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Citation: Applied Physics Letters **71**, 1041 (1997); doi: 10.1063/1.119721
View online: http://dx.doi.org/10.1063/1.119721
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Thin films of layered-structure $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ solid solution for ferroelectric random access memory devices

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(Received 6 March 1997; accepted for publication 24 June 1997)

We report on the thin films of solid–solution material $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ fabricated by a modified metalorganic solution deposition technique for ferroelectric random access memory devices. Using the modified technique, it was possible to obtain the pyrochlore free crystalline thin films at an annealing temperature as low as 600 °C. The solid–solution of layered perovskite materials helped us to significantly improve the ferroelectric properties, higher P_r and higher T_c, compared to $SrBi_2Ta_2O_9$; a leading candidate material for memory applications. For example, the films with $0.7\ SrBi_2Ta_2O_9-0.3Bi_3TiTaO_9$ composition and annealed in the temperature range 650–750 °C exhibited $2P_r$ and E_c values in the range 12.4–27.8 $\mu C/cm^2$ and 68–80 kV/cm, respectively. The leakage current density was lower than 10^{-8} A/cm^2 at an applied electric field of 200 kV/cm. The films exhibited good fatigue characteristics under bipolar stressing. © *1997 American Institute of Physics.* [S0003-6951(97)03034-9]

$SrBi_2Ta_2O_9$ is one of the leading candidate material for ferroelectric random access memory (FRAM) devices.[1–3] However, the realization of a commercially viable nonvolatile FRAM technology based on $SrBi_2Ta_2O_9$ has been hampered by problems related to high processing temperature (>750 °C), low P_r, and low Curie temperature which make the direct integration into high density CMOS devices extremely difficult.[4] The high crystallization temperature poses a problem for the selection of a suitable barrier layer, and low P_r and low T_c make these films unsuitable for high density memories and high temperature operation. In this letter, we report on the thin films of a new solid solution of layered perovskite materials, $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$, with much improved properties compared to $SrBi_2Ta_2O_9$ thin films at a low annealing temperature of 650 °C.

In general, it has been difficult to reduce the post-deposition annealing temperature of $SrBi_2Ta_2O_9$ thin films mainly due to poor ferroelectric properties at lower annealing temperatures. Additionally, pyrochlore phase formation has also been reported for $SrBi_2Ta_2O_9$ thin films at annealing temperatures lower than 700 °C.[5] It has been established that a critical grain size is required to get good ferroelectric properties on $SrBi_2Ta_2O_9$ thin films and annealing at higher temperatures is necessary to achieve the critical grain size.[6] Several attempts have been made to improve the film microstructure and, hence, the ferroelectric properties at lower annealing temperatures by either making the Sr/Bi/Ta atomic ratio slightly off-stoichiometric or annealing the films under low oxygen pressure conditions.[7,8] The problem of pyrochlore phase formation was eliminated by using the modified metalorganic solution deposition (MOSD) technique which provided pyrochlore free crystalline $SrBi_2Ta_2O_9$ thin films even at a low annealing temperature of 600 °C.[9] However, no well-defined approach has been established to solve the problems of high processing temperature, low P_r, and low T_c.

One of the approaches we have taken to enhance the grain growth at lower annealing temperatures is to use solid solution. The solid solution method was used to lower the processing temperature as well as to improve the low P_r and low T_c characteristics of $SrBi_2Ta_2O_9$. The solid solution $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ was selected for the present studies as $SrBi_2Ta_2O_9$ has a Curie temperature of 310 °C while $Bi_3Ti(Ta_{1-y}Nb_y)O_9$ has a Curie temperature in the range of 870–950 °C.[10] Both of these materials belong to the layered perovskite family. So the solid solution of these two materials is expected to exhibit a higher Curie temperature and improved ferroelectric properties compared to $SrBi_2Ta_2O_9$. Initial studies were conducted on bulk $(1-x)SrBi_2Ta_2O_9-xBi_3TiNbO_9$ material which exhibited much larger grain size and higher Curie temperature compared to $SrBi_2Ta_2O_9$ under similar annealing conditions.[11] So the thin films of the solid solution fabricated by the modified MOSD technique are expected to show pyrochlore-free crystalline phase and larger grain sizes at lower annealing temperatures compared to $SrBi_2Ta_2O_9$.

The thin films of $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ were prepared by the modified metalorganic solution deposition technique, similar to that reported for $SrBi_2Ta_2O_9$ thin films, using room temperature processed alkoxide–carboxylate precursor solution.[9] For the preparation of $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ thin films; strontium acetate, bismuth 2-ethylhexanoate, titanium isopropoxide, tantalum ethoxide, and niobium 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, niobium ethoxide, and titanium isopropoxide in 2-methoxyethanol to prepare a stoichiometric, clear, and stable $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ precursor solution. The precursor films were coated on to 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. In this letter, we report the structural, dielectric, and ferroelectric properties of $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ thin films

