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We have studied the microstructures of epitaxial $YbBa_2Cu_3O_7$ superconducting films grown on $SrTiO_3$[100] and [110] substrates by a new liquid-gas-solidification processing technique. Films grown on $SrTiO_3$[100] and [110] substrates are epitaxially oriented with [001] and [110] axes normal to the film surface. Twinned domains of ~200 Å in size are observed in the [001] oriented films. Most defects observed can be attributed to the presence of stacking faults along the *c* axis. The presence of Cu-O bilayer defects is also observed. Rapid oxygen diffusion in the liquid phase is found to play an important role in the microstructure of the thin films.

Recently, a new fabrication technique of superconducting thin films has been developed using the so-called liquid-gas-solidification processing.[1] The process consisted of (1) forming a melt composed of the metallic components of the compound (e.g., $YbBa_2Cu_3O_7$) to be formed, and (2) introducing the missing element, oxygen, into the precursor melt to form the oxide on a substrate. This new thin-film deposition technique is fundamentally different from other techniques such as sputtering,[2] molecular beam epitaxy (MBE),[3] pulsed laser evaporation,[4] and decomposition from solution.[5] This new processing technique is scalable and can produce single phase materials with uniform composition. In this work, we would like to report the microstructure and epitaxy of the thin films prepared by this new technique on $SrTiO_3$ substrates.

The detailed procedure of the new liquid-gas-solidification technique was described elsewhere.[1] Briefly, a precursor metallic alloy, $YbBa_2Cu_3$ in this case, was heated in an inert atmosphere to temperatures above the melting point. A $SrTiO_3$ substrate was then immersed into the melt forming a thin liquid film ~2 μm in thickness on the substrate surfaces. Oxidation of the liquid film was carried out *in situ* by introduction of oxygen gas into the melt. The resulting oxide film was annealed at 500 °C for 5 h and then furnace cooled. X-ray diffraction[1] has shown the resultant superconducting oxide film is single phase, and a T_c ($R = 0$) of 82 K with a transition width of 2 K has been achieved. The critical current density is typically 3×10^4 A/cm^2 and 10^5 A/cm^2 at 70 and 50 K, respectively. Samples for transmission electron microscopic studies were prepared by the standard method, i.e., mechanical polishing of the substrate followed by argon ion milling at 6 kV. During the final stage of ion milling, 4 kV ions were used to minimize the surface damages of the sample. We have examined both samples grown on $SrTiO_3$[100] and [110] substrates.

Examination of films grown on $SrTiO_3$[100] substrate reveals that most areas have *c* axis perpendicular to the substrate surface with *a* and *b* axes pointed along the cubic axes of the substrate. X-ray diffraction[1] has determined the crystal structure of $YbBa_2Cu_3O_7$ to be orthorhombic with lattice parameters $a = 3.808$ Å, $b = 3.887$ Å, and $c = 11.659$ Å. Since the lattice parameter of the cubic $SrTiO_3$ (3.89 Å) is within 0.2% of *b* and (1/3)*c* lattice parameters, natural epitaxial film would be [100] oriented with *b* and *c* axes in the film plane. $YBa_2Cu_3O_7$ thin films grown on $SrTiO_3$[100] by MBE, however, have exhibited both [100] and [001] orientations.[6] In the present case, we find that most of the film has [001] orientation with only a small portion of [100] orientations. It appears that the growth rate of $YbBa_2Cu_3O_7$ is highly anisotropic and it grows as a platelet with *c* axis normal to the substrate surface. Figure 1(a) shows an electron diffraction pattern from an area with [001] orientation. The sharpness of the diffraction spots and the absence of spurious spots from second phases reaffirm the high quality of the film. The splitting of diffraction spots at large scattering angles along the [110] direction due to the presence of twinning is also evident. Figure 1(b) shows a bright-field electron micrograph of the twinned domains. In general, within a small area of a few microns we find that the film grown by this new liquid-gas-solidification technique is cleaner than that obtained by the MBE technique.[3] In MBE-grown thin-film samples, the presence of Y_2O_3 particles of a few hundred angstroms in size was commonly observed. The presence of twinned domains is characteristic of $YBa_2Cu_3O_7$ superconductors in the forms of polycrystalline ceramics, single crystals, and thin films. However, the size of twinned domains could vary depending upon the details of the sample preparation procedure. For example, twinned domains varied from ~2000 Å observed in polycrystalline ceramics to ~750 Å in single crystals and to ≲350 Å in MBE films.[6] We note that the twinned domains varying in the range of 100–300 Å as shown in Fig. 1(b), are significantly smaller than that observed in samples prepared by other techniques. The size of twinned domains may play an important role in achieving high critical current density in oxide superconductors, as suggested by recent experimental evidences.[6] Figure 1(b) also shows two sets of perpendicular twinned domains with twin boundaries oriented parallel to the [110] and [1$\bar{1}$0] directions. In most cases, either in single crystals or polycrystalline ceramics, twin boundaries were formed along the [110] (or [1$\bar{1}$0]) direction throughout the whole grain typically a few microns in size. However, it is common in the present sample to find perpendicular twin domains in an area about a few microns in size. In an orthorhombic

