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Microstructural Properties of Laser Ablated $Ba_{0.5}Sr_{0.5}TiO_3$ Ferroelectric Films

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Abstract

The microstructural and ferroelectric properties of bulk $Ba_{1-x}Sr_xTiO_3$ and thin films prepared by excimer pulsed laser deposition on SiO_2/c-Si and Pt/Ti/SiO_2/c-Si are reported in this work. The films were amorphous in the as-deposited condition and randomly crystallized after post-annealing at 550°C. The x-ray diffraction patterns of the films and the ablation target match exactly indicating that excellent stoichiometry preservation is attained by pulsed laser deposition. Smooth and uniform films showing few cracked areas were obtained on SiO_2/c-Si substrates, while films deposited on Pt/Ti/SiO_2/c-Si substrates presented wider cracks that were promoted during the annealing process due to the thermal expansion mismatch between the films and the Pt coated substrates. The Curie temperature of the films was around -31°C with a maximum dielectric constant of 180.

Introduction

Ferroelectric thin films with a high dielectric constant (e) are needed in order to obtain giga-bit storage capacity on DRAM (Dynamic Random Access Memory) devices [1-5]. Optimally e=100-300 with a thickness of d=100-200 nm are required in order to improve the packing density in integrated capacitors. Bulk ferroelectric barium titanate ($BaTiO_3$) and barium strontium titanate $Ba_{1-x}Sr_xTiO_3$ (BST) are well characterized, however, the ferroelectric properties of thin films are not understood at a fundamental or even at a technical level. The microstructural features such as grain size, orientation (polycrystalline vs. epitaxial), thickness and surface roughness of the film have neither been systematically studied neither characterized.

BST films are interesting ferroelectric materials with perovskite-type structure that posses desirable values of dielectric permittivity for applications in integrated capacitors for dynamic random access memories (DRAM's) [1-5].

BST thin films have been successfully deposited by radio-frequency (RF) sputtering [2-4], metallorganic chemical vapor deposition (MOCVD) [5,6], ion beam sputtering [7] and pulsed laser deposition (PLD) [1,8,9]. PLD is known to be an excellent technique to produce thin films on various substrates while preserving the stoichiometry of multicomponent targets [10].

In the present study the ferroelectric properties were measured for $Ba_{0.5}Sr_{0.5}TiO_3$ thin films grown by PLD and the crystallinity, morphology, microstructure and stoichiometry were analyzed and compared to the ablation target properties.

Experimental Procedure

Stoichiometric barium strontium titanate ($Ba_{0.5}Sr_{0.5}TiO_3$) powders were fabricated by the conventional ceramic method by mixing and firing ultra-high purity oxides and carbonates (99.999, Alfa-Aesar). The target for laser ablation experiments was made by isostatically pressing the ceramic powders and sintering in air at 1450°C for 2 hours.

BST films were grown by PLD at 400°C on a-SiO_2/c-Si and Pt/Ti/SiO_2/Si substrates with a KrF laser (l=248 nm), pulsed at 30 ns, an energy fluence of 2.0 J/cm^2 and a repetition rate of 10 Hz during 60 min. The separation between the rastered target and the rotated substrate was maintained fixed at 50 mm. The $Ba_{0.5}Sr_{0.5}TiO_3$/SiO_2/c-Si and $Ba_{0.5}Sr_{0.5}TiO_3$/Pt/Ti/SiO_2/c-Si samples were cut into small pieces (1.5 x 1.5 cm^2) and annealed in air for 2 hours at 550, 575 and 600°C. The crystallinity of the films was determined by X-ray diffractometry (XRD) excited with Cu Ka radiation (λ=1.541 nm) and the surface morphology was exam-

