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Preparation and characterization of $(Ba_{1-x}Sr_x)TiO_3$ films by sol–gel processing

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Barium strontium titanate ((Ba, Sr)TiO_3) thin films were prepared on Pt/Ti/Si substrates by the sol–gel method using metal alkoxides. The dependence of the dielectric constant for the films on the film compositions and on the film thickness were investigated. The dielectric constant of the film of thickness 180 nm had the highest value of 230 at composition ratios of $[Ba+Sr]/[Ti]=1.04$ and $[Sr]/[Ba+Sr]=0.6$. The dielectric constant of the films with this composition decreased from 390 to 160 with a decrease in the film thickness from 440 to 100 nm. The decrease in the dielectric constant with increasing film thickness is attributed to the existence of a low-dielectric-constant interface layer adjacent to the electrodes.

1. Introduction

Dielectric thin films with a high dielectric constant such as Pb(Zr, Ti)O_3 (PZT), $SrTiO_3$ and (Ba, Sr)TiO_3 have been attractive for the application to the capacitor of dynamic random access memories (DRAMs). With the use of high-dielectric-constant films, the planar capacitor structure, which requires simpler processing than the stack or trench capacitor, realizes very-large-scale integration. In addition to a high dielectric constant, DRAM capacitor materials should have a low leakage current and be paraelectric in the operating temperature range to avoid fatigue phenomena by ferroelectric domain switching. The substitution of strontium for barium in $BaTiO_3$ decreases the Curie temperature, T_C, to make (Ba, Sr)TiO_3 a room-temperature paraelectric with both a high dielectric constant and a low leakage current.

(Ba, Sr)TiO_3 thin films have been prepared by various methods, such as radio-frequency (r.f.) sputtering [1, 2], ion-beam sputtering [3], laser ablation [4, 5], metal–organic chemical vapour deposition [6] and the sol–gel technique [7, 8]. The sol–gel method has been studied for preparing various thin films. Sol–gel processing has advantages over other methods such as homogeneity, purity, and ease of controlling the composition of the film.

In this study, $(Ba_{1-x}Sr_x)TiO_3$ thin films were prepared by a sol–gel method. The dependence of the dielectric constant for the films on the composition ratios $[Ba+Sr]/[Ti]$ and $[Sr]/[Ba+Sr]$ and on the film thickness were investigated.

2. Experimental procedure

Appropriate amounts of barium and strontium metals were dissolved in 2-methoxyethanol ($CH_3OC_2H_4OH$) at 60 °C. Titanium isopropoxide was then added to this solution. Finally, the solution was refluxed at 124 °C for 2 h. The above procedures were conducted in a dry nitrogen atmosphere. The concentrations of the $(Ba_{1-x}Sr_x)TiO_3$ solution were 0.3 and 0.15 $mol\,l^{-1}$. The solutions were used for coating without partial hydrolysis.

For the substrate preparation, a Si(1 0 0) wafer was cleaned with diluted HF solution and coated with 50 nm Ti and 50 nm Pt layers in a r.f. sputtering apparatus. The precursor films were prepared on the substrates by spin coating at 2000 rev min^{-1} for 30 s. After spinning, the films were dried at 120 °C for 10 min and fired at 750 °C for 10 min in an oxygen atmosphere at a heating rate of 5 °C min^{-1}. These procedures were repeated to achieve the desired film thickness. Each cycle of coating, drying and firing formed the film with thicknesses of about 60 nm and 20 nm from the 0.3 mol l^{-1} and 0.15 mol l^{-1} solutions, respectively. Finally, the films were heat treated at 750 °C for 1 h in an oxygen atmosphere.

The crystalline phases in the films were identified using X-ray diffraction (XRD). The thickness and microstructure of the films were observed by scanning electron microscopy (SEM). The dependence of the dielectric constant on the composition was determined using the films with a thickness of 180 nm prepared from solutions of concentration 0.3 mol l^{-1}. The dependence of the dielectric constant on the film thickness was obtained using the films prepared from the solutions with concentrations of 0.3 and 0.15 $mol\,l^{-1}$. Gold upper electrodes with a diameter of 0.5 mm were deposited by vacuum evaporation. The dielectric properties were measured at room temperature using a HP 4275A *LCR* meter at 100 kHz. The dielectric properties of the films with thicknesses less than 180 nm and 100 nm from the 0.3 $mol\,l^{-1}$ and 0.15 $mol\,l^{-1}$ solutions, respectively, could not be measured because of the short circuit.

