In situ growth and properties of single-crystalline-like $\text{La}_2-x\text{Sr}_x\text{CuO}_4$
epitaxial films by off-axis sputtering

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Excellent quality $\text{La}_2-x\text{Sr}_x\text{CuO}_4$ epitaxial films of $0.07 < x < 0.34$ in (001) and (103) orientations have been successfully grown in situ on SrTiO$_3$, LaAlO$_3$, and Y-stabilized ZrO$_2$ substrates using 90° off-axis sputtering. A record low ion channeling minimal yield $\chi_{\text{min}}$ of 1.9% is observed for the first time, and a $\chi_{\text{min}}$ of 3% is routinely attained. The surface exhibits a featureless morphology under high-resolution scanning electron microscope, suggesting a roughness $< 30 - 40$ Å. Superconductivity is maximized at $x = 0.15$ with a typical $T_c$ ($R=0$) of 35 K, a $J_c$ (4.2 K) of $1 - 3 \times 10^6$ A/cm$^2$, and a normal state resistivity two to three times lower than single crystals. $T_c$ shows a marked reduction with thickness, and the results are interpreted on the basis of partially relieved strained-layer growth coupled with a sensitive dependence of $T_c$ on uniaxial stress.

Thin-film synthesis and processing of high-temperature superconductors have progressed very rapidly, as motivated by the prospect of applications in superconducting electronics at 77 K. The contributions of thin-film materials to fundamental research on superconductivity, however, are less obvious than those of single crystals. Among the high $T_c$ cuprates $\text{La}_2-x\text{Sr}_x\text{CuO}_4$ has the simplest crystal structure, and is best suited for investigating the dependence of normal state and superconducting properties on carrier concentrations. It has been established that the material properties change progressively with Sr dopings ($x$) from an antiferromagnetic insulator to a superconductor with a maximum $T_c \approx 38$ K at $x = 0.15$, and further to a nonsuperconducting metal at $x > 0.2$. Due to material in homogeneities questions remain regarding exact phase boundaries of superconductivity, and possible existence of crossovers of different conduction mechanisms. Since large, good quality single crystals are scarce for $x > 0.12$, epitaxial films become very attractive for studying transport, optical, and electronic properties.

Extensive studies on epitaxial $\text{La}_2-x\text{Sr}_x\text{CuO}_4$ films were conducted by Suzuki. The lack of precise composition controls and the employment of high-temperature annealing resulted in substantial scatterings in the physical data. In this work the approach of in situ epitaxial growth has produced homogeneous $\text{La}_2-x\text{Sr}_x\text{CuO}_4$ films of precise stoichiometry and eliminated the need for high-temperature annealing. In addition to an excellent epitaxial order, a remarkably smooth film morphology was attained with a roughness less than 30 - 40 Å. The low normal-state resistivity and high $J_c$ are the best data reported for this system. A model based on lattice clamping effect resulting from unrelieved epitaxial strains is proposed to account for a significant decrease of $T_c$ with thickness.

The $\text{La}_2-x\text{Sr}_x\text{CuO}_4$ films were grown by dc magnetron sputtering in a 90° off-axis configuration. Films of variable Sr contents were obtained by adjusting the Sr/La ratio in sintered ceramic targets. Excess CuO of 15% was added to the targets to compensate for a slight Cu deficiency in the films. Substrates of MgO(100), Y-stabilized ZrO$_2$(100), LaAlO$_3$(100), and SrTiO$_3$(100) and (110) were used. The sputter gas consisted of a mixture of $\sim 60$ mTorr Ar and $\sim 20$ mTorr O$_2$. The dc sputter source, operated at low power of 6 and 16 W, produced deposition rates of 140 and 300 Å/h, respectively. The substrates were attached with silver paste to a heater which was held at 650 °C during growth as measured by an infrared pyrometer. After deposition the samples were cooled to 500 °C in one atmosphere O$_2$ over an 1.5 h period, and followed by slow cooling to room temperature. This cool-down procedure ensures that the films are fully oxygenated, and need no further external anneal.