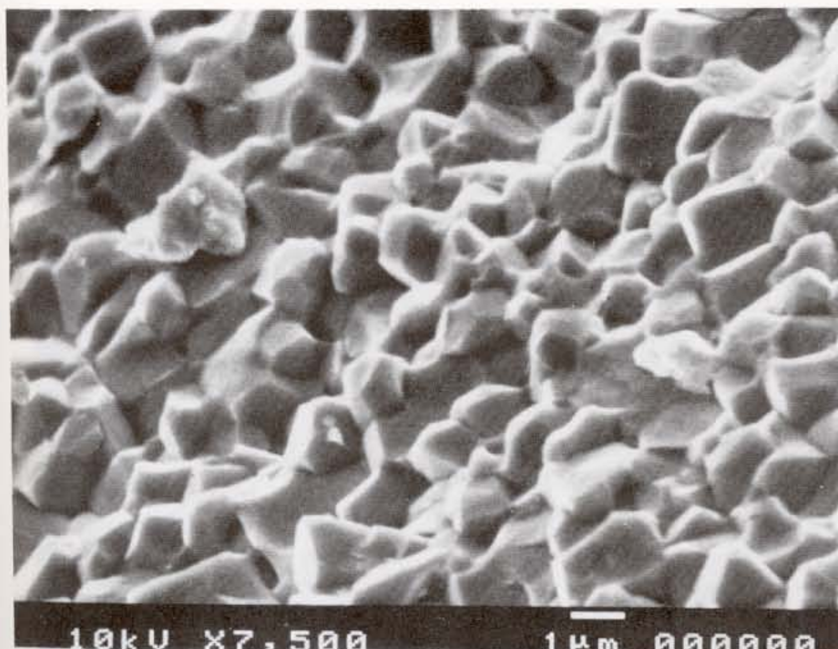


Fig. 1: *SEM micrograph of the $Ba_{0.5}Sr_{0.5}TiO_3$ target sintered at 1450ºC for 2 hr.*

ined by scanning electron microscopy (SEM). A chemical binding energy analysis to examine the stoichiometry of the ablation target and the PLD films was performed at the surface using x-ray photoelectron spectroscopy (XPS) operated with an Al Ka (1486.6 eV) x-ray source. In order to study the microstructure and thickness of the films high resolution transmission electron microscopy (HRTEM) was performed on cross-sectioned specimens prepared by gluing two samples together face-to-face, cutting a 3 mm disk and thinning by standard micropolishing and ion milling methods. For capacitance measurements, platinum electrodes (0.1 mm in diameter) were deposited on top of the BST/substrate films by DC sputtering through a metallic mask. The dielectric constant was calculated from the capacitance measured at 10 kHz with a LCR meter using the following equation: $\varepsilon = Cd/\varepsilon_0 A$

Where C is the capacitance (farads), ε_0 the free space dielectric constant value (8.85×10^{-12} F m), A the capacitor area (m^2) and d (m) the thickness of the ferroelectric film.

Results and Discussion

Figure 1 is an SEM micrograph of the surface of the $Ba_{0.5}Sr_{0.5}TiO_3$ target prior to the pulsed laser ablation experiments. A dense structure is observed with grains of the order of 1-2 μm that are well faceted. In Figure 2 the x-ray diffraction pattern obtained from the ablation target clearly confirms to be single phase and polycrystalline. The dependence of the dielectric constant response on temperature is displayed in Figure 3. The diffraction pattern (Figure 2), and the Curie temperature (Tc) observed around -25°C in Figure 3, confirm the stoichiometry of the $Ba_{0.5}Sr_{0.5}TiO_3$ target. The Curie temperature is a function of the Sr (strontium) content and it has been reported that for bulk $Ba_{0.5}Sr_{0.5}TiO_3$ to be Tc=-23°C [11]. Figures 4 (a) and 4 (b) correspond to XPS spectra measured on the ablation target and on the film post-annealed at 600°C. Both spectra are very similar indicating

