# *In situ* grown $YBa_2Cu_3O_{7-d}$ thin films from single-target magnetron sputtering

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Using single-target off-axis sputter deposition, high quality superconducting films of $YBa_2Cu_3O_{7-\delta}$ were made *in situ*. These films have properties which are distinctly different from those of bulk ceramics and of post-deposition annealed films. Their superconducting resistive transitions remain sharp regardless of the value of $T_c$ between 75 and 86 K. Normal-state conductivities are as high or higher than the best single crystals. Critical current densities are as high as $6\times10^7$ A/cm$^2$ at 4.2 K. $T_c\,(R=0)$ falls off with film thickness down to 10 K for 35–40 Å films. All of the above properties are relatively insensitive to compositional variation. The results can be explained if the *in situ* growth results in well-formed $CuO_2$ planes with defects occurring elsewhere.

In this letter, we report results on YBaCuO films grown *in situ* using an off-axis single-target magnetron sputtering technique that reproducibly exhibits novel physical and materials properties.

Stoichiometric targets were prepared from "freeze-dried" powders using the method developed by Johnson *et al.*[1] The depositions were performed in a high oxygen partial pressure environment. Substrates were placed on the side of a planar magnetron gun[2] to avoid backsputtering damage from negative oxygen ions as shown in Fig. 1. The sputtering atmosphere consisted of, in most cases, 10 mTorr $O_2$ (or $N_2O$) and 40 mTorr Ar. The rf power (125 W) on the sputter gun generated a self-bias of $-50$ to $-75$ V and gave a deposition rate of about 0.5 Å/s. The substrate temperature during deposition was measured by a thermocouple embedded in a block to which the substrates were clamped. The block temperature was held at 600–700 °C during film growth. Film thicknesses varied from 35 to 4000 Å. Substrate materials included MgO(100), $SrTiO_3$(100) and (110), $LaAlO_3$(100), yttria-stabilized zirconia, and *R*-plane sapphire. After deposition, the chamber was immediately vented to 600 Torr of oxygen.

The compositions of the films were measured with an electron microprobe; the results were verified in some cases by inductively coupled plasma spectroscopy or Rutherford backscattering. A small phase spread was found over an area of 1 in.$^2$ from which reproducibly good films could be obtained. In a typical run using a target of composition $Y_{17.7}Ba_{32.9}Cu_{49.4}$, the composition of the films at the extreme positions (Fig. 1) varied from $Y_{18.6}Ba_{32.8}Cu_{48.5}$ to $Y_{16.9}Ba_{33.1}Cu_{50.0}$, illustrating the 1:1 correspondence between target and film composition. In what follows we assume the films to have the composition of the two targets (1:2:3 and 1:2:3.5) from which they were fabricated. As will be shown below, the physical properties we discuss here are not very sensitive to the composition of the *in situ* grown films.

Characteristics of representative films are given in Table I. Even though transition temperatures at zero resistivity ($T_{c0}$) are somewhat lower than those of bulk materials, the transition widths $\Delta T$ (defined by the temperature between 90% of the normal state resistivity near $T_c$ and the temperature at zero resistivity) were sharp; $\Delta T\sim 3$–1 K for $T_c$'s varying from 75–86 K. Figure 2 shows representative $\rho$ vs $T$ transitions of films grown on MgO(100). The inset shows the narrow transition width of a high $T_c$ film. The normal-state resistivity of the good film is at least as low as that of the single crystal.[3] From the x-ray data discussed below, it is certain that this is not due to the high conductivity of the 2-4-8 phase.[4] Even for films as thin as 35 Å, the superconducting transition is still completed at 10 K [Fig. 2(d), dotted line], which implies a very sharp film-substrate interface with little interdiffusion. Sharp interfaces have also been seen on thicker films by cross-sectional transmission electron microscopy (TEM). The superconducting transition of the 35 Å film went away after four months vacuum storage, but partially recovers upon a 10 min, 400 °C oxygen anneal. This behavior seems to be consistent with the loss of surface oxygen in vacuum as has been seen by some surface anaysis work.