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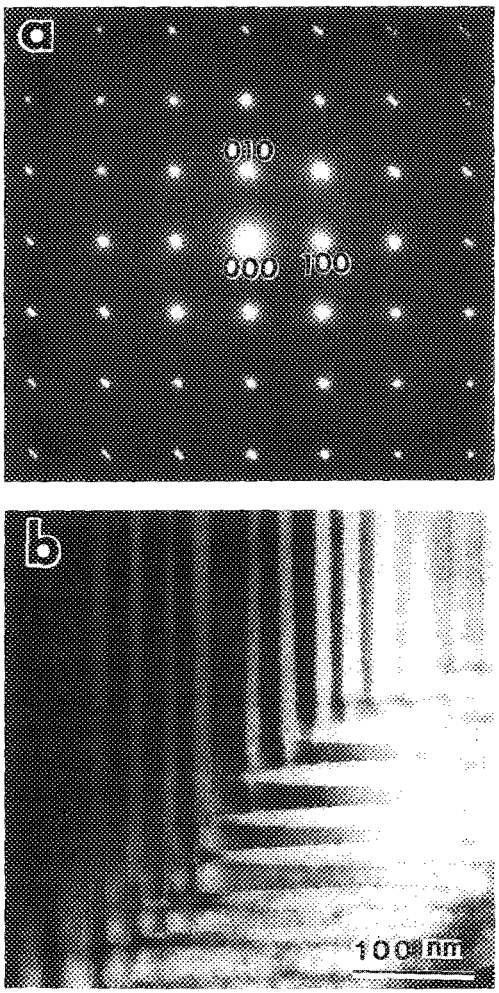

FIG. 1. (a) [001] oriented electron diffraction pattern of films grown on $SrTiO_3$[100]. (b) Bright-field electron micrograph of the twinned domains.

system the [110] and [1$\bar{1}$0] directions are equivalent crystallographically. Due to the small orthorhombicity present in the crystal structure of the 1-2-3 superconductors, the predominance of one type of twin boundaries over the other type can occur as result of anisotropic local strains during the grain growth. The anisotropic local strains could arise from different crystallographic orientation of adjacent grains of the same phase or different phases. The roughly equal abundance of [110] and [1$\bar{1}$0] twin boundaries observed in the sample prepared by the new liquid-gas-solidification technique suggests that the growth kinetics is near equilibrium due to the rapid oxygen diffusion in the melt. Oxygen diffusion in the solidified oxides is expected to be much slower. High-resolution lattice images of the [001] oriented film show regular, well ordered lattice spots reaffirming the high quality of the thin-film sample. In addition to the [001] oriented grains, we have also detected a small amount ($<10\%$) of grains with [100] orientation. Similar to the MBE-grown samples, in which the [001] and [100] oriented grains can be controlled by processing conditions, this new liquid-gas-solidification processing procedure could also produce samples with either [001] or [100] orientation on the $SrTiO_3$[100] substrate.

For films grown on the $SrTiO_3$[110] substrate, we find most areas are grown with [1$\bar{1}$0] and c axis in the plane, i.e., [110] axis normal to the substrate surface. Since the lattice spacing of (1$\bar{1}$0) planes in $SrTiO_3$ ($\sim$2.75 Å) is only about 1% bigger than the (1$\bar{1}$0) plane spacing of the 1-2-3 superconductors, we expect the [1$\bar{1}$0] and [001] directions of the substrate to be parallel to the [1$\bar{1}$0] and the c axis of the epitaxial films, respectively. A selected area electron diffraction pattern of the [110] oriented epitaxial film is shown in Fig. 2(a). The diffraction spots are again quite sharp and no extra spots due to the presence of second phases can be seen. In some areas, however, weak diffuse streaking of the diffraction spots along the c axis was observed, suggesting the presence of stacking disorder of the perovskite layers. Since the c axis lies parallel to the film surface in this case, stacking order of the perovskite layers along the c axis images, can be readily examined in the high-resolution lattice images. High-resolution images, indeed, show areas with varying degrees of stacking disorder along the c axis. Figure 2(b) shows an area exhibiting regular stacking of three perovskite layers with a periodicity of 11.7 Å. No stacking faults or other apparent defects are evident in this area. However, some areas are characterized by the presence of stacking faults as shown in Figs. 2(c) and 2(d). The 11.7 Å lattice fringes along the c axis in Fig. 2(c) are straight and regular whereas irregular spacing and slight bending of the c-axis lattice

