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Effect of Oxygen Plasma on Growth, Structure and Ferroelectric Properties of $SrBi_2Ta_2O_9$ Thin Films Formed by Pulsed Laser Ablation Technique

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Abstract. Growth of $SrBi_2Ta_2O_9$ (SBT) thin films has been carried out in the presence of O_2-plasma created by applying a potential at an auxiliary ring electrode placed near the substrate. Effect of plasma excitation potential and polarity, especially negative polarity, on the formation of a proper SBT phase at 700°C and in modifying crystallite orientation and microstructure of SBT films over (1 1 1) oriented Pt film coated over $TiO_2/SiO_2/Si(1\,0\,0)$ substrates has been demonstrated. Preferred *c*-axis orientation of SBT films changes to (*a*–*b*) orientation with decrease in plasma excitation potential from -700 to -350 V and eliminates secondary Bi_2Pt phase formation even at 600°C Microstructural study show a 2-dimensional large flat *c*-oriented crystallites formed at -700 V change to small crystallites in conformity with the changed aspect ratio for crystallites in (*a*–*b*) plane parallel to film plane. Spectroscopic ellipsometric results are in agreement with the microstructural data. These affects are attributed to O_2-ion bombardment during film growth which reduces nucleation barrier for growth of crystallites in (*a*–*b*) plane. O_2-plasma sustains the cationic species formed by laser ablation, which along with O_2^+ ions, provide necessary activation energy and enhance the oxidation rates required for SBT phase formation even at 700°C. SBT films grown in O_2-plasma show enhancement in remnant polarization value from 1.2 to 6.6 $\mu C/cm^2$ and display ferroelectric properties superior to those formed without plasma. Further O_2-plasma eliminates post deposition annealing step for observance of enhanced polarization values. This study shows O_2-plasma excitation potential could be exploited as a new process parameter in laser ablation growth of ferroelectric oxide thin films.

Keywords: SBT, plasma, ferroelectric, $SrBi_2Ta_2O_9$, pulsed laser ablation, film growth, oxygen plasma, film orientation

1. Introduction

Bismuth layered perovskite oxides belonging to $(Bi_2O_2)^{2+}$ $(A_{m-1}B_mO_{3m+1})^{2-}$ family have recently emerged as a most viable thin film ferroelectric material for application in non-volatile random access memory (NvRAM) devices [1–4]. Among several materials in this class such as $Bi_4Ti_3O_{12}$, $SrBi_2Nb_2O_9$, $SrBi_4Ti_4O_{15}$ etc., $SrBi_2Ta_2O_9$ (SBT) have been widely investigated owing to its high fatigue endurance up to 10^{12} switching cycles, excellent retention characteristics and low leakage currents over Pt electrodes. These properties have made it attractive in comparison to PZT based ferroelectrics which suffer from the loss of switched charges over 10^8 bi-polar cycles due to oxygen vacancies at the interface with metal electrodes [5,6]. Although, efforts to use oxide electrodes have met with some success, high contact resistance and interfacial growth of non-ferroelectric phases are

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still the issues to be reckoned with [7,8]. While the SBT films are free from such deficiencies, lower value of remnant polarization and high coercive fields exhibited by them are towards the lower limits of requirements for high density (4 Mbits) NvRAM applications. Further more, SBT films are processed at relatively higher $\sim 800^{\circ}$C temperatures and the films are often subjected to prolonged post-deposition crystallization anneals. At these temperatures, several issues related to the integration of SBT films with the Si-VLSI technology, particularly the compositional integrity of various interfaces, oxidation of barrier metal and a limited choice of contact metals etc. become an area of major concern.

In SBT, contribution to spontaneous polarization is due to perovskite lattice blocks comprising of two Sr-Ta-O units stacked alternatively between the $(Bi_2O_2)^{2+}$ layers in a pseudo-tetragonal crystal structure [9]. The dipole interaction between the perovskite blocks is prevented by non ferroelectric $(Bi_2O_2)^{2+}$ planes. Thus, very little polarization exists along the *c*-axis which is perpendicular to the $(Bi_2O_2)^{2+}$ planes and mainly resides along the (*a*–*b*) plane. Due to the anisotropic nature of ferroelectric properties on the crystal structure, orientation of the crystallites in SBT films is relevant for attaining high remnant polarization, P_r and low coercive field, E_c values. High temperature synthesis is required to eliminate pyrchlore phase formation, transformation of fluorite micrograins to Bi-layered structure [10], improve the microstructure and attain a critical grain size [11]. A major thrust of the several chemical and vapor phase techniques developed to deposit SBT films has been to overcome the twin issues, of minimizing the process temperature and time and improving the ferroelectric properties, e.g., P_r, E_c and dielectric constant $\varepsilon\varepsilon_0$. The essential approach of these techniques is crystallization of a proper Bi-layered phase with minimum defects without inclusion of any secondary phases and orientation of the crystallites with a preferred (*a*–*b*) plane along the film surface. As these are highly dependent on processing methods and parameters, several process variables have been attempted in the past to form SBT films meeting the structural criterion. In chemical techniques, namely, solgel [12] and metalorganic solution deposition (MOSD) [13–15], some important process variables such as, off stoichiometric Sr-deficient compositions [15], texture control by buffer layers [16], post growth crystallization at low oxygen partial pressures [17] and rapid thermal annealing [12] have been employed. SBT films deposited by solgel and metalorganic solution growth techniques are generally polycrystalline, fine grained and often with segregated metallic Bi, necessitating 800°C processing for improvement. In these methods, the SBT phase growth is by solid state reaction within the deposited precursors and depend essentially on the rates of precursor pyrolysis, oxidation and reaction, driven by the temperature of processing. The vapor phase techniques, on the other hand, depend on condensation of molecular species from a vapor phase and follow the kinetics of nucleation controlled growth. Here, the substrate temperature and vapor flux have a direct impact on the crystalline phase, microstructure and composition of the deposited film. Most studies on SBT film growth have been done by pulsed laser ablative deposition (PLD) due to its proven versatility for multi-component oxides [2,11,18–20]. Important variables attempted in this method are Sr/Bi ratio [18], oxygen pressure [20], use of N_2O as oxidizer gas [21] and substrate temperature [11]. In the present work, we have carried out PLD growth of SBT films in the presence of oxygen plasma containing energetic oxygen ions and neutrals. Under the plasma conditions employed here, the oxygen ions cause enhancement of reaction among the component oxides and modification of the film nucleation and growth kinetics through irradiation of energetic ions during the film growth. This has a profound effect on the film microstructure and crystalline orientation resulting in an improvement in ferroelectric properties and elimination of the severe post-growth crystallization step. We also demonstrate, plasma parameters especially the excitation potential as an important variable to obtain films in (*a*–*b*) orientation and lowering of the deposition temperature to 700°C. This paper reports the results of this study.

