Lattice distortions in $YBa_2Cu_3O_{7-\delta}$ thin films grown *in situ* by sequential ion beam sputtering

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We have analyzed epitaxial, *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films grown *in situ* by sequential ion-beam sputtering on (100) $SiTiO_3$ and (100) MgO substrates. X-ray diffraction studies showed the presence of both homogeneous and inhomogeneous lattice distortions along the *c*-direction. The *c*-axis lattice parameters ranged from 11.72 to 12.00 Å. The broadening of the (00*l*) Bragg peaks in excess of the broadening due to finite film thickness was found to be due to inhomogeneous lattice distortions. The overall trend in the data shows an increase of the inhomogeneous strains with the enlargement of the *c*-axis lattice parameter. The inhomogeneous lattice distortions are interpreted as fluctuations in the *c*-axis lattice parameter. The resistive transitions were found to be correlated to the lattice distortions. We show correlations between the midpoint T_c and the *c*-axis lattice parameter and between the transition widths and the inhomogeneous lattice distortions.

In recent years, the *in situ* growth of high-T_c superconductor thin films and their applications to devices has been a subject of intense work. Several techniques were reported for *in situ* growth of $YBa_2Cu_3O_{7-\delta}$ thin films.[1–8] Most of the attention was focused on films of optimized characteristics such as high-transition temperatures, sharp transitions, high-crystal quality, etc. The study of departures from these ideal characteristics is, however, important in understanding the *in situ* growth of high-T_c superconductor films.

The properties of sputtered "123" thin films, such as the transition temperature T_c, degrade as the deposition temperature is lowered.[9–11] This has been correlated to an expansion of the *c*-axis lattice parameter that increases as the deposition temperature is lowered.[10] The superconducting transition temperatures decrease with the enlargement of the *c*-axis lattice parameter as was shown for films grown *in situ* by magnetron sputtering,[12] sequential ion beam sputtering,[10] and *e*-beam evaporation.[13] In films grown by sequential ion beam sputtering, a broadening of the (00*l*) x-ray Bragg reflections that increases with the enlargement of the *c*-axis lattice parameter has also been reported.[10]

In this communication, we report an analysis of the lattice distortions and their correlations to characteristics of the superconducting transitions in "123" thin films grown *in situ* by sequential ion beam sputtering. The lowering of T_c with the enlargement of the *c*-axis lattice parameter is shown to hold over a wide range of lattice parameters. The broadening of the (00*l*) x-ray lines was analyzed for several orders of diffraction. This analysis showed that stacking faults are not an important cause of the broadening. The "size" and "inhomogeneous lattice distortions" contributions to the broadening were evaluated. The size coefficients were consistent with the film thicknesses. The main cause of broadening of the (00*l*) x-ray Bragg peaks in films with large *c*-axis lattice parameters was found to be inhomogeneous lattice distortions. The resistive transitions were found to be wider for higher values of the inhomogeneous lattice distortion coefficient. These results suggest that the superconducting resistive transition midpoint and width are related to the fluctuations and mean value of the lattice distortions along the *c*-direction, which cause the (00*l*) x-ray peak broadening (other than the broadening due to finite film thickness) and shift.

Epitaxial, *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ thin films were grown by sequential ion beam sputtering from elemental Y, Ba, and Cu targets. The stacking sequence of the "123" compound was followed with the individual layer thicknesses nominally equal to one monolayer. Films ranging from 300 to 1600 Å were grown on (100) $SrTiO_3$ and on (100) MgO substrates. The typical film thickness was 400 Å. Details on the deposition technique have already been reported.[8] The films have expanded *c*-axis lattice parameters ranging from 11.72 to 12.00 Å. The *c*-axis lattice parameters were evaluated by high-angle extrapolations using the (00*l*) series. Anneals in O_2 at 400 °C produced changes in the *c*-axis lattice parameter of <0.02 Å, and no significant changes in the superconducting transitions. Anneals in O_2 at 850 °C followed by anneals at 400 °C were effective in reducing the lattice parameter to approximately the bulk value of 11.68 Å.

Resistivity measurements were done by the standard AC four-point technique. Figure 1 shows the transition temperatures (midpoints) as a function of the *c*-axis lattice parameter. The tendency of T_c to decrease with the expansion of the *c*-axis lattice parameter was found to hold for a wide range of lattice parameters.