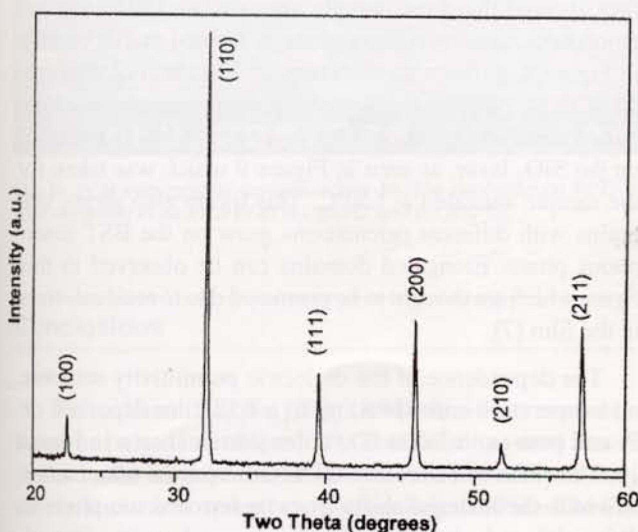


Fig. 2: *XRD pattern of the $Ba_{0.5}Sr_{0.5}TiO_3$ target sintered at 1450ºC for 2 hr.*

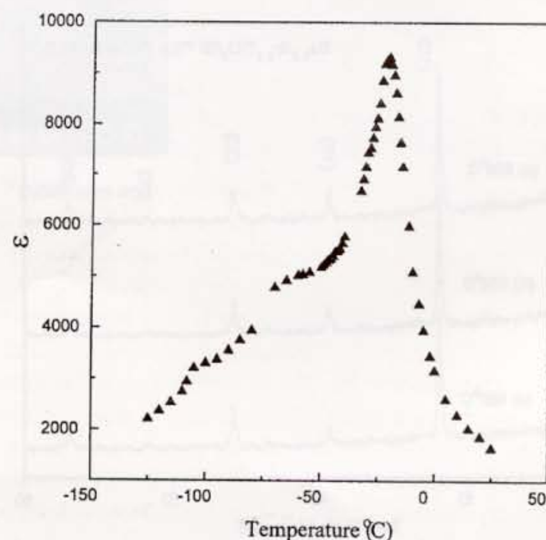
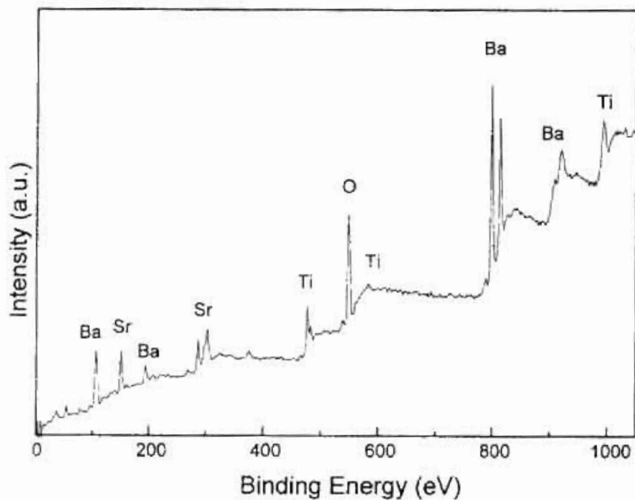


Fig. 3: *Dielectric permittivity as a function of temperature measured on the $Ba_{0.5}Sr_{0.5}TiO_3$ target sintered at 1450ºC for 2 hr.*



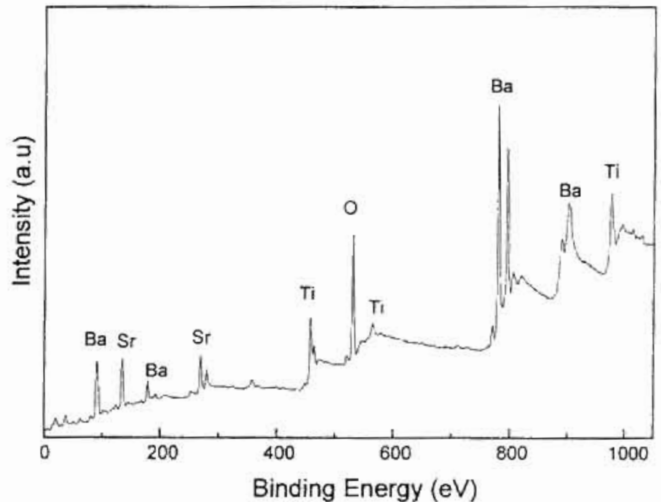


Fig. 4: *XPS spectra taken on: (a) BST target and (b) BST film post-annealed in air for 2 hr at 600°C.*

that excellent stoichiometric transfer is achieved by the PLD technique.

