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Annealing Effects on the Dielectric Properties of the (Ba, Sr) TiO_3 Films on RuO_2 Bottom Electrodes

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(Ba,Sr) TiO_3 (BST) thin films were prepared on RuO_2/Si substrates by rf magnetron sputtering and annealing was followed at temperatures ranging from 550 to 800°C in N_2 or O_2 atmosphere. The effects of annealing conditions on the properties of BST film deposited on RuO_2 bottom electrodes were investigated. It was found that the crystallinity, surface roughness, and grain size of BST films vary with the annealing temperature but they are not dependent upon the annealing atmosphere. The flat region in the current-voltage (I-V) curves of BST capacitors shortened with increasing annealing temperature under both atmospheres. This is believed to be due to the lowering of potential barrier caused by unstable interface and the increase of charge The shortening of the flat region by O_2-annealing was more severe than that by N_2-annealing. As a result, there was no flat region when the films were annealed at 700 and 800°C in O_2 atmosphere. The dielectric properties of BST films were improved by annealing in either atmosphere, however, a degradation with frequency was observed when the films were annealed at relatively high temperature under O_2 atmosphere.

Key words : (Ba,Sr) TiO_3, RuO_2, Annealing, Potential barrier, Leakage current, Dielectric constant

I. Introduction

With the increase in the integration density of dynamic random access memory (DRAM) devices, silicon dioxide and silicon oxynitride, which have long been used as capacitor dielectric materials, are no longer applicable because of their low dielectric constants. Therefore, a new material having a relatively high dielectric constant is required. Recently, a few materials with the perovskite structure, such as $SrTiO_3$, (Ba_{1-x}, Sr_x) TiO_3 (BST), and Pb $(Zr_{1-x}, Ti_x)O_3$ (PZT), have attracted much attention as new dielectric materials for the charge storage capacitors. Among them, BST is considered to be the most promising capacitor material for use in ultralarge scale integration (ULSI) DRAMs due to its high dielectric constant, low dissipation factor, and low leakage current density. In addition, since BST is paraelectric at room temperature when x is more than 0.3, it does not have aging and fatigue effects.[1,2] BST thin films have been deposited by a variety of deposition techniques, such as rf magnetron sputtering,[3] laser ablation,[4] metalorganic chemical vapor deposition (MOCVD),[5] and liquid source chemical vapor deposition (LSCVD).[6] Among these techniques, rf magnetron sputtering using multicomponent oxide target is an appropriate method to fabricate BST thin films owing to its excellent compositional reproducibility and controllability.[7]

Because a relatively high substrate temperature and an oxidizing atmosphere are usually necessary during the preparation of BST films, a noble metal bottom electrode, such as Pt, is required. However, the application of the metal electrode to the fabrication is limited due to its difficulties in precise submicron patterning. Therefore, an alternative bottom electrode material is required for BST film capacitors.[8] RuO_2 is one of the most promising bottom electrode materials because it has relatively low resistivity and high thermodynamic stability,[9] acts as a good diffusion barrier,[10] and shows easiness of etching.[11] Moreover, because RuO_2 appears to be a high work function material,[12] a contact between RuO_2 electrode and BST film forms a high potential barrier at the interface (Schottky-type barrier) These are the reasons why RuO_2 films have been studied as the bottom electrode, instead of a noble metal, for the BST film capacitors.[8,13,14] However, there are few reports about how the annealing conditions affects the properties of BST films deposited on RuO_2 bottom electrodes In our present study, in order to investigate this effect, we prepared BST films on RuO_2/Si substrates by rf magnetron sputtering and annealed them in various conditions. This paper describes the influence of annealing conditions on the microstructures and the electrical properties of BST films deposited on RuO_2 bottom electrodes.

Table 1. Typical Deposition Conditions of BST thin Films

Base pressure	$< 5.0 \times 10^{-6}$ Torr
Working pressure	2.5×10^{-3} Torr
Ar : O_2	50 : 50
Target	$(Ba_{0.5}, Sr_{0.5}) TiO_3$ (2-inch dia.)
rf power	50 W
Temperature	550°C
Substrate	RuO_2/p-Si (100)
Substrate rotation rate	2 rpm
Target to substrate distance	10 cm

II. Experimental Procedure

RuO_2 thin films, deposited on Si substrates by reactive rf magnetron sputtering at a temperature of 500°C, were used as bottom electrodes. The sputtering gas was 70% Ar + 30% O_2 mixture with total pressure of 3 mTorr. BST films (80 nm thick) were then deposited onto them by rf magnetron sputtering. Typical deposition conditions of BST thin films are shown in Table 1. The deposited films were annealed at temperatures ranging from 550 to 800°C in N_2 or O_2 atmosphere for 30 min. For electrical measurements, Al top electrodes with a diameter of 0.5 mm were deposited by thermal evaporation through a metal shadow mask.

