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Electrical properties of non *c*-axis oriented $SrBi_2(Ta_{0.95}V_{0.05})_2O_9$ thin films

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Pulsed laser deposition technique was used to grow off *c*-axis oriented $SrBi_2(Ta_{0.95}V_{0.05})_2O_9$ (SBTV) ferroelectric thin films. X-ray diffraction studies revealed the *c*-axis suppression in the films grown at lower substrate temperature (∼350°C) followed by annealing at higher temperatures (≥650°C). In-plane lattice parameters of the films were decreased with increase in annealing temperature. SBTV films annealed at 750°C exhibited enhanced ferroelectric properties with remanent polarization ($2P_r$) of ∼31.5 μC/cm^2 and coercive field (E_c) of ∼157 kV/cm. The dielectric permmitivity of the films increased with increase in annealing temperature and it was attributed to the grain size dependence. The films annealed at 750°C showed maximum value of dielectric permittivity ∼172 with a tangential loss of 0.1, at 100 kHz. Higher value of dissipation factor at lower annealing temperature is explained in terms of space charge accumulation at grain boundaries. The leakage current densities of the films follow ohmic behavior at low field regime and space charge limited current dominates at higher fields.

1. Introduction

Ferroelectric ceramics in thin film form have drawn much attention due to their manyfold applications, such as memory devices, IR sensors, microelectromechanical devices, etc. There is a global interest to fabricate non-volatile memory devices based on ferroelectric thin films which have low leakage current density, low operating voltage, fast switching, and fatigue endurance of up to 10^{12} switching cycles. Recently, $SrBi_2Ta_2O_9$ (SBT) has been a most intensively studied ferroelectric compound in bismuth-layered series due to its fatigue free nature [1, 2]. Two major drawbacks in SBT are: (i) low remanent polarization, and (ii) higher crystallization temperature. There has been a tremendous effort to overcome these inherent problems associated with SBT. Sr-deficient and Bi-excess composition $Sr_{0.8}Bi_{2.2}Ta_2O_9$was investigated by Noguchi *et al*. [3], according to them remanent polarization is doubled ($2P_r \sim 23$ μC/cm^2) compared to stoichiometric SBT, and this enhancement has also been confirmed by several groups [4, 5]. Previously we have reported, the Sr-site doping in SBT that lead to slight increase in remanent polarization [6]. There are a number of reports on thin films with compositions deviating from the stoichiometry of SBT to enhance the remanent polarization (P_r) and to further decrease the processing temperature for the application of non-volatile random access memory devices [7–9]. The substitution of A- and B-site cations has pronounced influence on ferroelectric properties of SBT thin films [10, 11]. Recently, Wu *et al.* have reported the reduction of processing temperature by partial substitution of Ta^{+5} ion by V^{+5} ion [12]. According to them SBT and SBN bulk ceramics crystallize at low temperature upon vanadium substitution and also show enhanced dielectric and ferroelectric properties. In this article, we have reported the effect of 5% vanadium substitution at Ta-site and studied the growth behavior of *c*-axis suppressed $SrBi_2(Ta_{0.95}V_{0.05})_2O_9$ (SBTV) ferroelectric thin films on platinized silicon substrate using laser ablation technique. The phase formation and electrical properties of these films were studied in close correlation with the annealing temperatures.

2. Experimental details

Bismuth layered ferroelectric thin films of composition $SrBi_2(Ta_{0.95}V_{0.05})_2O_9$ (SBTV) were grown on $Pt/TiO_2/SiO_2/Si$ substrates using the pulsed laser deposition technique. Ceramic targets of 35 mm diameter with 15% excess bismuth were used for the ablation of 150 nm SBTV thin films. Before deposition the base pressure was dropped down to 5×10^{-6} Torr. Thin films (∼150 nm) were grown at a substrate temperature of 350°C with an oxygen pressure of 200 mTorr. As-grown films were post-annealed at temperatures ranging from 650 to 750°C, in O_2 ambient. Siemens D5000 X-ray diffractometer, with Cu Kα radiation, was employed to identify the phase formation and crystallographic orientation of the films. Lattice parameters and crystallite sizes were calculated from the XRD data. Platinum top electrodes of 200 μm diameter and

