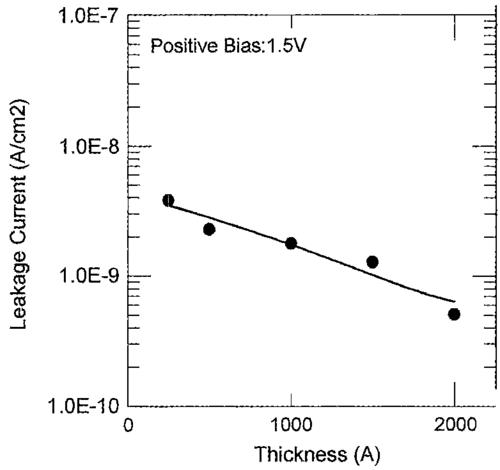

Fig. 7. Leakage current density with BST films thickness.

leakage current density less than 5.5 V but increased rapidly for applied voltage greater than 5.5 V. In the case of 2000 Å thick film, the leakage current density showed the lowest value of 5.0×10^{-10} at 1.5 V. While the leakage current densities increase with decreasing thickness, the films of 250~1500 Å show leakage cur-

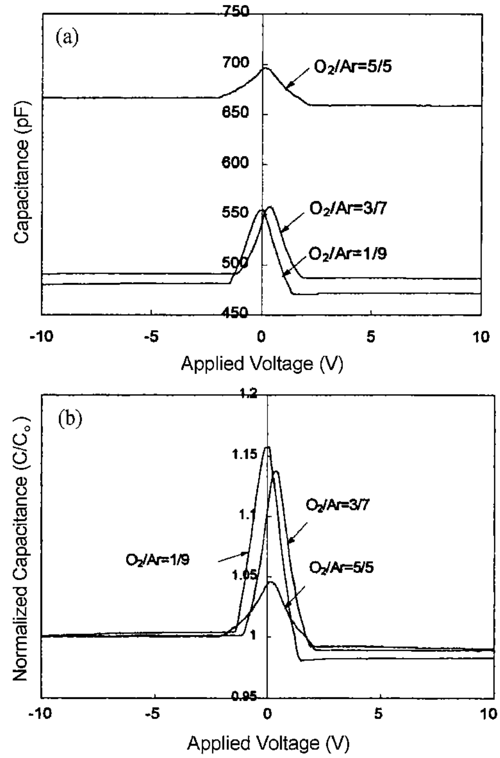

Fig. 8. C-V characteristics of BST film with various O_2/Ar ratio.

rent densities of 10^{-10} order (Fig. 7).

Figure 8 shows the C-V plot for BST film with MIS structure deposited at various O_2/Ar ratio in plasma gas. The BST +S iO_2 layer shows its maximum value of capacitance, 695pF, at O_2/Ar = 5/5 and the dielectric constant of 110 (Fig. 8(a)). As the O_2 ratio increases, the C-V plots shift to more positive bias. In Fig. 8(b), a positive flat band voltage shift of C-V plot implies effective negative charge residing at (BST + SiO_2)/Si interface [8].

The dependeces of capacitance on (Ba + Sr)/Ti ratio were shown in Fig. 9. The maximum capacitance was at (Ba + Sr)/Ti = 1.05 (Fig. 9(a)). And the C-V plots shift to more positive bias direction with increasing (Ba + Sr)/Ti ratio (Fig. 9(b)). As the deposition temperature increases, the capacitance increases. But, in this case, there was any remarkable flat band voltage shift with temperature (Fig. 10(a), (b)).

The increase of capacitance near zero field is considered as the result of ferroelectricity of BST films even though the Ba/Sr ratio is in the range of paraelectricity for bulk BST. The ferroelectricity of the epitaxial BST films, confirmed by X-ray pattern, is considered to be caused by the elongation of lattice constant in the direction of thickness. It is supposed that the elongation of the lattice constant enhances an ionic displacement and an interaction among dipoles [7].