2. Experimental

SBT thin films were deposited over (1 1 1) oriented Pt film (1800A) coated $TiO_2/SiO_2/Si(1\,0\,0)$ single crystal substrates by pulsed laser ablation technique. The target was 25 mm diameter disc of stoichiometric $SrBi_2Ta_2O_9$ prepared by conventional ceramic route by calcination at 1120°C and sintering at 1190°C in air for 3 h each. For film deposition, the rotating target

(at 11 rpm) was irradiated by excimer laser (Lamda Physik LPX300) utilizing 248 nm KrF radiation operating at 10 Hz and energy density of 1.5 J/cm^2. The substrate was mounted on a heater block having the facility of rotation at 4 rpm and kept at a distance of 60 mm from the target. The deposition was carried out at a nominal oxygen pressure of 200 m Torr while the substrate was held at 600 and 700°C in different deposition runs. In the present deposition system, O_2-plasma was excited by applying a high dc potential to a ring electrode of $\sim$ 30 mm dia. placed in between the target and substrate/heater holder coplanar with the substrate at a distance of 10 mm from it. A dc potential of 300–700 V of either polarity can be applied to the auxiliary ring electrode with respect to the target which is kept electrically grounded to create the O_2-plasma glow discharge under typical oxygen partial pressures of 80 to 400 m Torr in the PLD chamber. The discharge region extends on either side of the ring electrode. Geometric location of the substrate was within the plasma zone and thus exposed to energetic species, neutrals and electrons in the glow discharge depending on the bias applied at the excitation electrode. The substrate was kept electrically floated by using a suitable design of the heater and rotation system. The plasma was excited and sustained by voltage application simultaneous to triggering of the excimer laser pulse which initiates the ablation process. Film deposition rates were dependent on whether O_2-plasma was present or not. Typically average film deposition rate was 0.3 nm/s without the plasma and $\sim$ 0.23 nm/s with the plasma. Some films were subjected to a post growth oxygen annealing for periods ranging from 30 to 90 min, especially when a comparison was required with SBT films grown without the plasma assistance which needed to be optimized for ferroelectric properties. Ferroelectric properties were measured by RT66A tester (Radiant Technology) under virtual ground conditions. For this, an array of Pt contacts each of nominal area 3×10^{-4} cm^2 were sputter deposited using appropriate shadow mask to form metal-ferroelectric-metal capacitors. The thickness and optical properties of films were determined by variable angle spectroscopic ellipsometry (J.A. Woollam Co., Inc.). The crystallographic structure was analyzed by X-ray diffraction (XRD) measurements using CuK_α radiations by SCINTAG XDS200 instrument. The microstructure studies have been carried out using the atomic force microscope (Digital Instruments) in the tapping mode with amplitude modulation.

3. Results

3.1. Ferroelectric Properties

(a) Effect of deposition temperature. SBT films formed without the presence of O_2-plasma at a substrate temperature, T_s, of 600°C in the as-deposited state were either shorted or showed very poor ferroelectric behavior. Post-deposition anneal at 700°C for 90 min eliminated the shorts and improved the polarization characteristics, *P–E*, as shown in Fig. 1(a). The

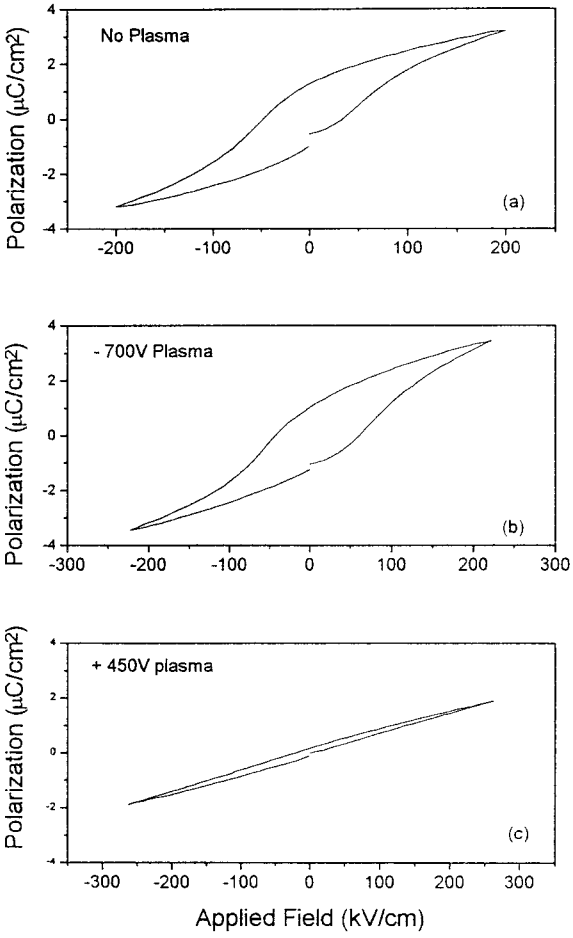

Fig. 1. P–E hysterisis loops of SBT films deposited at 600°C substrate temperature (a) without plasma and with O_2-plasma excited at potential (b) -700 V and (c) $+450$ V.

remnant polarization, P_r values of 1.27 and saturation polarization, P_s values of 3.2 μC/cm^2 and coercive field of 35 KV/cm were recorded. These films showed high leakage currents, typically $\sim 1.3 \times 10^{-5}$ A/cm^2. Figure 1(b) shows *P–E* curves for the SBT films deposited under similar conditions except for the presence of O_2-plasma during the film growth excited by applying -700 V at the auxiliary ring electrode. Although, the polarization values are not much different, the coercive field increases to 60–62 KV/cm and the leakage currents are now much lower, typically $1\text{–}2 \times 10^{-10}$ A/cm^2. The *P–E* hysterisis for films grown in O_2-plasma when a positive potential of 450 V is applied at the ring electrode for plasma generation showed extremely poor ferroelectric properties (Fig. 1(c)). Clearly, the plasma does affect the SBT film properties, but to observe its favorable impact, further optimization is required. Since the SBT films were required to be annealed to 700°C in order to observe a ferroelectric response, in the next experiment, the film growth itself was carried out at the substrate temperature of 700°C. Figure 2 shows a comparison of ferroelectric parameters at different fields for a SBT film deposited at 700°C without the plasma and the one deposited at 600°C with the plasma (-700 V) assistance. More dramatic effect of the plasma in improving the remnant polarization value is observed when the SBT film deposition is done at 700°C. Figure 3 shows a comparison of *P–E* hysterisis for SBT films deposited at $T_s = 600$ and 700°C in the presence of O_2-plasma excited by applying -700 V at the auxiliary ring electrode. Since, 600°C deposited films required a post growth anneal at 700°C for 90 min, the SBT films deposited at 700°C was also subjected to a similar treatment for comparing the results. Our experiments described in the following section have however shown, the post-growth annealing step is not necessary for SBT films deposited in the O_2-plasma under optimum conditions of plasma potential As

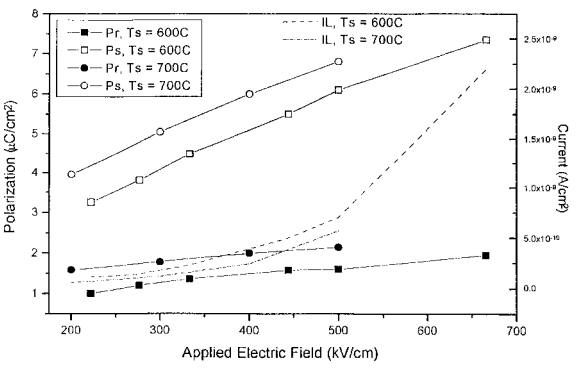

Fig. 2. Dependence of remnant (P_r) and saturation (P_s) polarization values and leakage current on applied electric field for SBT films formed at $T_s = 600$°C in the presence of O_2-plasma and at $T_s = 700$°C without O_2-plasma.