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150 nm thickness were deposited using DC magnetron sputtering. The polarization-field hysteresis loops were measured using RT 6000HVS ferroelectric tester (Radiant Tech.) at virtual ground mode. The dielectric behavior of the films was examined by the frequency dispersion of capacitance and dissipation factor in the frequency range of 1 kHz to 1 MHz, using an impedance analyzer HP4294A. Leakage current behavior of the films was studied using an electrometer (Keithley 6517 A) with a staircase dc-bias voltage of an amplitude ~0.2 V and a delay time of 30 s at each voltage step.

3. Results and discussion

Aurivillius layered perovskites have strong anisotropic characteristics. The ferroelectric properties of this family of compounds depend entirely upon the orientation of the domains along a particular axis. It is a challenge to grow thin films of bismuth-layered perovskites, along the polarization axis (which is in *a-b* plane). The typical X-ray diffraction (XRD) patterns of as-grown and post-annealed SBTV films are depicted in Fig. 1. It was noticed that the films grown at 350°C had an amorphous structure, but crystallization started after annealing them at/above 650°C. On increasing the annealing temperature to 750°C the crystalline peaks became more intense and sharper with reduced half width implying better crystallinity and increased crystallite size. It was also observed that, the (00l) crystalline orientation was suppressed in the polycrystalline SBT films, which is desired, since SBT has polarization axis along *a-b* plane. There was no evidence of secondary phase formation even at annealing temperature of 750°C. There is a small and systematic shift of XRD patterns towards higher diffraction angle with the increase in annealing temperature (inset Fig. 1). This shows that the lattice parameter decreases with increase in annealing temperature. Fig. 2 shows the variation of lattice parameters calculated from XRD patterns, for different annealing temperatures. The in-plane lattice parameters (*a*,*b*) decrease and the out of plane *c*-parameter increases with increase in annealing temperature. The variation of lattice parameter with annealing temperature could be attributed to the growth strain during annealing. At different annealing temperature the grain size is different and the thermal mismatch

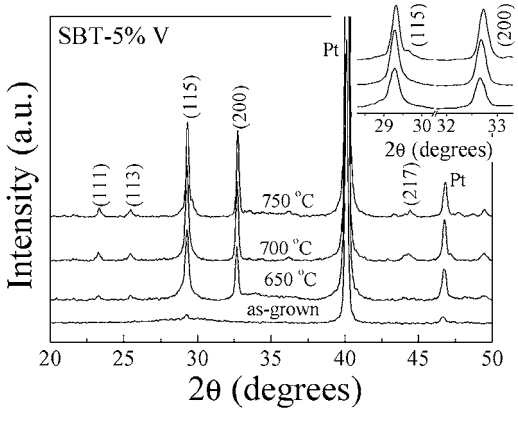

Figure 1 X-ray diffractograms of as-grown and annealed SBTV thin films.

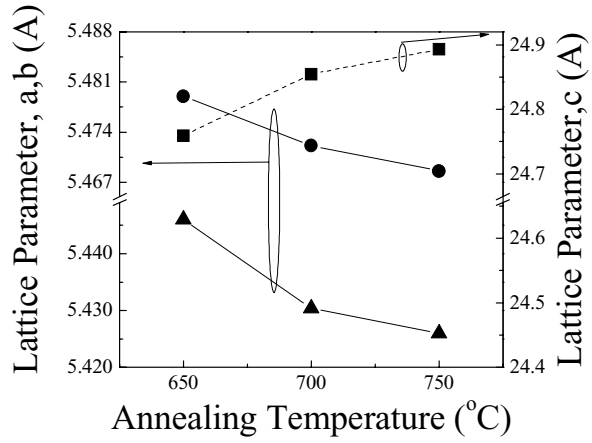

Figure 2 Lattice parameter variation of SBTV thin films with annealing temperature.

