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We compare the superlattice modulation, microstructure, and epitaxy of $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films grown on MgO [100] and $SrTiO_3$ [100] substrates by dc diode sputtering. Films grown on MgO were found to be quite clean with the *c* axis perpendicular to the substrate. However, no in-plane orientational relationship to the substrate was found. Films grown on $SrTiO_3$, on the other hand, showed very good epitaxy to the substrate despite the presence of second phases. Films grown on MgO also exhibited a longer coherence length of the superlattice modulation than those grown on $SrTiO_3$ under identical conditions.

Immediately following the discovery of superconductivity in the bulk Tl-Ba-Ca-Cu-O system,[1,2] successful preparation of superconducting thin films of this system on the substrates of MgO, $SrTiO_3$, and yttrium-stabilized ZrO_2 has been reported.[3–6] Although high zero-resistance temperature ($T_c \simeq 120$ K) and high critical current density ($J_c \sim 10^5$ A/cm^2 at 100 K) have been achieved, the microstructure of the thin films and their epitaxy to the substrates are still largely unknown. Furthermore, the incommensurate superlattice modulation observed in the bulk samples[7–9] has not been reported in the thin-film samples.

In this letter, we report results obtained from $Tl_2Ba_2Ca_2Cu_3O_{10}$ (2223) thin films deposited on MgO [100] and $SrTiO_3$ [100] substrates. We compare the superlattice modulation, microstructure, and epitaxy of the thin-film samples grown on these two substrates. The detailed deposition procedure has been described elsewhere.[6] Briefly, thin-film samples ~ 2000 Å thick were deposited onto MgO [100] and $SrTiO_3$ [100] substrates by a dc diode getter sputtering technique. The as-deposited films were amorphous and insulating and required post-annealing at temperatures above 800 °C to become superconducting. The samples exhibit a T_c ($R = 0$) at 116 K and a $J_c \gtrsim 10^5$ A/cm^2 at 100 K. Plan-view samples were prepared by mechanical polishing followed by ion milling from the substrate side at liquid-nitrogen temperature. After the appearance of pinholes in the samples, a brief cleaning by 3 kV Ar^+ ions from both the thin-film and the substrate sides was carried out to minimize the possible damages due to ion thinning and to remove any possible deposit on the film surface during the substrate thinning process. Electron diffraction and transmission electron microscopy studies were carried out in a JEOL 2000 FX electron microscope operating at 200 kV.

We shall first present results obtained from the samples grown on a MgO (100) substrate. Electron microscope examinations show that, at least for a small area of a few microns, the film is quite clean without the presence of second phase or other inclusions. This is consistent with the x-ray diffraction study which showed that the film was single phase and impurity phases, if any, are below 1% level. Most areas (> 90%) in the sample were found to consist of large grains (~ 1 μm in size) oriented with [001] axis perpendicular to the substrate surface, although [100] oriented grains can still be seen. Since the orientation of the single crystalline substrate is fixed, epitaxial or nonepitaxial relationship between the film and the substrate can be determined by comparing the substrate orientation and the orientations of many grains in the deposited films. The orientation comparisons were carried out by electron diffraction studies. For the [001] oriented grains, we did not observe any well-defined in-plane orientation relationship between the film and the substrate. In other words, the growth of $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin film on MgO (100) substrate is not epitaxial. The preferred orientation of most grains with *c* axis perpendicular to the substrate is simply a restatement of the fact that the *c* axis is an easy-growth direction due to the nature of layer-type structure of the lattice.

Shown in Fig. 1 is a selected area electron diffraction

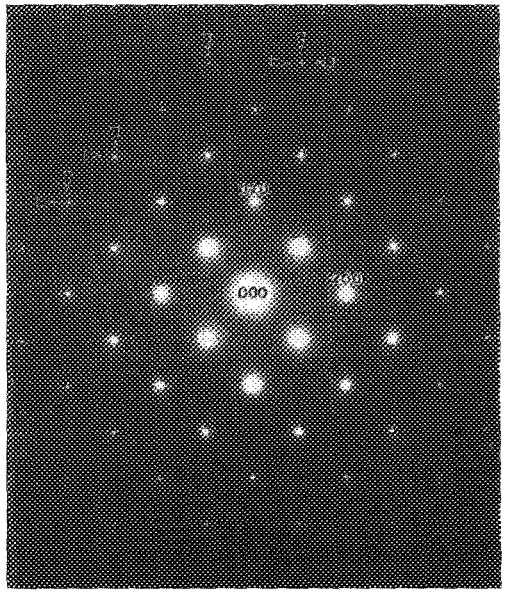

FIG. 1. [001] zone-axis electron diffraction obtained from films grown on MgO. Note the presence of superlattice spots along the [100] and [010] direction at the large scattering angles ($\theta > \theta_{200}$ or θ_{020}). Some of the superlattice spots are indicated by arrows.