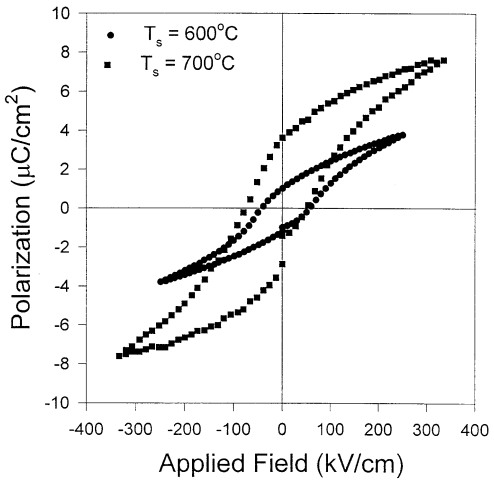

Fig. 3. Comparison of *P–E* hysterisis loops of SBT films deposited at $T_s = 600$ and 700°C in the presence of O_2-plasma excited at -700 V.

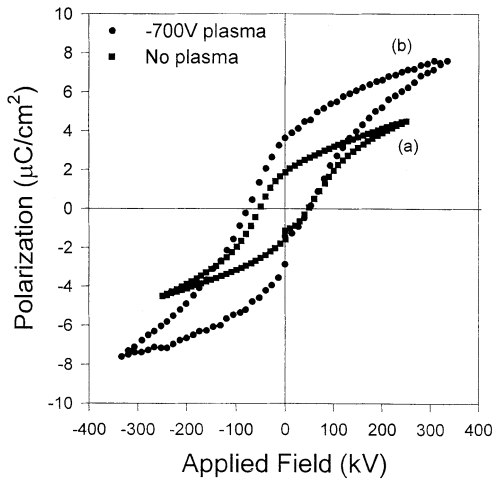

Fig. 4. Comparison of *P–E* hysterisis loops of SBT films deposited at $T_s = 700$°C (a) without O_2 plasma and subjected to a 700°C anneal for 90 min and (b) in the presence of O_2-plasma excited at -700 V without any post deposition anneal.

inferred from Fig. 3, P_r improves from a low value of 1.1 to 3.6 μC/cm^2. P_s and E_c values in the two cases were 3.8 and 7.6 μC/cm^2 and 56.7 and 50 KV/cm, respectively. Figure 4 shows a comparison of *P–E* hysterisis curves of SBT films deposited at 700°C with and without the oxygen plasma excited at -700 V. Whereas, P_r values of conventionally deposited SBT films are still poor, ~ 1.7 μC/cm^2, (curve a), those deposited with the assistance of O_2-plasma show a considerable improvement to 3.6 μC/cm^2 (curve b).

(b) Optimization of plasma parameters. SBT films deposited by pulsed laser ablation at $T_s = 700$°C were used for optimization of ferroelectric properties in view of enhanced effect of O_2-plasma observed for such films. This study focuses on variation in plasma excitation potential and its polarity as applied at the auxiliary ring electrode. We observed that plasma potential has a pronounced two fold effect on the synthesis and ferroelectric properties of SBT films. Firstly, use of oxygen plasma eliminates any post-growth crystallization step, otherwise required for observing ferroelectric properties for SBT films deposited without the plasma assistance. Secondly, it enables attaining higher remnant polarization values which were not achievable for SBT films grown by pulsed laser ablation under the processing conditions applied in these experiments.

(i) Elimination of post-growth anneal. Ferroelectric P-E hysterisis characteristics of SBT films deposited by laser ablation in the presence of O_2-plasma were studied in the as-deposited state without subjecting them to any post-deposition crystallization anneal. Figures 5 and 6 show the polarization curves for SBT films deposited in O_2-plasma at potentials of -450 and -350 V, respectively. *P–E* curves for similarly processed but without the plasma are also included for comparison. P_r values improve from 1.2 μC/cm^2 to 2.3 μC/cm^2 and more substantially to 6.6 μC/cm^2 by depositing in O_2-plasma at -450 V and -350 V, respectively. Some earlier studies [18,19] on pulsed laser deposition of SBT films have found that post deposition annealing at 800°C is an inevitable process step in order to form a fully crystallized SBT phase and increase remnant polarization values. Clearly, the O_2-plasma during SBT film growth by laser ablation process, under optimum plasma excitation potentials, do not require any post-deposition anneal for improving the ferroelectric properties. Proper choice of plasma excitation potential not only ameliorates the process related problems associated with subjecting these films to a more severe, 700–800°C. 60–90 min post-growth crystallization anneal step but also improves the remnant polarization values. A replot of the data of Figs. 5 and 6 in Fig. 7 makes it more evident. An important observation is that for SBT films deposited in O_2-plasma, improvement in P_r values are invariably associated with increased coercive field. As compared to an E_c value 39.7 KV/cm for films deposited without O_2-plasma, typically, E_c rises to ~ 51 KV/cm for example in films formed at -350 V plasma. This behavior is due to change in crystallite orientation as discussed later.

(ii) Effect of plasma potential polarity. O_2-plasma can be excited and sustained in between the target and the substrate, irrespective of the polarity of the voltage applied to auxiliary ring electrode. However, we find that most improvements in the ferroelectric property of the SBT films were possible only when a potential of negative polarity was applied. Figure 8 shows a typical polarization curve for a SBT film deposited in the O_2-plasma excited by applying $+450$ V at the ring electrode. P_r and P_s values were 0.45 and 3.35 μC/cm^2, respectively and

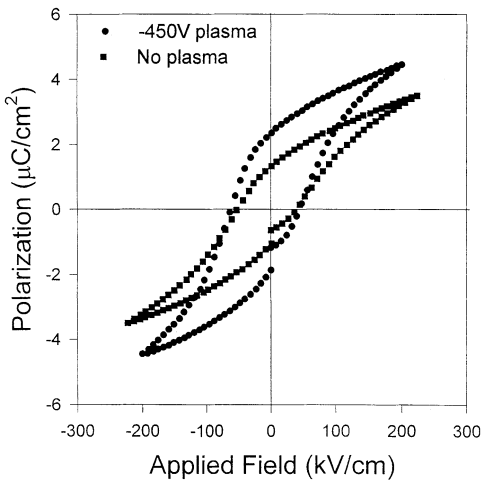

Fig. 5. Comparison of *P–E* hysterisis loops of SBT films deposited at $T_s = 700$°C without O_2 plasma and subjected to a 700°C anneal for 90 min and in the presence of O_2-plasma excited at -450 V without any post deposition anneal.

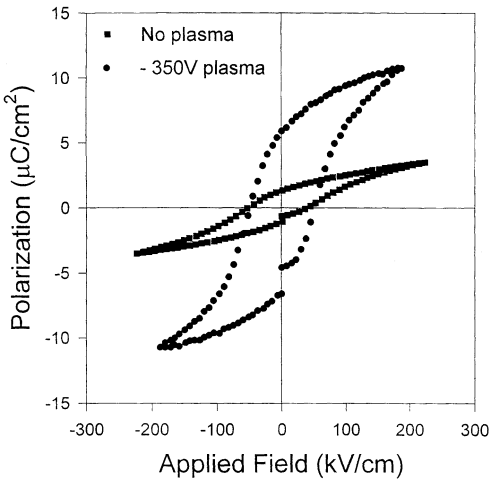

Fig. 6. Comparison of *P–E* hysterisis loops of SBT films deposited at $T_s = 700°C$ without O_2 plasma and subjected to a 700°C anneal for 90 min and in presence of O_2-plasma excited at -350 V without any post deposition anneal.

leakage currents of $\sim 7 \times 10^{-9}$ A/cm^2. Further, in this case, on post-growth annealing, P_r and P_s values instead of showing an expected improvement were found detrimental although E_c improved from a low value of 16 KV/cm to 35 KV/cm and leakage current marginally to 3×10^{-10} A/cm^2.