The film thickness was measured by α-step surface profilometry. The crystallinity of the films was examined by X-ray diffraction (XRD) measurement. Atomic force microscopy (AFM) was used to determine grain size and surface roughness. Current-voltage (I-V) and capacitance-frequency (C-F) characteristics of Al/BST/RuO_2 capacitors were measured using HP 4155A semiconductor parameter analyzer and HP 4284A LCR meter, respectively.

III. Results and Discussion

Fig. 1 shows the XRD patterns of BST films annealed in N_2 and O_2 atmospheres at 600 and 800°C. Typical perovskite structure BST films were obtained under all annealing conditions. In both annealing atmospheres, the intensity of the perovskite peaks increased with increasing annealing temperature but no preferred orientation was observed. Therefore, it is believed that the crystallinity of BST films does not depend on annealing atmosphere although it depends on the temperature. For the RuO_2 films, however, the peak intensity and orientation did not change significantly even the temperature was raised up to 800°C which implies that RuO_2 bottom electrode is suitable for the MIM capacitor in terms of stability even at high temperature.

The surface roughness and the grain size of BST films were investigated by AFM measurement. Figs. 2 (a) to 2 (d) are the 3-dimensional AFM images showing the grain sizes of BST films deposited at 550°C and annealed in N_2 atmosphere at 550, 600, 700 and 800°C. As shown in the figures, the grain size dose not increase markedly by annealing at temperatures up to 700°C, however, the sample annealed at 800°C shows much larger grain size than the other films. The morphologies of BST films annealed in O_2 atmosphere are similar to those of the films annealed in N_2 atmosphere.

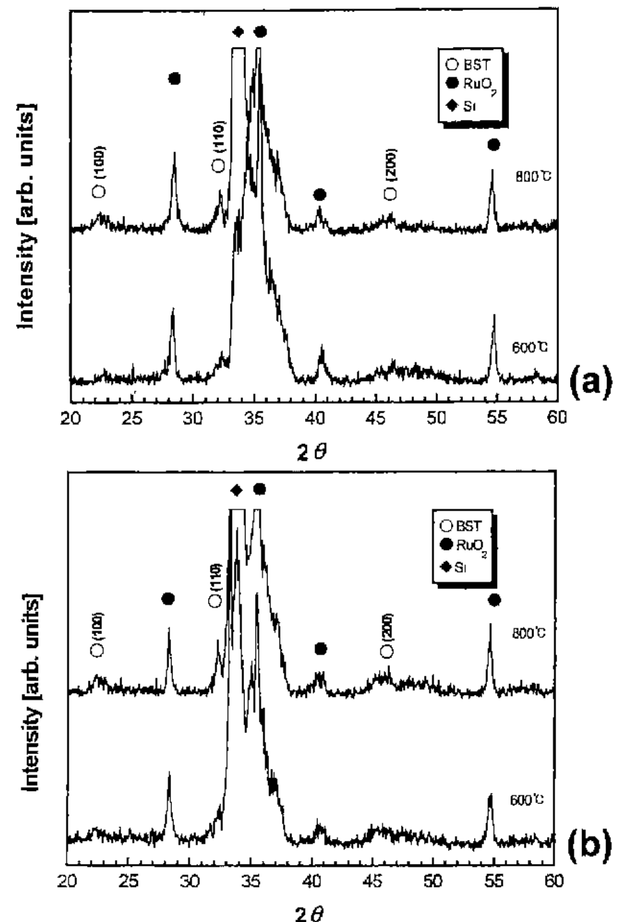

Fig. 1. XRD patterns of BST films deposited at 550°C and annealed at 600 or 800°C in (a) N_2 and (b) O_2 atmosphere.

Fig. 3 shows the rms surface roughnesses of BST films annealed in N_2 and O_2 atmosphere as a function of annealing temperature. The result indicates that the effect of annealing on the surface roughness of BST films is not significant at temperatures up to 700°C. The roughness, however, is increased markedly from 39Å to near 55Å for both atmospheres as the temperature increased from 700 to 800°C. The Surface roughness of the film is also independent of the annealing atmosphere.

