Surface and Coatings Technology 160 (2002) 277–281

SURFACE & COATINGS TECHNOLOGY

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Improving leakage currents of Pt/$Ba_{0.8}Sr_{0.2}TiO_3$/Pt capacitors using multilayered structures

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Received 12 April 2002; accepted in revised form 17 June 2002

Abstract

Pt/$Ba_{0.8}Sr_{0.2}TiO_3$ (BST)/Pt capacitors fabricated by the sol–gel process generally show abnormally high leakage currents. In this paper, we report the reduction of this leakage current in multilayered sol–gel Pt/BST/Pt thin film capacitors. The multilayered structure also provided the flexibility of adjusting the dielectric constant of the film. The thin films were fabricated by a step-by-step annealing scheme at 750 °C except that the top and bottom layers were annealed at less than 750 °C. The observed results are explained by an amorphous/polycrystalline structure, which was confirmed by scanning electron microscopy and X-ray diffraction analysis.

Keywords: (Ba, Sr)/TiO_3 films; Sol–gel process; Leakage current

1. Introduction

Barium strontium titanate (BST) film has been investigated extensively for the application in the high density dynamic random access memories (DRAMs) [1–5]. One of the most crucial electrical parameters of these films has been the leakage current level of DRAM cells [6–9]. Once data has been written in DRAM, charges stored in each capacitor must maintain more than the refresh time so that the information stored in each DRAM cell can be read out correctly. Therefore, leakage current must be kept sufficiently low such that the capacitor does not discharge before it is refreshed.

In recent years, many investigations have been conducted on the mechanism of leakage current in various perovskite thin film capacitors including Pt/BST/Pt [6–12]. It is generally recognized that the conduction mechanism of BST films is Schottky emission in which leakage currents are controlled by the Schottky barriers between the Pt/BST interfaces [10]. Thus, the Schottky emission is an interface-controlled mechanism and strongly depends on the conditions of the Pt/BST interfaces and the polarity of the applied voltage. On the other hand, it has been reported recently that the leakage current is more related to some sort of tunneling. Tunneling can dominate the emission process in forming gas annealed sample due to strong band bending in the film resulting from high space charge concentrations introduced into the films during forming gas exposure [13–15]. Many methods have been considered to improve the leakage by annealing the capacitors in different atmospheres [10,11]. Mostly, these methods effectively improve the reverse currents (negative voltages are applied to the top electrodes). Unfortunately, the forward current (positive voltages are applied to the top electrodes) is difficult to reduce.

It was reported [12] that amorphous BST films show good insulating property and low dielectric constants in comparison with the polycrystalline BST films. Thus, by combining the amorphous and polycrystalline BST film ‘in series’, the effective leakage current level and dielectric constant of the whole film can be adjusted

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0257-8972/02/$ - see front matter
PII: S0257-8972(02)00402-4

and controlled. In this paper, we report an effort to improve the characteristics of leakage currents of Pt/BST/Pt thin film capacitors by a multilayered structure of amorphous and polycrystalline BST layers. The sol–gel method was adopted because it is easy to control the deposition conditions. There are two reasons that the Ba content 0.8 was selected [16]: (1) BST films with this content shows a maximum relative permittivity in the room temperature and the dielectric loss remains essentially constant. (2) The grain size for the sol–gel derived BST films is in the submicron range, which explain the little spontaneous polarization and the small variation in dielectric constant with temperature.

2. Experimental details

The BST films were obtained by a spin-coating deposition process. The raw materials for the solution synthesis were barium acetate $Ba(CH_3COO)_2$, strontium acetate $Sr(CH_3COO)_2$, and titanium butoxide $Ti(OC_4H_{9-n})_4$. Glacial acetic acid (CH_3COOH) and methanol (CH_3OH) were used as stabilizer and solvent, respectively. Barium acetate and strontium acetate in the ratio of 8:2 were dissolved into heated acetic acid. The solutions were then mixed and stirred. The titanium butoxide was added into the mixture with addition of moderate HAcAc and then the mixture was stabilized by appropriate amount of methanol. A clear yellowish solution was prepared, which was stored in sealed bottles for several months without crystallite formation. The concentration of the final solution can be adjusted to different values by adding appropriate quantity of solvent. The preparation of the precursor solution was performed in ambient atmosphere.

