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Structure-Property Relationships in W Doped (Ba,Sr)TiO₃ Thin Films Deposited by Pulsed Laser Deposition on (001) MgO

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ABSTRACT

Ba_xSr_(1-x)TiO₃ films (BST) with $x=0.5, 0.6, 0.7$, containing 1% W, were grown by pulsed laser deposition on MgO (001) substrates in an oxygen pressure from 3 to 500 mTorr, at a substrate temperature of 720 C. The crystal structure of the film, as determined from x-ray diffraction, was fit to a tetragonal distortion of a cubic lattice having two in-plane lattice parameters. The in and out-of-plane lattice parameters c , a , a' , and lattice distortion (a/c and a'/c) were calculated from the positions of the measured BST reflections ((004), (024) and (224)). The dielectric properties of the film at 2 GHz were measured using gap capacitors deposited on top of the dielectric film, at room temperature. For all compositions, as a function of the oxygen deposition pressure, a peak in the change in the dielectric constant, as a function of an applied electric field (0 – 80 kV/cm), was observed for films deposited in 50 mTorr of oxygen. Unlike the pure BST, the dielectric Q was insensitive to the oxygen deposition pressure. The largest K-factor ($K=(\epsilon(0)-\epsilon(V))/\epsilon(0) \times Q(0)$) for films deposited from Ba_{0.6}Sr_{0.4}TiO₃ target were observed in a film that had a minimum in-plane strain, where $a \sim a'$.

INTRODUCTION

The large electric field induced change in dielectric constant of (Ba_xSr_{1-x})TiO₃ ($0 \leq x \leq 1$), is currently being used to develop a new class low of loss, tunable microwave devices, such as tunable oscillators, delay lines and phase shifters [1]. These devices will reduce the size and the operating power of the current semiconducting and ferrite based devices, and will soon have a significant impact on both radar and wireless communication systems [2]. An issue in the fabrication of these devices is optimizing the processing of the material such that it exhibits a large change in the dielectric constant with an applied bias while minimizing the dielectric loss at microwave frequencies.

The dielectric properties of thin films are affected by many factors, such as Ba/Sr ratio, grain size, defect chemistry, oxygen vacancies, strain, and dopants. A strong relationship between structural and dielectric properties of the film has been reported in (Ba_xSr_{1-x})TiO₃ $x=0.4$ and $x=0.5$ films grown by pulsed laser deposition (PLD) with different oxygen deposition pressures [3,4]. As-deposited (Ba, Sr)TiO₃ films with minimal stress, grown in a relatively low pressure of O₂, exhibited the highest microwave figure of merit (% change ϵ with DC bias $\times Q_{0V}$) [5-7].

Normally, oxygen deposition pressures around 300 mTorr are used during the PLD of oxide thin films to minimize the formation of oxygen vacancies. The lattice of an oxygen

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deficient perovskite film expands beyond the size reported for the corresponding bulk ceramic. During heteroepitaxial thin film growth, strain due to the lattice mismatch between the film and the substrate changes the structure of the film. In addition, strain due to the thermal expansion difference between the film and the substrate also alters the structure of the deposited film during cooling from the deposition temperature to room temperature. The resulting strain in the film at room temperature has been correlated with the microwave dielectric properties of the films [3,4].

In previous studies [5,6], it was observed that a minimum in the film strain was realized for BST films deposited in a relatively low partial pressure of oxygen (~ 50 mTorr). The reduction in film strain resulted in a high overall microwave FOM for the deposited film. However, the improvement in the microwave loss due to minimizing film strain is at the cost of additional free carriers introduced into the film as a consequence of oxygen vacancies. Acceptor and donor dopants such as Mn and W have been used to minimize microwave losses due to the presence of free carriers [3,8-10]. In this paper, we report a systematic study of the influence of the oxygen deposition pressures on the structure and microwave dielectric properties of W doped, BST thin films grown on (001) MgO by PLD. Here we use oxygen vacancies, to control BST film strain and W, as a dopant, to reduce the number of free carriers generated by the additional oxygen vacancies.

