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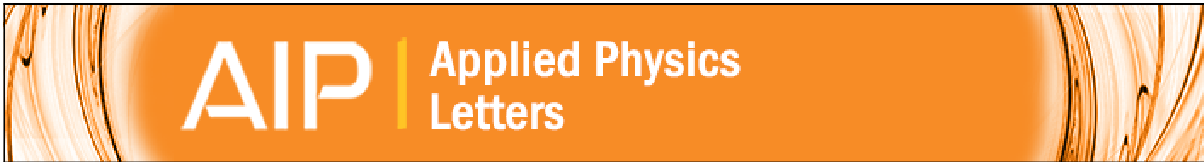

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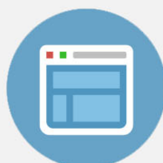

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Properties of $SrBi_2Ta_2O_9$ ferroelectric thin films prepared by a modified metalorganic solution deposition technique

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Polycrystalline $SrBi_2Ta_2O_9$ thin films having a layered-perovskite structure were fabricated by a modified metalorganic solution deposition technique using room temperature processed alkoxide-carboxylate precursor solution. It was possible to obtain a complete perovskite phase at an annealing temperature of 650 °C and no pyrochlore phase was observed even up to 600 °C. In addition, the $SrBi_2Ta_2O_9$ thin films annealed at 750 °C exhibited better structural, dielectric, and ferroelectric properties than those reported by previous techniques. The effects of postdeposition annealing on the structural, dielectric, and ferroelectric properties were analyzed. The electrical measurements were conducted on $Pt/SrBi_2Ta_2O_9/Pt$ capacitors. The typical measured small signal dielectric constant and dissipation factor at 100 kHz were 330 and 0.023 and the remanent polarization and the coercive field were 8.6 $\mu C/cm^2$ and 23 kV/cm, respectively, for 0.25-μm-thick films annealed at 750 °C. The leakage current density was lower than 10^{-8} A/cm^2 at an applied electric field of 150 kV/cm. The films showed good switching endurance under bipolar stressing at least up to 10^{10} switching cycles. © *1997 American Institute of Physics.* [S0003-6951(97)00209-X]

Ferroelectric thin films have attracted considerable attention for their potential applications in electronic devices such as pyroelectric infrared detectors, optical switches, actuators, displays, dynamic random access memories (DRAMs), and nonvolatile random access memories (NVRAMS).[1–3] Ferroelectric nonvolatile memories have the potentials to replace current state-of-the-art nonvolatile memories such as floating and flash erasable programmable read only memories (EEPROMs) because of their lower writing voltages, faster writing speeds, better endurance, and potentially fewer processing steps.[4] Recently, there has been a surge in research activity on bismuth layer-structured ferroelectric materials for NVRAM applications. In particular, strontium bismuth tantalate, $SrBi_2Ta_2O_9$, which is one of the bismuth layer-structured compounds, is the most promising candidate for ferroelectric random access memories (FRAMs) with high fatigue endurance and good retention. $SrBi_2Ta_2O_9$ has high potential for device applications because of its high dielectric constant, high Curie temperature, low leakage current, and good ferroelectric switching characteristics. In this letter, we report the fabrication of $SrBi_2Ta_2O_9$ thin films by a modified metalorganic solution deposition (MOSD) technique using a stable alkoxide-carboxylate precursor solution prepared under ambient room temperature conditions. It was possible to obtain a perovskite phase at an annealing temperature of 650 °C and no pyrochlore phase was observed even up to 600 °C;[5] however, the ferroelectricity was found to be weaker in films annealed at 650 °C due to smaller grain sizes. But their is a possibility to enhance the grain growth in the $SrBi_2Ta_2O_9$ thin films prepared by the present technique at lower annealing temperatures due to the absence of the pyrochlore phase. The present $SrBi_2Ta_2O_9$ thin films exhibited better structural, dielectric, and ferroelectric properties than those reported by other methods under similar postdeposition annealing conditions.