Fig. 4 represents the current-voltage (I-V) characteristics of the BST films annealed in N_2 atmosphere. The current was measured at 25°C and the voltage was applied up to ±6 volts with a step of 0.1 V. It is generally accepted that the leakage current density of a BST film increases with the surface roughness.[15] The film annealed at 800°C, however, does not show the highest cur-

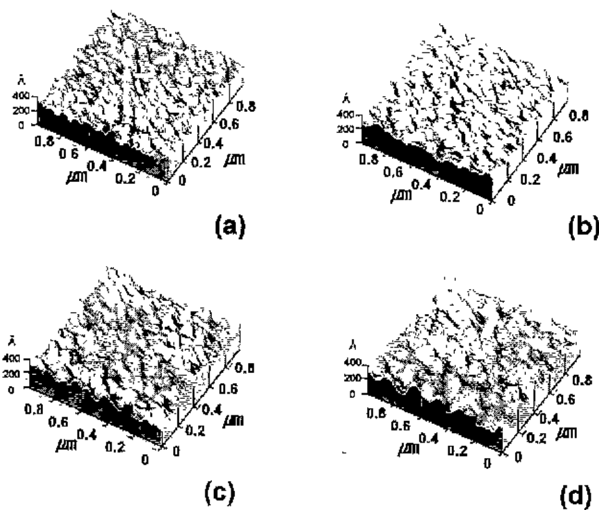

Fig. 2. 3-dimensional AFM images of BST films deposited at 550°C and annealed in N_2 atmosphere at (a) 550, (b) 600, (c) 700 and (d) 800°C.

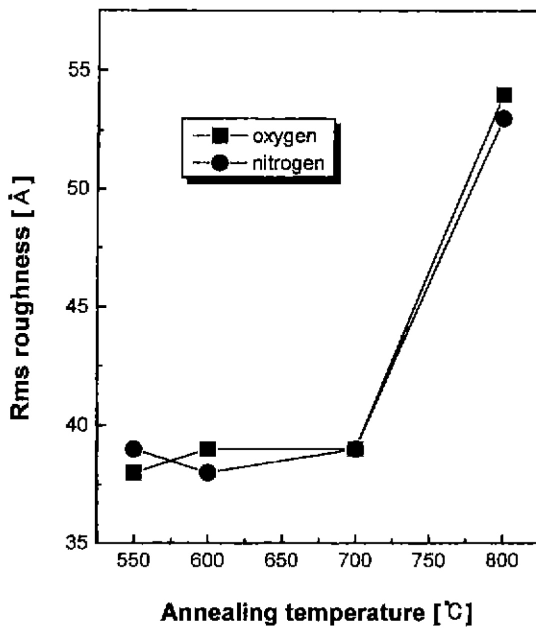

Fig. 3. Rms surface roughnesses of BST films annealed in N_2 and O_2 atmosphere as a function of annealing temperature.

rent density even though it has the largest value of surface roughness. This is because the area of grain boundaries, which act as current path,[16] is decreased due to grain growth for the film annealed at 800°C.

It is verified from the I-V characteristics that the current through BST film capacitor is electrode-limited, because the shape of curve for negative bias is different from that for positive bias. Since Al has relatively low work function, the potential barrier height between Al and BST is small at the contact. This results in the absence of the flat region in the I-V curve when the ne-

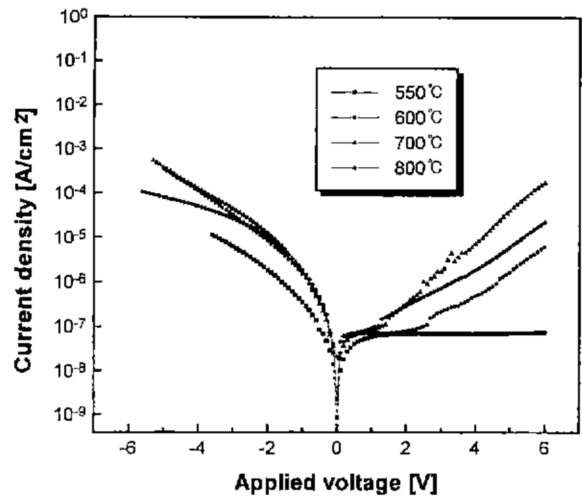

Fig. 4. Current-voltage characteristics of the BST films annealed in N_2 atmosphere for various annealing temperatures.

