TEM study of ordering domains in $PbSc_{0.5}Ta_{0.5}O_3$ and threading dislocations in $Ba_{0.7}Sr_{0.3}TiO_3$ epitaxial films

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Microstructure of two technologically relevant perovskites, $PbSc_{0.5}Ta_{0.5}O_3$ (PST) and $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) is investigated using (HR) TEM. PST, because of its high figure of merit, is a promising pyroelectric sensor for intruder sensing, flame detection, spectroscopic analysis etc. [1]. BST thin films are potential materials for application in microelectronic devices like dynamic random access memories and microwave devices [2]. The physical properties of thin films are influenced by the type of substrate and the microstructure and mechanical stress within the film and the film/substrate interface.

Films were grown by pulsed laser deposition (PLD) at elevated substrate temperatures, e.g. 550-650 °C, in oxygen atmosphere. 60 nm thick PST films with 45 nm thick $SrRuO_3$ (SRO) bottom electrode were grown on (001) and (111) oriented $SrTiO_3$ (STO) vicinal single-crystal substrates. BST films of thickness greater 100 nm with $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bottom electrode were grown on (001) oriented STO and $LaAlO_3$ (LAO) single crystal substrates. Their microstructure was investigated by XRD using Philips X'pert MRD diffractometer, diffraction contrast imaging using a CM20T TEM operated at 200 kV and (HR) TEM using a Jeol 4010 TEM operated at 400 kV. Macroscopic ferroelectric properties were measured by standard methods.

Reports on the TEM investigation of PST ceramics are few [3] and the first TEM investigation on epitaxial PST thin films has recently been communicated by the authors group [4]. Selected area electron diffraction (SAED) patterns (Fig. 1(a-b)) indicate single crystalline epitaxial growth of PST; the out-of-plane direction of the substrate is carried over into the PST film. The SAED patterns yielded a smaller in-plane lattice parameter in comparison to bulk values reported in literature, indicating compressive strain. Misfit dislocations with a spacing of about 10 nm are observed at the PST/SRO interface and appear to produce threading dislocations in the PST film. SAED patterns (Fig. 1 (b-c)) show {½, ½, ½} superstructure reflections indicating cation ordering. A dark field image (Fig. 1 (c)) acquired using one of these superstructure reflections shows ordering domains with a size of about 10 nm. The corresponding bright-field images showed anti-phase boundaries where ordering domains meet. Pyrochlore secondary phase was not observed in the (001) oriented film in agreement with the XRD investigations. Remnant polarization of (001) oriented film is 3.4 $\mu C/cm^2$ at room temperature, which is considerably higher than the previously reported values. Preliminary investigations indicate that ordering is influenced by annealing. A systematic (HR) TEM investigation of the Burgers vectors of misfit and threading dislocations, size of ordering domains and domain boundaries will be presented.

Dislocations and strain are believed to deteriorate the ferroelectric properties of BST thin films. Recently single crystalline $Ba_{1-x}Sr_xTiO_3$ films of various compositions (x=0.3, 0.4, 0.5 etc) on different substrates like STO, LAO and MgO have been prepared by PLD [2, 6]. Misfit and threading dislocations have been widely reported, but the mechanism of their formation and dissociation is still not well understood [6-7]. Microstructure studies of BST films grown on conducting bottom electrode layers like SRO, LSMO are rare but essential to