Spin-coating was employed to deposit the filtered solution (syringe filters with 0.1 μm pore diameter) at 4500 rpm for 40 s onto the $Pt/Ti/SiO_2/Si$ substrates. The wet films were pyrolyzed at 120 °C for 2 min just after deposition, prebaked to get rid of the organic material at 400 °C for 20 min and then annealed at different temperatures for 10 min. The films were obtained by multiple repetitions of the deposition.

The structure of the film was analyzed by a Rigaku D/MAX 3C X-ray diffraction (XRD) diffractometer using Cu Kα radiation at 40 kV. The microstructure of the film was investigated using a Hitachi S-5750 SEM. The electric measurements were performed on the films in Metal–Insulator–Metal (MIM) configuration. The electrodes, made of Pt dots 0.25 mm in diameter, were prepared by RF-sputtering through a mask on the films to form MIM capacitors. The films were not post-annealed after the top Pt fabrication. The dielectric constant and loss measurements were carried out with a HP4294A LF impedance analyzer. The film thickness was determined with an ET350 Talysurf profilometer (Kosaka Laboratory Ltd) after selective etching in buffered HF. In order to determine the leakage current of dielectric thin film as a function of the applied voltage, a voltage-step technique can be employed [6–8]. A Keithley 6517A electrometer/high resistance meter was used in our experiment.

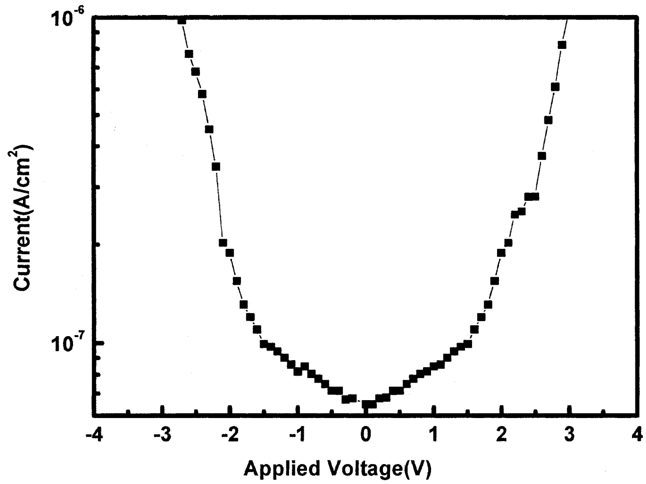

Fig. 1. The dependence of the leakage currents of Pt/BST/Pt capacitor on the applied DC field for the BST films prepared by the conventional sol–gel process.

3. Results and discussion

In the first attempt, a film was prepared by a conventional step-by-step annealing process [17]. The 0.2 mol/l solution was used and each layer was annealed at 750 °C for 10 min after the organic material was burned off. The procedure was repeated until the film had five layers. The thickness of the final film is 200±2 nm, and the I–V characteristic of the corresponding capacitor is shown in Fig. 1. It can be seen that both the forward and reverse leakage currents are approximately 1×10^{-6} A/cm^2 at the applied voltage of 3 V, though the dielectric constant is relatively high, near 500 at 10 kHz.

Using a similar process, a series of BST films were prepared with the top layer annealed at different temperatures ranging from 400 to 700 °C at an interval of 50 °C in attempt to improve the reverse leakage current level which is determined by the top Pt/BST interface. The top layer is different from the other four layers (bulk layers) due to different annealing temperatures, and thus a two-layer structure was formed. The corresponding I–V characteristics of these samples are shown in Fig. 2. The forward currents demonstrate similar characteristic as that of the conventional film capacitors because the bottom layers are the same. However, reverse currents decrease with the decreasing of the annealing temperatures until they are below 500 °C, indicating that the top layers may be amorphous at annealing temperatures lower than 500 °C. This has