3. Results and discussion

Figure 1 shows the XRD patterns for the films with the composition ratio [Sr]/[Ba + Sr] = 0.5–0.8. The (1 1 1) peak of perovskite type (Ba, Sr)TiO_3 overlapped the very strong (1 1 1) peak of Pt. No diffraction peak other than those of (Ba, Sr)TiO_3 and Pt was observed. All four patterns showed weak (1 1 0) preferred orientation. With increase in strontium content, the diffraction lines of the perovskite phase shifted towards larger angles. This indicates that the lattice constant of (Ba, Sr)TiO_3 becomes smaller with increasing strontium content, owing to the difference between the ionic radii of Ba^{2+} and Sr^{2+} ions.

The $SrTiO_3$ thin films prepared by a sol–gel method showed a composition dependence of the dielectric constant with a maximum at [Sr]/[Ti] = 1.04 [9]. The change in the dielectric constant for the films with [Ba + Sr]/[Ti] was obtained using the constant composition ratio of [Sr]/[Ba + Sr] = 0.6. Fig. 2 shows the dependence of the dielectric constant for the films on the [Ba + Sr]/[Ti] ratio. As in the case of the $SrTiO_3$ films, the dielectric constant showed a maximum of 230 at [Ba + Sr]/[Ti] = 1.04. This result agreed with the previous results obtained using ion-beam sputtering [3]. The XRD peaks of the film with [Ba + Sr]/[Ti] = 1.04 were slightly sharper than those of the other two films. The excess A-site ions (Ba^{2+} and Sr^{2+} ions) could be substituted for the B-site ions (Ti^{4+} ions) and compensate for oxygen vacancies; this could make the dielectric constant higher through the improvement in crystallinity of the perovskite phase.

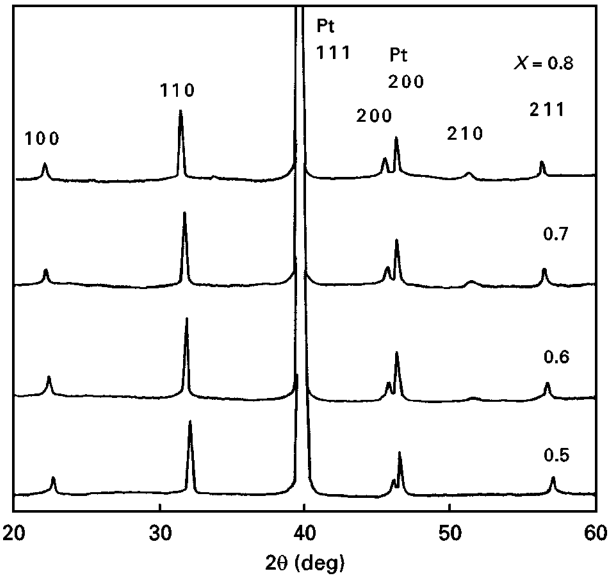

Figure 1 XRD patterns of the films with [Sr]/[Ba + Sr] ratios x of 0.5, 0.6, 0.7 and 0.8.

The change in the dielectric constant for the films with [Sr]/[Ba + Sr] ratio is shown in Fig. 3. The dielectric constant increased from 180 to 230 with increase in [Sr]/[Ba + Sr] from 0.5 to 0.6. On further increase in [Sr]/[Ba + Sr], the dielectric constant decreased slightly to 190 at [Sr]/[Ba + Sr] = 0.8. Bulk (Ba, Sr)TiO_3 ceramics show a maximum at around [Sr]/[Ba + Sr] = 0.7. The (Ba, Sr)TiO_3 thin films obtained by ion beam sputtering were reported to show a maximum of the dielectric constant at [Sr]/[Ba + Sr] = 0.5 [10]. On the other hand, those films prepared by a sol–gel method showed the maximum dielectric constant at [Sr]/[Ba + Sr] = 0.75 at room temperature [8]. The result of this work lies between those of the previous two reports.

The dissipation factors (tan δ) for all the films prepared were almost constant between 0.02 and 0.03, irrespective of the film compositions.