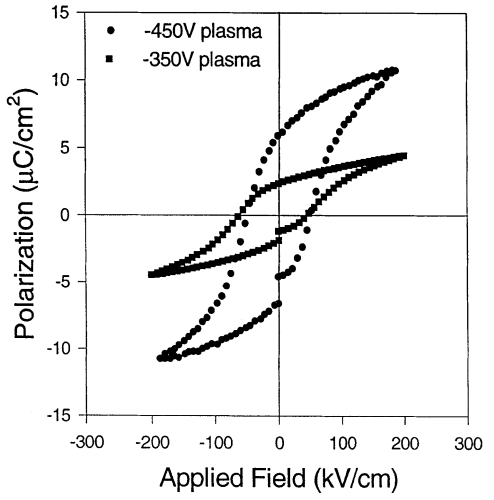

Fig. 7. Comparison of *P–E* hysterisis loops of SBT films deposited at $T_s = 700°C$ in presence of O_2 plasma excited at potential of -450 and -350 V without any post deposition anneal.

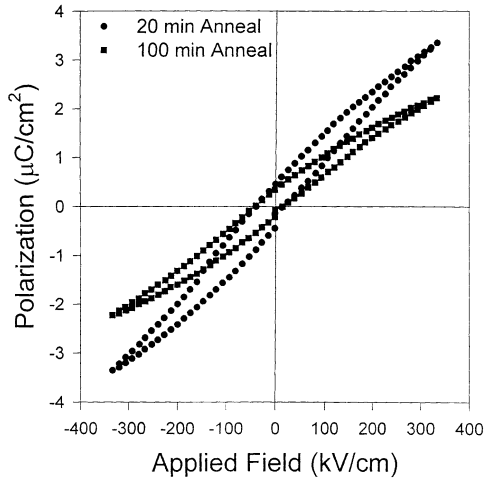

Fig. 8. P–E hysterisis loops of SBT films deposited at $T_s = 700°C$ in presence of O_2-plasma excited at $+450$ V and subjected to a post deposition anneal at 700°C for 20 and 100 min.

3.2. Crystalline Structure

Figure 9 shows the effect of substrate temperature, T_s on the crystallite orientation in SBT films grown without any O_2-plasma assistance. Both films, deposited at $T_s = 600$ and 700°C are well crystallized. At $T_s = 600°C$, we observe strong (1 1 5) peak and another one (2 1 7) of the same family belonging to perovskite phase. The diffraction line at $2\theta = 26.2°$ and 38.75° not belonging to the SBT system are attributed to Bi_2 Pt phase indicating insufficient oxidation of Bi during film growth which results in

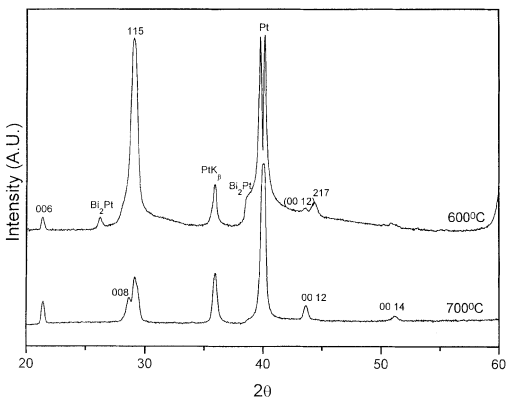

Fig. 9. Comparison of XRD patterns of SBT films formed at $T_s = 600$ and 700°C without any O_2-plasma.

its reaction with bottom Pt electrode. Other diffraction lines belong to (*00l*) orientation. The tendency for a stronger *c*-axis orientation normal to the film plane increases with the increase in the deposition temperature as is evident from stronger (0 0 6), (0 0 8), (0 0 1 2) and (0 0 1 4) diffraction lines in XRD pattern for films deposited at $T_s = 700°C$. Here, a dominant number of crystallites grow with their *c*-planes lying parallel to the film plane. There is no peak belonging to Bi_2Pt suggesting absence of any O_2-deficient phase of constituents of SBT. Crystalline state of SBT films deposited at $T_s = 600°C$ in O_2-plasma excited at -700 V continues to show *c*-axis orientation normal to film plane as its XRD spectra in Fig. 10 does not differ appreciably form that of the SBT film formed without O_2-plasma. However, secondary phase at $2\theta = 26.2°$ and 38.75° due to Bi_2Pt is not observed suggesting O_2-plasma has helped in improving the oxide growth for which higher deposition temperature was needed initially (Fig. 9). This is in general agreement with the ferroelectric hysterisis data which have shown no perceptible improvement in polarization values. Absence of more conducting secondary phase Bi_2Pt reduces the leakage current as is indeed observed. For SBT films grown in O_2-glow discharge at excitation potential of opposite polarity of $+450$ V, the randomly oriented crystallite formation is preferred. The relative peak heights of (*00l*) reflections decrease and additional (*hkl*) peaks appear. The full width at half maximum (FWHM) for (1 1 5) peak decreases

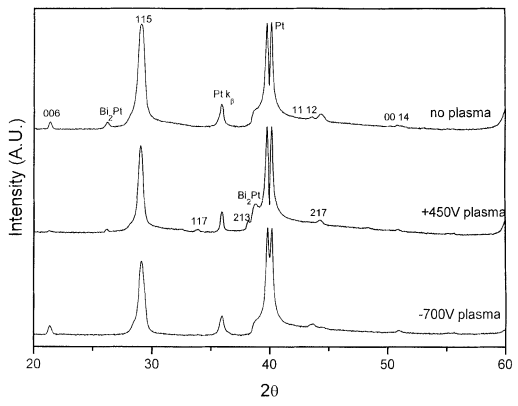

Fig. 10. Comparison of XRD patterns of SBT films formed at $T_s = 600°C$ without plasma and in the presence of O_2-plasma excited at -700 and $+450$ V.

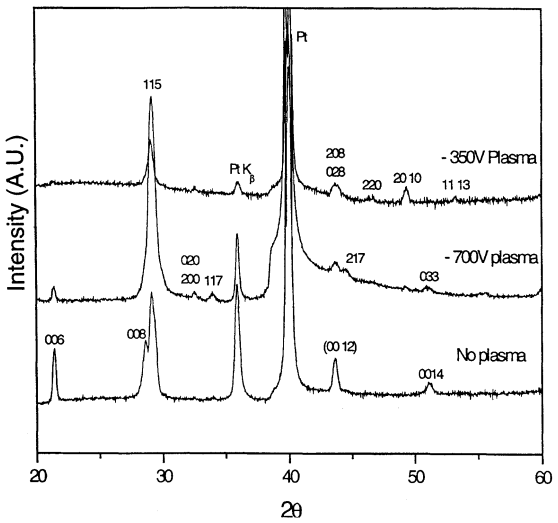

Fig. 11. Comparison of XRD patterns of SBT films formed at $T_s = 700°C$ without plasma and in the presence of O_2-plasma excited at -700 and -350 V.

from 0.73° for without plasma to 0.66° and 0.55°, respectively for -700 and $+450$ V plasma excitation potentials showing an improved crystallite growth of perovskite stacks of Sr-Ta-O in SBT film. It may be noted that the secondary peak belonging to Bi_2Pt still exists in the SBT films formed in $+450$ V plasma, as opposed to the one in -700 V plasma. This implies that the positive potential at the ring electrode does not have any effect in enhancing the oxidation state of component oxides in SBT film growth.

