Correlations between deposition parameters and structural and electrical properties of $YBa_2Cu_3O_{7-\delta}$ thin films grown *in situ* by sequential ion beam sputtering

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We have studied the correlations between deposition parameters and structural and electrical properties of $YBa_2Cu_3O_{7-\delta}$ thin films grown *in situ* by sequential ion beam sputtering. Epitaxial, *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films were grown both on (100) $SrTiO_3$ and on (100) MgO substrates following the stacking sequence of the "123" compound, with deposited layer thicknesses nominally equal to 1 monolayer. The *c*-axis lattice parameters obtained were larger than the corresponding lattice parameter in bulk samples, even after low-temperature anneals in O_2. The transition temperatures were found to decrease with the enlargement of the *c*-axis lattice parameter. A clear correlation between growth temperature and the value of the *c*-axis lattice parameter was observed. The *c*-axis lattice parameter and the x-ray linewidth of Bragg reflections with the G vector along the *c*-axis were also found to be correlated. This suggests a relationship between the *c*-axis lattice parameter and the structural coherence of the epitaxial films.

Several *in situ* techniques are now available for the growth of $YBa_2Cu_3O_{7-\delta}$ films.[1–7] This has raised a set of new issues not previously encountered in bulk samples or films obtained by high-temperature post-deposition anneals. One of the special characteristics often seen in *in situ* grown films is the expansion of the *c*-axis lattice parameter relative to the bulk value of 11.68 Å.[8–10] Early interpretations associated this expansion to an oxygen deficiency in the films by analogy to the well known expansion of the *c*-axis lattice parameter in oxygen-deficient bulk samples. However, it was soon recognized that the properties of *in situ* grown films with a given lattice parameter were intrinsically different from those of an oxygen-deficient bulk sample with the same lattice parameter.[8–10] An important characteristic of the *in situ* grown films with expanded *c*-axis lattice parameter is their behavior under heat treatments in oxygen. Contrary to what is observed in bulk samples, the lattice parameter of the films cannot be reduced by anneals in oxygen at low temperatures ($T < 650$ °C).[8,9] Recently, data were published for films grown *in situ* by magnetron sputtering, showing that the superconducting transition temperatures decrease linearly with the enlargement of the *c*-axis lattice parameter while the transitions remain sharp.[9] Understanding the nature of this lattice expansion and its dependence on deposition parameters is crucial for the successful control and optimization of the superconducting properties of *in situ* grown films.

In this letter we present an analysis of the general trends in the x-ray and resistive data obtained for $YBa_2Cu_3O_{7-\delta}$ thin films grown *in situ* by sequential ion beam sputtering.

Epitaxial, *c*-axis oriented $YBa_2Cu_3O_{7-\delta}$ films were grown on (100) $SrTiO_3$ and on (100) MgO substrates. The *c*-axis lattice parameters of the films were larger than the corresponding lattice parameter of bulk "123" samples, even after low temperature anneals in O_2. We investigated the dependence of the *c*-axis lattice parameter on deposition parameters over a wide range, finding that the growth temperature was the predominant factor in determining its value. The x-ray lines corresponding to Bragg reflections with the G vector along the *c* axis showed a broadening that is correlated to the value of the *c*-axis lattice parameter. The transition temperatures were found to decrease with the enlargement of the *c*-axis lattice parameter.

Films were grown using a Kaufman-type ion source operated with Ar to sputter sequentially from elemental Y, Ba, and Cu targets. A shuttering mechanism was used to control the deposition time for each layer. The stacking sequence of the "123" compound was followed with the individual layer thicknesses approximately equal to 1 monolayer. Typical deposition rates were on the order of 10 s for each monolayer. A detailed description of this technique will be given in a separate publication.[11]

Most of the films were grown under an enhanced local partial pressure of oxygen (P_{O_2}), introducing the oxygen through a nozzle or a ring situated at 1.5 cm from the sample. Some films were grown in a controlled background oxygen pressure. The local P_{O_2} at the substrate was estimated to range from 1×10^{-4} Torr to low 10^{-1} Torr, while the background P_{O_2} ranged from 1×10^{-4} Torr to 1×10^{-3} Torr. The substrates were clamped to a sample holder which was heated radiatively. Films were grown at sample holder temperatures ranging from 650 to 850 °C. The temperature at the surface of the substrate is estimated to be 100 °C lower than the temperature of the sample holder. Immediately after deposition the partial pressure of oxygen was increased, typically by a factor of four, and the samples were cooled to room temperature at a rate of 10 °C per minute.

