Fabrication Process of Sol-Gel Spin Coating for $SrBi_2Ta_2O_9$ Films Applied to FeRAM *

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We investigate $SrBi_2Ta_2O_9$ (SBT) films prepared by the sol-gel spin method with different spin rates or different anneal conditions for the first layer of SBT, as promising ferroelectric layer materials applied to ferroelectric random access memory (FeRAM). All the specimens in this experiment have similar SBT crystal orientations of (115), (020), (220), and (135). The Pt/SBT/Pt capacitor with coating of 3000 rpm spin rate has a perfect rectangle shape of hysteresis loops, remanent polarization of 7.57 $\mu C/cm^2$ and coercive voltage of 0.816 V at 5 V voltage amplitude. These characteristics are better than those with coating of 3500 rpm spin rate, which is attributed to the influence for thickness and grain size of the film from depressed spin rate. Slow-rate anneal in the furnace for the first layer of SBT can improve the crystallization processes and properties for SBT layers slightly, compared with rapid thermal annealing. The ion damage from etching for the top electrode can influence leakage current characteristics of the Pt/SBT/Pt capacitor at positive voltage bias.

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Ferroelectric random access memory (FeRAM) has attracted considerable attention due to its advantages of nonvolatile data retention, low power consumption, and fast write/read speed.[1] Among the several ferroelectric materials applied to FeRAM, such as $Pb(Zr_{1-x}Ti_x)O_3$(PZT), $SrBi_2Ta_2O_9$ (SBT) and $(Bi_{1-x}La_x)_4Ti_3O_{12}$ (BLT),[2−4] $SrBi_2Ta_2O_9$ (SBT) with a layered structure[4] appears to be one of the most promising ferroelectric layer materials due to its excellent reliability properties, such as fatigue and retention endurance.[5] However, the fatigue-free SBT materials have several disadvantages of very high processing temperature and low remnant polarization. In particular, the high temperature annealing process puts a strong limitation on the application of SBT films in high density ferroelectric devices.[4] The SBT films applied to FeRAM can be prepared by several methods, such as metal-organic chemical vapour deposition (MOCVD), metalorganic decomposition (MOD), pulsed laser deposition (PLD) and sol-gel spin coating.[6−9] Among them, sol-gel spin coating is most suitable for experiments of materials due to its simple and flexible processes. In addition, the materials for the bottom electrode can play critical role in determining the texture and quality of ferroelectric films, which are closely correlated with remanent polarization.[4] Pt films are most widely used as bottom electrodes for ferroelectric films prepared by chemical solution technique.[4] In this study, an SBT film for Pt/SBT/Pt capacitor is prepared by the sol-gel spin method on a $Pt/Ti/SiO_2/Si$ substrate in experiment. The fabrication process, texture and characteristics of the Pt/SBT/Pt capacitor are investigated.

In this experiment, platinum (Pt) layers in thicknesses of 1800 Å and 1200 Å prepared by dc sputtering are used as the bottom and top electrodes, respectively. The substrate for ferroelectric capacitor is thermal-oxidized Si wafer. A layer of Ti (300 Å) prepared by dc sputtering is fabricated as an adhesive layer between the bottom electrode and the substrate. Figure 1 shows the structure of ferroelectric capacitors. The SBT film is prepared by sol-gel spin coating. Strontium acetate, bismuth 2-methoxyethanol, and tantalum ethoxide were selected as precursors; and acetic acid, 2-ethylhexanonic acid, and 2-methoxyethanol were selected as solvents; 15% bismuth was added. In sol-gel processes of this experiment, different spin rates, different anneal conditions for the first layer of the SBT film and their influences are investigated. Three specimens in this experiment and their conditions are displayed in Table 1. The counts of SBT layers in all the specimens are four layers. Every layer of the SBT film has an annealing process of 650°C in O_2 atmosphere after coating and pyrogenation. Among them, rapid thermal anneal (RTA) of 1 min and slow-rate anneal in furnace of 10 min are applied in the sol-gel process for the first SBT layer, respectively. The 1-min RTA is used for other layers of the SBT films in all the specimens. All the heating rate in the RTA is 90°C/s in this experiment. After the four layers of the SBT film deposited, a crystalliza-