The preparation of $SrBi_2Ta_2O_9$ thin films has been reported by pulsed laser deposition,[6] metalorganic chemical vapor deposition,[7] metalorganic decomposition,[8–10] and sol-gel techniques.[5,11] The electrical and optical properties of bismuth layer-structured ferroelectrics are dependent on their crystallographic orientation due to their large structural anisotropy. So the properties of these materials are strongly dependent on the nature of substrate, preparation technique, and the postdeposition annealing treatment. The selection of precursor compounds and solvents is the most important step in the MOSD technique. The final film properties are strongly dependent on the selected precursor compounds and the solvents, and the preparation conditions. The $SrBi_2Ta_2O_9$ thin films were prepared by alkoxide-salt method using alkoxide-carboxylate precursors. The precursor solution was prepared under ambient room temperature conditions. For the preparation of $SrBi_2Ta_2O_9$ thin films; strontium acetate, bismuth 2-ethylhexanoate, and tantalum ethoxide were selected as precursors, and acetic acid, 2-ethylhexanoic acid, and 2-methoxyethanol were selected as solvents. In the experiment, bismuth 2-ethylhexanoate and strontium acetate were initially dissolved in 2-ethylhaxanoic acid and acetic acid, respectively, under room temperature conditions. These solutions were then added to the solution of tantalum ethoxide in 2-methoxyethanol to prepare a stoichiometric, clear, and stable $SrBi_2Ta_2O_9$ precursor solution. The viscosity of the solution was controlled by varying the 2-methoxyethanol content. Dust and other suspended impurities were removed from the solution by filtering through 0.2 μm syringe filters. The precursor films were coated onto Pt-coated Si substrates by spin coating using a photoresist spinner. The thickness of the films was controlled by adjusting the viscosity of the solution and the spin speed. After spinning onto various substrates, films were kept on a hot plate (at ~350 °C) in air for 10 min. This step was repeated after each coating to ensure complete removal of volatile matter. In this letter, we report the structural, dielectric, and ferroelectric properties of $SrBi_2Ta_2O_9$ thin films. The film microstructure and properties were found to be strongly dependent on the excess bis-

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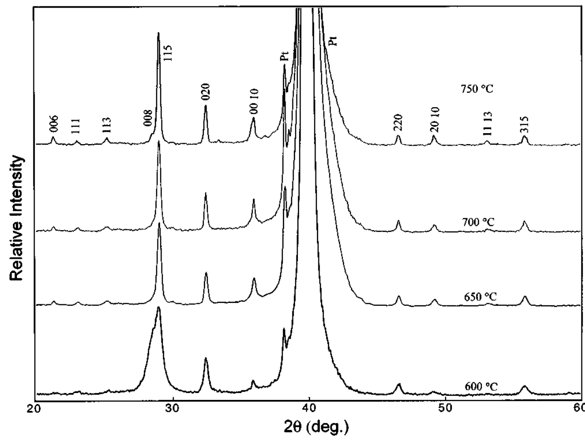

FIG. 1. X-ray diffraction patterns of $SrBi_2Ta_2O_9$ thin films annealed at various temperatures for 30 min.

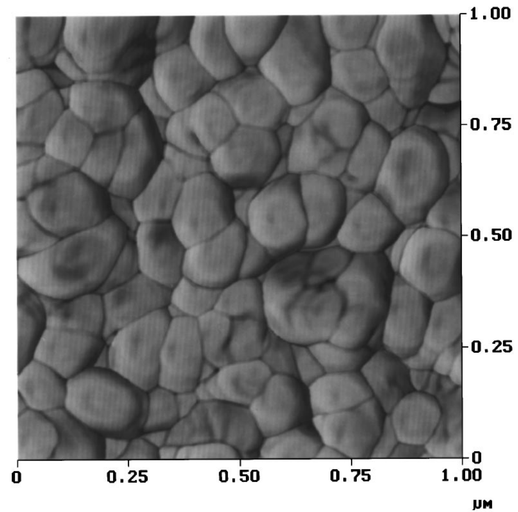

FIG. 2. AFM photograph of $SrBi_2Ta_2O_9$ thin film annealed at 750 °C for 30 min.

muth content. The best results were obtained for 30% excess bismuth content. So this letter focuses on the structural and electrical characteristics of $SrBi_2Ta_2O_9$ thin films with 30% excess bismuth. The effects of the postdeposition annealing temperature on the film microstructure and properties are also analyzed.