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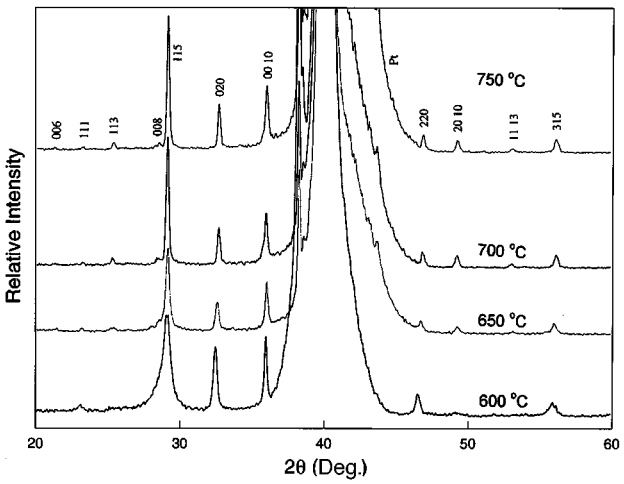

FIG. 1. X-ray diffraction patterns of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films annealed at various temperatures for 60 min.

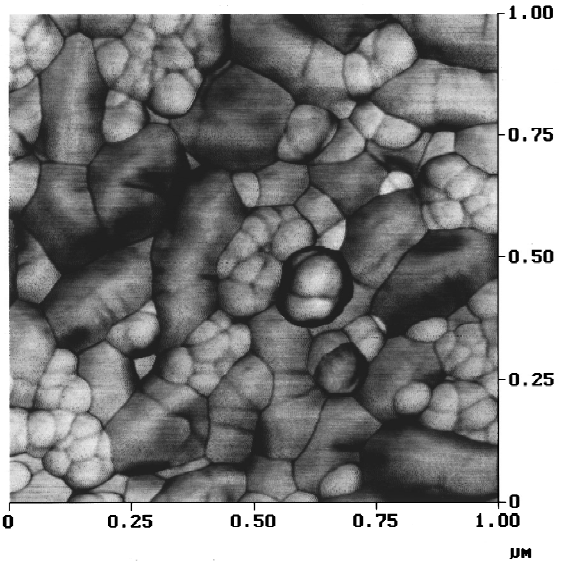

FIG. 2. AFM photograph of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films annealed at 750 °C for 60 min.

for 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 and 0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9 compositions belonging to end members $(1-x)SrBi_2Ta_2O_9-xBi_3TiTaO_9$ and $(1-x)SrBi_2Ta_2O_9-xBi_3TiNbO_9$, respectively. The properties of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films are described in detail and a comparison has been made with $SrBi_2Ta_2O_9$ and 0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9 thin films. The film microstructure and electrical properties were found to be strongly dependent on the excess bismuth content. The best results were obtained for about 20% excess bismuth content. So this letter focuses on the structural and electrical characteristic of the films with 20% excess bismuth.

The structure of the films was analyzed by x-ray diffraction (XRD). The XRD patterns were recorded on a Scintag XDS 2000 diffractometer using CuK_α radiation at 40 kV. The post-deposition annealing of the films was carried out at various temperatures for 60 min in an oxygen atmosphere. Figure 1 shows the XRD patterns of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films, deposited on Pt-coated Si substrates, as a function of annealing temperature. It was possible to obtain a perovskite phase at an annealing temperature of 600 °C. A longer annealing time was required for the solid solution compositions to get well crystallized phase as compared to $SrBi_2Ta_2O_9$ thin films.[9] 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.

The surface morphology of the films was analyzed by Digital Instrument's Dimension 3000 atomic force microscope (AFM) using tapping mode with amplitude modulation. The scan area was 1×1 μm. The surface morphology of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films was smooth with no cracks and defects, as shown in Fig. 2, and the average surface roughness was less than 10 nm for films annealed in the temperature range 600–750 °C. The grain size of both 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 and 0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9 thin films was found to be larger than that of $SrBi_2Ta_2O_9$ thin films as expected (Table I).

The dielectric properties of 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films were measured in terms of the dielectric constant ϵ_r and loss factor tan δ. The dielectric measurements were conducted on metal–ferroelectric–metal (MFM) capacitors with an HP 4192A impedance analyzer at room temperature. Several platinum electrodes (area$=3.1\times10^{-4}$ cm^2) were sputter deposited through a mask on the top surface of the films to form MFM capacitors. The films were annealed at 600 °C for 20 min after top electrode deposition to get good electrical contact. For 0.25-μm-thick films annealed at 750 °C, the small signal dielectric constant and dissipation factor at a frequency of 100 kHz were 200 and 0.025, respectively. The dielectric constant for both the compositions, 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 and 0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9 was found to be smaller than that of $SrBi_2Ta_2O_9$ thin films (Table I). The permittivity showed no dispersion with frequency up to about 1 MHz indicating that the values were not masked by any surface layer effects or electrode barrier effects in the measured frequency range.

Ferroelectric hysteresis measurements were conducted on 0.25-μm-thick 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 thin films in MFM configuration at room temperature using standardized RT66A ferroelectric test system. Figure 3 shows the typical hysteresis loops of films annealed at 650 and 750 °C. The measured remanent polarization (P_r) and the coercive

TABLE I. Comparison of the properties of $SrBi_2Ta_2O_9$, 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9, and 0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9 thin films annealed at 750 °C.