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tion process of anneal in furnace at 750°C is performed for 30 min to obtain perovskite crystal texture of the SBT film. The thickness of every layer of the SBT film is 500 Å or so, so the thickness of the ferroelectric film applied to the capacitor is 2000 Å or so. Pt films as electrodes and SBT films are both etched by ion beam etching (IBE) to obtain the Pt/SBT/Pt capacitor in measurement, as shown in Fig. 1. After the top electrode is deposited, the 1-min RTA in O_2 atmosphere at 650°C is applied to the ferroelectric capacitor for the amelioration of the top electrode/SBT interface conditions. Then, slow-rate anneal in furnace for 20 min at 750°C is applied to the Pt/SBT/Pt capacitor for crystallization repeatedly after the etching process for ferroelectric capacitor is completed.

Table 1. Three specimens in this experiment and their conditions.

Specimens	Spin rate	Anneal mode for the first SBT layer
1	3000 rpm	RTA
2	3500 rpm	RTA
3	3500 rpm	slow-rate anneal in furnace

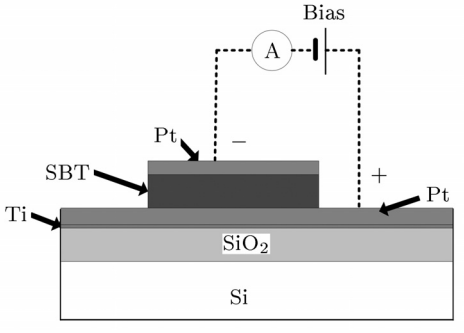


Fig. 1. Schematic diagram of the device structure of ferroelectric capacitor and specimen in the measurement system.

Figure 2 shows the crystal orientations of three specimens of Pt/SBT/Pt capacitors in this experiment by x-ray diffraction (XRD) patterns. The crystal orientations of SBT films in the three specimens are very similar. SBT peaks of (115), (020), (220), and (135) are displayed in Fig. 2. Among them, peaks of (115) have the largest intensity in XRD patterns of three specimens. The Pt (111) peak originates from the Pt electrodes. Figure 3 shows hysteresis loops of three specimens at 5 V voltage amplitude. All the data in Fig. 3 about the Pt/SBT/Pt capacitor are measured at a frequency of 100 Hz. It is shown that specimen 1 has less coercive voltage, larger remanent polarization, larger saturated polarization and better rectangle shape than the other two, obviously. Pt/SBT/Pt capacitor has remanent polarization of 7.57 μC/cm^2 and coercive voltage of 0.816 V at 5 V voltage amplitude. The other two specimens have similar remanent polarization and coercive voltage. Specimen 3 has slightly larger saturated polarization than the one of specimen 2 because slow-rate anneal in furnace can help to obtain good crystal orientations of the first layer of SBT and to improve the crystallization processes for SBT layers.