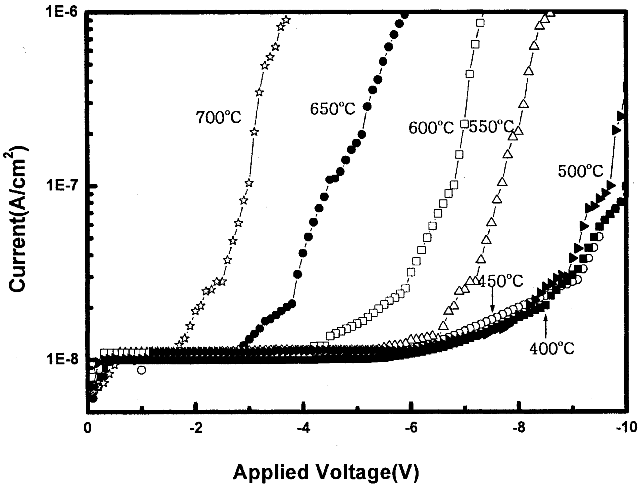

Fig. 2. The dependence of the reverse leakage currents of Pt/BST/Pt capacitor on the DC applied field for the films with the top layers annealed at temperatures ranging from 400 to 700 °C at an interval of 50 °C.

been confirmed by the SEM micrography and XRD patterns of the BST films. The SEM micrographs (not shown here) clearly show different microstructures of the surfaces. The grains become obvious on the surfaces of those films with the top layers annealed above 500 °C and the size of the grains increases with increasing of the annealing temperature, consistent with the work of other authors [18]. The XRD (shown in Fig. 3) patterns of the BST films with a top layer which was annealed at temperatures lower than 600 °C show the presence of an amorphous phase (Fig. 3b), which are consistent with the SEM results. When the top layers were annealed at temperatures higher than 600 °C, the films show typically polycrystalline BST peaks as can be noted from Fig. 3a.

Table 1
The relationship between the thickness and different solution for top layer

	Solution (mol/l)		
	0.2	0.1	0.08
T1 (nm)	220±2	212±2	200±2
T2 (nm)	60	52	40

The above results indicate that the reverse leakage current level of the Pt/BST/Pt capacitor can be greatly reduced by introducing an amorphous top layer. However, the dielectric constants of this kind of films were relatively small (approximately 150 at the frequency of 100 kHz) due to the presence of a low-dielectric-constant top layer, and the forward leakage current was not improved.

Focusing on this problem, another series of samples were prepared. All the top layers of the samples were annealed at 500 °C, which was the favored conditions selected because of their relatively high dielectric constants and low leakage currents. The concentration of the solution for the top layer was reduced so that the thickness of the top layer can be reduced, which will increase the effective dielectric constant of the film. In addition, the annealing temperature of the first layer (bottom layer) was also lower than 600 °C in an attempt to improve the forward leakage current level. The concentration of the solution used to deposit the top layer was 0.2, 0.1 and 0.08 mol/l, respectively. In this way, the thickness of the top amorphous layer can be controlled. The relationship between the thickness and different solutions for top layers is shown in Table 1, where T1 is the thickness of the films and T2 is the correspondingly thickness of top layers. The thickness of the bulk layers was 160 nm. It is obvious that the

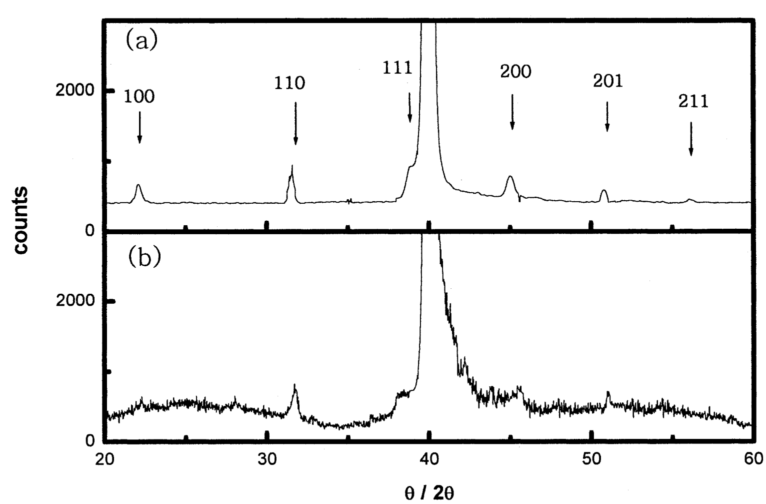

Fig. 3. The XRD patterns of films with the top layer annealed at (a) high temperatures (600–700 °C); and (b) low temperatures (450–550 °C).