The dependence of the dielectric constant on the film thickness was determined by the films with [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6. The films with thickness greater than 180 nm and less than 180 nm were prepared from the 0.3 mol l^{-1} and 0.15 mol l^{-1} solutions, respectively. Fig. 4 shows the change in the dielectric constant with the film thickness. The film with a thickness of 440 nm had a dielectric constant of 390. The dielectric constant decreased with decrease in the film thickness, to 160 for the film with a thickness of 100 nm. This tendency of the

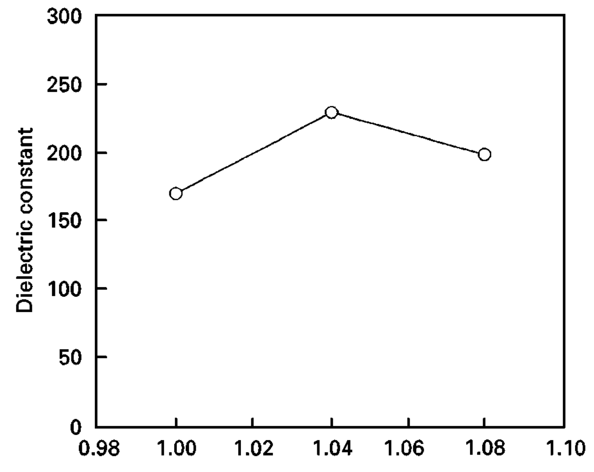

Figure 2 Change in the dielectric constant for the films with [Ba + Sr]/[Ti] at constant [Sr]/[Ba + Sr] = 0.6.

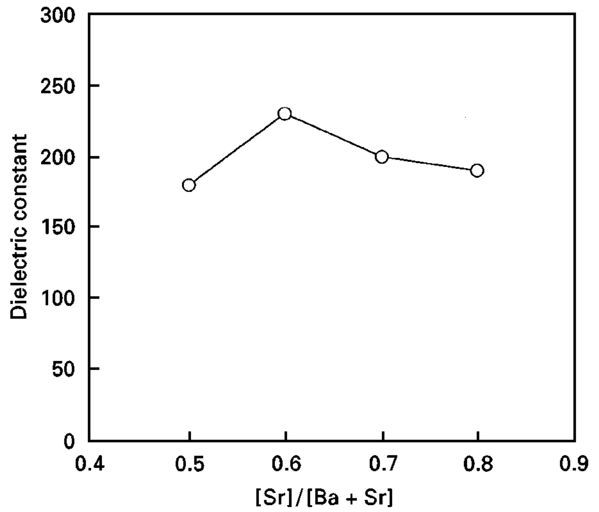

Figure 3 Change in the dielectric constant for the films with [Sr]/[Ba + Sr] at constant [Ba + Sr]/[Ti] = 1.04.

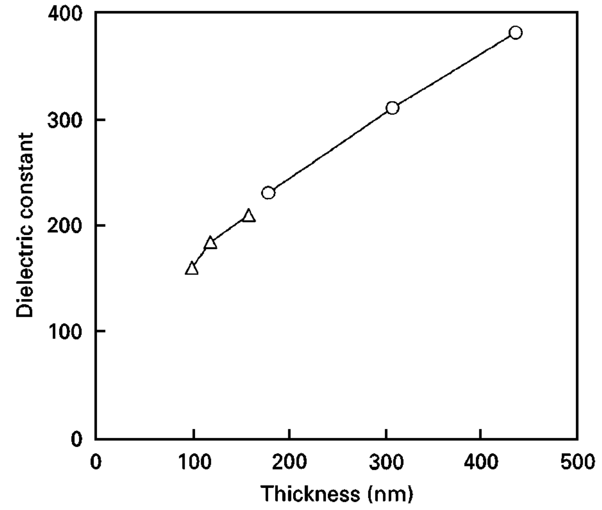

Figure 4 Change in the dielectric constant with the film thickness with [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6. (–○–), 0.3 mol l^{-1} solution; (–△–) , 0.15 mol l^{-1} solution.

dielectric constant for the thin films was reported for (Ba, Sr)TiO_3 [3] and PZT [11].

The surfaces of the films were observed by SEM in order to examine the effect of the grain size on the dielectric constant. Fig. 5 a and b shows SEM photographs of the films with thickness of 180 nm and 440 nm, respectively, prepared from the 0.3 mol l^{-1} solution. The 180 nm film had very shallow dimples on the surface and did not show a distinct grain structure under SEM observation. The 440 nm film showed a grain structure with a grain size of about 70–100 nm. The dielectric constant decreased from 390 to 230 with decrease in the film thickness from 440 to 180 nm. Fig. 6 shows a SEM photograph of the film with a thickness of 160 nm prepared from the 0.15 mol l^{-1} solution. This film had a grain structure with almost the same grain size as the 440 nm film. The dielectric constant of this film decreased to 210 in spite of its grain size.

