Molecular beam epitaxy of layered Dy-Ba-Cu-O compounds

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Heteroepitaxial Dy-Ba-Cu-O films have been grown *in situ* on $SrTiO_3$ substrates using an oxygen plasma beam and elemental source beams in a modified molecular beam epitaxy machine. By periodically shuttering the Dy and Ba beams during growth, flat surfaces of layered Dy-Ba-Cu-O compounds have been obtained. Periodic oscillations in the intensity of the *in situ* reflection high-energy electron diffraction pattern were observed during shuttered growths. Depending on growth conditions, the as-grown layers have ranged from insulating to superconducting with onset temperatures above 60 K.

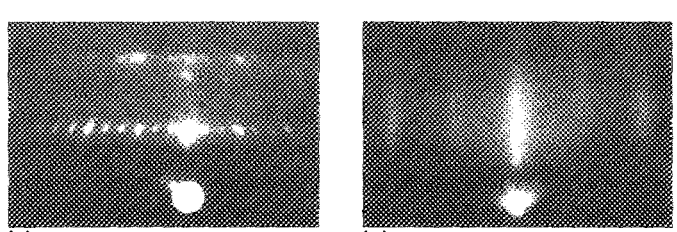
Molecular beam epitaxy (MBE) offers several potential advantages in the preparation of the recently discovered layered perovskite-related oxide superconductors. The precise thickness control available in MBE suggests that it might be possible not only to atomically layer these oxide superconductors, but also to sequentially grow layers of superconductors, metals, semiconductors, and insulators and thus create novel electronic devices. To achieve such goals, epitaxial superconducting layers must be formed *in situ*.

Using reflection high-energy electron diffraction (RHEED) to monitor the crystal structure of the growing layer, we previously demonstrated[1] that copper is not oxidized by molecular oxygen at pressures less than 10^{-5} Torr (further experiments with oxygen at pressures up to 5×10^{-4} Torr yielded the same result). Other researchers have grown superconducting layers *in situ* by electron beam (*e*-beam) evaporation,[2,3] pulsed laser deposition,[4] and sputtering[5,6] using an oxygen plasma or relatively high pressures of oxygen during growth and subsequent cool down. This letter describes our efforts to grown *in situ* epitaxial layers of Dy-Ba-Cu-O compounds by MBE using an oxygen plasma. We find that these compounds, including $DyBa_2Cu_3O_{7-x}$ superconducting phases, can be epitaxially grown on $SrTiO_3\{100\}$ substrates.[7]

The Dy-Ba-Cu-O layers were grown in a modified Varian 360 MBE machine. Conventional resistively heated MBE furnaces were used to provide stable fluxes of the constituent metals. A gridless magnetron plasma source was fabricated with a small orifice to leak oxygen species out of the plasma cavity and onto the grounded substrate. It produced a visible plume of excited oxygen which extended from the plasma source to the substrate, completely engulfing it. All the films described here were grown using this oxygen plasma source.

The growths described here were all on $SrTiO_3\{100\}$ substrates, prepared and mounted as previously described.[8] Growth temperatures between 530 and 640 °C were used. The growth rate was typically 0.6 Å/s. During growth the oxygen pressure at the substrate was typically in the mid 10^{-4} Torr range, but remained on the low 10^{-4} Torr scale in the rest of the chamber due to differential pumping.

Figure 1(a) shows the observed RHEED pattern during growth where the $SrTiO_3$ substrate was exposed continuously to dysprosium, barium, and copper beams and to an oxygen plasma beam. The presence of spots (as opposed to rings or streaks) indicates an epitaxial, atomically rough surface producing the reflection-transmission diffraction pattern observed. This diffraction pattern is not similar to the patterns observed during growth with molecular oxygen where the copper was not oxidized [compare to Fig. 1(c) of Ref. 1 or Fig. 1(b) of Ref. 8]. The presence of two dim spots between bright spots along the horizontal rows of the RHEED pattern denotes a tripled superstructure in real space. Further, the horizontal (in-plane) spot spacing is consistent with the *c* axis of the desired superconducting $DyBa_2Cu_3O_{7-x}$ phase (11.68 Å, three times as long as $SrTiO_3$, $a = 3.905$ Å) lying in the plane of the substrate. The vertical (growth direction) RHEED spacing corresponds to the growth of a (110) oriented film ($DyBa_2Cu_3O_{7-x}$