gative bias was applied to the top electrode. On the contrary, when the positive bias was applied to the top electrode, the flat region appeared because of relatively high potential barrier between RuO_2 and BST. However, the flat region shortens as the annealing temperature increases, as shown in the figure. This is believed to be due to the lowering of Schottky barrier height. High-temperature annealing of undoped perovskite titanate, such as BST, under nonoxidizing atmosphere generally produces electrons with oxygen vacancies.[17] The reduction reaction can be represented by

$$O_O \rightarrow 1/2\ O_2 + V_O^{\cdot\cdot} + 2e' \quad (1)$$

As the annealing temperature increases, the number of produced electrons increases.[17] It is known that the Schottky barrier height depends on the work function of electrode, barrier lowering by Schottky effect due to charges and the interface states.[18] In this study, the bottom electrode was fixed to RuO_2. Therefore, the other possible factors, which can affect the barrier lowering, are the increase of produced electrons and the degradation of interface state by annealing. Hence, it can be said that the Schottky barrier height between RuO_2 and BST was decreased by annealing, which results in the shortening of flat region in the I-V curve with increasing annealing temperature when the positive bias was applied to the Al top electrodes.

The I-V curves of BST films annealed in O_2 atmosphere are different from those of the films annealed in N_2 atmosphere as shown in Fig. 5. It is seen that the shortening of the flat region by O_2-annealing is more severe than that by N_2-annealing. There are two sources of oxygen vacancies in the undoped perovskite titanates[19]: a) Reduction by equilibration with a low oxygen activity which produce electrons, b) Nonstoichiometry in the cation ratios which does not produce electrons. W. J. Lee

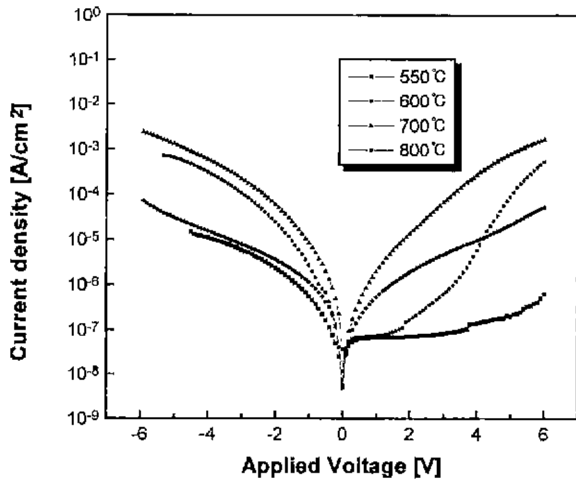

Fig. 5. Current-voltage characteristics of the BST films annealed in O_2 atmosphere for various annealing temperatures.

reported[20] that the (Ba + Sr)/Ti ratio was 0.68 when the BST film was deposited by RF magnetron sputtering using stoichiometric target and this was ascribed to the resputtering and different sticking coefficients of each element. Since the stoichiometric target was used in the present study, (Ba + Sr)/Ti ratio of the film must be less than unity. Therefore, the oxygen vacancies in the as-deposited films was made dominantly by nonstoichiometry in the cation ratio. When the undoped perovskite titanate having nonstoichiometry in the cation ratio, such as BST deposited using stoichiometric target, is annealed in oxidizing atmosphere at relatively high temperature, the neutral oxygen atoms that enter the lattice require two electrons from the valence band leaving equivalent number of holes.[21] The oxidation reaction can be represented by

$$V_O^{\cdot\cdot} + 1/2\ O_2 \rightarrow O_O + 2h^{\cdot} \quad (2)$$

It is believed that these holes play an important role in the decreasing of the flat region in the curve. Like the case of N_2-annealing, the flat region in the I-V curve of O_2 -annealed films shortened with the annealing temperature. This is believed to be to due to the barrier lowering caused by degradation of interface and the increase of image force by annealing. As shown in Fig. 5, there are no flat regions in the I-V curves of BST films annealed at 700 and 800°C. This means that there is no effect of potential barrier between RuO_2 and BST on the current through the capacitor.