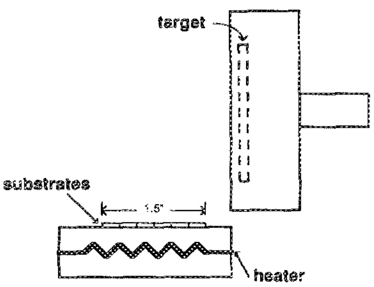

FIG. 1. Sputtering system geometry.

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TABLE I. Properties of films grown with *in situ* off-axis magnetron sputtering.

| Comp. | Substrate | $T_{sub}/P_{O_2}$ | Texture | $T_{c0}$ (K) | $\Delta T_c$ (K) | $J_c$ (A/cm$^2$) |
|---|---|---|---|---|---|---|
| 1:2:3 | MgO (100) | 660 °C/10 mT | $c$ | 85 | <1 | $6\times10^7$ |
| 1:2:3 | MgO (100) | 660 °C/10 mT | $c+a$ | 82 | <1 | $2\times10^7$ |
| 1:2:3.5 | MgO (100) | 630 °C/10 mT | $c+a$ | 82 | 1 | $9\times10^6$ |
| 1:2:3 | $SrTiO_3$ (100) | 700 °C/100 mT | $c$ | 86 | <1 | ··· |
| 1:2:3.5 | $SrTiO_3$ (100) | 660 °C/10 mT | $c+a$ | 85 | 3 | $5\times10^6$ |
| 1:2:3.5 | $LaAlO_3$ (100) | 660 °C/10 mT | $c+a$ | 84 | 3 | $4\times10^6$ |
| 1:2:3 | YSZ (100) | 660 °C/60 mT | $c$ | 84 | 1 | $5\times10^6$ |
| 1:2:3 | $Al_2O_3$ $(1\bar{1}02)$ | 700 °C/100 mT | $c$ | 87 | 1.5 | $2\times10^6$ |

Structural studies show that films less than 4000 Å thick on MgO(100) are purely $c$-axis oriented and epitaxially aligned in the substrate plane. The surfaces are very smooth; no features could be detected within the ~200 Å resolution of the scanning electron microscopy (SEM). Figure 3 shows a typical x-ray diffraction scan normal to a stoichiometric $c$-axis film's surface. Impurity peaks were absent in 1:2:3 samples. The high phase purity of one of such film was confirmed using a slow scan and a thin-film diffractometer. An $\omega$ rocking on the $YBa_2Cu_3O_7(005)$ peak was found to be only 0.2° of full width at half maximum (FWHM). More quantitative studies of the x-ray data revealed an interesting relationship between the $c$-lattice parameter and the transition temperature.

In Fig. 4(a), the transition temperatures ($T_{c0}$) of films grown at various deposition temperatures and oxygen partial pressures are plotted against the $c$-lattice parameters, together with similar data obtained from studies on bulk ceramics.[5,6] The $c$-lattice parameter increased with decreasing substrate temperature and oxygen pressure. In our experience, the $T_{c0}$ corresponds well with the onset of $T_c$ measured by magnetization. Accordingly, in Fig. 4 we used onset for the bulk $T_c$'s. It is clear from Fig. 4(a) that the $T_c$ of our *in situ* grown thin film has a much weaker dependence on the $c$-lattice parameter, and that even our best as-grown films have longer $c$-lattice parameters than those of bulk ceramics or post-annealed films. Also, in films with mixed $a$ and $c$ orientations, the $a$-lattice parameter was measured. It was confirmed by off-axis x-ray diffraction that the $c$-lattice parameter of $a$-axis grains is equal to the $c$-lattice parameter of $c$-axis grains on two films that contain a mixture of $a+c$ oriented grains. That result rules out the possibility that differential thermal expansion between the films and the substrates makes a large contribution to the difference in the $c$-lattice parameters. The relation between the $c$-lattice parameter and $a$-lattice parameter is shown in Fig. 4(b). Unlike the bulk ceramics where an expansion of the $c$-lattice parameter is accompanied by a similar expansion of the $a$ axis, our *in situ* films tend to have a rather constant $a$-lattice parameter, even when the $c$-lattice parameter varies.