EXPERIMENTAL

Thin ($\sim 0.5 \mu\text{m}$) $(\text{Ba}, \text{Sr})\text{TiO}_3$ (BST) films were deposited onto (001) oriented MgO single crystals by pulsed laser deposition. A KrF excimer laser pulse (248 nm, 30 ns FWHM) was focused on a rotating target, at a fluence of 1.5-2.0 J/cm². Three commercial BST targets from Target Materials Inc., that were 2 in. diameter by 0.125 in. thick, were used. The target compositions were $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$, $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$. All the targets contained 1 mole % W as a dopant. The (001) MgO substrate temperature was maintained at 720 C while the oxygen pressure was varied from 3 to 500 mtorr. A deposition rate calibration at 50 mTorr was made prior to every deposition series. The film thickness was measured using a Tencor P-10 surface profilometer to determine the number of shots required for 0.5 μm thick BST film. An array of straight gap capacitors were fabricated on the BST films by photolithography and metal lift-off patterning using a multi-level resist process. A thin Cr adhesion layer ($\sim 100 \text{ \AA}$) was used for the gold capped silver electrode. The silver was deposited in an e-beam evaporator over the patterned multi-level resist, to a thickness of 4 μm . Lift-off was then used to delineate the gap capacitor pattern. Thick silver is used to reduce the conductor loss of the capacitor caused by the skin effect at the microwave frequency. The gap length of the capacitor varied from 20 to 50 mil, and gap width was fixed a 5 μm .

The structural properties of the film were determined by analysis of x-ray diffraction pattern using Cu K_{α} radiation from a Rigaku rotating anode source and a powder diffractometer using standard θ -2 θ geometry. The lattice parameter c , along the film normal direction, was calculated from the positions of the measured BST symmetric (004) peak. Using the calculated value for c , the in-plane lattice parameters, a and a' , were calculated from the positions of the measured BST asymmetric reflections ((024) and (224)) assuming a tetragonal structure. Differences between a and a' values indicated an additional in-plane distortion. The lattice parameter a , is defined as the larger value between a and a' since the a and a' directions could not be distinguished from the XRD data. Each BST peak was fitted with either a Gaussian/Lorentzian (or a combination of them) function to obtain the maximum intensity peak

position. The diffraction peaks of the MgO substrate were used as an internal reference for each BST peak. The lattice parameters were used to calculate the degree of distortion, a'/c and a/c . Rutherford Backscattering Spectrometry (RBS) analysis was used to determine composition of films that deposited from $Ba_{0.6}Sr_{0.4}TiO_3$ target. The microwave dielectric properties of the deposited films were measured at 2 GHz with HP8510C network analyzer and 250- μ m pitch GS probe. The capacitance and Q of the gap caps were calculated from the measured S11-parameters of the caps using a parallel resistor-capacitor circuit model. The conformal mapping technique for the analysis of gap capacitors on layered substrates is used to extract the dielectric constant of the BST films from the calculated capacitance values.

RESULTS AND DISCUSSION

Recently, we have shown a strong correlation between the structure and microwave dielectric properties of BST thin films deposited onto MgO substrates. As deposited BST films have lattice parameters that are different from the corresponding bulk materials. In addition, oriented films, deposited onto (001) MgO, show deviations from the expected cubic structure. These deviations occur as a consequence of the strain generated by the difference between the lattice parameter of the film and the substrate as well as differences between the thermal expansion coefficients between the film and the substrate. A correlation has been observed between the magnitude of the deviation from expected cubic and the microwave dielectric properties. For $(Ba_{0.5}Sr_{0.5})TiO_3$ films that are nearly cubic (i.e., with minimal stress) we observe the highest microwave figure of merit (%tuning $\times Q_{0V}$, where Q_{0V} is Q at 0 kV/cm) [5-7]. These films were deposited in a relatively low partial pressure of oxygen (50 mTorr). Normally a higher oxygen deposition pressure is used during film growth in PLD to prevent the formation of oxygen vacancies. The lattice of an oxygen deficient perovskite film expands beyond the size reported for the corresponding bulk ceramic. The strain induced modification of the dielectric properties has been reported for BST $x=0.5$ [6] as well as $x=0.4$ [7].