Figures 5 (a-c) show the XRD patterns for the films grown on SiO_2/c-Si substrates and subsequently annealed at 550°C, 575°C and 600°C for two hours. The films were amorphous in the as-deposited condition and crystallized even at the lowest annealing temperature (T_A=550°C). The XRD patterns of the films match exactly with those obtained from the ablation target. In this narrow temperature range (550-600°C) the films crystallized with a random orientation on both substrates.

Figures 6 (a) and 6 (b) show SEM micrographs for films grown on SiO_2/c-Si substrates and post-annealed at 550°C and 600°C, respectively. A smooth and uniform surface for both annealing temperatures can be observed, however the films are slightly cracked. SEM micrographs shown on Figure 7 (a) and 7 (b) correspond to films deposited on Pt/Ti/SiO_2/c-Si substrates and heat-treated at 600°C and 650°C, respectively. In this case larger cracks are promoted during the post-annealing process. The thermal expansion coefficients for the substrates (SiO_2 and Pt) are α_{SiO2} = 3.5 x 10^{-6} °C^{-1} and α_{Pt} = 9 x 10^{-6} °C^{-1} [12-13], respectively. Assuming a thermal expansion coefficient value for BST to be similar to that reported for $BaTiO_3$ thin films [12] (α_{BaTiO3} = 4 x 10^{-6} °C^{-1}) it is reasonably to expect larger cracks on the Pt coated substrates due to the larger thermal expansion mismatch.

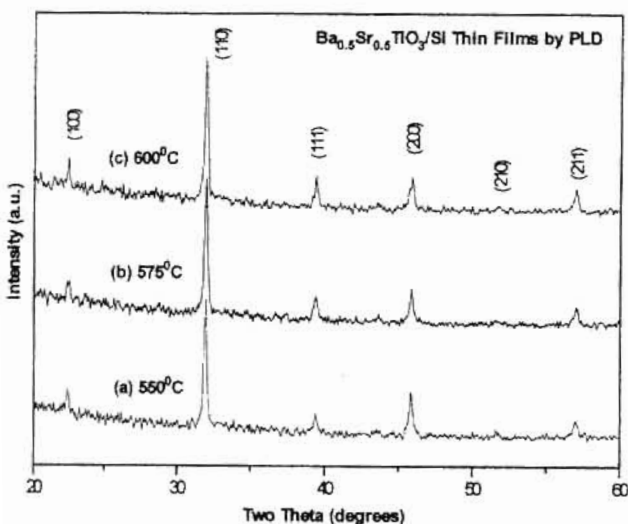
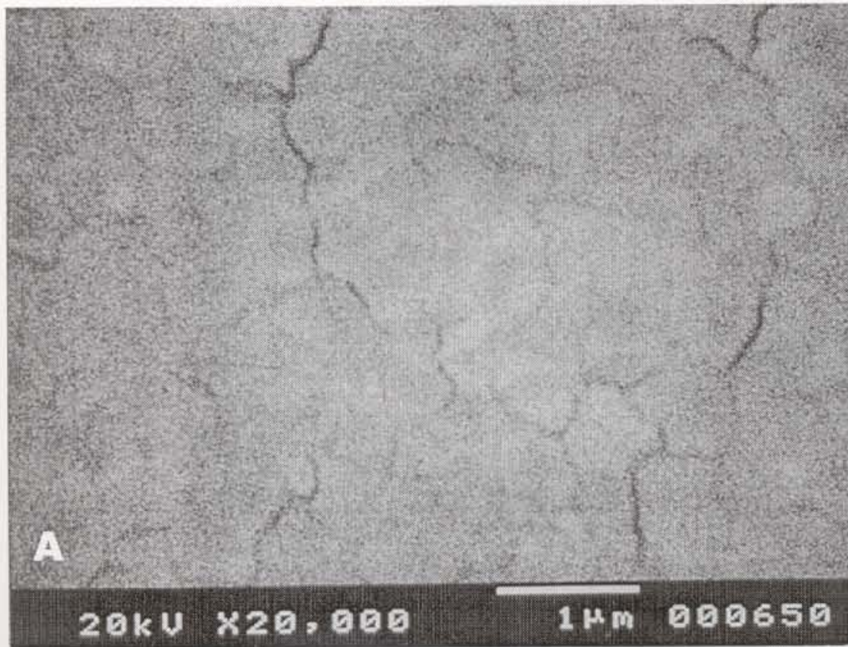


