In situ epitaxial growth of Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ films by molecular beam epitaxy with an activated oxygen source


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Highly oriented, epitaxial Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ thin films were prepared on MgO(100) by molecular beam epitaxy at a substrate temperature of 550–600°C. The in situ growth was achieved by incorporating reactive oxygen species produced by a remote microwave plasma in a flow-tube reactor. The epitaxial (001) orientation is demonstrated by x-ray diffraction and ion channeling. In situ reflection high-energy electron diffraction showed that a layer-by-layer growth has produced a well-ordered, atomically smooth surface in the as-grown tetragonal phase of an oxygen stoichiometry of 6.2–6.3. A 500°C anneal in 1 atm of O$_2$ converted the oxygen content to 6.7 to 6.8. Typical superconducting transport properties of an Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ film 1000 Å thick are $\rho(300 \text{ K}) = 325 \mu \text{Ohm cm}$, $\rho(300 \text{ K})/\rho(100 \text{ K}) = 2.4$, $T_c$ (onset) = 92 K, and $T_c (R = 0) = 82$ K. The transport $J_c$ at 75 K is $1 \times 10^6 \text{ A/cm}^2$, and increases to $1 \times 10^8 \text{ A/cm}^2$ at 70 K.

Rapid progress has been made on the preparation of high-temperature superconducting oxide films. Earlier studies were largely based on low-temperature (<400°C) deposition of amorphous oxide films followed by high-temperature (>800°C) O$_2$ furnace annealing. Recent emphasis has been directed toward in situ production of the high $T_c$ phase at relatively low growth temperature to eliminate completely the high-temperature annealing step. The in situ method offers the obvious advantage of fabricating superconducting thin-film devices at a temperature compatible with semiconductor processing. It also holds a better prospect of attaining a highly perfect film surface suitable for surface-sensitive measurements such as electron tunneling. Furthermore, it promotes the possibility of producing metastable superconducting phases or artificially structured oxides in thin-film form.

Advanced film deposition technique of molecular beam epitaxy (MBE) is well known for its versatility and precise control. As is generally agreed, one of the crucial parameters in forming superconducting perovskites is the abundance of activated oxygen species with a chemical reactivity with metal much greater than molecular oxygen. This work reports in situ low-temperature growth of Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ films using a combination of MBE and a reactive oxygen source generated from a microwave discharge in a flow-tube reactor. The activated oxygen species are predominantly excited molecular oxygen and atomic oxygen. MgO(100) substrates were used because the films produced are suitable for real applications. X-ray diffraction and ion channeling demonstrate a high degree of epitaxial order of the (001) orientation. Most important, in situ reflection high-energy electron diffraction (RHEED) studies indicated that a layer-by-layer growth maintained a well-ordered perovskite oxide structure to the uppermost surface. A smooth surface morphology on a scale finer than 1000 Å was observed by scanning electron microscopy. Typical transport properties for nearly stoichiometric films are $\rho(300 \text{ K}) = 325 \mu \text{Ohm cm}$ and $\rho(300 \text{ K})/\rho(100 \text{ K}) = 2.4$. The resistive transition is $T_c$ (onset) = 92 K, and $T_c (R = 0) = 82$ K. The fact that the transport $J_c$ increases rapidly to $1 \times 10^6 \text{ A/cm}^2$ at a temperature 15% below $T_c$ suggests that the current carrying capabilities are comparable to state of the art results obtained by high-temperature annealing.

The samples were prepared in a versatile ultrahigh vacuum molecular beam epitaxy system previously described. Coevaporation of three metal sources was used, i.e., the Y and Cu were from electron beam heated sources, and the Ba was from an effusion cell oven. No shuttered growth of individual source was employed. The substrate temperature was calibrated by the optical pyrometer method. The optimal growth temperature extends over a finite range of 550–600°C. The overall oxide growth rate was 0.5 Å/s with total film thickness of ∼1000 Å.

In order to enhance the oxidation of the metal species in the growing film a beam of activated oxygen was directed at the substrate. The activated oxygen species were generated by passing a flow of molecular oxygen through a discharge contained in a flow-tube reactor made of a 10-mm-i.d. untreated quartz tube. The discharge was excited in a magnetic cavity using a microwave power of 120 W at 2.45 GHz. The gas flow in the reactor tube was sampled with a 1.6-mm-i.d. quartz tube. The flow velocity down the tube was kept at 400 mTorr, which produces a flux of $2 \times 10^{17}$ species/cm$^2$ s impinging upon the substrate located approximately 2 cm from the orifice. This flux is equivalent to a pressure of $6 \times 10^{-4}$ Torr, which is two orders of magnitude over the pressure of $5 \times 10^{-5}$ Torr maintained in the growth chamber.