The expansion of the $c$-lattice parameter was found not to be due to oxygen deficiency. A series of annealing experiments was conducted. Anneals at 650 °C in oxygen caused no significant change in lattice parameters and $T_c$, suggesting that the origin of the expanded $c$-lattice parameter and the rather insensitive dependence of $T_c$ on the $c$-lattice parameter is not simply due to oxygen deficiencies. Anneals at 850 °C in oxygen, however, did increase the $T_c$ up to above 87 K and did shrink to the 11.68 Å $c$-lattice parameter characteristic of bulk $YBa_2Cu_3O_7$. Such temperatures are high enough to cause recrystallization of the films[7,8] and thus it is not surprising that the films become more like bulk material and post-annealed films. The 400 °C anneals in 10 mTorr of oxygen show depletion of oxygen from films; $T_c$ degraded to around 30 K, and the $c$-lattice parameter and $a$-lattice parameter expanded significantly, closely approaching that of

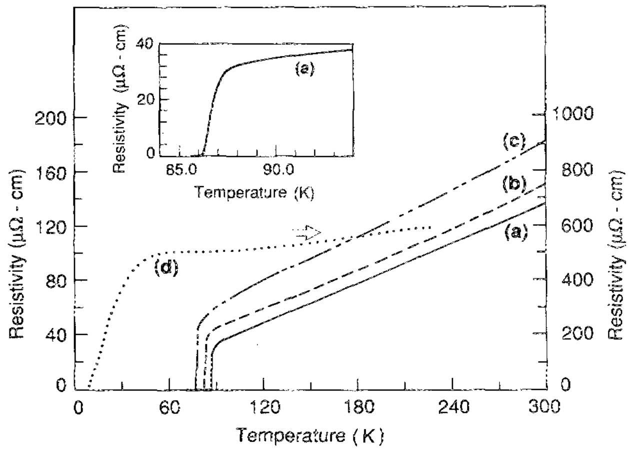

FIG. 2. Typical resistive transitions for films on MgO. (a) $T_{c0}$ = 86.2 K, (b) $T_{c0}$ = 82.5 K, (c) $T_{c0}$ = 79 K. Lower $T_c$ films are grown at lower temperature and oxygen pressure. (d) The resistance transition for 35-Å-thick film. ($T_{c0}$ = 10 K).

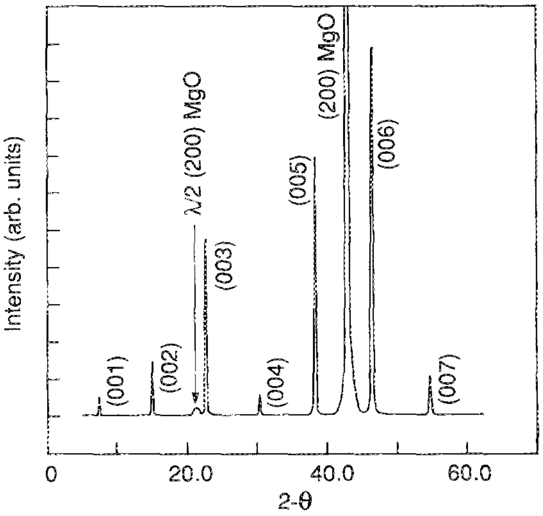

FIG. 3. X-ray diffraction pattern using Cu $K\alpha$ source showing clear $c$-axis orientation.