Analysis of our results and those of Eom *et al.*[13] show

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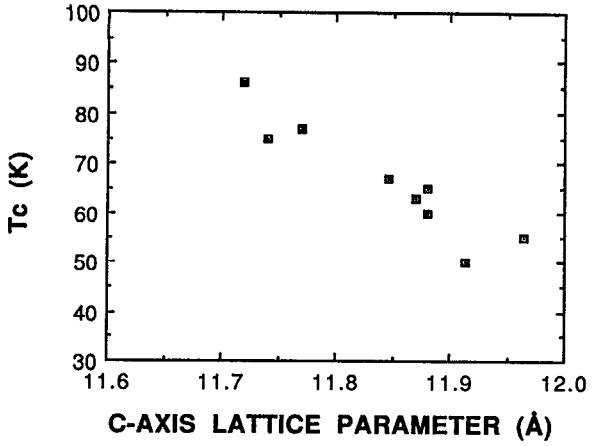

FIG. 1. Plot of the transition temperature (midpoint) as a function of the c-axis lattice parameter.

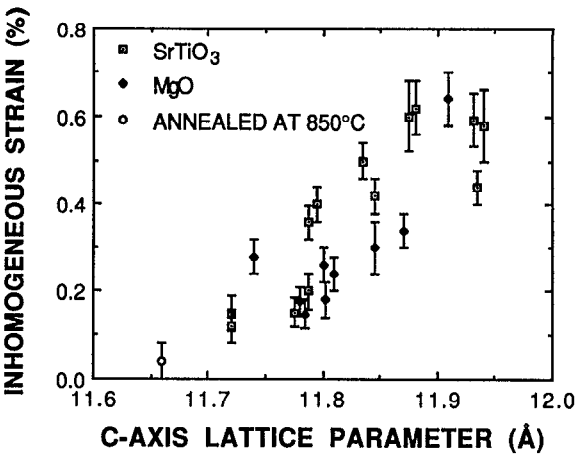

FIG. 3. Inhomogeneous strain ϵ_{rms} as a function of the c-axis lattice parameter.

that the relation between T_c and the c-axis lattice parameter, and the effects of anneals, are the same in different *in situ* growth techniques. This indicates that films grown by these various techniques present the same type of defects.

X-ray diffraction θ-2θ spectra were taken with a Siemens D500 diffractometer in a high-resolution geometry, using Cu$K\alpha$ radiation. The x-ray scans were corrected for $K\alpha$ and instrumental broadening. The full widths at half maximum of the (00l) Bragg peaks, ΔK, were plotted in reciprocal space as a function of their K values. The plots show a monotonic increase of ΔK with K. Figure 2 shows the plots for several films grown on MgO with different c-axis lattice parameters.

The line broadening due to finite crystal size along the film surface normal (c-direction) is constant in reciprocal space and given by

$$\Delta K \cong 0.9(2\pi/L),$$

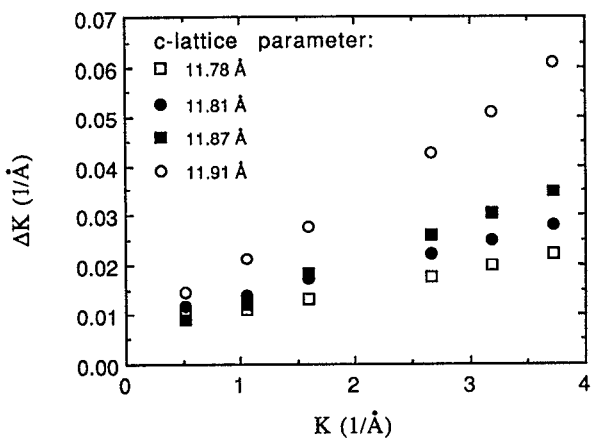

FIG. 2. Full widths at half maximum of the (00l) x-ray Bragg peaks ΔK as a function of their K values, for several films grown on MgO. The data were corrected for $K\alpha$ and instrumental broadening.

where L is the crystal size. The line broadening due to inhomogeneous lattice distortions along the c-direction is given by

$$\Delta K \cong 2.4\epsilon_{rms}K,$$

where $\epsilon = \delta c/c$ is the local inhomogeneous lattice distortion along the c-direction, $\langle\epsilon\rangle = 0$, and $\epsilon_{rms} = \langle\epsilon^2\rangle^{1/2}$ is the root mean square inhomogeneous lattice distortion.[14]

The contributions to line broadening due to finite size and to inhomogeneous lattice distortions were evaluated by least square fits assuming particular peak shapes for each contribution. The best fits were obtained in most cases assuming Cauchy size broadening and Gaussian lattice distortions broadening. The values of crystal size obtained were consistent with the film thicknesses as measured by Rutherford backscattering spectrometry and by cross sectional transmission electron microscopy.