Fig. 5: *XRD patterns for the films grown on SiO_2/c-Si substrates and post-annealed for 2 hr. at: (a) 550°C, (b) 575°C and (c) 600°C.*

The as-deposited amorphous films crystallized with grain sizes between 50-200 nm after the annealing treatment. A cross-sectional HRTEM analysis at the film/substrate interface showed that for a sample annealed at 550°C a mixed amorphous/nanocrystalline phase is formed as can be seen in Figure 8, a film with thickness of 220 nm. For temperatures above 600°C films with XRD sharper peaks were obtained however, an amorphous layer of 4-6 nm is observed on the SiO_2 layer, as seen in Figure 9 which was taken for the sample annealed at 650°C. This figure also shows that grains with different orientations grow on the BST amorphous phase. Elongated domains can be observed in this figure which are thought to be promoted due to residual stress in the film [7].

The dependence of the dielectric permittivity response on temperature corresponding to a BST film deposited on Pt and post-annealed at 600°C for 2 hr is shown in Figure 10. The value of Tc around -31°C indicates the temperature at which the material shifts from its ferroelectric phase to the paraelectric state. This result is in good agreement with the Tc value obtained in bulk BST as indicated in Figure 3 and to that reported in Ref. 11.



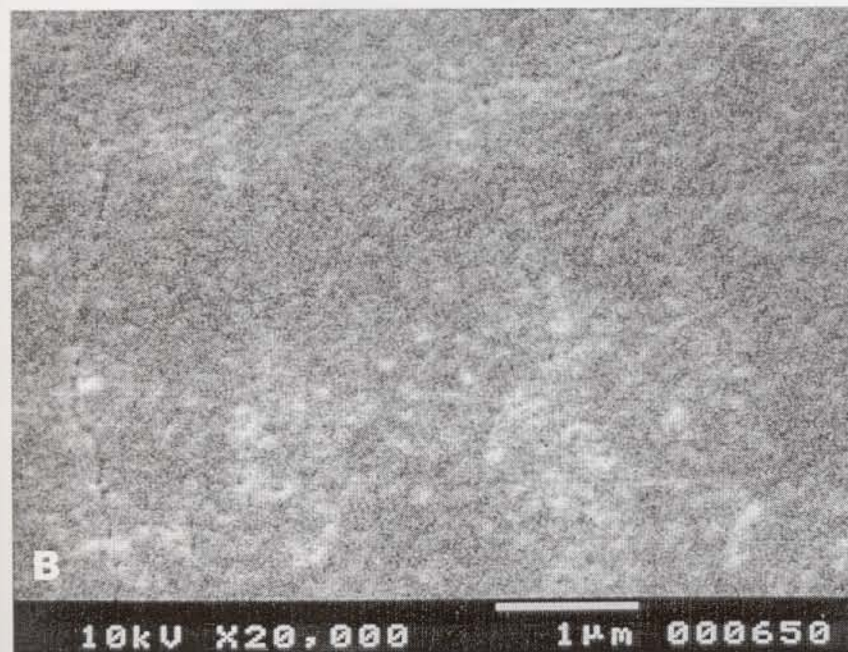


Fig. 6: *SEM micrographs corresponding to films deposited on Pt/Ti/SiO_2/c-Si substrates and post-annealed in air for 2 hr at (a) 600ºC and (b) 650ºC.*

Conclusions

Ferroelectric $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films were obtained by pulsed laser deposition. The BST films were amorphous in the as-deposited condition and crystallized randomly under low temperature annealing (550°C). The X-ray diffraction patterns of the films matched exactly with those obtained from the ablation target indicating that excellent stoichiometric preservation is attained by the pulsed laser deposition. Smooth and uniform films with minimal cracking were obtained on SiO_2/c-Si substrates, while films deposited on Pt/Ti/SiO_2/c-Si substrates presented pronounced cracks that were promoted during the annealing process due to the thermal expansion mismatch between the film and the Pt substrates. The films annealed at 600°C exhibits a Curie temperature at around -31°C in good agreement with the Tc value obtained for bulk materials.