The films with thicknesses of 180 nm and 440 nm were prepared from the 0.3 mol l^{-1} solution by three and seven cycles, respectively, of coating, drying and firing. On the other hand, the film with a thickness of 160 nm was prepared from the 0.15 mol l^{-1} solution by eight cycles of coating, drying and firing. For the lower numbers of coating–drying–firing cycles, the surface of the films have shallow dimples and the grain growth does not take place well. The above results on the dielectric constant indicate that the decrease in the film thickness does not necessarily lower the grain size and that the decrease in the dielectric constant with the decrease in the film thickness is mainly caused by another mechanism.

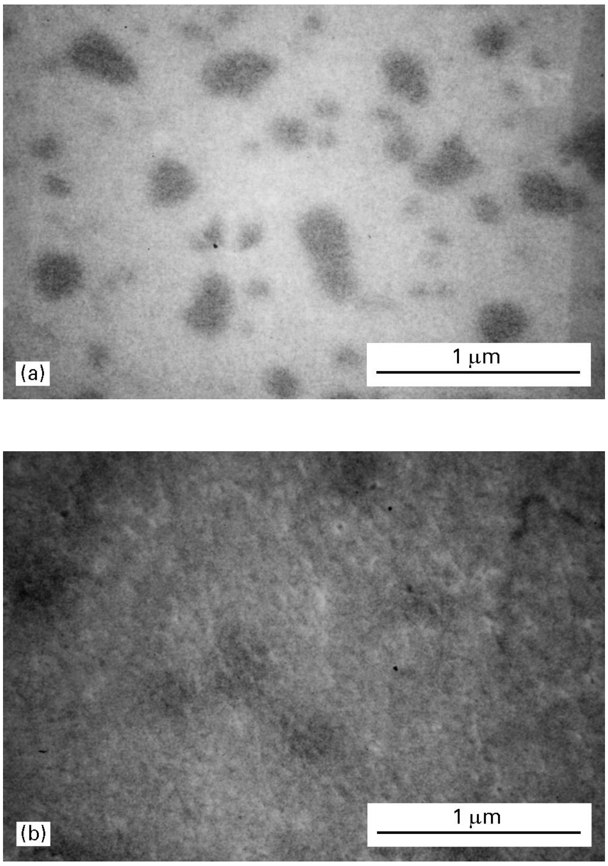

Figure 5 SEM photographs of the surface for the films prepared from the 0.3 mol l^{-1} solution with [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6: (a) thickness of 180 nm; (b) thickness of 440 nm.

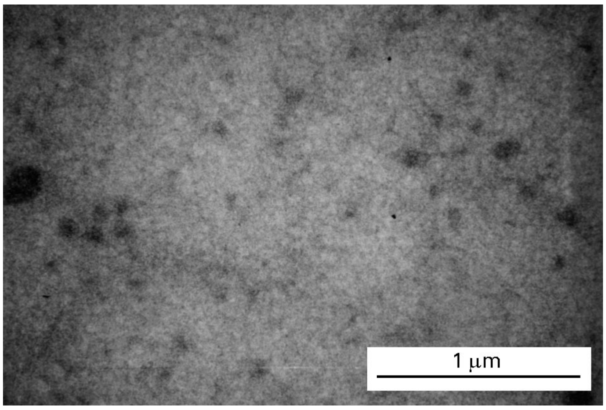

Figure 6 SEM photograph of the surface for the film 160 nm thick prepared from the 0.15 mol l^{-1} solution with [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6

The double-layer capacitor model, where two series capacitors are assumed to exist, is used to explain the thickness dependence of the dielectric constant [12] (Fig. 7). It is assumed that a layer with a low dielectric constant exists adjacent to the electrode and that the remaining part of the film has a high dielectric constant. The measured capacitance, C_m, is related to the capacitance C_i of the low-dielectric constant layer at the interface and the capacitance, C_b, of the remaining layer as follows:

$$\begin{aligned}\frac{1}{C_m} &= \frac{1}{C_b} + \frac{1}{C_i} \\ &= \frac{d_b}{\varepsilon_0 \varepsilon_b A} + \frac{d_i}{\varepsilon_0 \varepsilon_i A} = \frac{d_m - d_i}{\varepsilon_0 \varepsilon_b A} + \frac{d_i}{\varepsilon_0 \varepsilon_i A} \qquad (1)\end{aligned}$$

where d_b and ε_b are the thickness and the dielectric constant, respectively, of the major layer in the film, d_i and ε_i are the corresponding values of the interface