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pattern from a single grain oriented along the [001] direction. It is evident that no superlattice reflections can be seen in the zeroth-order Laue zone (smaller scattering angles). Weak superlattice reflections along both [100] and [010] directions, however, are clearly visible in the first Laue zone (i.e., larger scattering angles). This observation, therefore, suggests that the superlattice reflections do not lie in the a^*-b^* plane and must have a component along the c^* direction. This is consistent with the superlattice reflections observed in the bulk ceramic samples.[7–9] The presence of the superlattice reflections can be best demonstrated by an electron diffraction pattern obtained from a grain oriented with [100] axis normal to the film surface, as shown in Fig. 2. The measured c lattice parameter of 35.6 Å from Fig. 2 is consistent with what we expect for the 2223 phase. Figure 2 shows that the superlattice reflections are characterized by an incommensurate periodicity approximately six times the b lattice parameter ($b = 3.8$ Å) and a commensurate periodicity along the c axis. In other words, the positions of the superlattice reflections are given by $\mathbf{Q} = \mathbf{G} \pm \mathbf{q}$, with $\mathbf{q} \simeq (0,1/6,1)$ being the reduced wave vector of the superlattice modulation and $\mathbf{G}$ being the reciprocal lattice vectors of the parent lattice. We note that the reduced wave vector $\mathbf{q}$ observed here for thin films is in good agreement with that reported for bulk samples.[8,9] From Fig. 1 we know that the incommensurate modulation occurs along both [100] and [010] directions; therefore, the incommensurate modulation can be described as a two-$\mathbf{q}$ incommensurate phase with $\mathbf{q} \simeq (1/6,0,1)$ and $(0,1/6,1)$.

We would like to emphasize that the intensity of the superlattice reflections observed in our thin-film samples is very uniform across the entire sample, in contrast to the polycrystalline ceramics in which fluctuation of superlattice intensity from sample to sample or grain to grain in a given sample was commonly observed. This indicates that the thin film sample is far more homogeneous than the bulk ceramic samples.

A high-resolution lattice image obtained from a [100] oriented grain is shown in Fig. 3. The stacking of Tl bilayers is very regular without stacking defects such as the intergrowth of perovskite layers of different number of Cu-O layers—a defect commonly observed in the Bi-based superconductors.

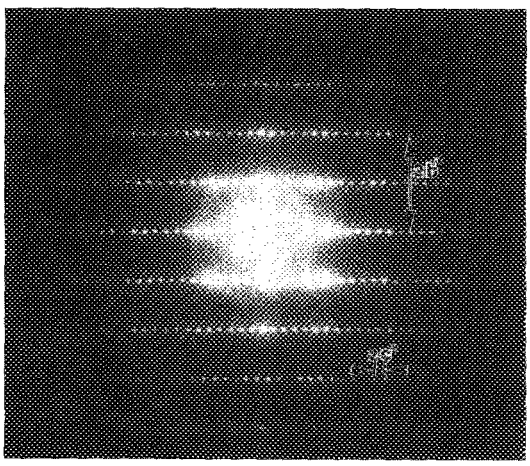

FIG. 2. [100] zone-axis electron diffraction pattern showing the existence of the superlattice reflections.

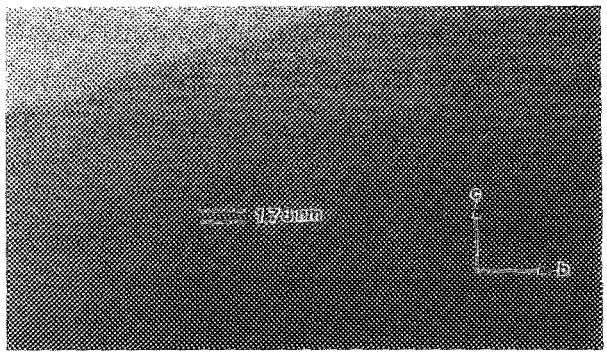

FIG. 3. High-resolution lattice image along the [100] zone axis. It shows very regular stacking of the perovskite layers without any apparent defects.

The incommensurate superlattice reflections shown in Fig. 2 are very similar to that observed in the Bi-based superconductors, in which the incommensurate periodicity is 4.76 times the b lattice parameter. However, it should be noted that the a and b axes of the orthorhombic Bi-based superconductors are defined to be 45° off from the a, b axes ($a = b$) in the tetragonal Tl-based superconductors, and therefore, the lattice parameters of a and b in the Bi superconductor are $\sqrt{2}$ times larger than the a lattice parameter in the Tl superconductors. The periodicity of the incommensurate modulation is ~23.4 Å (i.e., 6×3.9 Å) in the Tl-based superconductors, which is close to the 25.6 Å periodicity observed in the Bi-based superconductors. We also note that the intensity of the superlattice reflections as shown in Fig. 2 is much weaker than that observed in Bi superconductors. The incommensurate modulation in the Tl-superconductors is believed to be due to periodic chemical substitution by Ba/Ca ions[7] in the Tl-double layers along the a and b axes, in a manner similar to that observed in the Bi-based superconductors.[10,11] The weaker intensity of the superlattice in the Tl-based superconductors is probably a result of smaller lattice distortion induced by the chemical substitution. It has been shown that the lattice distortion associated with superlattice formation is quite large (up to 0.4 Å) in the Bi superconductors.[12]