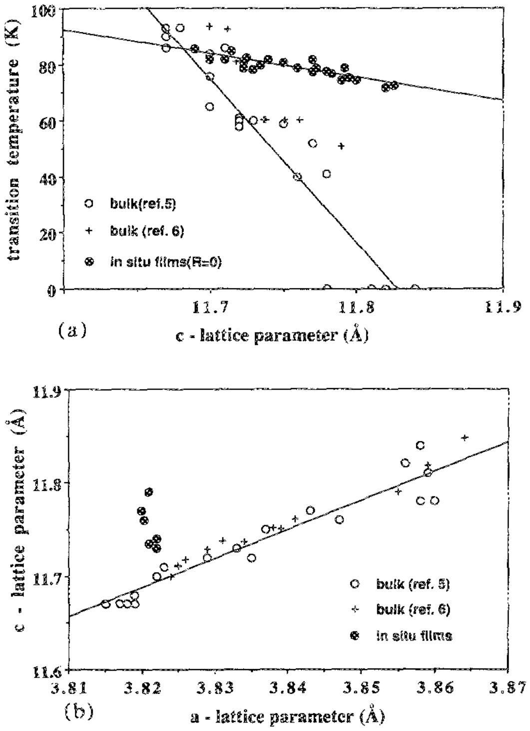

FIG. 4. (a) Transition temperatures vs *c*-lattice parameters for *in situ* film (closed circle) compared with the bulk ceramic's (open circles,[5] crosses[6]). (b) *c*-lattice parameters vs *a*-lattice parameters of thin and bulk ceramic films grown *in situ*.[5,6]

the bulk values for the same $T_c$ (Fig. 4). Subsequent 400 °C anneals of the same films in 1 atm oxygen returned $T_c$, and the *c*-, and *a*-lattice parameters to their orginal values. Reversible entry and exit of oxygen in bulk material is well known to be caused by oxygen movement on the chain sites; the same evidence occurs in the *in situ* films. It is evident that depletion of oxygen content from *in situ* samples is not the same degradation as is caused by nonoptimal *in situ* growth [Fig. 4(a)].

The critical currents of these films were calculated from magnetization data using Bean's formula, which for thin films with large demagnetization factors could be applied down to quite low fields ($\sim 1$ kG). The zero field current density was then estimated by extrapolation. Typical values of critical current densities for our 1:2:3 films are around $(2-6)\times10^7$ A/cm$^2$ at 4.2 K. In general, the critical currents have a weaker field dependence than do post-annealed films, dropping only by a factor of 2 from zero to 1.5 T, rather than $>3$ for post-annealed films.[7] Two tests were made with patterned films. The critical current for a 250-$\mu$m-wide, wet-etched film exceeded the limit of the measuring probe, $1\times10^5$ A/cm$^2$ at 1.3 K below $T_c$. In an experiment being carried out at Stanford with S. Tahara, a film patterned to make a 1-$\mu$m-wide bridge by ion milling $T_c$ was degraded by 10 K, however, the transport critical current at 4.2 K was $2\times10^7$ A/cm$^2$.

$T_c$ and critical current densities of post-annealed films are very sensitive to composition. A 10% deviation from stoichiometry seriously degrades the critical current density and $T_c$.[8] In contrast, the superconducting properties of the *in situ* grown films were found to be quite insensitive to overall cation compositional variations. As can be seen in Table I, off composition 1:2:3.5 films have only slightly poorer critical current densities, $9\times10^6$ A/cm$^2$ at zero field. Furthermore, the critical currents remain relatively insensitive to field.

In conclusion, high quality epitaxial YBaCuO films, which have a high degree of orientation, smooth surfaces, and high critical current densities, have been grown *in situ* via magnetron sputtering at intermediate pressures and relatively low substrate temperatures. The transition temperatures of the best films are slightly lower than bulk values and the *c*-axis lattice parameters are longer. These properties are not due to oxygen deficiencies at the chain sites. It is rather possible that the low-temperature growth of thin films introduces disorder or defects. Such defects on the oxygen "bridge" sites, for example, could account for the increased *c*-lattice parameter and might act as additional pinning sites. An overall more uniform distribution of defects resulting from the low-temperature growth might also account for the unusual dependence of $T$ upon lattice parameters. The large normal-state conductivity, high critical current density, and the constant near-single-crystal value of the *a*-axis support the idea that the CuO$_2$ planes are left intact. The fact that ultrathin superconducting films below 50 Å can be grown sets a limit on substrate-film interaction.

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