The use of donor/ acceptor dopants such as W and Mn is well documented as a means to correct for oxygen vacancies in BST thin films. Presumably, the high oxidation state of these ions reduces the number of free carriers. There have been no reports of the effect of lattice distortion on the structure and microwave dielectric properties of doped BST materials. Here we report the lattice induced distortion in $Ba_xSr_{(1-x)}TiO_3$ thin films ($x=0.5, 0.6,$ and 0.7) for 1% W doped thin films deposited on MgO.

The composition, structure, and microwave dielectric properties of W doped BST were measured as a function of the oxygen deposition pressure. The deposition rate typically increased up to ~60% as the oxygen deposition pressure was increased from 200 to 500 mTorr. For all composition investigated, as deposited BST films on (001) MgO are single phase, and well oriented with respect to the substrate, both in-plane and normal to the surface. A typical specular $\theta/2\theta$ XRD pattern taken with Cu K_α for BST film on MgO is shown in Figure 1.

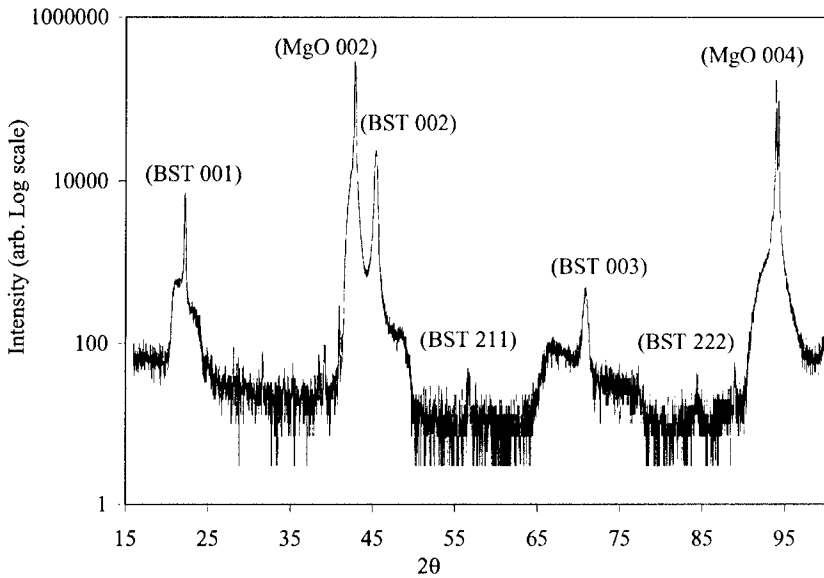


Figure 1: XRD patterns for BST film ($x=0.6$) deposited on MgO in 50 mTorr of oxygen at 720 C.

Film Structure

An analysis of the x-ray diffraction data for $x=0.5$, 0.6 and 0.7 film (1% W) shows a strong dependence of the film structure on the oxygen pressure with. For $x=0.5$ and 0.6, the deposited film is expected to be cubic at room temperature. All deposited films exhibit tetragonal distortion. The largest distortion is typically observed for films deposited at low partial pressures of oxygen (≤ 50 mTorr). Typical in-plane lattice compression ($c > a$, a') is observed up to 200 mTorr. An in-plane tension ($c < a$, a') is observed at higher oxygen deposition pressures (figure 2).