Composition	Grain size (nm)	ϵ_r	tan δ	$2P_r$ (μC/cm^2)	E_c (kV/cm)
$SrBi_2Ta_2O_9$	165	330	0.023	17.2	23
0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9	240	200	0.025	27.8	68
0.8 $SrBi_2Ta_2O_9-0.2$ Bi_3TiNbO_9	200	245	0.030	26.9	75

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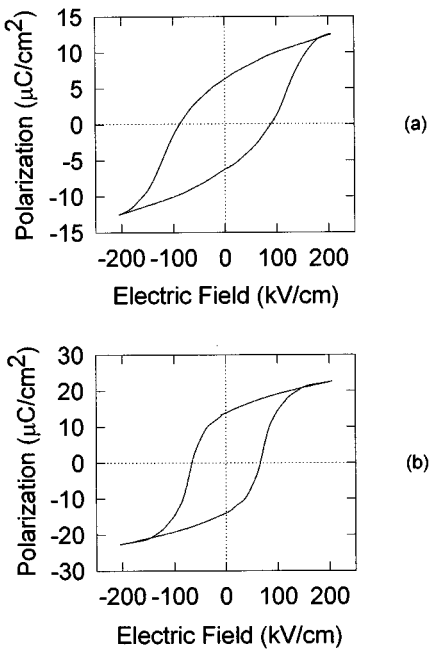

FIG. 3. Hysteresis loop of 0.25-μm-thick 0.7 $SrBi_2Ta_2O_9-0.3$ Bi_3TiTaO_9 film annealed at (a) 650 °C and (b) 750 °C for 60 min.

field (E_c) values at an applied electric field of amplitude 200 kV/cm were 13.9 μC/cm^2 and 68 kV/cm, respectively, for films annealed at 750 °C. The remanent polarization value was found to be improved compared to $SrBi_2Ta_2O_9$ thin films, however, the value of coercive field was found to be larger (Table I). The films annealed at 650 °C also showed much improved ferroelectric characteristics, as shown in Fig. 3(a), compared to $SrBi_2Ta_2O_9$ thin films.[9] The 2 P_r and the E_c values were measured to be 12.4 μC/cm^2 and 80 kV/cm, respectively. The much improved ferroelectric properties at 650 °C show the possibility of further decreasing the processing temperature by optimizing the composition and post-deposition annealing treatment. Low leakage current density is an important consideration for memory device applications. The leakage current density of the $0.7\ SrBi_2Ta_2O_9-0.3\ Bi_3TiTaO_9$ thin films was found to be lower than 10^{-8} A/cm^2 at an applied electric field of 200 kV/cm, indicating good insulating characteristics.

The switching endurance of a 0.25-μm-thick $0.7\ SrBi_2Ta_2O_9-0.3\ Bi_3TiTaO_9$ 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 4 shows the decay of the remanent polarization as a function of polarization reversing switching cycles. 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 $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ to be an attractive material for memory devices with operating voltage levels of 3–5 V.

In conclusion, polycrystalline $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ thin films, with much improved ferroelectric properties compared to $SrBi_2Ta_2O_9$ at an annealing temperature of 650 °C, were successfully fabricated on Pt-coated Si substrates by the modified MOSD technique using room temperature processed alkoxide–carboxylate precursor solution. It was possible to obtain a complete perovskite phase at an annealing temperature of 600 °C. The ferroelectric properties for the solid solution were found to be much improved compared to $SrBi_2Ta_2O_9$. For example, the films with $0.7\ SrBi_2Ta_2O_9-0.3\ Bi_3TiTaO_9$ composition and annealed in the temperature range 650–750 °C exhibited $2P_r$ and E_c values in the range 12.4–27.8 μC/cm^2 and 68–80 kV/cm, respectively. The leakage current density was lower than 10^{-8} A/cm^2 at an applied electric field of 200 kV/cm. The films exhibited good fatigue characteristics under bipolar stressing up to 10^{10} switching cycles. The structural, dielectric, and ferroelectric measurements on the films suggest that $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ has great potential to solve major problems with $SrBi_2Ta_2O_9$ for the realization of a practical memory device. Detailed studies are being done to optimize the composition and analyze the effects of excess bismuth content and the post-deposition annealing treatment on the structural, dielectric, and ferroelectric properties of $(1-x)SrBi_2Ta_2O_9-xBi_3Ti(Ta_{1-y}Nb_y)O_9$ thin films.

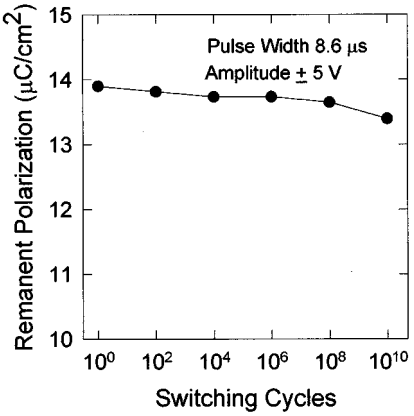

FIG. 4. Decay in remanent polarization as a function of number of bipolar switching cycles.

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