The chemical composition of the film was determined by Rutherford backscattering spectroscopy (RBS). A four-circle x-ray diffractometer using Cu $K\alpha$ radiation assessed the structural order. The surface morphology was examined by phase-contrast optical microscopy, scanning electron microscopy (SEM) of both standard and high resolutions, and scanning tunneling microscopy (STM). The resistivity was measured by the standard van der Pauw method. The electrodes were formed by evaporating Ag contacts. Critical current densities ($J_c$) were determined by the magnetic method using a vibrating sample magnetometer, and verified by the transport method.

Highly oriented epitaxial films were obtained on the aforementioned substrates with only one exception of MgO(100), on which polycrystalline films were formed. Growth on the (100) face of SrTiO$_3$, LaAlO$_3$, and Y-stabilized ZrO$_2$ produced purely c-axis oriented films with complete absence of a-axis grains, whereas growth on the SrTiO$_3$ (110) face led to (103) orientation of two variants, (103) and (103). Both types of films showed excellent crystallinity of narrow mosaic spreads. The x-ray rocking curve measurements in Fig. 1(a) indicated a full width of half maximum (FWHM) of 0.29° for the (006) reflection of (001) films, and a slightly larger width of 0.32° for the (206) reflection of (103) films. The instrumental broadening is 0.16° as measured on a SrTiO$_3$ substrate. Very low
levels of impurities were detected in the longitudinal scan in Fig. 1(b). The longitudinal widths of the peaks in Fig. 1(b) are resolution limited, indicating crystalline order in a length scale exceeding 500 Å. The fact that the signal-to-noise ratio of a typical Bragg reflection exceeds four orders of magnitude attests to a remarkable phase purity.

The RBS measurement in conjunction with ion channeling also showed excellent alignment of the crystal axes with the substrates. Shown in Fig. 2 are RBS channeled and random spectra of a (001) film 7700 Å thick using 2.0 MeV He\(^+\) ion beam. The ratio of the backscattered yield along (100) to that in random direction, called \(X_{\text{min}}\), is about 3% for most (001) films. For the spectra in Fig. 2, a record low \(X_{\text{min}}\) of 1.9% is obtained, which equals to the theoretical prediction for high \(T_c\) single crystals, and is for the first time demonstrated in epitaxial films. Note that the ratio of channelled to random yield increases only slightly to \(\sim 10\%\) at the interface with substrates. Typical \(X_{\text{min}}\) of (103) films is \(\sim 7\%\), indicating a slightly poorer epitaxial order than (001) films.

The (001) film surface showed reproducibly an extremely smooth morphology with little evidence of outgrowths or precipitates. This is illustrated by the SEM micrograph in Fig. 3 taken under standard resolution. No visible features were detected by optical microscope, either. Further examinations under high-resolution SEM revealed similar featureless morphology, suggesting a surface roughness occurring on a scale less than 30-40 Å. Consistent observation was also made by STM which indicated the presence of growth steps corresponding to one or half unit cell height; however, no clear evidence of screw dislocations was seen. Undoubtedly the surface smoothness of \(La_{2-x}Sr_xCuO_4\) films is superior to those of \(Y_1Ba_2Cu_3O_7-x\) or other high \(T_c\) films reported to date. Three possibilities may be responsible, including the lower growth temperature by \(-50-100\) °C, better thermodynamic phase stability, and a simpler crystal structure of a smaller growth unit, i.e., 7 Å in \(La_{2-x}Sr_xCuO_4\) as opposed to 12 Å in \(Y_1Ba_2Cu_3O_7-x\).

The temperature dependence of the normal-state resistivity \(\rho\) is shown in Fig. 4 for the (001) oriented \(La_{2-x}Sr_xCuO_4\) films with \(x=0.07, 0.15,\) and 0.34. Upon increasing Sr doping, the functional dependence of \(\rho\) vs \(T\) changes systematically from variable range hopping, to \(T\) linear, and onto \(T^{1.5}\), for \(x=0.07, 0.15,\) and 0.34, respectively, in accord with single-crystal behavior. Note that the magnitude of \(\rho\) in our films is better (lower)
Evidence for interdiffusion within a resolution of 50 Å. This is sufficient to account for the data in Fig. 5. The interface by Auger electron spectroscopy, and found no evidence for a reasonably sharp interface is also supported by the RBS measurements. The rate of decrease depends on the magnitude and 3.5 K for the thickness >5000 Å, and decreases less rapidly with the thickness (5000 Å).