For SBT films formed at $T_s = 700°C$, effect of O_2-plasma on crystallite orientation is more profound. Figure 11 compares the XRD patterns of SBT films deposited without and with O_2-plasma excited with -700 and -350 V applied at the ring electrode. At -700 V excitation potential, (*00l*) diffraction peaks have either diminished in intensity or disappeared. In the diffraction pattern, the peaks corresponding to (0 0 8) and (0 0 1 4) planes are no longer seen and only (0 0 6) is observed. At still lower plasma excitation potential of -350 V, there are multiple peaks belonging to (*hk0*) or (*h0l*), but none from (*00l*) planes. The (1 1 5) peak present in both sets of SBT films is the main peak corresponding to perovskite phase. A sharp narrow peak indicates a large grain size. The full width at half maximum (FWHM) of (1 1 5) peak for (*00l*) oriented SBT film formed

without plasma is 0.68°. It decreases for films deposited in the presence of plasma to 0.60° for -700 V and remarkably to 0.35° for -350 V plasma excitation potentials indicating a growth of large (*a–b*) oriented crystallites in SBT films deposited with plasma assistance. The intensity ratios $I\Sigma(00l)/I\Sigma(hkl)$ decreases from a high value of 1.53 in the case of films formed without the plasma to 1.22 and 0 for SBT formed in O_2-plasma at -700 V and -350 V, respectively. It is thus inferred that, pulsed laser deposition of SBT film in the presence of O_2-plasma has strong effect on the crystallite orientation, with lower plasma potentials enhancing the growth of (*a–b*) planes. The preferred *c*-axis orientation normal to the film plane in films formed without the plasma, progressively changes the orientation with plasma excitation potential to a preferred *c*-axis direction nearly inclined along the film plane at lower excitation potentials. With the assumption that SBT film crystallizes in *pseudo*-tetragonal structure, lattice constants were determined from (1 1 5), (2 0 8) and (0 0 6) reflections. We obtained $a = b$ lattice parameters as 0.5498, 0.5480 and 0.5493 nm and *c*-axis lattice parameters as 2.4876, 2.4876 and 2.4918 nm for no plasma, -700 V and -350 V plasma, respectively. Lattice constants show no specific dependence on plasma conditions. These values are reasonably close to standard values, $a = b = 0.5534$ and $c = 2.4984$ nm.

Similar to the case of 600°C deposited films (Fig. 10), the effect of positive plasma potentials on the XRD pattern of SBT films deposited at $T_s = 700$°C is also not as appreciable. As shown in Fig. 12, a randomly oriented crystallite growth is preferred and (*00l*) reflections either diminish in intensity or are not observed. Random orientation and formation of highly crystallized perovskite Sr-Ta-O stacks is a common effect of the positive plasma on the structure of SBT films. Although, crystallinity of the perovskite phase also improves in SBT films grown in O_2-plasma excited at negative voltages, a much stronger effect on the change in crystallite orientation is observed in this case.

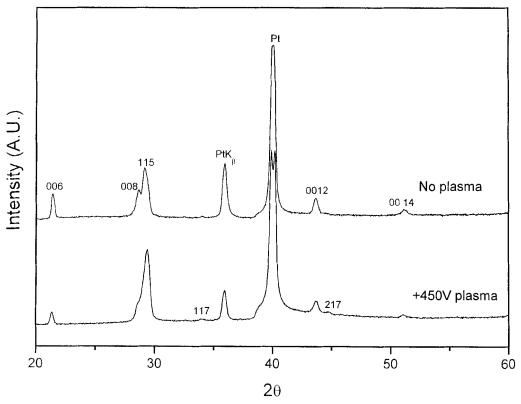

Fig. 12. Comparison of XRD patterns of SBT films formed at $T_s = 700$°C without plasma and in presence of O_2-plasma excited at $+450$ V.

3.3. Microstructure

Both, O_2-plasma and the substrate temperature considerably effect the crystallite surface microstructure of the SBT films grown by laser ablation. The microstructure studies have been carried out using the atomic force microscope (AFM) in the tapping mode with amplitude modulation over an area of $1\,\mu m \times 1\,\mu m$. Figure 13 shows the effect of the O_2-plasma on SBT films deposited at $T_s = 600$°C. Films deposited without the plasma (Fig. 13(a)) display small nodular crystallites of an average size between 34–52 nm. Deposition of films in O_2-plasma with negative excitation potential at the electrode significantly affects the film morphology. One observes the formation of large, average size 0.13 μm, platelet like crystallites alongside the usual small $\sim$ 20–30 nm nodular grains. These flat crystallites represent those having a strong *c*-axis orientation normal to the film plane belonging to $[Bi_2O_2]^{2+}$ planes in SBT as already established by the XRD analysis. The microstructure of SBT films deposited in O_2-plasma with a positive excitation potential at the ring electrode are not much different from the films deposited without any plasma. The crystallites are closely packed having an average size $\sim$ 45 nm. A general effect of increase in substrate temperature is on corresponding increase in the crystallite size [11]. More significant effect of the O_2-plasma on the microstructure is evident from Fig. 14 and is generally supportive of the inferences drawn from ferroelectric and XRD studies. It may be recalled XRD pattern of SBT film formed at $T_s = 700$°C exhibit an improved *c*-axis orientation as compared to the one formed at $T_s = 600$°C. Consequently, films grown without the plasma having a preferred (*00l*) orientation display well formed large Bi-layered structure flat platelet