The flow velocity down the tube after the discharge was only ∼280 cm/s which resulted in a residence time of the activates species in the flow tube of 0.21 s. Over this period of time the species undergo deactivation. Using literature values for a wall recombination efficiency of $10^{-4}$ and a volume recombination rate constant of $7 \times 10^{7}$ cm$^3$ mol$^{-1}$ s$^{-1}$, the depletion of the activated species is estimated to be ∼60%. Taking the production efficiency of atomic oxygen and excited molecular oxygen by the plasma to be 10%, the

flux of the activated oxygen at the substrate is \( \sim 6 \times 10^{15}/\text{cm}^2\text{s} \), about one order of magnitude over the amount of oxygen required at the given growth rate.

According to isocompositional plots of \( \log P(\text{O}_2) \) vs temperature\(^1\) determined for bulk ceramics of \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \), the low partial pressure of oxygen of \( 10^{-1} \) Torr during growth resulted in a deficient oxygen stoichiometry of 6.2–6.3 in the as-deposited films. After the growth, the samples were cooled down in the same oxygen pressure. They were then annealed in 1 atm O\(_2\) flow at 500–550 °C for 1 h, and slowly cooled to room temperature.

The substrates used in this work are MgO(100), of which the lattice mismatch with the film is about 9%. The surface of the natural cleavage plane (100) is atomically smooth; however, it has many cleavage steps. Figure 1 shows the \( \text{in situ} \) RHEED patterns for MgO(100) surface along azimuthal (a) [100] and (b) [110] axes using 10 keV electrons of a 1.0° grazing incidence. The diffusive streaks are presumably related to the multistep surface. After the growth was initiated, the diffraction patterns changed immediately to those shown in Figs. 1(c) and 1(d) for an \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \) film 150 Å thick along [100] and [110], respectively. The increase of the streaking spacing by about 8% is evident. The in-plane epitaxial relationship is [100] \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \parallel [100] \text{MgO} \) and [100] \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \parallel [110] \text{MgO} \). The presence of distinct streaks along with Kikuchi arcs suggests that a layer-by-layer growth has produced an atomically smooth, highly ordered surface even for films thinner than 150 Å. Figures 1(e) and 1(f) are diffraction patterns obtained for an as-grown \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \) film of 1000 Å along [100] and [110], respectively. The relative intensities of the diffraction streaks and the background, as a measure of the relative amounts of the \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \) phase and impurity components, vary critically with small compositional deviations from the ideal stoichiometry.

The sample composition was determined from Rutherford backscattering spectrometry (RBS) analysis using a \( ^4\text{He}^+ \) ion beam of 2.0–3.0 MeV depending on the film thickness. The sample in Fig. 1 has a composition of \( \text{Y}_1\text{Ba}_{1.8}\text{Cu}_{3.2} \). The ratio of the aligned [100] backscattered yield to the random yield in the Ba region of the spectrum, called \( \chi_{\text{min}} \), was measured to be 21%. This value, which measures the degree of alignment along [100] of MgO, compares favorably to the best value of 30% reported for \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x \) films prepared by high-temperature anneal.\(^1\)

Scanning electron microscopy (SEM) was used to examine the film surface morphology. At a magnification of 95 000, the surface appeared smooth with roughness occurring on a scale finer than 100 Å. Dispersed \( \text{Cu}_2\text{O} \) precipitates of submicron size were detected on top of the film surface, with an effective area coverage of \( \sim 15\% \). This partly accounts for the measured \( \chi_{\text{min}} \) being six times larger than that measured in single crystals.\(^1\)