Aknowledgements

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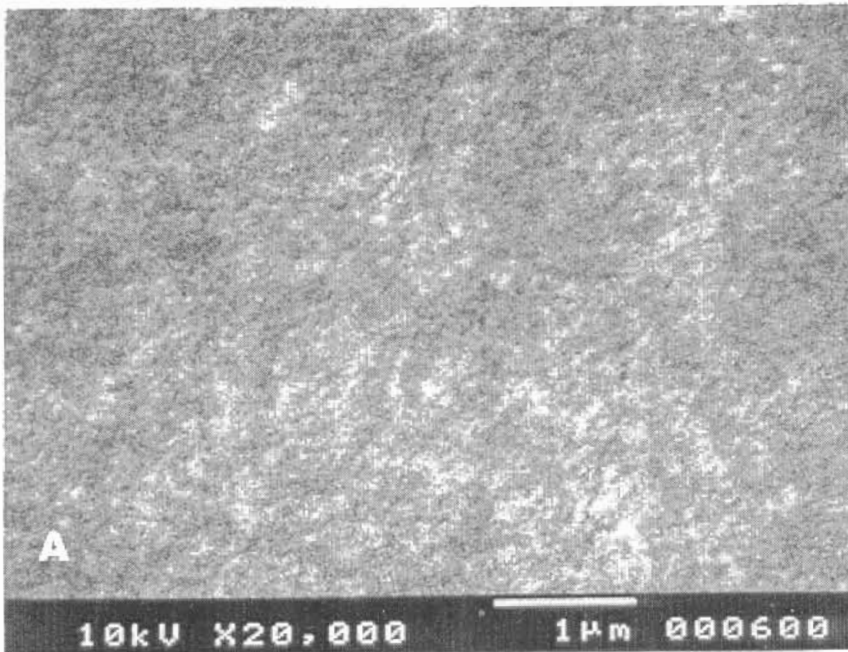

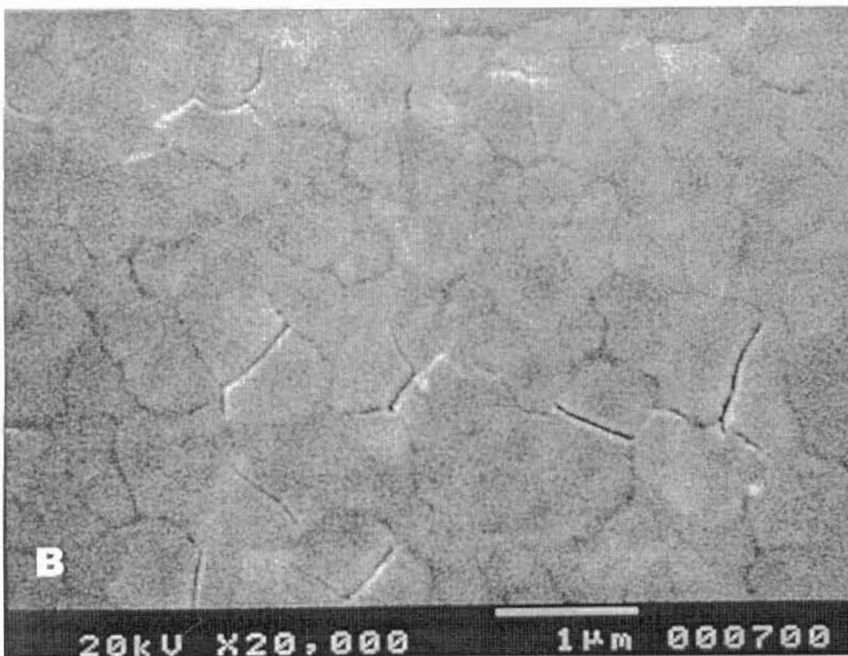

Fig. 7: *SEM micrographs for films grown on SiO_2/c-Si and post-annealed in air for 2 hr at: (a) 550ºC and (b) 600ºC.*