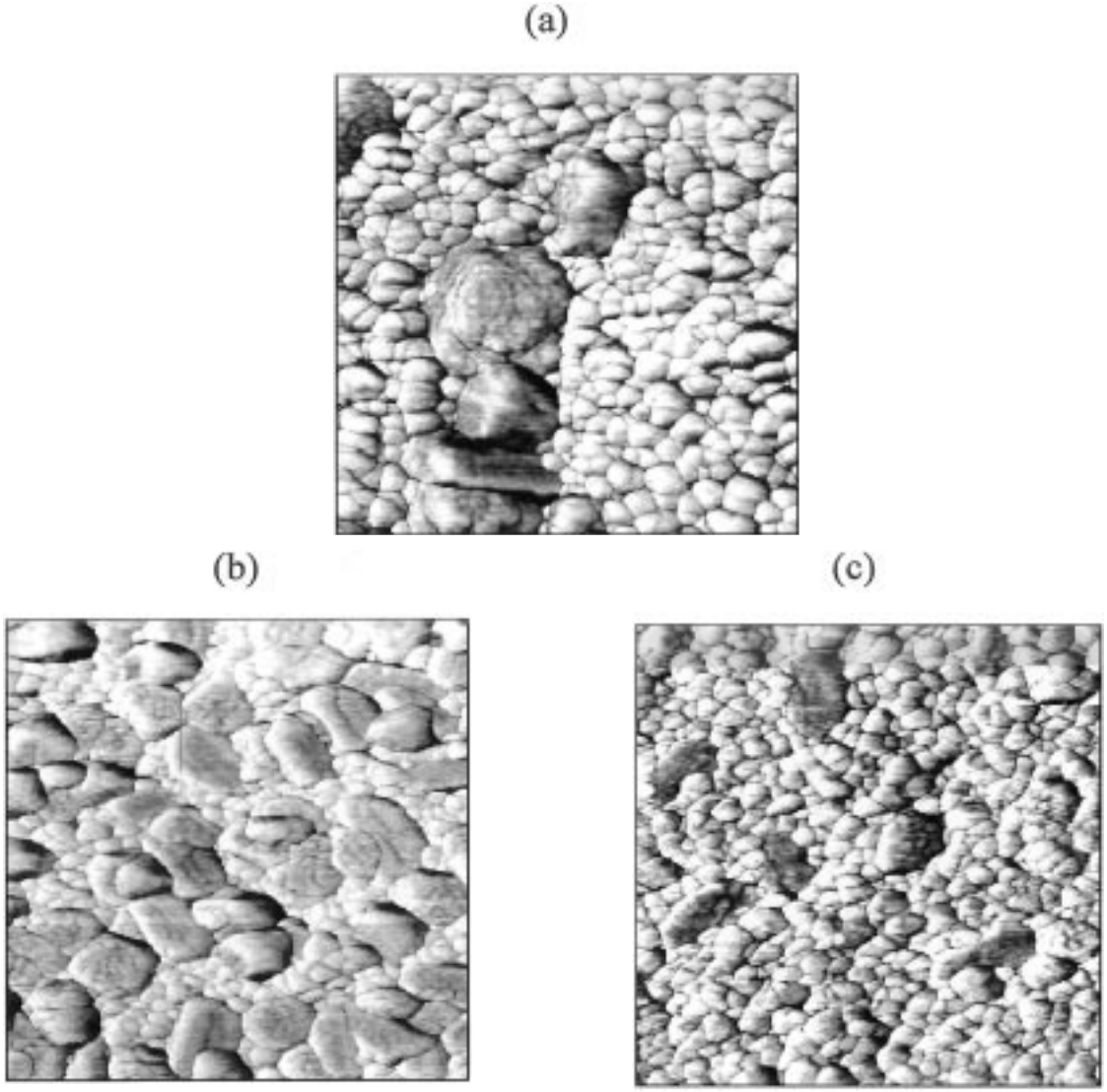

Fig. 13. AFM microstructure of SBT films deposited at $T_s = 600°C$, (a) without O_2-plasma and with O_2-plasma excited at (b) -750 V and (c) $+450$ V.

grains of a larger average size between 130–170 nm. These grains are loosely packed and show voids in the inter-grain regions. The large grains appear to have superimposed small flat grains. These could be the crystallites developing into larger platelets in a two dimensional growth mode as suggested by the staircase-like growth steps. These flat crystallites grow larger, average size $\sim$ 240–350 nm and are well formed when films are grown in O_2-plasma at -700 V as excitation potential. Smaller crystallites are not observed suggesting the crystallite formation is complete. The morphology of SBT films grown in O_2-plasma at low excitation potential of -350 V is quite different. It shows crystallites are semi-rectangular grains which appear as standing blocks of smaller average size of $\sim$ 90 nm. The surface morphology is quite uniform, without cracks or defects and has no inclusion of small size grains as observed in films grown without plasma. The different aspect ratios of crystallites in the two cases is in

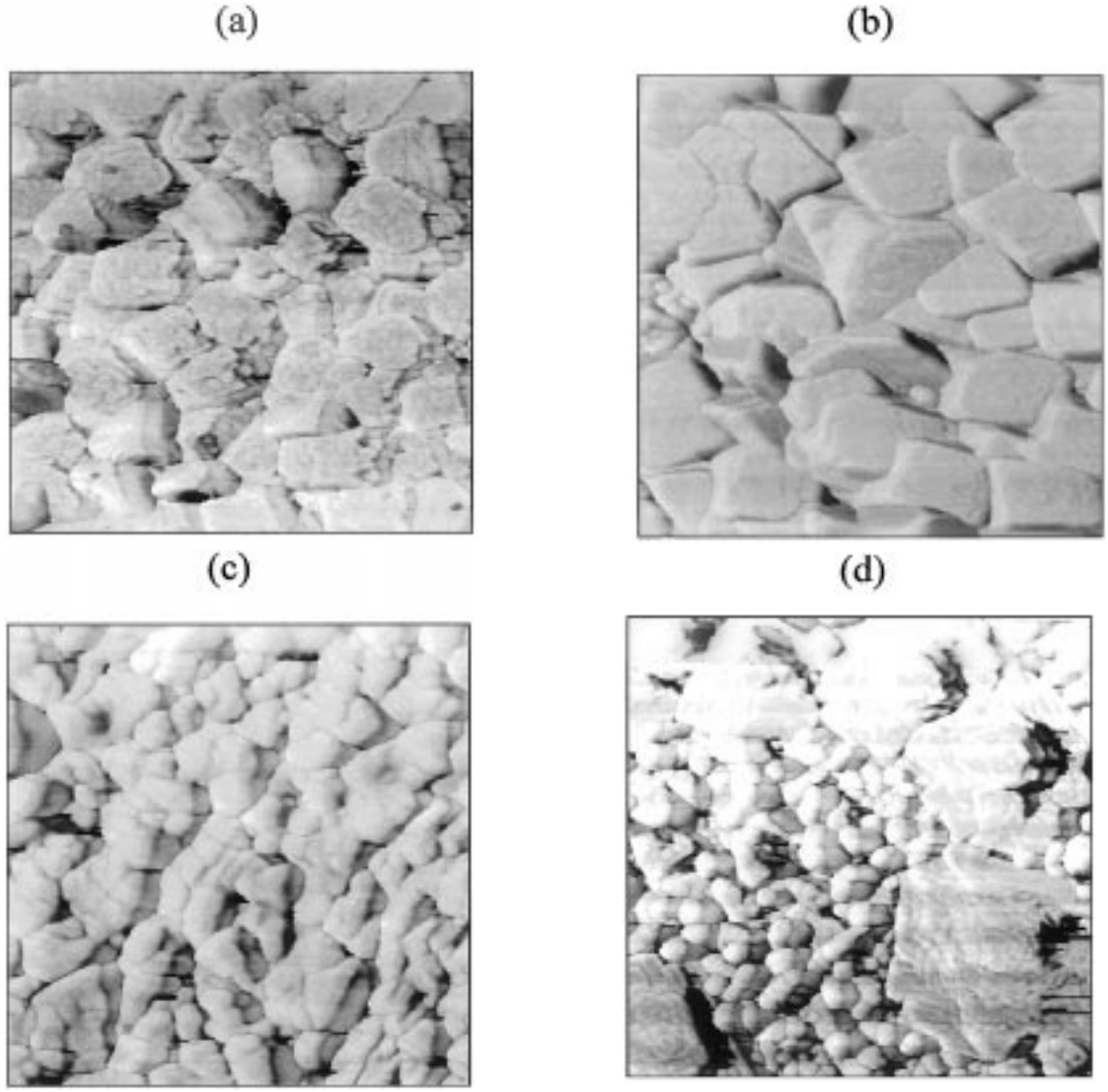

Fig. 14. AFM microstructure of SBT films deposited at $T_s = 700°C$, (a) without O_2-plasma and with O_2-plasma excited at (b) -450 V and (c) -350 V (d) $+450$ V.

accordance with the inference drawn from XRD analysis and agree well with the anisotropic lattice constant for preferred *c*-axis orientation normal and near parallel to the film plane. Surface morphology of SBT films formed in O_2-plasma generated by application of a positive potential of 450 V is a mix of small nodular and large flat crystallites. These are randomly scattered across the film surface. The heterogeneous morphology is riddled with macroscopic defects, particularly voids.