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fully understand the microstructure-ferroelectric properties relationship in BST thin films [5, 8]. SAED showed single crystalline epitaxial growth of BST/LSMO films on STO and LAO substrates. Dislocations are not observed (Fig. 1(e)) in the LSMO film or at its interface with the STO substrate; this LSMO film is therefore completely strained. Threading and misfit dislocations with a spacing of about 65 nm are observed in the BST film and at its interface with the LSMO electrode grown on STO. The misfit dislocation density is smaller by about 2.5 times than what is essential for the complete relaxation of the BST/LSMO/STO heteroepitaxial strain. In comparison, the BST film as well as the LSMO electrode grown on LAO substrate showed a significantly larger density of dislocations because of the larger misfit strain (-4.5 %) in this system (Fig. 1(d)). Majority of the threading dislocations in this BST film are out of contrast in the dark-field images with 002 reflections indicating [100] or [010] burgers vectors, in agreement with literature reports [6-7]. As a consequence of larger density of dislocations at the BST/LSMO interface and in the BST films grown on LAO, their Polarisation-Voltage curves are leaky and asymmetrical in comparison to those of BST/LSMO films grown on STO. A systematic (HR) TEM investigation of dislocation densities, dislocation dissociation and their influence on ferroelectric properties of BST films prepared in different growth regimes will be presented.

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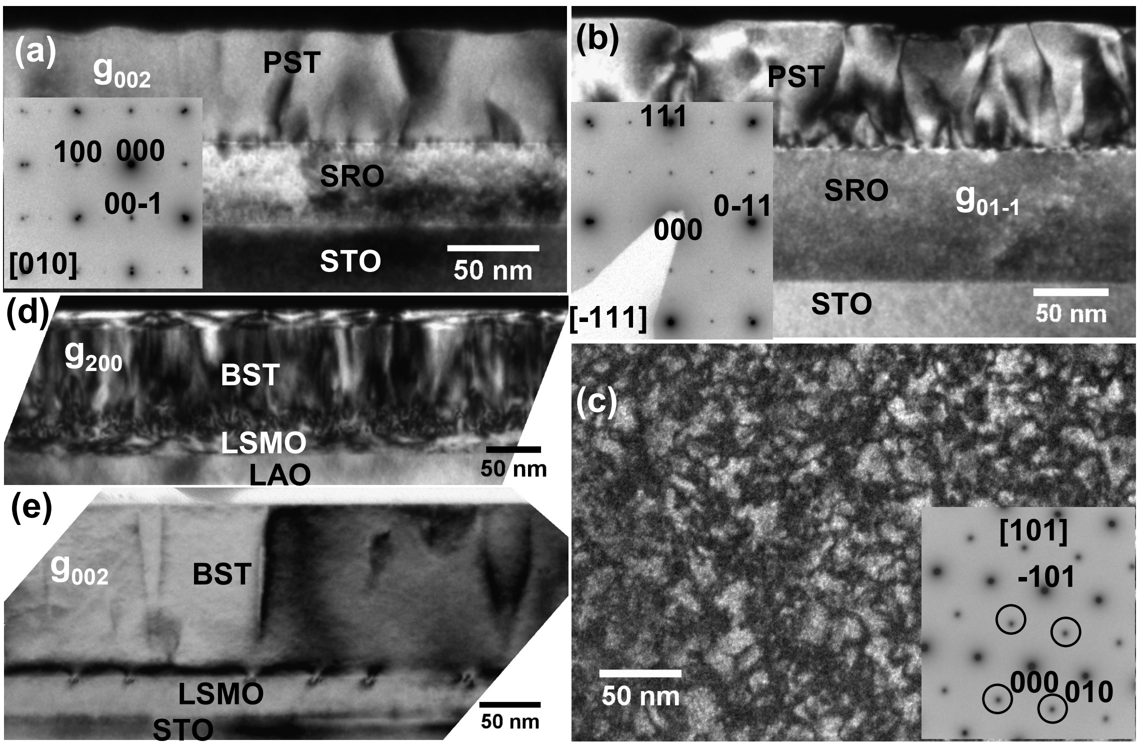

Figure 1. TEM two-beam dark-field (a-d) and bright-field (e) images of: (a) PST(001)/SRO/STO(001) cross section, (b) PST(111)/SRO/STO(111) cross section, (c) plan view of (a) – superstructure reflections are encircled, (d) BST/LSMO/LAO cross section, (e) BST/LSMO/STO cross section.

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