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Effect of thermal strain on the ferroelectric phase transition in polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ thin films studied by Raman spectroscopy

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We have applied Raman spectroscopy to study the influence of thermal strain on the vibrational properties of polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ films. The films were grown by rf magnetron sputtering on Pt/SiO_2 surface using different host substrates: strontium titanate, sapphire, silicon, and vycor glass. These substrates provide a systematic change in the thermal strain while maintaining the same film microstructure. From the temperature dependence of the ferroelectric A_1 soft phonon intensity, the ferroelectric phase transition temperature, T_C, was determined. We found that T_C decreases with increasing tensile stress in the films. This dependence is different from the theoretical predictions for epitaxial ferroelectric films. The reduction of the ferroelectric transition temperature with increasing biaxial tensile strain is attributed to the suppression of in-plane polarization due to the small lateral grain size in the films. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1813625]

Thin film ferroelectrics, such as barium strontium titanate, $Ba_xSr_{1-x}TiO_3$ (BST), continue to attract broad research attention due to their potential for novel device applications.[1] The differences between thin-film dielectric properties and those of corresponding bulk materials remain a major issue. Possible causes of this difference include nonstoichiometry, defects such as oxygen vacancies, interface and size effects, and strain.[2–7] Strain reduces the dielectric constant in BST films[6] and changes the ferroelectric phase transition temperature, T_C, and Curie–Weiss constant.[4,5] In most experimental studies of BST films, the critical thickness is exceeded at the high growth temperatures and the films become fully or nearly fully relaxed. Biaxial stress is imposed on the films due to the thermal expansion mismatch upon cooling to room temperature. In epitaxial films, in which the crystalline structure matches that of the substrate, strain can be fairly well characterized and its effects on the ferroelectric properties have been theoretically described.[4,5] Strain effects in polycrystalline films, on the other hand, are more complex. Fiber textured films may be similar to the epitaxial films, whereas in films with randomly oriented grains one may expect different behaviors.

Lattice dynamics determines the fundamental properties of ferroelectrics, therefore, it is important to study the vibrational properties of ferroelectric thin films under the influence of strain. In particular, Raman spectroscopy data on the soft mode behavior are very valuable for determining the phase transition temperature in ferroelectric thin films. The temperature dependence of the dielectric constant of thin films is often broad, and it deviates from the Curie–Weiss behavior at temperatures significantly higher than bulk T_C. This makes the precise determination of T_C difficult as discussed by Vendik and Zubko[8] and exemplified by the result of Taylor *et al.*,[9] in which the fitting to the Curie–Weiss behavior resulted in the values of T_C below 0 K. The temperature dependence of the soft phonon modes can provide a more physical measurement of T_C in ferroelectric thin films, since the soft mode behavior reflects the ferroelectric phase transition. In our previous studies, we have investigated soft phonon modes and the ferroelectric phase transitions in epitaxial BST films using Raman spectroscopy.[10,11] Recently, the impact of thermal strain on the renormalized Curie–Weiss temperature and constant in polycrystalline BST films was investigated[9] by growing BST films on substrates with different thermal expansion coefficients using the same thin buffer layer of Pt/SiO_2. This approach allows one to obtain BST films of similar morphology with different thermal strain. In the present letter, we report a lattice dynamics study in polycrystalline BST films with different thermal strain.

The $Ba_{0.5}Sr_{0.5}TiO_3$ films for this study were grown by rf magnetron sputtering on four different substrates: $SrTiO_3$ (STO), sapphire, Si, and vycor glass, covered by 60 nm SiO_2 and 100 nm platinum layers. The sample growth was described previously.[9] X-ray diffraction measurements revealed polycrystalline BST films with weak (110) and (111) texture.

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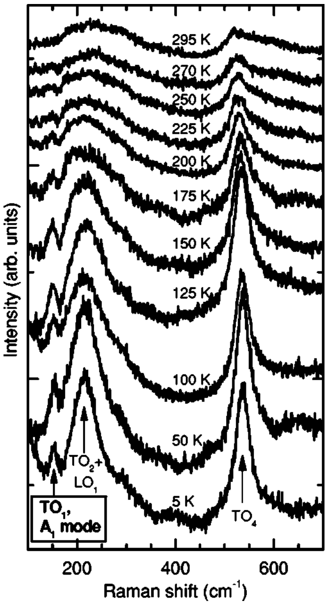

FIG. 1. Raman spectra of $Ba_{0.5}Sr_{0.5}TiO_3$ films in the temperature range 5–300 K measured in parallel polarization configuration.