3.4. Optical Dispersion by Ellipsometry

Dispersion of complex index of refraction for SBT films deposited under various O_2-plasma conditions at a substrate temperature of 700°C was determined from the spectroscopic ellipsometeric studies using Lorentz dispersion theory [22]. The optical parameters were determined by visualizing realistically the SBT films are composite of voids, grains and roughness by modeling the data for Bruggemann

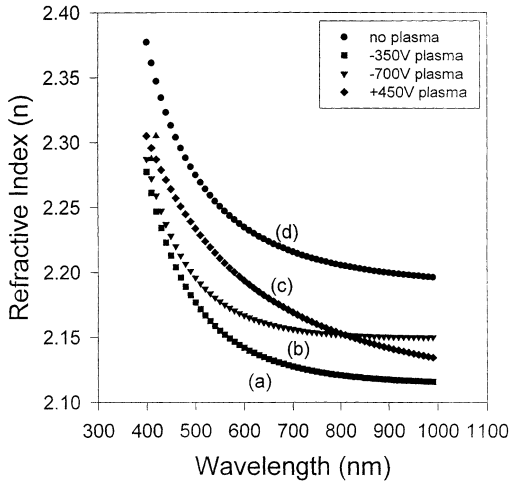

Fig. 15. Dispersion of index of refraction of SBT films deposited at $T_s = 700°C$, with O_2-plasma excited at (a) $-350\,V$ and (b) $-700\,V$ (c) $+450\,V$ (d) without any O_2-plasma.

effective media approximation [23]. This modeling mimics the peak envelope in the oscillation of Δ and Ψ representing the polarization state of light reflected by SBT film and are the parameters measured by the ellipsometer. Figure 15 shows the variation of real part of complex index of refraction with the wavelength for SBT films deposited in O_2-plasma under various excitation potentials and without the plasma. At higher photon energies significant dispersion is seen as one approaches the band edge and decreases monotonously with decreasing photon energy. Direct band edge of SBT occurs at 5.1 eV [24] and is not observed due to limited wavelength range of measurements. Void percentage in SBT film corresponding to which best fit with the experimental data are observed are 3% for film formed without the plasma and 9.36% for film deposited in plasma at $+450\,V$ at the excitation electrode. For plasma at negative excitation voltages, minimum voids $<0.5\%$ at $-700\,V$ and 4.3% at $-350\,V$ were estimated. These are consistent with the microstructure data described above. SBT films displaying large flat crystallites representing a dominant 2-dimensional growth have less than 3% voids and minimum for films with larger crystallites. Since, films formed at $+450\,V$ plasma have shown morphology of mixed small and flat large crystallites, void percentage is large here. Deviation in the dispersive nature and values of index of refraction ***n*** in Fig. 15 is attributed to crystalline orientation of the SBT films deposited under these conditions. Primarily the (*a–b*) oriented films yield lower n values with minimal dispersion (curve a) as compared those with *c*-planes along the film surface. Randomly oriented films such as formed in O_2-plasma with $+450\,V$ have intermediate values to both.

4. Discussion

Growth of SBT films in the present case is affected by (i) interaction of O_2-plasma with the laser ablated material in the vapor form and (ii) bombardment of the film during the deposition by energetic ions and neutrals in the plasma. Conventional pulsed laser ablation process generates cationic species, in this case Sr^{2+}, Bi^{3+} and Ta^{5+} along with atomic and molecular oxygen in the vicinity of the SBT target. These ionized/excited species are significantly attenuated by elastic scattering in transit towards the substrate. Thus, these have little or no effect on the subsequent film growth steps such as, adsorption, oxidation and recombination which are important for the formation of SBT phase and development of a desired crystallite structure. Presence of a continuous glow discharge plasma excited by external means between the target and substrate sustains the species emanating from the SBT target by a process of electron impact ionization. Low pressure glow discharge in oxygen generates O_2^+-ions [25]. These O_2^+-ions are also formed by electron impact ionization creating a substantial population in the metastable $a^4\Pi_4$ state having a life time between 1–100 ms. Plasma interaction with the ablated vapor flux and oxygen could also create excited or ionized cations as well as O_2^+-ions and atomic oxygen. One direct effect of the presence of cationic species as well as O_2^+-ion and atomic oxygen is that they provide necessary activation energy and enhance the oxidation reaction required for the growth of compound oxide film. Thus, irrespective of the lower substrate temperature, secondary phases e.g., $PtBi_2$ were not formed in the SBT films laser deposited in the presence of O_2-plasma (see Figs. 9 and 10). The cationic species appear to undergo chemical reaction including the oxidation leading to the formation of intermediate reaction products during the transit towards the substrate. These re-react at the substrate surface to crystallize SBT film. Energetic ions enhancing the

reactivity provide better thermodynamic stability for the SBT phase formation significantly affecting the film properties. Consequently, the films grown with plasma assistance neither require any post-deposition crystallization anneal nor higher substrate temperatures for SBT crystalline phase formation or for observing improved ferroelectric properties. On the other hand, in the conventional pulsed laser ablation deposition in the presence of background oxygen gas, depending upon the laser fluence and pressure, the species on the substrate surface are the molecular fragments of constituent oxides. Reaction among the molecular fragments leading to the growth of $SrBi_2Ta_2O_9$-single phase compound film follows the reaction kinetics of heterogeneous system of condensed phase satisfying the thermodynamic criterion. Thus, here higher substrate temperature (800°C) during film growth and post-deposition annealing are required for SBT phase formation, improve its crystallinity and increase remnant polarization values [18,19]. Further, in the present experiment, the substrate has been located inside the glow discharge plasma zone. It is therefore quite likely that highly excited or ionized species (Sr^{2+}, Bi^{3+}, Ta^{5+} and O_2^+) formed in the plasma also arrive at the substrate surface. Thus in this case, the reactions among the constituent ions can occur at a faster rate. It is also evident from the microstructure studies. The films formed by plasma assistance, even at relatively low temperature show larger crystallites (Figs. 13(b), 14(b)) and compact morphology characteristics of a two dimensional growth.

The other important effect of the plasma on the SBT film growth and properties as mentioned in (ii) above is attributed to bombardment by energetic ions and neutrals during the growth. In this experiment, the substrate is electrically isolated both from the ring electrode and the target, the later always kept at a ground potential. When the auxiliary ring electrode acts as a cathode, the target and chamber walls act as anode at ground potential, and plasma glow discharge pervades on either side of the ring electrode. Due to its proximity, the substrate is immersed in the plasma and exposed to bombardment by energetic particles. Since the substrate is electrically isolated, it acquires a floating potential which is more negative than the plasma potential. This is evident from Fig. 16 which shows typical current-voltage characteristics of the plasma excited by applying 500 V of either polarity at the interposing ring electrode and using the substrate as a probe. For plasma excitation potentials of -500 V, the cutoff value at which the current begins to rise provides an idea of the floating potential at the substrate, although some inaccuracy may arise due to large area of the substrate This potential is a consequence of the formation of a space charge region adjacent to the substrate which repels the more mobile electrons in order to balance the ion and electron currents and maintains the steady state of no net current flow. When the steady state condition is disturbed by initiation of the laser ablation process, the ions generated by the plasma interaction between the ring electrode and the substrate are accelerated across this space charge and impinge on the substrate. The energetics of the process is determined by the plasma excitation parameter due to its strong influence on the electron energy and distribution function [26,27]. Ions and excited species generated between the target and the ring electrode are attracted by the negative potential at the ring electrode acquire a drift energy and impinge on the substrate. This bombardment by ionic species significantly influences the nucleation and growth of SBT film. The effect of ions in enhancing the physical and chemical processes during thin film growth by conventional vapor deposition techniques have been well known [28]. In pulsed laser ablation deposition also some past studies have found that increase in ion density at the substrate by biasing helps in epitaxy of PbTe films [29]. Beside enhancing the reactivity at the substrate, these ions impart sufficient ad- atom mobility, thus affecting the nucleation, crystal orientation, morphology and grain size of SBT film.