Figs. 6 and 7 show the dielectric constants and dissipation factors as a function of frequency for the BST films annealed in N_2 and O_2 atmosphere, respectively. These values are evaluated at the applied bias of 1 V. With increasing the annealing temperature, both of the dielectric constant and the dissipation factor of the films increase. This trend is well agreed with D. M. Tahan *et al.*'s report.[22] The dielectric constants of the films annealed at 800°C were 320 and 346 for N_2 and O_2 atmosphere, respectively. The dielectric constant of the film annealed in O_2 atmosphere is a little bit higher than that of the film annealed in N_2 atmosphere. However, as the frequency increases, the dielectric properties of the films annealed in O_2 atmosphere degraded more significantly than did the films annealed in N_2 atmosphere, especially for the high temperature annealed films.

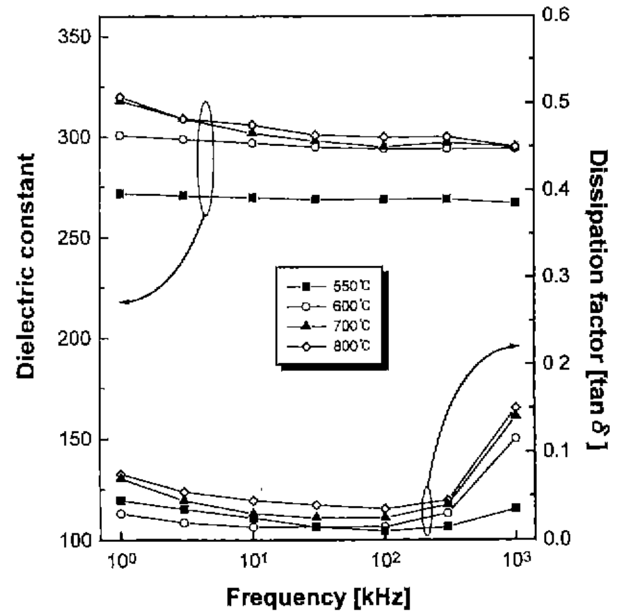

Fig. 6. Dielectric constants and dissipation factors as a function of frequency for the BST films annealed in N_2 atmosphere

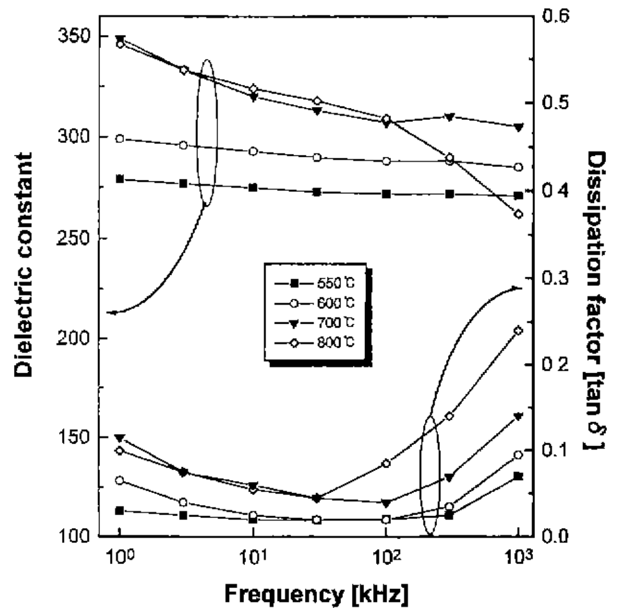

Fig. 7. Dielectric constants and dissipation factors as a function of frequency for the BST films annealed in O_2 atmosphere.

IV. Conclusions

BST thin films were deposited on RuO_2/Si substrates and annealed in N_2 and O_2 atmosphere at temperatures ranging from 550 to 800°C. The perovskite structure BST films were obtained in all annealing conditions. Though the crystallinity of the films was improved with increasing the temperature, it was independent on the annealing atmosphere. While the surface roughness and the grain size of BST films did not change significantly at annealing temperatures between 550 and 700°C, they were increased markedly at 800°C. The film annealed at 800°C, does not show the highest current density even though it has the largest value of surface roughness. This is because the grain boundary area, which act as current path, is decreased due to grain growth. In both annealing atmospheres, the flat regions in the I-V curves of BST capacitors shortened with increasing annealing temperature. This is believed to be due to the lowering of barrier height caused by degradation of interfacial quality and increase of charges. Annealing improved the dielectric properties of the BST films in both atmospheres. However, the properties of the films annealed at high temperature degraded with frequency. This degradation is more significant in O_2 atmosphere than in N_2 atmosphere.

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