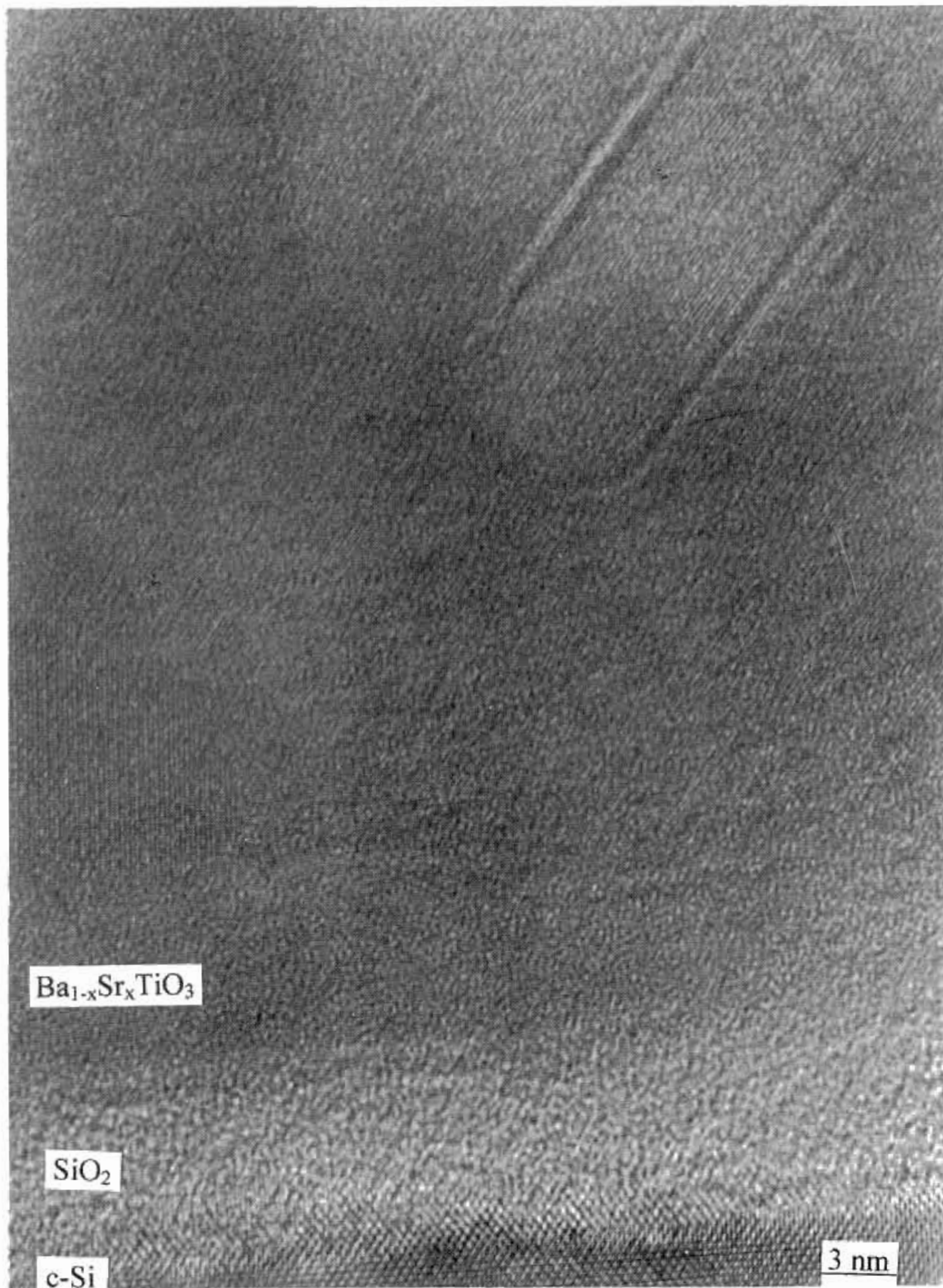

Fig. 8: *HRTEM micrograph showing the BST/SiO_2/c-Si cross-section. This specimen was post-annealed in air at 550°C for 2 hr.*