Figure 3 shows a plot of the inhomogeneous strains, ϵ_{rms}, as a function of the c-axis lattice parameter. The error bars were evaluated by assuming Cauchy–Cauchy and Gaussian–Gaussian peak profiles. There is an overall tendency for films with larger c-axis lattice parameters to present higher inhomogeneous lattice distortions.

Comparison of the x-ray spectra for films before and after annealing in O_2 at 400 °C showed no change in the widths and positions of the (00l) Bragg peaks. Films annealed at 850 °C in O_2 showed a sharpening of the (00l) Bragg peaks and a shift to the bulk "123" lattice constant, indicating a relaxation of the strains (Fig. 3).

The resistivity data showed that films with large c-axis lattice parameters and high inhomogeneous strains had considerably broad transitions. The transition widths were best correlated to the inhomogeneous strains. Typically, films with ϵ_{rms} of 0.15, 0.30, and 0.60% had transition widths of 5, 10, and 30 K, respectively (Fig. 4). A relation between the broadening of diffraction lines and the broadening of superconducting transitions was proposed in perovskite superconductors.[15] These broadenings have been attributed to fluctuations in the lattice parameter[15] and to the proximity of phases with different oxygen ordering.[15,16]

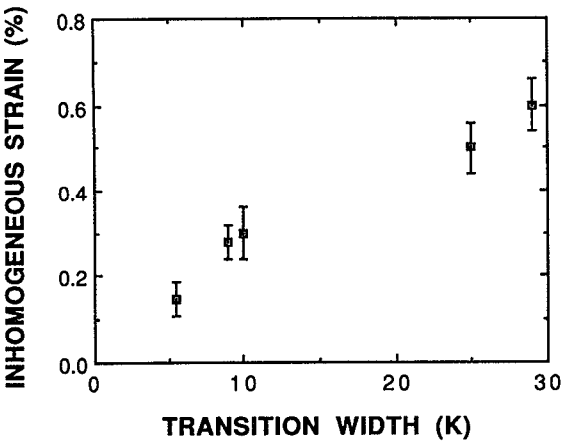

FIG. 4. Plot of inhomogeneous strains ϵ_{rms} vs resistive transition widths.

Off-axis x-ray diffraction studies in films grown by magnetron sputtering rule out a substrate-induced stress as the main cause of the *c*-axis lattice parameter expansion.[12]

We speculate that the *c*-axis lattice parameter expansion is related to defects trapped in the film during growth. Films grown at lower temperatures would present a higher density of defects, resulting in larger *c*-lattice parameters. This would explain the dependence of the *c*-lattice parameter on the deposition temperature.[10] Furthermore, it is tempting to assume that both the homogeneous and inhomogeneous lattice distortions are due to the same cause. The inhomogeneous lattice distortions would then be related to the fluctuations in the density of defects, or to the microscopic strain fields associated with the defects.

Results from deposition techniques that use activated oxygen sources suggest a relation between the oxygen content of *in situ* grown films and the lattice expansion and degradation of T_c.[17,18] The effect of anneals and the relation between the T_c and the *c*-axis lattice parameter in *in situ* grown films are different than in bulk samples.[16] This indicates that the lattice expansion cannot be attributed to oxygen vacancies in the chain sites as in bulk samples, but may be due to other oxygen defects. Another possible defect structure was proposed[11] consisting of substitutional disorder between the Y and Ba sublattices.

In conclusion, we have analyzed "123" films grown *in situ* by sequential ion-beam sputtering. We found that the broadening of the (00*l*) x-ray peaks is due to inhomogeneous strains. We have shown that there is a relation between the inhomogeneous and homogeneous lattice distortions along the *c*-direction, that can be interpreted as a relation between the fluctuations and mean value of the strain. We have found relations between the characteristics of the superconducting transition and the lattice distortions. Further studies are being carried out to elucidate the nature of the defect structure in the films.

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