(a) (b)

FIG. 1. *In situ* RHEED pattern (7.5 keV beam energy) observed during growth with the following conditions: (a) *unshuttered*, $T_{sub}\approx550$ °C, composition $Dy_{0.18}Ba_{0.33}Cu_{0.49}O_{7-x}$, $\approx\langle110\rangle SrTiO_3$ azimuth, thickness ≈0.5 μm, oxygen plasma run with dc power supply. X-ray diffraction indicates $c = 11.60\pm0.04$ Å. (b) *"shuttered,"* $T_{sub}\approx550$ °C, composition $Dy_{0.14}Ba_{0.34}Cu_{0.52}O_{7-x}$, $\langle100\rangle SrTiO_3$ azimuth, thickness ≈0.6 μm (490 Dy-Ba-Ba layers), oxygen plasma run with rf power supply. The in-plane RHEED streak spacing is constant ($\pm2\%$), implying a tetragonal structure.

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[110]//$SrTiO_3$[001]). However, x-ray diffraction data revealed that the film was primarily *c*-axis oriented ($DyBa_2Cu_3O_{7-x}$[001]//$SrTiO_3$[001]), with only a small (110) film component. X-ray diffraction also indicated that the *c*-axis regions were aligned to the substrate with the $DyBa_2Cu_3O_{7-x}$ [100] film axis parallel to the ⟨110⟩ and ⟨100⟩ $SrTiO_3$ surface directions.

The apparent contradiction between the *in situ* RHEED orientation data and the x-ray data was resolved by examining the surface morphology of the $DyBa_2Cu_3O_{7-x}$ film. Scanning electron microscopy (SEM) revealed that the as-grown surface was quite rough with a characteristic cross-hatched structure similar to that reported by Fujita *et al.*[6] Since the RHEED beam is incident on the sample at a grazing angle, it is sensitive to only the highest portions of the film, which shade the lower portions of the film from the beam. On the other hand, x-ray diffraction is sensitive to the entire thin film. Thus, an explanation consistent with both the RHEED orientation data and the x-ray data is that (110) $DyBa_2Cu_3O_{7-x}$ plates stick up the farthest, whereas short *c*-axis plates cover the majority of the substrate surface. Growth with predominantly $DyBa_2Cu_3O_{7-x}$[110]//$SrTiO_3$[001] has been observed by transmission electron microscopy (TEM) of *in situ* superconducting films grown by *e*-beam evaporation.[2,9] We speculate that simultaneous exposure of all the elements to the substrate during growth encourages (110) film growth since $DyBa_2Cu_3O_{7-x}$ (110) planes contain all the atoms whereas the better lattice-matched $DyBa_2Cu_3O_{7-x}$ (100), (010), and (001) planes do not. The slower growth rate employed in our growth method compared to Ref. 9 allows more time for surface diffusion, perhaps allowing more of the better lattice-matched *c*-axis growth to occur in our samples.

In an attempt to obtain entirely *c*-axis film growth, the effect of periodic shuttering during growth was investigated. During a "shuttered" growth, the copper and oxygen fluxes are not interrupted, but the dysprosium and barium fluxes are periodically shuttered in order to encourage the Dy-Ba-Ba-Dy-Ba-Ba-··· *c*-axis layering of the desired $DyBa_2Cu_3O_{7-x}$ structure. Ideally, the total number of atoms in each flux burst and in each Dy-Ba-Ba cycle would equal an integral number of "monolayers."

Figure 1(b) shows the RHEED pattern observed during "shuttered" growth of a Dy-Ba-Cu-O film grown at the same substrate temperature, growth rate, and with nominally identical metal composition (as measured by electron microprobe) as the film shown in Fig. 1(a). The presence of streaks indicates either an atomically smooth epitaxial surface or one-dimensional disorder in the growth direction.[10] Since the as-grown surface appeared almost featureless when observed under a Nomarski phase-contrast microscope, we believe the former to be the case. Note that since RHEED is only sensitive to the highest portions of the film, an atomically flat surface with pits spaced farther apart than the electron penetration depth (several hundred angstroms) would still give rise to a streaked RHEED pattern. Thus, the observed streaked RHEED pattern is indicative of reflection diffraction from atomically flat terraces at least several hundred angstroms in lateral extent.