For the films deposited on $SrTiO_3$ [100] substrate, we found that they were not as clean as those grown on MgO. Transmission electron microscopy and electron diffraction studies showed the existence of at least two impurity phases, although no effort was taken to identify these phases. The typical grain size of the superconducting 2223 phase is ~1μm. Selected area electron diffraction studies (see Fig. 4) of the 2223 phase showed that the film exhibited very good epitaxy to the substrate, in contrast to the films deposited on MgO. Electron diffraction studies of many grains revealed that the epitaxial thin film was grown with the c axis perpendicular to the substrate and the a and b axes of the films parallel to the two cubic directions of the $SrTiO_3$ [100] surface. The epitaxial growth has also been confirmed by x-ray diffraction studies.[13] Apparently, the good epitaxy arises from the close lattice match between the $SrTiO_3$ substrate and a/b lattice parameters of the 2223 phase. Although the film was dominated by grains with c axis perpendicular to

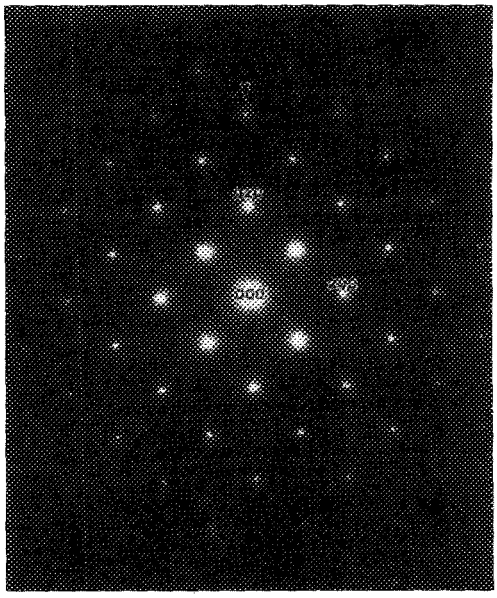

FIG. 4. [001] zone-axis electron diffraction pattern obtained from films deposited on $SrTiO_3$ substrate. Note the presence of diffuse rings around each main Bragg reflections at large scattering angles. The diffuse ring around the (040) Bragg spot, for example, is indicated by an arrow.

the substrate, grains with c axis parallel to the substrate surface were also present.

Incommensurate modulations for films grown on $SrTiO_3$ can also be seen at large scattering angles in the [001] zone axis diffraction pattern shown in Fig. 4. However, close examination of the incommensurate superlattice reflections reveals that it is not as sharp as those obtained from films deposited on MgO (Fig. 1). Instead, diffuse rings surrounding the main Bragg reflections at large scattering angles were observed. The diffuse diffraction intensity was observed at reciprocal lattice positions of $\mathbf{q} = \mathbf{G} + A\mathbf{a}^* + B\mathbf{b}^*$ with $A^2 + B^2 \simeq 1/6$ and G a reciprocal lattice vector of the main lattice. The intensity around the diffuse rings, however, is not uniform; it peaks along the [100] and [010] directions. The diffuse diffraction rings shown in Fig. 4 are very similar to those observed in the rapid-quenched bulk 2212 ceramic sample.[7] The coherence length of the incommensurate modulation is ~ 30 Å as estimated from the diffuse scattering intensity. This is much shorter than the coherence length of ~ 150 Å observed in films grown on MgO substrates. The reason for this difference in coherence length is not clear at this moment, although it is possible that the presence of second phases and other inclusions in the films grown on $SrTiO_3$ might alter the stoichiometry of the 2223 phase, which in turn could affect the coherence length of the incommensurate modulation. In fact, electron micrographs obtained from the superconducting 2223 phase show the presence of very small (~ 30 Å) speckles all over the sample which could be indicative of slight phase separation or decomposition in the films deposited on $SrTiO_3$. We have also confirmed the weak and diffuse modulation reflection in the electron diffraction patterns obtained from grains oriented with the c axis parallel to the substrate surface.

In summary, we have studied the epitaxy, microstructure, and incommensurate modulation of $Tl_2Ba_2Ca_2Cu_3O_{10}$ thin films grown on MgO [100] and $SrTiO_3$ [100] substrate. Very good epitaxy was observed for films deposited on $SrTiO_3$ substrates. However, these films were not as clean as those deposited on MgO. Stronger and sharper superlattice reflections from the incommensurate modulation are observed in films grown on MgO. The coherence length of the incommensurate modulation was estimated to be ~ 150 Å in MgO-grown films and ~ 30 Å in $SrTiO_3$-grown films.

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