Raman spectra were measured using a SPEX Triplemate spectrometer equipped with a liquid nitrogen-cooled multichannel coupled charge device detector. Spectra were recorded in the temperature range 5–300 K in backscattering geometry using the 514.5 nm Ar^+ laser line as the excitation source. The laser power density was kept at a low level ($\lesssim 30\ W/cm^2$) to avoid heating of the samples.

Figure 1 shows the temperature evolution of the Raman spectra of a BST film grown on STO substrate. The spectra were recorded in parallel polarization configuration $z(x,x)\overline{z}$ (z direction is normal to the film plane). The Pt layer below the BST film completely screens the substrate, and the spectra contain only the phonon lines of BST films. The low-temperature Raman scattering signals are strong, indicating that although the films are polycrystalline, the crystallinity of each grain is very good. Two peaks were observed at all temperatures at around 215 and 536 cm^{-1}. The 215 cm^{-1} peak is attributed to the mixed TO_2–LO_1 phonon mode, and the 536 cm^{-1} peak corresponds to the TO_4 phonon.[10] The frequencies of the hard mode do not change much with temperature. At low temperatures a peak at around 153 cm^{-1} was observed, which is the A_1 component of the soft phonon mode TO_1. Another soft mode component, the E mode, can be observed in the low-frequency spectral range in perpendicular polarization geometry $z(x,y)\overline{z}$.[10] Unlike in pure $BaTiO_3$, where the A_1 soft mode line merges into the broad feature of TO_2 phonon,[12] the two phonon lines remain distinctly separated in $Ba_{0.5}Sr_{0.5}TiO_3$. The cubic-tetragonal phase transition leads to the splitting of the triple degenerated F_{1u} mode in the paraelectric phase into the E (double degenerated) and A_1 modes in the ferroelectric phase.[12,13] The square of the E soft mode frequency is inversely proportional to the dielectric constant in the a–b plane while the square of the A_1 mode frequency is proportional to the spontaneous polarization.[12,13]

Because the E soft mode is overdamped near the ferroelectric phase transition,[11] its frequency is difficult to measure near T_C. The temperature dependence of the spontaneous polarization, thus the A_1 soft mode frequency, can be weak in the case of the first-order phase transition. Therefore, it is difficult to determine T_C by measuring the frequencies of either one of the soft modes. On the other hand, the intensity of the A_1 mode decreases to zero when the temperature increases to T_C, since this mode exists in the ferroelectric phase only. Therefore, while the absolute A_1 soft mode intensities cannot be compared between different samples, its relative change with temperature can be used to determine the value of T_C for a sample. This approach is especially valuable in the case of the first-order phase transition, when the polarization does not go to zero continuously, but has a discontinuity at T_C. The phase transition in $Ba_{0.5}Sr_{0.5}TiO_3$ is of the first order, as follows from our studies of both single crystals and films.[11,14]

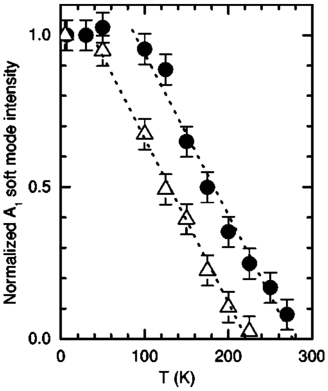

FIG. 2. Temperature dependence of the A_1 soft mode intensity (normalized to the Bose factor $n+1$) for $Ba_{0.5}Sr_{0.5}TiO_3$ films grown on STO (circles) and vycor glass (triangles) substrates.

Taylor *et al.*[9] have shown that the tensile thermal strain influences the dielectric constant, the Curie–Weiss temperature, and the Curie–Weiss constant in the polycrystalline BST films. Since the dielectric constant is inversely proportional to the square of the soft mode frequency, the variation in the dielectric constant due to thermal strain reported in Taylor *et al.*[9] is too small to observe by measuring the frequencies of the broad soft mode peaks. However, the impact of the thermal strain on T_C is very clearly observed. Figure 2 shows the temperature dependence of the A_1 soft mode Raman intensity for two BST films grown on STO and vycor glass substrates. [The intensity is normalized by the Bose factor $n+1=(1-\exp(-\hbar\omega/kT))^{-1}$ to correct for the general temperature dependence of Raman intensity.] While the thermal expansion coefficients for BST and STO are nearly equal,[15] the glass has significantly lower thermal expansion coefficient.[9] Therefore, the thermal strain is very small in the film on STO, but much larger and tensile in the film on vycor. As one can see, the A_1 soft mode intensity in the sample grown on glass goes to zero at ~220 K, while for the case of STO substrate this temperature is ~275 K. Figure 2 clearly demonstrates that the tensile strain causes a large decrease of the ferroelectric phase transition temperature.