X-ray diffraction of the as-grown "shuttered" sample of Fig. 1(b) confirms that it is a highly oriented epitaxial film, layered in the growth direction. The 2θ–θ scan aligned to the $SrTiO_3${100} substrate is shown in Fig. 2. Figure 2 also shows the same 2θ–θ scan after rocking off the {100} substrate peak. The signal has been virtually reduced to background noise indicating very little random nucleation. This sample was not a superconductor as grown.

Data from a "shuttered" growth that did produce an as-grown superconductor are shown in Fig. 3. Figure 3(a) shows the RHEED pattern along the ⟨110⟩$SrTiO_3$ azimuth after the growth of about 50 Dy-Ba-Ba layers. The presence of half-order streaks indicates a doubling of the unit cell along the ⟨110⟩ direction. We have observed this same doubling in other copper-deficient samples.[11] After increasing the total amount of incident copper and dysprosium by changing the shutter parameters, these half-order streaks became more faint.[7] The substrate temperature was briefly increased until the RHEED pattern showed polycrystalline growth[7] (rings were observed above $\approx$610 °C), then lowered to 600 °C for the duration of the growth. X-ray diffraction of this sample revealed that it was mainly epitaxial, but with some randomly oriented polycrystalline material in agreement with the observed RHEED pattern.

Figure 3(b) shows the resistivity versus temperature curve for this as-grown sample. The onset temperature around 65 K is typical of nearly tetragonal $YBa_2Cu_3O_{7-x}$ with oxygen deficiency, incomplete oxygen ordering,[12] or impurity substitution.[13] Similar onsets (and broad transitions) have been observed in *in situ* layers grown by other techniques.[3,4]

A cross-sectional TEM image of the $SrTiO_3$ substrate and the first few hundred angstroms of this same Dy-Ba-Cu-O film is shown in Fig. 3(c). This TEM area corresponds to the material that was grown during the initial growth conditions of Fig. 3(a); it is most likely not the superconducting portion of the film. The abruptness of the film/substrate interface and the epitaxial alignment between the film and the substrate is evident. Single and double height layers [near the scale marker in Fig. 3(c)] coexist

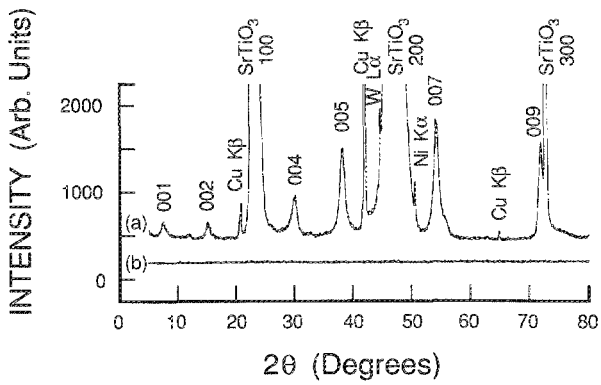
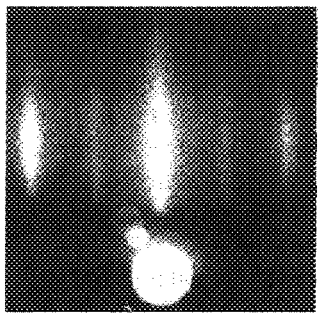
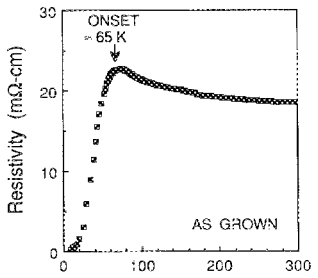
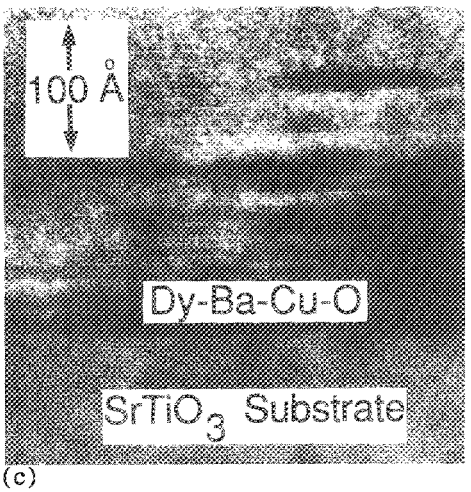