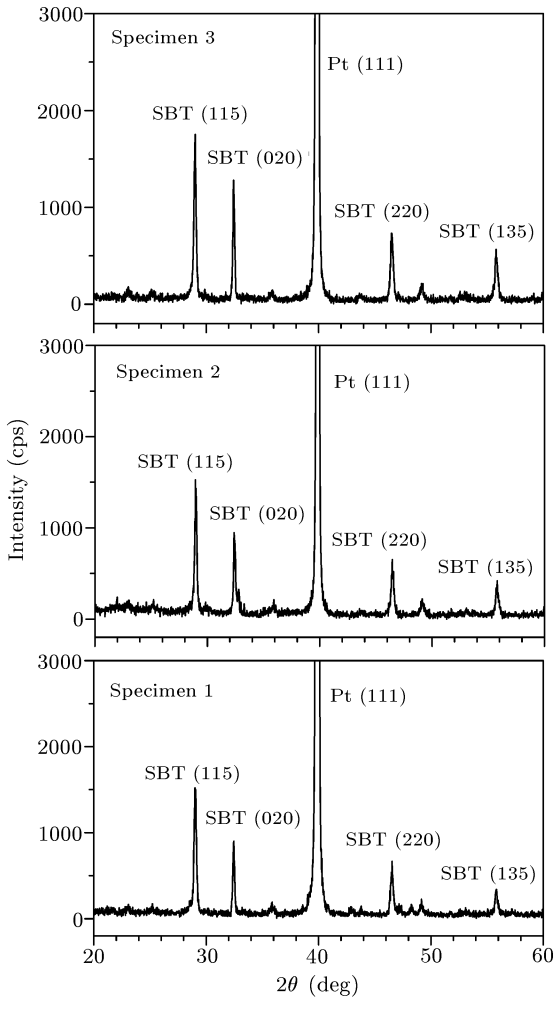


Fig. 2. XRD patterns of Pt/SBT/Pt capacitor in this experiment.

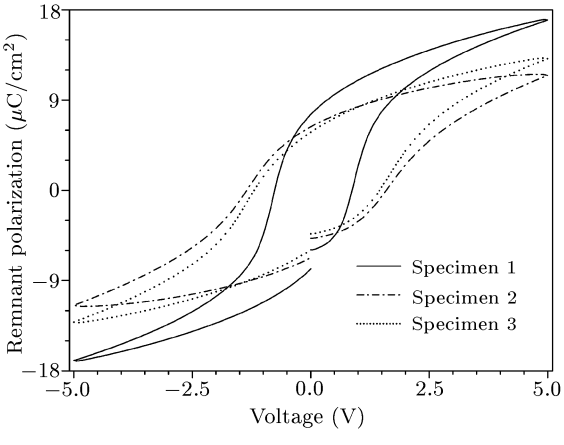


Fig. 3. Hysteresis loops of three capacitor specimens.

Compared to the other two specimens, a ferroelectric capacitor of specimen 1 has been prepared by a little slow spin rate in coating process for SBT. The depressed spin rate of SBT coating can augment the thickness and grain size of ferroelectric films. Larger thickness can compensate for the vacancies at the interfaces between different layers in the SBT film, which can result in improving the crystallization results of the SBT film. Larger grain size can make the surface of the SBT film more compact. Thus specimen 1 with slightly slower spin rate has properties better than the other two. Figure 4 shows the hysteresis loops of specimen 1 at different voltage amplitudes of 2–10 V. It is displayed that the hysteresis loops of specimen 1 all have a perfect rectangle shape. With the amplitude increasing, remanent polarization and coercive voltage of capacitor trend to respective saturated values gradually, while the saturated polarization increases obviously with amplitude increasing.

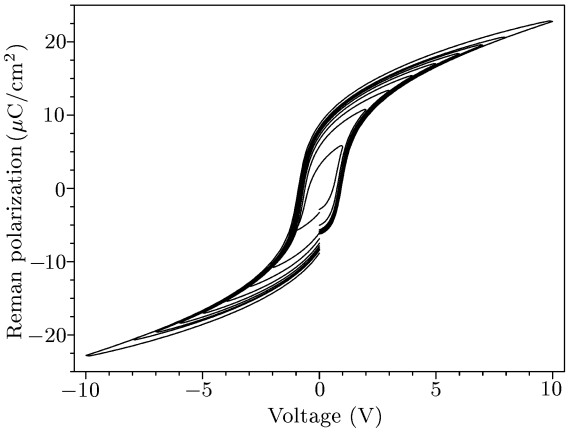


Fig. 4. Hysteresis loops of No 1 specimen at different voltage amplitudes.