The data for the films on all the substrates studied are summarized in Fig. 3. From the differences in the thermal expansion coefficients between BST and the substrates,[15] thermally induced strain at 250 K is calculated, which is tensile for vycor glass (−0.71%), Si (−0.54%), and sapphire (−0.28%), and slightly compressive for STO (0.03%). As the magnitude of the tensile strain increases, the ferroelectric phase transition temperature decreases. The values of T_C de-

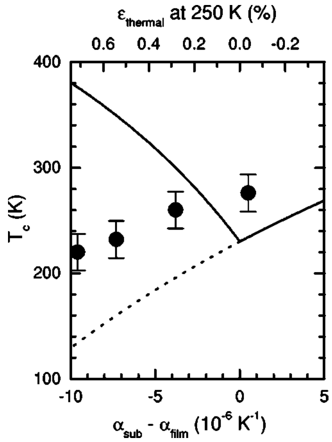

FIG. 3. The Curie–Weiss temperature as a function of the thermal mismatch and thermal strain, determined from the A_1 soft mode Raman intensity for all types of substrates (circles) and calculated within the thermodynamic model (Ref. 5). The dotted line shows the predicted behavior of T_C if the polarization is fixed normal to the film surface.

rived in this work from the soft mode measurements show the trend of the strain dependence consistent with that determined by Taylor *et al.*[9] from the linear extrapolation of the inverse susceptibility as a function of temperature.

The strain dependence shown in Fig. 3 is very different from the theoretically predicted behaviors in epitaxial thin films. From thermodynamic theories,[4,16] compressive strain in epitaxial ferroelectric film promotes the polarization in the ferroelectric phase to be out of plane (*c* domain), and T_C increases with increasing strain. Tensile strain favors in-plane polarization in the ferroelectric phase (*a* domain), and T_C also increases with increasing strain. In both cases, theories predict increase of T_C when the magnitude of the strain becomes larger. This is in clear contradiction with our result in polycrystalline BST films.

The observed reduction in T_C with increasing tensile strain is attributed to the suppression of in-plane polarization due to the small lateral grain size in the BST film. Fine grain size suppresses in-plane polarization in part due to formation of large fixed charges at grain boundaries due to discontinuities in the normal component of the polarization vector when crossing the grain boundary.[17,18] If domains with only a largely normal component of polarization can form, then increasing tension will cause a decrease in the Curie temperature. We estimate an in-plane grain size $\lesssim$100 nm and this grain size is sufficiently small to suppress in plane polarization.

It should be noted that the values of T_C determined from Raman data are higher than the thermodynamic predictions,[4,16] including the film on STO where the thermal strain is negligible. Recently, it was demonstrated by scanning optical microscopy studies[19] that the ferroelectric transition in films occurs over a broad temperature range, and local ferroelectric regions exist well above the bulk T_C. The appearance of the A_1 soft mode in Raman spectra likely corresponds to the temperature at which local ferroelectric regions start to develop in the films. This temperature can be significantly higher than bulk T_C, and is analogous to the Burns temperature in relaxor ferroelectrics.[11] Polar defects like oxygen vacancies and inhomogeneous strain caused by defects were suggested as possible causes for broadened ferroelectric phase transition in films.[11,19]

In summary, we have studied the soft phonon modes of a series of polycrystalline $Ba_{0.5}Sr_{0.5}TiO_3$ films with different thermal strain by Raman spectroscopy. Raman data on the soft mode behavior are used to determine the ferroelectric phase transition temperature T_C. The temperature dependence of the A_1 soft mode intensity reveals that T_C decreases with increasing the magnitude of the thermally induced tensile strain. Our results suggest that the *c* domain is fixed in the polycrystalline BST films during the growth and cooling processes. The complex structural nature of the polycrystalline films has to be taken into account when studying the strain dependence of the ferroelectric phase transition in these films.

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