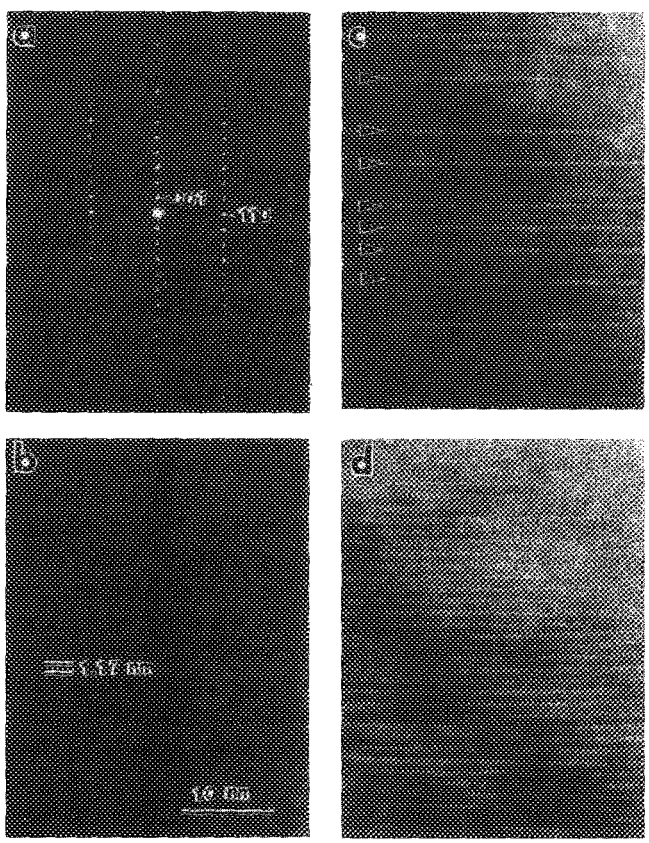

FIG. 2. (a) [110] oriented electron diffraction pattern of films grown on $SrTiO_3$[110] substrate, (b) high-resolution lattice image showing the regular layer stacking of 11.7 Å, (c) lattice image of stacking faults, as indicated by arrows, in the 1-2-3 structure, (d) lattice image showing the presence of Cu-O bilayer structure. Note that the lattice fringes along the c axis shown in (d) are now slightly curved and irregular.

fringes are observed in Fig. 2(d). The brighter lattice fringes as indicated by arrows in Fig. 2(c) are due to stacking faults which appear to be just one perovskite layer thick. Since the spacing of the stacking fault is always multiples of 11.7 Å, we conclude that the defective crystal structure still consists of three perovskite layers stacking along the c axis with no extra layers inserted. We think the stacking faults in Fig. 2(c) are defects of chemical origin such as the possibility of substituting Cu in the Cu-O layer by Y. Further studies are needed to confirm this possibility. Figure 2(d), on the other hand, shows a more irregular and defective area. The c-axis lattice fringes are no longer at a regular spacing of 11.7 Å and slight bending of the lattice fringes occurs. In many areas, 13.6 Å layers, instead of 11.7 Å, can be found. We believe that the 13.6 Å lattice spacing is due to the insertion of an extra copper-oxide layer along the c axis in the normal 1-2-3 structure. An ordered defect of this Cu-O bilayer structure occurring in a macroscopic scale has recently been produced in Y-Ba-Cu-O thin film.[7] Pure phase sample of this Cu-O bilayer structure has now been made and T_c is found to be about 80 K.[8] Most of the Cu-O bilayer defects in Fig. 2(d) are incoherent and isolated, and, as a result, the c-axis lattice fringes are now irregular and curved slightly. The presence of the Cu-O bilayer defects can be attributed to the slight excess Cu in the precursor melt. Since the diffusion kinetics in the liquid phase is much faster, the excess Cu is unlikely to confine in a macroscopic scale to form the Cu-rich phase. This is consistent with our observation that the bilayer Cu-O structure occurs as defects in the 1-2-3 structure and no ordered phase of Cu-O bilayer structure was found.

In conclusion, we have presented studies of microstructures and epitaxy of $YbBa_2Cu_3O_7$ films grown by a new liquid-gas-solidification technique on $SrTiO_3$ [100] and [110] substrates. We find that films grown by this new technique are, in general, cleaner than those obtained by the MBE technique due to rapid oxygen diffusion in the liquid phase. Twinned domains in the (001) oriented film are smaller than that observed in other types of samples. Defects of Cu-O bilayer structure along the c axis are commonly observed in these samples.

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