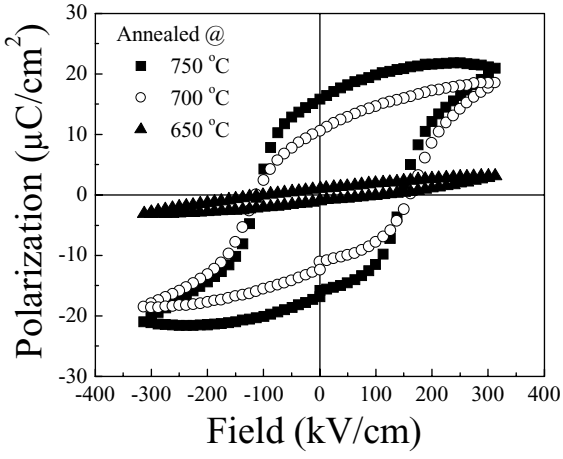

Figure 3 Hysteresis loop of SBTV thin films annealed at different temperatures.

coefficient between the SBTV film and the Pt substrate will be different. The exact nature of strain is not clearly understood.

The ferroelectric properties of typical 200 nm SBTV thin films were measured at an applied field of 250 kV/cm. Polarization-field hysteresis loops of SBTV thin films annealed at different temperatures are illustrated in Fig. 3. Films annealed at 650°C showed poor ferroelectric properties with remanent polarization of 3 μC/cm^2. This could be due to the poor crystallinity of the material. As we increase the annealing temperature, the loop became more saturated with improved ferroelectric properties. SBTV films annealed at 750°C exhibit enhanced ferroelectric properties with a remanent polarization ($2P_r$) of 31.5 μC/cm^2 and coercive field of (E_c) of 157 kV/cm. Previously, we have reported the ferroelectric properties of SBT thin films with partial replacement of Sr-site cations by Ba which exhibited $2P_r$ of 25 μC/cm^2 [6]. By substituting 5% vanadium at Ta-site enhanced the ferroelectric characteristics of SBT thin films. The possible reasons for the enhancement of the ferroelectric properties could be: (i) the growth of off *c*-axis oriented SBTV thin films and/or (ii) the increase in structural disorder in the material by partial substitution of a small size cation inside the TaO_6 octahedra. This enhancement is consistent with the reported results of Wu *et al.* [13].

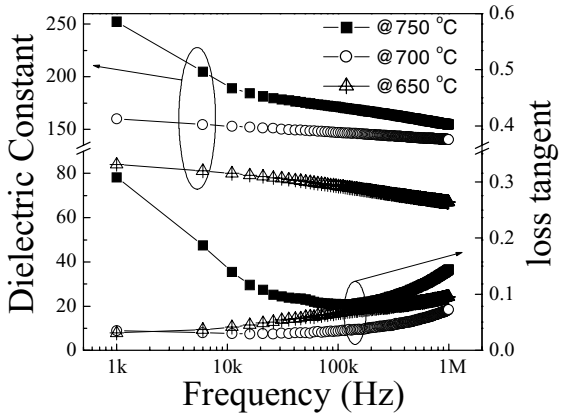

Figure 4 Frequency dispersion of dielectric constant and loss tanget of SBTV thin films at various annealing temperatures.

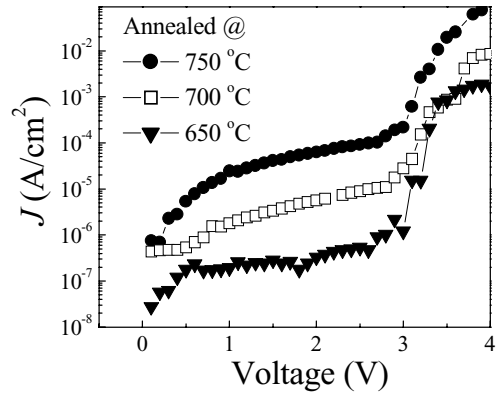

Figure 5 Leakage current behavior of SBTV thin films at different annealing temperatures.