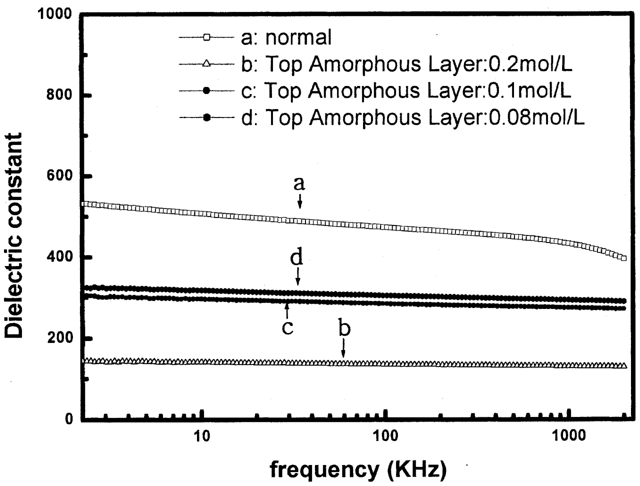

Fig. 4. The frequency dependence of dielectric constant of BST films with top layer (a) annealed at 750 °C and produced by 0.2 mol/l solution; and annealed at 500 °C and produced by (b) 0.2 mol/l; (c) 0.1 mol/l; and (d) 0.08 mol/l solutions.

thickness of top amorphous layer decreases with the decreasing of the concentration of the solution. The dielectric constant as a function of frequency at room temperature is shown in Fig. 4. As expected, the dielectric constant increases with decreasing of the thickness of the top amorphous layer, while the dielectric loss keep almost unchanged, and remains approximately 3%. Fig. 5 shows the I–V characteristics of these samples. The reverse leakage current increases with the decreasing of the thickness of the top layer, and the forward leakage current of these films decreased two orders of the magnitude at the applied voltage of 3 V compared to those having the bottom layer annealed at 750 °C. This trend can be understood in terms of tunneling of electrons through the interfacial Schottky barrier [13,14]. Banieck [14] reported that if the hydrogen present in the film, high space charge concentrations can be introduced into BST thin films. In our experiment thin films were derived by sol–gel technique. There must be a small amount of organic material (including hydrogen) left in the film after it was prebaked. We propose that when the bottom layer is annealed at 600 °C, less space charges are formed near the bottom layer and electrode, compared with that annealed at 750 °C. This may cause in the decrease of the forward leakage currents. The present result indicates that it is also an effective way to reduce the forward leakage current of Pt/BST/Pt by lowering the annealing temperature of the bottom layer.

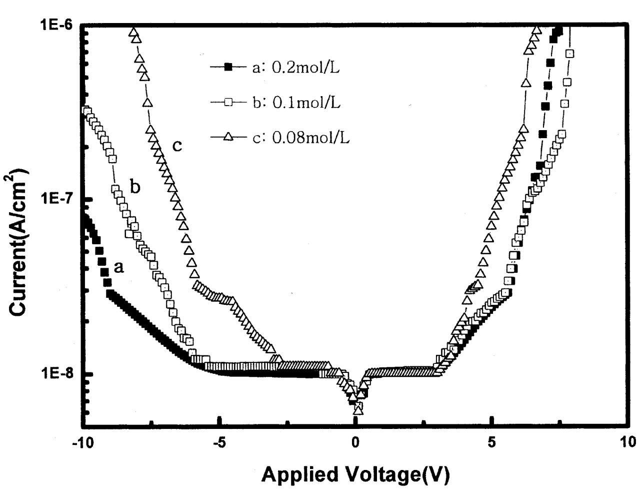

Fig. 5. The dependence of the leakage currents of Pt/BST/Pt capacitor on the DC applied field for the BST films with the top layers annealed at 500 °C and produced by (a) 0.2 mol/l; (b) 0.1 mol/l; and (c) 0.08 mol/l solutions.

4. Conclusions

In this study, we found that both the reverse and forward leakage currents of the Pt/BST/Pt capacitors can be reduced several orders of magnitude by employing a multilayered structure with top and bottom layers annealed at low temperatures during the sol–gel deposition of BST films. The observed results could be explained by an amorphous/polycrystalline structure, which was confirmed by scanning electron microscopy and XRD patterns. In addition, by varying the concentration of the organic solution of the top amorphous layer, the effective dielectric constants of the capacitors can also be controlled.

Acknowledgments

The authors wish to express their appreciation for the financial support from the Natural Science Foundation for youth of Jiangsu, China (Grant No. BQ 98037).

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