The structure of the films was analyzed by x-ray diffraction (XRD). The XRD patterns were recorded on a Scintag XDS 2000 diffractometer using Cu Kα radiation at 40 kV. The as-pyrolyzed films were found to be amorphous and postdeposition annealing was required to develop crystallinity. The postdeposition annealing of the films was carried out at various temperatures for 30 min in an oxygen atmosphere. Figure 1 shows the XRD patterns of the films, deposited on Pt-coated Si substrates, as a function of annealing temperature. It was possible to attain a perovskite phase at an annealing temperature of 650 °C. The films annealed at 650 °C exhibited better crystallinity than those reported by Amanuma *et al.*[8] and Boyle *et al.*[5] using chemical methods. As the annealing temperature was increased, the peaks in the XRD pattern became sharper and the full width at half-maximum (FWHM) decreased indicating better crystallinity and an increase in grain size with increasing annealing temperature. The XRD patterns also revealed that films were polycrystalline in nature with no evidence of preferred orientation or secondary phases. No pyrochlore phase formation was observed in the XRD patterns of the $SrBi_2Ta_2O_9$ thin films (0%–30% excess Bi) prepared by the present method as was observed in the films prepared by sol-gel method.[5]

The surface morphology of the $SrBi_2Ta_2O_9$ thin films was analyzed by Digital Instrument's Dimension 3000 atomic force microscope (AFM) using tapping mode with amplitude modulation. The scan area was $1 \mu m \times 1 \mu m$. The surface morphology of the films was smooth with no cracks and defects, as shown in Fig. 2, and the average surface roughness was less than 12 nm for films annealed in the temperature range of 650–750 °C. The films exhibited a dense microstructure and the grain size was found to increase with the increase in annealing temperature, as shown in Table I, and was in the range of 85–165 nm for films annealed in the temperature range of 650–750 °C.

The dielectric properties of $SrBi_2Ta_2O_9$ thin films were measured in terms of the dielectric constant ε_r and loss factor $\tan\delta$. The dielectric measurements were conducted on metal-ferroelectric-metal (MFM) capacitors with an HP 4192A impedance analyzer at room temperature. Several platinum electrodes (area$=3.1\times 10^{-4}$cm^2) were sputter deposited through a mask on the top surface of the films to form MFM capacitors. Figure 3 shows the low field dielectric constant and dissipation factor as a function of frequency for a 0.25-μm-thick film annealed at 750 °C. The small signal dielectric constant and dissipation factor at a frequency of 100 kHz were 330 and 0.023, respectively. The dielectric constant was larger than that for bulk ceramics; however, the dielectric constant and the loss factor values for the present films were found to be smaller than those reported by others.[5,8] The permittivity showed no dispersion with frequency up to about 1 MHz, as shown in Fig. 3, indicating that the values were not masked by any surface layer effects or electrode barrier effects in the measured frequency range. The dielectric constant and the dissipation factor were found to increase, as shown in Table I, with the increase in annealing temperatures from 650 to 750 °C. This increases in dielectric constant with annealing temperature may be attributed to an increase in grain size and density of the films as was observed in AFM studies.

Ferroelectric hysteresis measurements were conducted on 0.25-μm-thick $SrBi_2Ta_2O_9$ films in MFM configuration at room temperature using standardized RT66A ferroelectric test system. Figure 4 shows a typical hysteresis loop of a film annealed at 750 °C. The measured remanent polarization (P_r) and the coercive field (E_c) values at an applied electric field of amplitude 150 kV/cm were 8.6 μC/cm^2 and 23 kV/

TABLE I. Dependence of grain size, dielectric parameters, and ferroelectric properties on postdeposition annealing temperature.

Temperature (°C)	Grain size (nm)	ε_r	$\tan\delta$	$2P_r$ (μC/cm^2)	E_c (kV/cm)
650 °C	85	240	0.007	4.4	30
700 °C	125	310	0.020	12.8	23
750 °C	165	330	0.023	17.2	23

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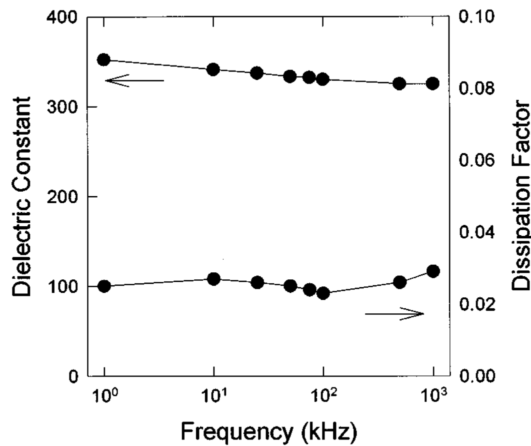

FIG. 3. Dielectric constant and dissipation factor as a function of frequency for $SrBi_2Ta_2O_9$ thin film annealed at 750 °C for 30 min.