Figure 11 shows the dielectric constant as a function

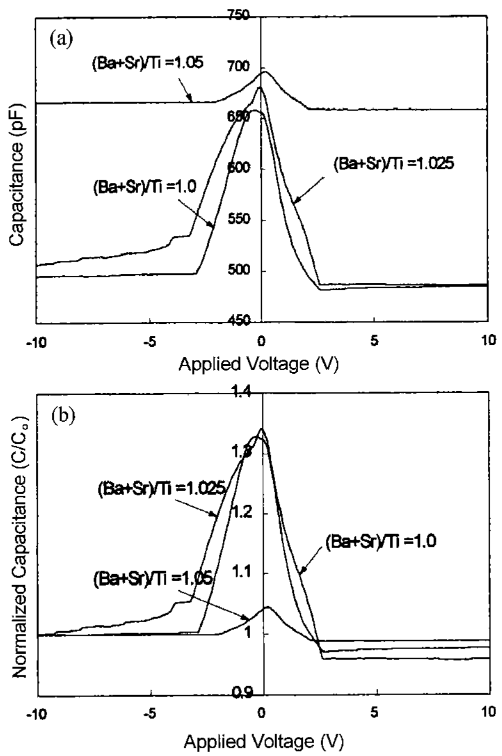

Fig. 9. C-V characteristics of BST film with various (Ba + Sr)/Ti ratio.

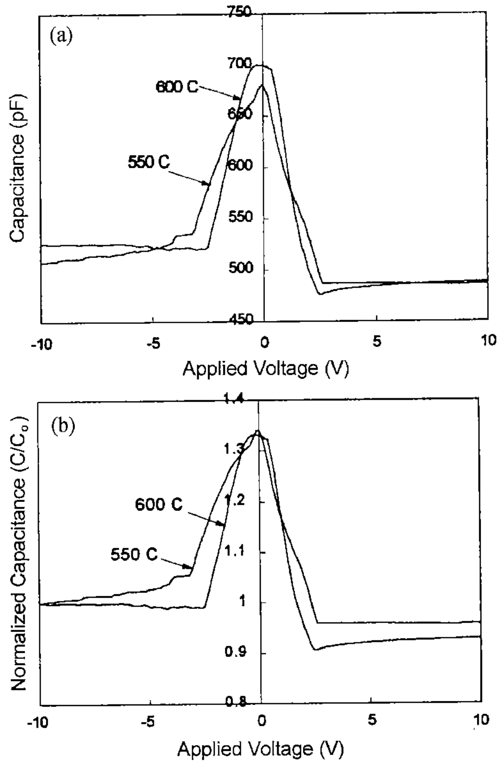

Fig. 10. C-V characteristics of BST film with temperature.

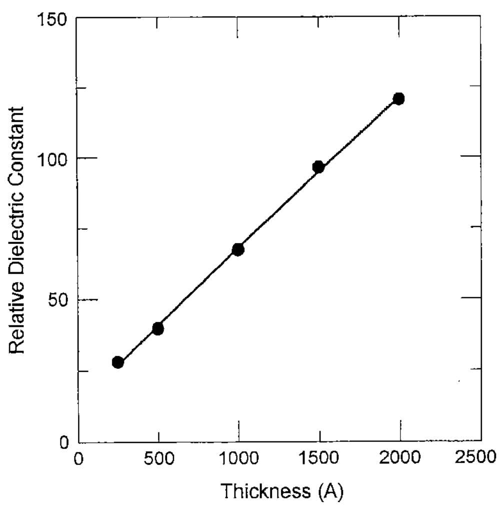

Fig. 11. Relative dielectric constant BST films.

of the film thickness. Dielectric constants of (BST + SiO_2) layer decreased with the decrease of the film thickness. It is assumed that the local field induced by space-charge layer at the dielectric-electrode interfaces would cause lowering of the dielectric constant.

4. Conclusion

The electrical properties of BST films were investigated for the application of MIS sturucture. BST films were deposited on SiO_2/Si substrate by controlling the O_2/Ar ratio and the (Ba + Sr)/Ti ratio in the films. The leakage current densities have the dependences on the O_2/Ar ratio in plasma gas, the (Ba + Sr)/Ti ratio and the deposition temperature. The dielectric constant of (BST + SiO_2) film calculated at the maximum capacitance was 110 and the leakage current density was 10^{-10} A/cm^2 at 5 V. The improved results can be introduced giga bit DRAM capacitors.

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