Films deposited from $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$ targets show larger differences between the in-plane lattice parameters, a and a' , than the $Ba_{0.7}Sr_{0.3}TiO_3$ composition, suggesting an anisotropic in-plane strain for those compositions (figure 2). This could be due to a large lattice mismatch between the film and the substrate. Figure 2 also shows lattice distortion and $(Ba+Sr)/Ti$ as a function of oxygen pressure for films deposited from $Ba_{0.6}Sr_{0.4}TiO_3$ target. The in-plane lattice compression is associated with a Ti deficiency whereas an in-plane tension is associated with a Ti excess. An analysis of the FWHM from ω scan of (002) film planes shows a minimum at high oxygen deposition pressures. That suggests a minimum number of film defects at high oxygen deposition pressures.

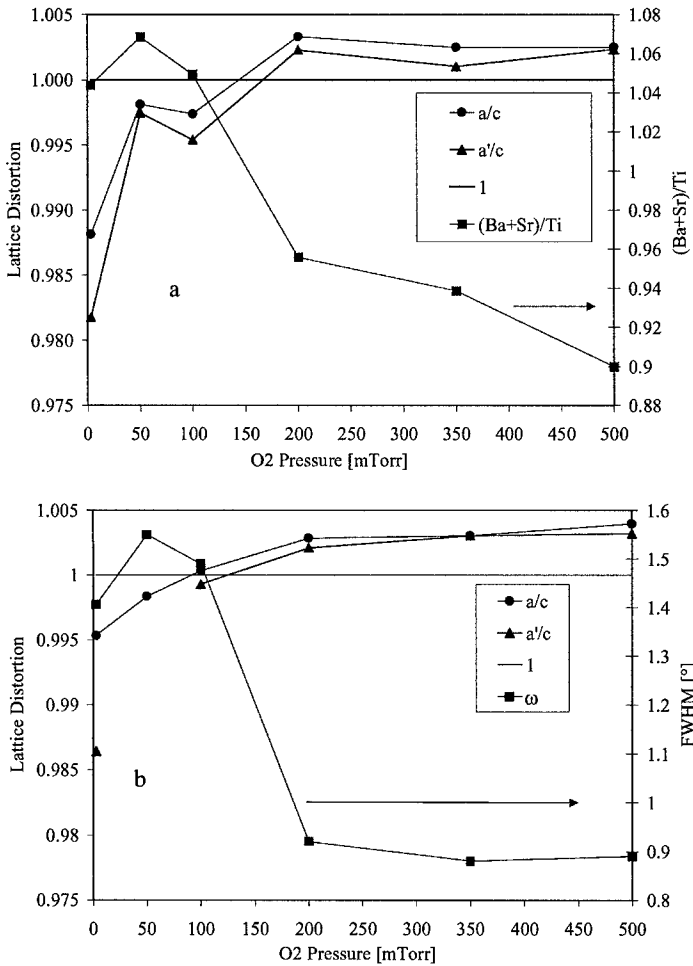


Figure 2: (a) Lattice distortion and cations ratios as a function of oxygen deposition pressure for films deposited from $Ba_{0.6}Sr_{0.4}TiO_3 + 1\% \text{ mole W}$ target. (b) Lattice distortion and ω scan of (002) for films deposited from $Ba_{0.7}Sr_{0.3}TiO_3 + 1\% \text{ mole W}$ target.

Dielectric properties

The capacitance, electric field dependence and capacitor Q for W doped BST films was measured for gap capacitors as a function of the oxygen deposition pressure for $x=0.5, 0.6$ and 0.7 . The dielectric Q for the paraelectric phase composition ($Ba_{0.6}Sr_{0.4}TiO_3$ 1%W doped) and the ferroelectric phase composition ($Ba_{0.7}Sr_{0.3}TiO_3$ 1%W doped) are similar and do not show any

significant dependence on the oxygen pressure or film composition (figure 3). The Q is relatively independent of the oxygen deposition pressure, therefore, the K factor observed in these films follows the oxygen pressure dependence of the tunability, which is observed to have a peak at 50 mTorr for all compositions.