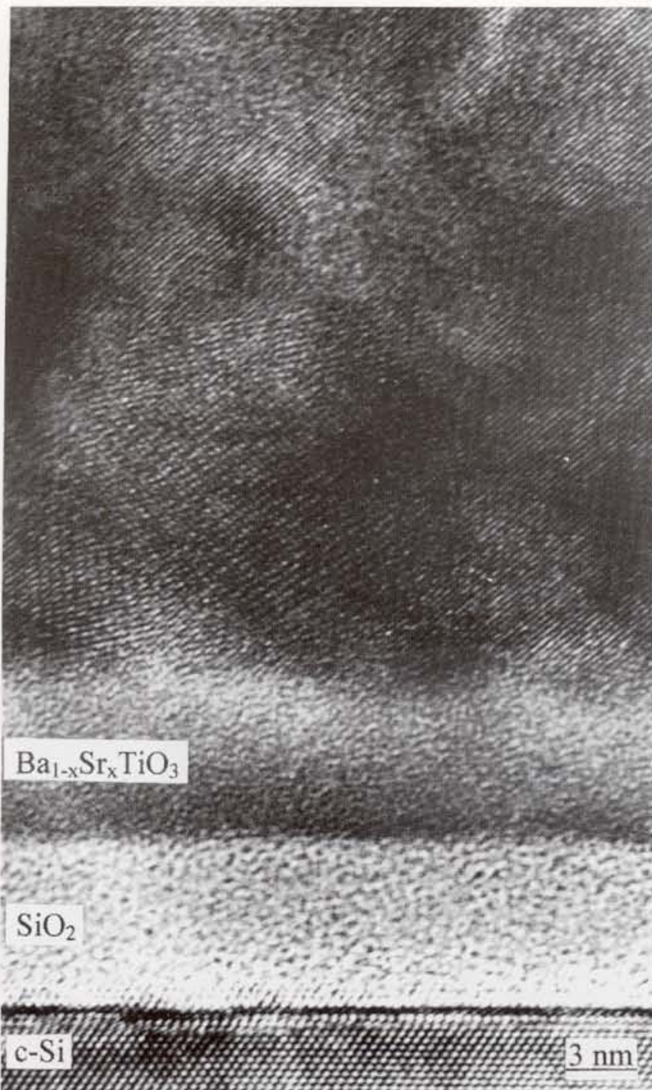

Fig. 9: *Cross-sectional image taken from the BST SiO_2/c-Si sample post-annealed at 650ºC for 2 hr.*

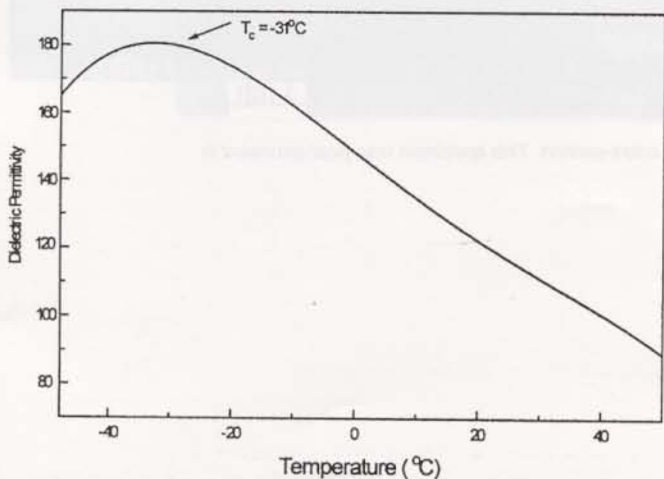

Fig. 10: *Dielectric permittivity as a function of temperature measured on the $Ba_{0.5}Sr_{0.5}TiO_3$ film post-annealed at 600ºC for 2 hr.*

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