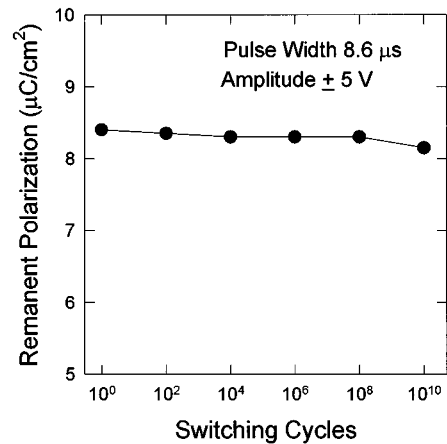

FIG. 5. Decay in remanent polarization as a function of number of bipolar switching cycles.

cm, respectively. The remanent polarization value was found to be improved compared to that reported by others and the value of the coercive field was found to be smaller.[5,8–10] The P_r and E_c were also measured as a function of annealing temperature, as shown in Table I. The remanent polarization ranged from 2.2 to 8.6 $\mu C/cm^2$ and the coercive field was between 23 and 30 kV/cm under an applied electric field of amplitude 150 kV/cm. This trend may be found consistent with the XRD and AFM data which indicate improvement in crystallinity with increasing annealing temperature. Low leakage current density is an important consideration for memory device applications. The leakage current density of the $SrBi_2Ta_2O_9$ thin films was found to be lower than 10^{-8} A/cm^2 at an applied electric field of 150 kV/cm for films annealed in the temperature range of 650–750 °C, indicating good insulating characteristics.

The switching endurance of a 0.25-μm-thick $SrBi_2Ta_2O_9$ capacitor as a function of switching cycles was studied. This was done by applying 8.6-μs-wide bipolar pulses of 5 V amplitude. Figure 5 shows the decay of the remanent polarization as a function of polarization reversing switching cycles N. During initial cycles, no rapid fall off in P_r was observed. There was an initial long period (up to about 10^8 cycles) over which P_r was nearly constant which was then followed by a final decay period. Even after 10^{10} cycles, the decay in P_r was observed to be less than 5% of the initial value, suggesting $SrBi_2Ta_2O_9$ to be an attractive material for memory devices with operating voltage levels of 3–5 V.

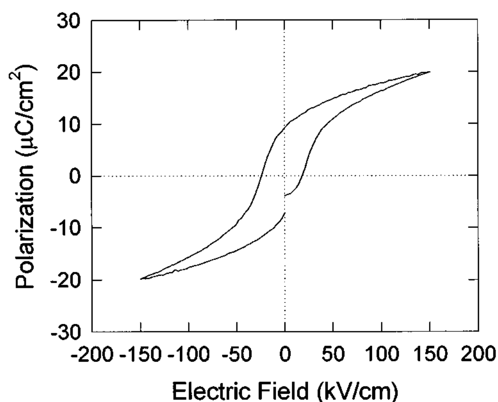

FIG. 4. Hysteresis loop of 0.25-μm-thick $SrBi_2Ta_2O_9$ film annealed at 750 °C for 30 min.

In conclusion, polycrystalline $SrBi_2Ta_2O_9$ thin films were successfully produced on Pt-coated Si substrates by a modified MOSD technique. The precursor solution was prepared under ambient room temperature conditions using alkoxide-carboxylate precursors. It was possible to obtain a complete perovskite phase at an annealing temperature of 650 °C. The surface morphology of the films was smooth with no cracks or defects while the grain size was found to increase with the increase in annealing temperature. For a film annealed at 750 °C, the small signal dielectric constant and dissipation factor at 100 kHz were 330 and 0.023 and the remanent polarization and the coercive field were 8.6 $\mu C/cm^2$ and 23 kV/cm, respectively. The leakage current density was lower than $10^{-8} A/cm^2$ at an applied electric field of 150 kV/cm for films annealed in the temperature range of 650–750 °C. The decay in remanent polarization was less than 5% up to at least 10^{10} bipolar switching cycles. The dielectric and ferroelectric measurements on the films suggest that $SrBi_2Ta_2O_9$ has good potential for applications in memories. Detailed studies are being done to analyze the effects of excess bismuth content and the postdeposition annealing treatment on the structural, dielectric, and ferroelectric properties of the $SrBi_2Ta_2O_9$ thin films.

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