SBT films formed by various techniques generally show a greater tendency to crystallize in *c*-axis orientation due to lower interfacial energy. The *c*-oriented nuclei thus form in abundance and grow at a faster rate. Same is the case for SBT films grown by laser ablation without the plasma (Figs. 9–12). Ion bombardment at the substrate controls the nucleation by imparting sufficient kinetic energy to enable lower the nucleation barrier for the initiation of differently oriented crystallites as well. Since for SBT, there is no thermodynamic limitation for the stability of crystallites form different orientations, once these are nucleated their growth continues unabated. As our XRD studies have already established, the SBT film grown in O_2-plasma show a growth of (*hk0*) and (*h0l*) crystallites alongside (*00l*). A systematic dependence of *c*-axis orientation from normal to the film plane to

near parallel to the film plane on plasma excitation potential is a consequence of change the energy of impinging ions. Low energy of impinging ions at lower excitation potential (− 350 V) been found beneficial for a preferred (*a–b*) oriented crystallite growth. Enhanced crystallization orientation of perovskite nuclei in this case also improves the film morphology and grain structure. Together, these improve the ferroelectric properties as described in Figs. 1–7. Polarization in Bi-layered compounds is dependent on orientation exhibiting larger spontaneous values in the (*a–b*) orientation than along the *c*-axis. For dipoles arranged in (*a–b*) plane, the internal field is large as dipoles aligned in (*a–b*) direction support each other [30]. Coercive filed values are thus expected to be large as is indeed observed in SBT films deposited in O_2-plasma. In *c*-axis oriented films example those grown without O_2-plasma, the dipoles are aligned perpendicular to the film plane act on each other, reducing the coercive field. The ferroelectric and crystalline structure data are well correlated. At higher potentials (− 700 V), increased kinetic energy of these ions at the film surface lead to reduction in nucleation density by a process of resputtering as well as create defects negating the effect of plasma. As a consequence, these films showed a nominal change in crystallite orientation and had little or no effect on the ferroelectric properties of the SBT films (Figs. 12, 13 and 3, 4).

Detrimental effect on the crystallite structure and ferroelectric properties of SBT films for in presence of O_2^+-plasma excited by a positive potential on the auxiliary ring electrode is explicable on a similar basis. In this case the target is cathode and most plasma-ablated vapor interaction takes place in the region between the target and the interposing ring electrode. The positively charged ionic species generated are attracted towards the target and repelled by the ring electrode. The ring electrode acts as an anode and thus bombarded by the electrons in the glow discharge. The substrate is closely placed to anode glow region surrounding the ring electrode. Indeed this situation exists is evident from the plasma characteristics shown in Fig. 16. The discharge is very conducting as a large number of electrons are present in the region adjacent to the substrate and the cut-off potential value is quite small. Consequently, the substrate is continually bombarded by high density of electrons and energetic ion species, including O_2^+ ions are largely excluded from impinging the

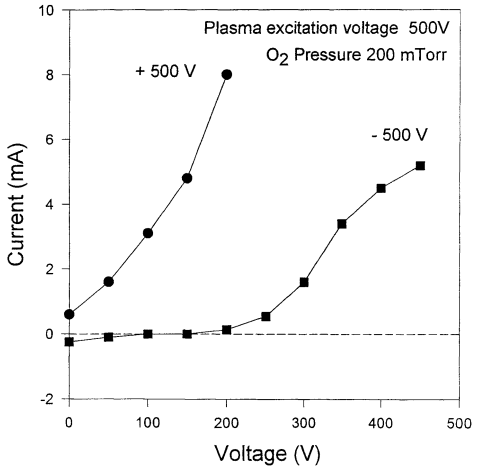

Fig. 16. Current–Voltage characteristics of O_2-plasma excited at − 500 and + 500 V using substrate as a probe inside the glow discharge plasma zone.

substrate during film growth. It may be recalled from XRD data in Fig. 10, unlike the case of − 700 V plasma, at + 450 V plasma formation of Bi_2Pt due to insufficient oxidation of Bi is still observed. Since the growth of SBT film here occurs primarily by partially or un-ionized ablated vapor flux, the crystallite orientation and microstructure of these films is not much different from those deposited without the plasma, as has indeed been observed, see Figs. 13 and 14. Possibly electron irradiation during film growth in this case could result in some damage resulting in ferroelectric properties much too inferior to those deposited even without any O_2^+-plasma (see Figs. 1(c) and 8).

The ionization rate for the formation of ionized species is strongly dependent on the electron energy and distribution function in the plasma [26,27]. Change in concentration of various ion species can therefore be independently controlled by external parameters such as nature of glow discharge gas, its partial pressure and excitation potential as well as geometry and location of interposing ring electrode with respect to the target and substrate. Since the ionic species produced by the laser ablation process are no longer required to be controlled by laser fluence, target composition etc, plasma potential provides an unique new process variable to influence the film growth and properties. Limited study of the effect of plasma excitation potential and polarity and its effect on the SBT film properties particularly ferroelectric and crystallite orientation described in the present

work supports this inference. More rigorous investigation using other process variables would be required to exploit the O_2^+-plasma in the formation of laser ablated SBT films displaying a further improvement in the ferroelectric properties and reduction in processing temperature.

5. Conclusions

1. Presence of O_2-plasma has profound effect on the microstructure, crystallite orientation and ferroelectric behavior of SBT films grown by pulsed lase deposition process. Plasma excitation potential and polarity offers a new process variable for optimizing the film properties.
2. O_2-plasma sustains the cationic species emanated by laser ablation of the SBT target along with O_2^+ ions which provide necessary activation energy for SBT phase formation at 700°C and elimination of long term post-growth 800°C anneal step otherwise needed for optimization of ferroelectric properties of these films.
3. Reduction in plasma excitation potential from -700 to-350 V results in change in a 2-dimensional growth mode of film with *c*-axis normal to film plane to a 3-dimensional growth corresponding to *c*-axis nearly parallel to the film plane. This is attributed to lowering of nucleation barrier for (*a–b*) crystallites by impinging energetic O_2^- ions.
4. Improvement in ferroelectric properties, especially P_r values of SBT films formed in O_2-plasma are a result of improvement in microstructure and crystallite orientation. This correlation is clearly borne out of this study.
5. O_2-plasma excitation potential could be exploited further as a process variable along with other variables such as laser fluence, O_2 pressure and target composition for further improvement of ferroelectric properties and reduction in processing temperature of SBT films.

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