Stoichiometry and thickness calibrations were done by Rutherford backscattering spectrometry (RBS). Most samples were grown within 5% of the ideal "123" composition,

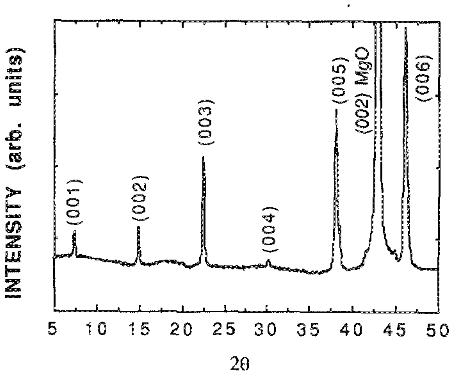

FIG. 1. X-ray diffraction pattern (Cu radiation) of a film grown on MgO showing c-axis orientation.

with the average individual layer thicknesses equal to 1 monolayer to within 10%. The total thicknesses of the films ranged from 300 to 1500 Å.

Not all combinations of growth temperatures and oxygen pressures produced $YBa_2Cu_3O_{7-\delta}$ films. At a given growth temperature there is a partial pressure of oxygen below which stoichiometric films contained multiple phases such as $BaCuO_2$, Cu_2O, etc. Films grown in a controlled background P_{O_2} of 2×10^{-4} Torr showed this phase separation at a sample holder temperature of 800 °C, while films grown at a sample holder temperature of 700 °C were predominantly single-phase $YBa_2Cu_3O_{7-\delta}$.

Figure 1 shows the x-ray diffraction pattern of a typical film, grown on MgO at a sample holder temperature of 775 °C. The films are c-axis oriented and epitaxial as was confirmed by transmission electron microscopy.

Analysis of the x-ray diffraction data showed that the c-axis lattice parameter had values ranging from 11.72 to 12.00 Å. In contrast, the lattice parameter of fully oxygenated bulk samples or films grown by post-deposition anneal in O_2 at 850 °C is 11.68 Å. Annealing in O_2 at low temperatures ($T < 650$ °C) had little or no effect on the lattice parameter, resulting in changes of less than 0.02 Å. Anneals in O_2 at 850 °C were effective in reducing the lattice parameter to 11.68 Å. Similar results have been reported for other *in situ* techniques.[8,9]

Resistivity measurements were done by the standard ac four-point technique. Figure 2 shows resistivity data for 400-Å-thick films grown on MgO with c-axis lattice parameters of 11.77 and 11.87 Å, and for a 1000-Å-thick film grown on $SrTiO_3$ with a c-axis lattice parameter of 11.72 Å. For optimum films, the transition temperatures were found to decrease with increasing lattice parameter. The highest transition temperature obtained is $T_c(R=0) = 79$ K for a film grown on $SrTiO_3$.

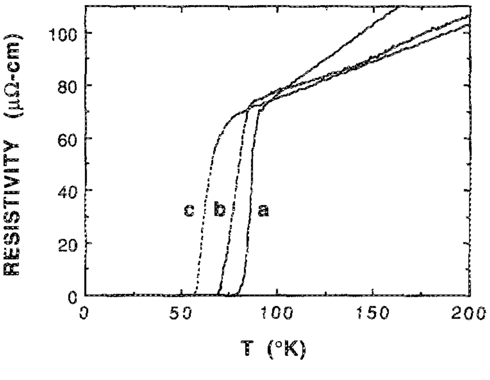

FIG. 2. Resistivity vs temperature for (a) 1000 Å film grown on $SrTiO_3$ with a c-axis lattice parameter of 11.72 Å, and 400 Å films grown on MgO with c-axis lattice parameters of (b) 11.77 Å and (c) 11.87 Å.