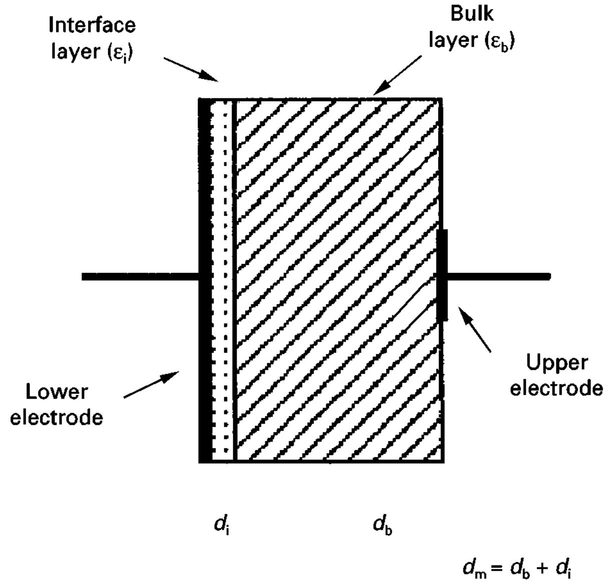

Figure 7 Schematic diagram of the double-layer capacitor.

layer, A is the electrode area and ε_0 is the dielectric constant of free space. It is also assumed that the thickness, d_i, of the interface layer is independent of the total film thickness, d_m. If $d_b \gg d_i$, $d_m = d_b$. Hence Equation 1 can be modified to

$$\frac{1}{C_m} = \frac{d_m}{\varepsilon_0 \varepsilon_b A} + \frac{d_i}{\varepsilon_0 \varepsilon_i A} \qquad (2)$$

The inverse, $1/C_m$, of the measured capacitance should have a linear dependence on the thickness, d_m. Fig. 8 shows the relationship between $1/C_m$ and d_m. All the experimental data on $1/C_m$ from both the 0.3 mol l^{-1} solution and the 0.15 mol l^{-1} solution are on one line. From the slope of the $1/C_m$ line, ε_b is calculated to be 620. This result indicates that a high-dielectric-constant layer is formed even when the thickness is only 100 nm. From the intercept of the $1/C_m$ line on the ordinate axis, d_i/ε_i can be also calculated to be 0.48 nm. Assuming that the interface phase is amorphous SiO_2 ($\varepsilon_r = 4$) formed by the diffusion of silicon from Si substrate, the thickness of the interface layer is 1.9 nm. The existence of the interface layer with a low dielectric constant has a detrimental effect on the dielectric properties of the films.

4. Conclusion

The (Ba, Sr)TiO_3 thin films were prepared on a Pt/Ti/Si substrate by a sol–gel technique using metal alkoxides. The dependence of the dielectric constant on the film composition and on the film thickness were examined. The dielectric constant of the films with a thickness of 180 nm showed a maximum of 230 at [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6. The dielectric constant decreased from 390 to 160 with a decrease in the film thickness from 440 to 100 nm.

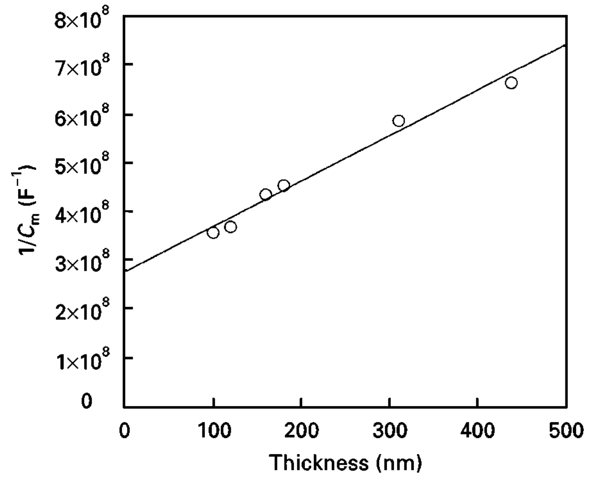

Figure 8 Thickness, d_m, dependence of the inverse measured capacitance, $1/C_m$, for the films with [Ba + Sr]/[Ti] = 1.04 and [Sr]/[Ba + Sr] = 0.6.

This behaviour was well explained by the existence of the interface layer with a low dielectric constant. It is necessary to minimize the thickness of the interface layer in order to obtain thin films less than 100 nm thick with a high dielectric constant.

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