The striking dependence of $T_c(R=0)$ on film thickness suggests a close interplay between superconductivity and lattice structures at low temperature. Studies along this direction are underway, and will be extended to $\La_{2-x}\Sr_x\CuO_4$ epitaxial films.

In conclusion, we have demonstrated single-crystal-like $\La_{2-x}\Sr_x\CuO_4$ epitaxial films by in situ growth using off-axis sputtering. The perfection of crystallinity and surface morphology is exemplary for high $T_c$ films. The systematics of superconductivity and transport as a function of doping provide opportunities to probe conduction mechanisms and to correlate with electronic structures.

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One surprising finding is a marked broadening and a rapid reduction of $T_c(R=0)$ with decreasing film thickness. The rate of decrease depends on the magnitude and the sign of lattice mismatch as well as the tilt angle between the Cu-O$_2$ plane and the substrate face. A subset of data of $T_c(R=0)$ versus thickness are plotted in Fig. 5 for samples grown on SrTiO$_3$ (100) and (110), and a complete report and analysis on this subject will be given elsewhere. Compared to (001) films, the $T_c$ of (103) films saturates near 35.0 K for the thickness >5000 Å, and decreases less rapidly with the thickness <5000 Å.

Our analysis of these results suggests that the chemistry-related effect is unlikely the cause. We have examined the interface by Auger electron spectroscopy, and found no evidence for interdiffusion within a resolution of 50 Å. This reasonably sharp interface is also supported by the RBS result that the interfacial structure is slightly disordered. Although interdiffusions at our growth temperature may not be entirely absent, previous studies on the interfacial layer suggested a thickness limited to 10–20 Å. It seems unlikely that such a thin layer could affect the rest of growth persistently to a thickness of 8000 Å. Furthermore, the mismatches of thermal expansion coefficients between the films and the substrates are quite small, and are insufficient to account for the data in Fig. 5.

A plausible interpretation is based on a picture of tially relieved strained-layer growth. The mismatches of lattice parameters between $\La_{2-x}\Sr_x\CuO_4$ and SrTiO$_3$ along two in-plane axes are −3.3%, −3.3% for [010], [001] in (001) films, and −3.3%, +5.5% for [010], and (103) in (103) films. X-ray diffraction indicated that the in-plane lattice parameters of a 8000 Å film are expanded by 0.2% compared to bulk ceramics, whereas those of (103) film of similar thickness are essentially bulk-like. This suggests that the coherency strains are better relieved for epitaxial growth of a larger lattice-mismatch-like (103) films. Furthermore, the presence of unresolved strains may affect superconductivity negligibly. This effect is expected to be pronounced especially for $\La_{2-x}\Sr_x\CuO_4$ epitaxial films, because the pressure dependence of $T_c$ in this materials is about one order of magnitude stronger than other high $T_c$ cuprates. Simple estimates using known compressibility and $dT_c/dP$ value showed that an average expansion of in-plane lattices by 0.2% could suppress the $T_c$ by as much as 2 K, in agreement with the (001) film results.

In conclusion, we have demonstrated single-crystal-like $\La_{2-x}\Sr_x\CuO_4$ epitaxial films by in situ growth using off-axis sputtering. The perfection of crystallinity and surface morphology is exemplary for high $T_c$ films. The systematics of superconductivity and transport as a function of doping provide opportunities to probe conduction mechanisms and to correlate with electronic structures. The striking dependence of $T_c$ on film thickness suggests a close interplay between superconductivity and lattice structures at low temperature. Studies along this direction are underway, and will be extended to $\La_{2-x}\Da_x\CuO_4$.

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