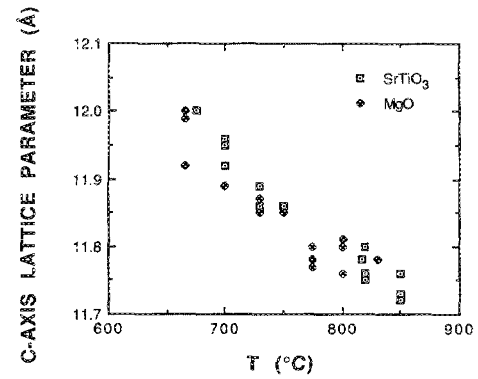

FIG. 3. Plot of c-axis lattice parameter vs sample holder temperature during growth.

Superconducting films were obtained over a range of compositions, including films as far off stoichiometry as $Y_1Ba_{2.5}Cu_4O_{7-\delta}$.

Figure 3 shows a plot of the c-axis lattice parameter as a function of the sample holder temperature during growth, for a large number of films. We include films grown under different partial pressures of oxygen, and a few films grown off stoichiometry by as much as 20%.

These results show that, under the conditions investigated, there is a strong correlation between the growth temperature and the c-axis lattice parameter. The growth temperature is clearly the principal variable in determining the value of the c-axis lattice parameter, with other variables having only secondary effects. The oxygen pressure during deposition did not seem to affect the value of the c-axis lattice parameter; it is, however, constrained to be above a critical value corresponding to the boundary for phase separation.

The x-ray data also show a broadening of the (00l) Bragg reflections which can be correlated to the expansion of the c-axis lattice parameter. Figure 4 shows a plot of full width at half maximum for the (005) diffraction peak as a function of the c-axis lattice parameter. This correlation sug-

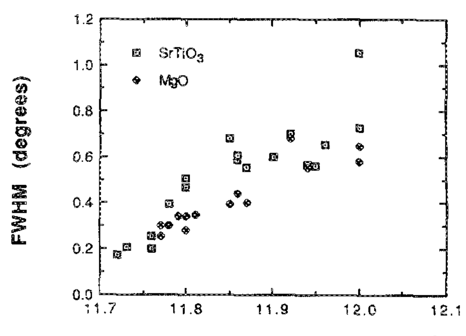

FIG. 4. Full width at half maximum for the (005) x-ray Bragg reflection vs c-axis lattice parameter.

gests that the expansion of the *c*-axis lattice parameter is related to a structural coherence length along the *c* direction of the epitaxial crystals.

In both the plot of the *c*-axis lattice parameter versus sample holder temperature and x-ray linewidth versus lattice parameter, the data for films grown on MgO and on $SrTiO_3$ follow the same trend, suggesting that the expansion of the lattice parameter is not caused by the substrate.

In conclusion, we have found clear correlations between the growth temperature of our films and the expansion of the *c*-axis lattice parameter, as well as between this expansion and the linewidths of the (00*l*) x-ray Bragg reflections. Although the nature of this expansion is not understood, it is known to degrade the superconducting properties of the films. The results suggest a relationship between a structural coherence length along the *c* axis and the expansion of the lattice parameter. We speculate that this structural coherence length may be determined by the density of defects such as stacking faults, low-angle tilt boundaries, etc., trapped within the film. Apparently, rather high temperatures ($\geqslant 750\,^\circ$C) are required to eliminate these trapped-in defects. We are carrying out further studies to elucidate the nature of the defect structures in the epitaxial films, and to understand the mechanism by which structural imperfections are trapped in the film during growth and relaxed in subsequent thermal treatments.

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