FIG. 2. (a) 2θ-θ x-ray diffraction scan aligned to $SrTiO_3${100} substrate. One film phase or orientation with set of reflections with spacing $c = 11.83 \pm 0.04$ Å (00*l* labeled peaks) and another with spacing 7.55 ± 0.1 Å (small peak at $2\theta \approx 11.7°$). Cu Kα, Cu Kβ, W Lα, and Ni Kα $SrTiO_3$ substrate reflections are labeled. Intensity offset by 250 units for clarity. (b) Same x-ray scan after rocking omega axis 5° off $SrTiO_3$ {100} peak.



(a)





(c)

FIG. 3. (a) *In situ* RHEED pattern (7.5 keV beam energy) observed during a "*shuttered*" growth with the following conditions: $T_{sub} \approx 583$ °C, ⟨110⟩ $SrTiO_3$ azimuth, thickness ≈600 Å (50 Dy-Ba-Ba layers), oxygen plasma run with rf power supply. (b) Resistivity vs temperature of as-grown sample with composition $Dy_{0.15}Ba_{0.35}Cu_{0.49}O_{7-x}$. X-ray diffraction indicates three phases: one with $a = 3.86 \pm 0.05$ Å, $c = 11.82 \pm 0.04$ Å; the second with orthogonal spacings of 4.04 ± 0.01 Å and 4.11 ± 0.04 Å; and a third with spacing 7.55 ± 0.1 Å. (c) Cross-sectional TEM photo of same sample.

along the growth direction in close proximity. This implies that the diffusion length is short under these "shuttered" growth conditions.

During several growths with an oxygen plasma, the intensity of the RHEED pattern was observed to oscillate with the shuttering period. Figure 4 shows the intensity of the central RHEED streak as a function of time for several different growths. It is not surprising that the period of the oscillation corresponds to that of the shuttering, but it is interesting to note that the shape of the oscillation changes for different growth conditions. In particular, the maximum intensity was observed to occur during the Dy burst early in growth, but later in the same growth the maximum occurred during the middle of the Ba burst (not shown). Oscillations of the RHEED pattern intensity during nonshuttered MBE growth of semiconductors and metals have been shown to correspond to a layer-by-layer two-dimensional growth mode.[14] It seems inappropriate to apply this model here; it seems more natural to attribute the oscillations shown in Fig. 4 to microscopic responses of the surface structure to changes in the incident flux. A deeper understanding of these oscillations may allow the growth conditions to be altered during growth to optimize the properties of these films.

In conclusion, the presence of an oxygen plasma is found to be crucial to the growth of epitaxial Dy-Ba-Cu-O

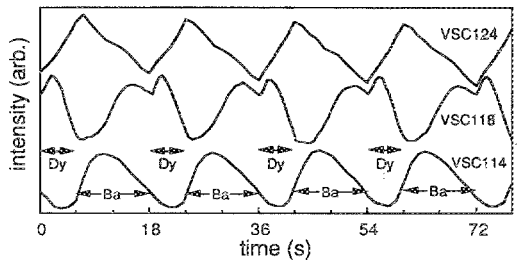


FIG. 4. Intensity of the central RHEED streak as a function of time during three different "*shuttered*" growths. During the white region the Ba shutter is open (Dy closed); during the shaded region the Dy shutter is open (Ba closed).

phases *in situ* at MBE compatible pressures ($\lesssim 10^{-4}$ Torr). Shuttering the incident Dy and Ba fluxes seems to encourage *c*-axis film growth, and yields atomically smooth surfaces under proper growth conditions. Periodic oscillations in the intensity of the RHEED pattern accompany shuttering, but are not yet understood.

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