In general the dielectric permmittivity of ferroelectric thin films is affected by various factors, such as orientation of the domains, bulk permmittivity of the material, low permmitivity depleted layer at the film and electrode interface, grain size etc. The deviation in the bulk properties of the materials is maximum for thinner films [14]. Room temperature frequency dispersed dielectric behavior of the SBTV thin films was studied at a frequency range of 1 kHz to 1 MHz, as depicted in Fig. 4. Films exhibited dielectric permittivity of 74, 147, and 172 (at 100 kHz) at an annealing temperature of 650, 700, and 750°C, respectively. Since all of the films have same orientation irrespective of the annealing temperature, low dielectric constant of the film annealed at 650°C could be due to poor cystallinity and smaller grain size. As we increased the annealing temperature the grain size increased causing an increase in the dielectric permmitivity. Influence of annealing temperature has strong influence on the dielectric loss ($\tan\delta$) of a ferroelectric thin film. The measured values of the tangential loss of SBTV thin films were 0.06, 0.03, and 0.1% (at 100 kHz) at the annealing temperature of 650, 700, and 750°C, respectively. Higher dielectric loss at lower annealing temperature (650°C) might be due to the contribution of finer grains with higher density grain boundaries. The possibility of maximum amount of space charge accumulation at grain boundaries leads to higher dielectric loss. The grain boundary density in the films was reduced with increase in annealing temperature to 700°C, causing reduction in the tangential loss (∼0.03). Films annealed at 750°C exhibited higher value of tangential loss (∼0.1). The origin of dielectric loss at higher annealing temperature could be due the interdiffusion of Bi into Pt electrode.

Influence of 5% vanadium at Ta-site has pronounced influence on leakage current characteristics of SBT thin films. Fig. 5 shows the variation of leakage current density (J) with applied voltage for SBTV thin films annealed at different temperatures. It was noticed that the leakage current density of SBTV thin films exhibit higher values than SBT thin films [15]. As we increase the annealing temperature the leakage current density start increasing. It is well established that the dc leakage current follow power law ($I \propto V^n$) behavior with applied voltage. The power index $n \simeq 1$ and $n \geq 2$ defines the Ohmic and space charge regions in the I–V curve respectively [16]. It was clearly visible, from Fig. 5, that the leakage current density behaves differently at low and high voltage regions. At low voltage the slope of J-V curve became 0.81, 1.1, and 1.3, at an annealing temperature of 650, 700, and 750°C, respectively. Low voltage region was considered as Ohmic region. Above applied field of 150 kV/cm the slopes became 19, 21, and 17 for the films annealed at 650, 700, and 750°C. In high field region the current density shoots up with few orders of magnitude and could be due to space charge limited current [17]. This sudden increase in the current is due to the filling of deep traps present inside the sample. A pure space-charge law would give a square law voltage dependence, which means a slope of 2.0 in the log-log plot. Higher leakage current density at higher annealing temperature could be due to the contribution of depleted layer at the interface of the film and Pt electrode. Detailed studies on leakage current behavior of SBTV thin films is in progress.

4. Conclusion

In summary, we have successfully grown c-axis suppressed SBTV ferroelectric thin films using PLD technique. Decrease in in-plane lattice parameters (a,b) and increase in the size of the unit-cell along pseudo tetragonal c-axis is attributed to the growth strain developed by the mismatch of thermal expansion coefficient between the film and the platinum electrode. The electrical properties of SBTV thin films were strongly dependent upon the annealing temperature. Films annealed at 750°C show enhanced ferroelectric properties with $2P_r$ of ∼31.5 μC/cm^2 and E_c of ∼157 kV/cm, at an applied field of 250 kV/cm. The increase in dielectric constant of SBTV thin films with increase in annealing temperature is explained in the framework of grain size dependence. The origin of tangential loss (0.06) at the annealing temperature (650°C) is attributed to the finer grains with the higher grain boundary density. However, larger dissipation factor (0.1) at higher annealing temperature (750°C) is explained in terms of interdiffusion of Bi into Pt electrode. The leakage current density of the films was found to be larger in SBTV in comparison with SBT thin films. Space charge limited current dominates at high field regime, irrespective of the annealing temperature.

Acknowledgements

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