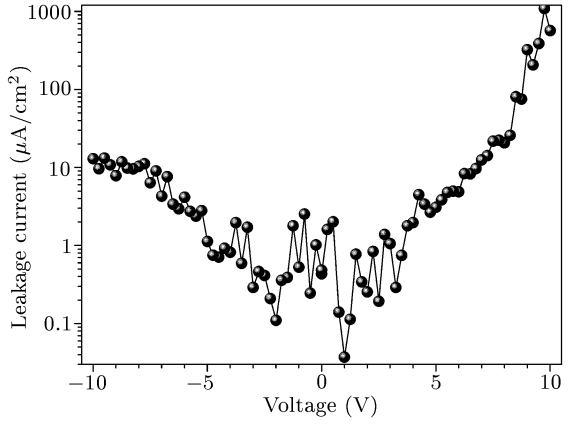


Fig. 5. Leakage current characteristics of the SBT capacitor of No 1 specimen.

Figure 5 shows the leakage current characteristics of the SBT capacitor of specimen 1 during ±10 V voltage bias. It is observed that the leakage current densities of Pt/SBT/Pt increase obviously at positive voltage bias when amplitude applied to capacitor exceeds 8 V, compared with those at negative voltage bias. The leakage current at positive bias corresponds to electron injection to the ferroelectric film from the top electrode[10] in this experiment. Thus the leakage current at positive bias is correlative to the SBT/top electrode interface. The differences on leakage current characteristics at positive and negative bias may attribute to the SBT/electrode interface properties.[11] The differences between conditions of the SBT/electrode interfaces result from properties of materials and processes. Different leakage current characteristics of the Pt/SBT/Pt capacitor at positive and negative bias voltages may attribute to different process conditions for the same SBT/Pt interfaces at different positions because more ion damages from etching for top electrode can influence the conditions of the SBT/top electrode interface.

Figures 6 and 7 show the surface photograph of the SBT film and lateral photograph of the Pt/SBT/Pt capacitor in this experiment by scanning electron microscopy (SEM), respectively. Perovskite crystal grains of the SBT film with nanometre size are observed to nucleate from the amorphous film matrix on the Pt substrate of (111) crystal texture. Protrudent boundaries are observed and are considered to be grain boundaries.

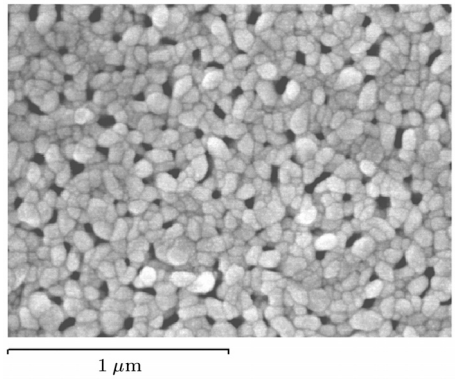


Fig. 6. Surface photograph of the SBT film by scanning electron microscopy.

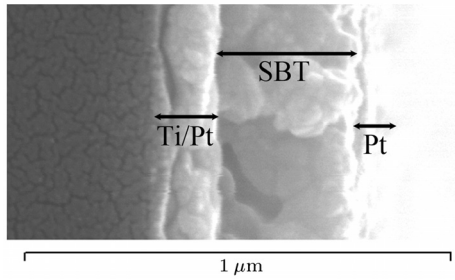


Fig. 7. Lateral photograph of Pt/SBT/Pt capacitor in this experiment by scanning electron microscopy.

In summary, SBT films prepared by the sol-gel spin method with different spin rates or different anneal conditions for the first layer of the SBT film have been investigated. Three capacitor specimens have similar crystal orientations of SBT. The capacitor with relatively low spin rate coating has characteristics obviously better than that with relatively high spin rate coating, because a depressed spin rate of coating can augment the thickness and grain size of the film, which can compensate for the vacancies at the interfaces between different layers and improve the crystallization results. Slow-rate anneal in furnace for the first layer of SBT can help to obtain good crystal orientations of the first layer and to improve the crystallization processes for SBT layers. The ion damage from etching for the top electrode can influence leakage current characteristics of the SBT capacitor at positive voltage bias. Protrudent grain boundaries and compact surface morphological structure of the SBT film are observed by SEM photograph.

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