The transport resistivity was measured in a standard four-point geometry using an ac method. The resistivities of as-grown films increase dramatically with small deviations of compositions from the ideal ratio. Typical room-temperature resistivity, \( \rho(300 \text{ K}) \) of nearly stoichiometric samples are \( \sim 10–20 \text{ m}\Omega \text{cm} \), consistent with an oxygen composition of 6.2–6.3.\(^6\) After annealing at 500 °C in 1 atm O\(_2\) for 1 h, \( \rho(300 \text{ K}) \) is reduced to 340 \( \mu\Omega \text{cm} \). The temperature dependence of resistivity shows a metallic behavior with a ratio \( \rho(300 \text{ K})/\rho(100 \text{ K}) \) of 2.4. Typical resistive superconducting transition is \( T_c \text{(onset)} = 87 \text{ K} \) and \( T_c (R = 0) = 77 \text{ K} \). Additional annealing of the same sample at 550 °C for 30 min reduces \( \rho(300 \text{ K}) \) slightly to 325 \( \mu\Omega \text{cm} \). The superconducting transition temperature, however, is improved to a \( T_c \text{(onset)} = 92 \text{ K} \) and \( T_c (R = 0) = 82 \text{ K} \) as shown in Fig. 2. The critical current density \( J_c \) was measured by the dc transport method using a criterion of 1 μA/cm\(^2\). At 75 K, \( J_c \) is \( 1 \times 10^5 \text{ A/cm}^2 \), and at 70 K, \( J_c \) increases to \( 1 \times 10^6 \text{ A/cm}^2 \). The temperature dependence of \( J_c \), as plotted in Fig. 2 inset,
is similar to those of state of the art epitaxial films with a $T_c$ of 90 K prepared by high-temperature anneal.\textsuperscript{14}

The x-ray analysis is summarized in Fig. 3. The films are highly oriented with little evidence of polycrystalline second phase. The film mosaic is about 0.5° as compared to a resolution of 0.2°, and longitudinal peak widths are 0.038 Å\textsuperscript{-1} full widths at half maximum as compared to the resolution of 0.025 Å\textsuperscript{-1}. Scans along [001] indicate that the c axis is 11.72 Å instead of 11.677 Å seen in fully oxygenated ceramics.\textsuperscript{16} Comparison with measurements of lattice parameters and superconducting transition temperatures of ceramics\textsuperscript{16} suggests that the films are oxygen deficient with a stoichiometry of 6.7–6.8.

In contrast with other Y$_3$Ba$_2$Cu$_3$O$_{7-x}$ films grown on SrTiO$_3$\textsuperscript{10,14} scans parallel to [002] such as the one shown in Fig. 3(a) show no evidence of domains with the c axis in the plane of the substrate. In one sample, however, minor amounts of domains rotated by 45° about the c axis are present as indicated by the peak at (2 0 6). The bulk of the film (~90%) consists of fully populated domains with either the a or the b axis parallel to the substrate [100].

A surprising feature of the Y$_3$Ba$_2$Cu$_3$O$_{7-x}$ films on MgO is the presence of an oriented phase with a c-axis spacing near that of MgO. The presence of this phase is demonstrated in Fig. 3(b) in the (h 0 5.56) scan. (l = 5.56 corresponds to l = 2 in MgO units.) Three peaks from MgO can be identified in the scan: (002) at (0, 0, 5.56), the forbidden (102) at (0.91, 0, 5.56), and (202) at (1.83, 0, 5.56). The two peaks marked x result from a phase with the c axis nearly equal to that of MgO (4.21 Å) and an in-plane lattice parameter nearly equal to that of Y$_3$Ba$_2$Cu$_3$O$_{7-x}$ ($\sim$ 3.85 Å). The presence of a similar peak at (1, 1, 5.56) suggests that the new phase is orthorhombic or tetragonal. So far the new phase has not been identified, although it appears to be epitaxial with the film as evidenced by the presence of 45°-rotated domains in Fig. 3(b).

In conclusion, highly oriented, epitaxial Y$_3$Ba$_2$Cu$_3$O$_{7-x}$ films have been produced in situ by molecular beam epitaxy aided with a reactive oxygen source generated by a microwave plasma. The new technique offers the dual advantages of low-temperature and low-pressure depositions. The attainment of high $J_c$ in the films grown on MgO suggests a useful application in strip line technology. Finally, the ability of maintaining a highly ordered perovskite structure in the uppermost layer represents one significant progress toward meaningful surface studies and tunnel junction fabrications.

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\textsuperscript{1}For a complete review, see D. W. Murphy, D. W. Johnson, Jr., S. Jin, and R. E. Howard, Science 241, 922 (1988), and references therein.