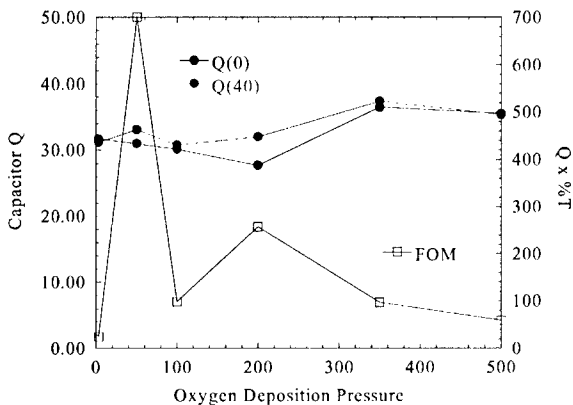


Figure 3: Q and K measured at 2 GHz as a function of oxygen deposition pressure for films deposited from $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3 + 1\%$ mole W target.

Figure 4 show a summary of the K-factor as a function of oxygen deposition pressure for all W doped compositions. All films show peak in the oxygen deposition pressure dependence at 50 mTorr where the film is observed to be in compressional distortion ($c > a, a'$). From figure 2, we can see that for the $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ composition this maximum occurred where an isotropic in-plane lattice parameter exist ($a \sim a'$). The $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ composition shows only a local maximum K at 50mTorr. It is possible that a lack of significant maximum is a consequences of the highly anisotropic strain observed for the in-plane lattice parameters ($a \neq a'$) at 50mTorr.

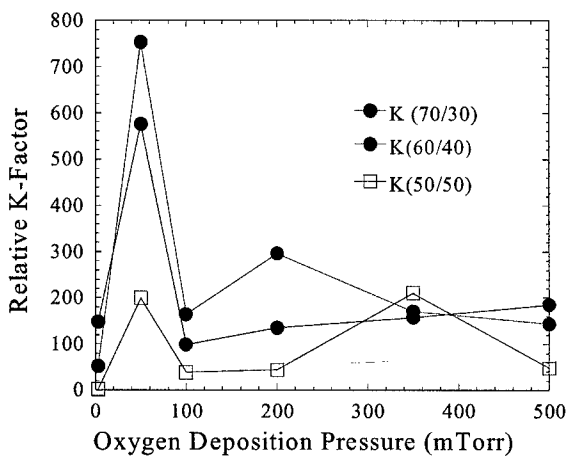


Figure 4: K-factor (2 GHz) as a function of oxygen pressure for all W doped films compositions.

SUMMARY

BST thin films, $x=0.5, 0.6, 0.7$ containing 1% mole W, were grown by PLD on MgO (001) substrates with oxygen deposition pressures from 3 to 500 mTorr, at a substrate temperature of 720 C. The crystal structure of the films was determined by x-ray diffraction using the (004), (024) and (224) reflections. The dielectric properties ($\epsilon(V)$ and $Q(V)$) were measured at 2 GHz. Q was relatively insensitive to the oxygen deposition pressure for all compositions (unlike pure BST [6]). Presumably, W^{+6} substitutes for Ti^{+4} and reduces the number of free carriers generated by the oxygen vacancies. As a consequence, a peak in oxygen deposition pressure dependence of the K-factor corresponds to a deposition condition that yields the largest tunability. In all materials investigated here, this was observed at an oxygen deposition pressure of 50 mTorr. An analysis of the diffraction data, assuming a tetragonal structure, indicates that $Ba_{0.6}Sr_{0.4}TiO_3$ and $Ba_{0.5}Sr_{0.5}TiO_3$ films could have an anisotropic in-plane distortion ($a \neq a'$). The anisotropy is larger if an orthorhombic distortion is assumed. The largest K-factor was observed in $Ba_{0.6}Sr_{0.4}TiO_3$ film corresponded to a deposition condition which resulted in a minimum of the in-plane strain, where $a \sim a'$, suggesting that in-plane anisotropic strain might also play a significant role in the dielectric properties of the film. It has been reported previously that anisotropic dielectric behavior occurs due to differences between in-plane and out-plane lattice parameters [11]. The effect of the in-plane anisotropy could have an influence on capacitors geometry and is currently being investigated.

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