Structural characterization of YBa$_2$Cu$_3$O$_{7−δ}$/Y$_2$O$_3$ composite films

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Using 4-circle x-ray diffraction and transmission electron microscopy we have studied the microstructure and in-plane orientation of the phases present in thin film composite mixtures of YBa$_2$Cu$_3$O$_{7−δ}$ and Y$_2$O$_3$. We see a high degree of in-plane orientation and have verified a previous prediction for the in-plane order of Y$_2$BaCuO$_5$ on (110) MgO. Transmission electron microscopy shows the composite films to be a mixture of two phases, with YBCO grain sizes of $\approx 1 \mu m$. We have also compared our observations of the in-plane order to the predictions of a modified near coincidence site lattice model.

I. INTRODUCTION

In thin film growth of YBa$_2$Cu$_3$O$_{7−δ}$ (YBCO), it is useful to understand the nature of the epitaxial relationships present between impurity phases in the films. This knowledge provides a guide for finding these phases by x-ray diffraction, as seen in the study of CuO in YBCO films by Watson et al. [1] Also, in a previous report on thin film composites of YBCO and yttria, [2] we predicted the in-plane orientation of the phase Y$_2$BaCuO$_5$ (Y-211) which was found in composites grown on (110) MgO. In this work, we have studied the microstructure and in-plane orientation of the phases present in thin film composites of YBCO and yttria grown on (100) and (110) MgO. In particular, we have studied how the YBCO, yttria, and Y-211 phases grow in relation to the underlying substrate, to understand how these phases appear as impurities in YBCO and to verify our previous prediction.

II. SAMPLE PREPARATION

The samples were grown by off-axis sputtering onto commercially polished (100) and (110) MgO substrates. [3] YBCO and yttria were cosputtered in a 100 mTorr gas mixture of 80% argon and 20% oxygen at a total growth rate of $\approx 440$ Å/hour. Under the growth conditions used they would ideally be composed of 91% YBCO and 9% yttria by volume. The substrates were at a temperature of $\approx 700 \, ^\circ C$, and after the growth were furnace cooled in 100 Torr of oxygen. Film thicknesses were $\approx 1900$ Å. The samples were studied by 4-circle x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD was carried out on a Phillips 4-circle diffractometer. The orientation of the films was determined by standard $\theta−2\theta$ scans with diffraction along the sample normal. The crystal quality was studied using rocking curves for diffraction along and at various angles to the sample normal. In-plane order was measured by taking $\phi$ scans where the diffraction vector for a particular value of $2\theta$ is at an angle (90- $\chi$) to the sample normal and $\phi$ is the angle of rotation about the sample normal. The TEM analysis was performed on a JEOL 200CX microscope using conventional bright field (BF) and selected area diffraction (SAD) conditions on plan view specimens.

To interpret the in-plane order observed and compare lattice matching of the phases to the substrate and to each other, previous work has used a near coincidence site lattice theory (NCSL). [4] In this model (for the case when the lattice direction along the growth direction is already determined) the mismatch between the film surface mesh and the substrate surface mesh is given as the percentage difference of the respective position vectors with respect to their average lengths. Since this approach only compares discrete orientations between the two meshes, we have used a computer model to study the matching of an N x N mesh of an overlayer onto the substrate mesh for arbitrary angles between the two meshes. We have a rectangular overlayer with lattice constants a and b in the directions $\hat{x}$ and $\hat{y}$, and a rectangular substrate mesh with corresponding lattice constants c and d in the directions $\hat{x}'$ and $\hat{y}'$, where the primed system is rotated by an angle $\theta$ with respect to the unprimed system. Then for each overlayer lattice point, $i,j = ia\hat{x} + jb\hat{y}$, the program finds the corresponding closest lattice point in the substrate layer, $i,j = kc\hat{x}' + ld\hat{y}'$, computes the strain for that point, and averages over all overlayer points (excluding the origin):
We then look for minima in the strain as a function of angle between the lattices that will indicate a preferred orientation of the overlayer on the substrate.

\[ Strain = \frac{1}{N^2 - 1} \sum_{i,j=0 \atop (i,j) \neq (0,0)}^{N} 2 \left( \frac{\vec{r}_{ij}^s - \vec{r}_{ij}^o}{\vec{r}_{ij}^s + \vec{r}_{ij}^o} \right) \]  

(1)

III. RESULTS

We first consider the composite on (100) MgO, which from \( \theta - 2\theta \) XRD shows the presence of YBCO and yttria in the film. The YBCO phase is c-axis oriented with a lattice constant of 11.714 \pm 0.004 \text{ Å}. The rocking curve width for the YBCO 005 peak is 0.64°, with a comparable width for the YBCO 309 peak. The yttria in the film is oriented (001) with a lattice constant of 10.594 \pm 0.004 \text{ Å}, with a rocking curve width for the yttria 004 peak of 0.98°. The width for the yttria 226 peak is comparable to that of the 004 peak.

In Fig. 1, we present plots of x-ray intensity versus the angle \( \phi \) for the MgO 402, YBCO 309, and the yttria 226 peak. We find in contrast to the case of pure YBCO on (100) MgO \( \| \) [010] MgO. A smaller amount of YBCO is in the usual cube-on-cube orientation. We find from the \( \phi \) scans that the bulk of the yttria is oriented as cube-on-cube, or [100] YBCO \( || \) [001] MgO. A smaller amount oriented at 45°, or [110] yttria \( || \) [010] MgO. We also see that the mosaic spread in the \( \phi \) scan is substantially broader for the yttria peaks, with the FWHM being \( \approx 7° \), but only \( \approx 2.5° \) for the YBCO peaks. This larger peak width is consistent with the larger rocking curve width seen for the yttria. Comparing the YBCO \( \phi \) scan to that for the yttria, we see that the YBCO is oriented with respect to the yttria as [110] YBCO \( || \) [100] yttria, which was seen in studies of yttria on YBCO layers. We also see that the intensities of the two phases track as a function of the angle \( \phi \). This tracking implies that the matching for the YBCO present in this sample is predominantly with the yttria, not the MgO.

Figure 2 shows a TEM BF image of the composite sample on (100) MgO. There are two phases clearly present: equiaxed, highly-faceted islands approximately 1 \( \mu \text{m} \) in diameter partially surrounded by a thin phase. We see a high degree of connectivity between the islands in this sample. Analysis of SAD images (not shown) reveals that the islands are c-axis oriented YBCO and the phase between the YBCO grains is (001) oriented yttria. In addition, SAD analysis shows an in-plane orientation relationship of the [101] direction of yttria parallel to the [100] or [010] axis of YBCO, which agrees with what was seen in the XRD analysis. The variation in contrast among the YBCO islands is due to their varying thickness. We estimate that the volume fraction of YBCO is 93 \pm 4\%, with the uncertainty being due to contrast variation.

Using our lattice model for the case of the composite film on (100) MgO, we compared the matching of yttria (001) to MgO (100), and because the YBCO in this sample seemed to be oriented with the yttria, we also compared the matching of yttria (001) to YBCO (001). For yttria we used \( a=b=10.6 \text{ Å} \). For yttria (001) on (100) MgO, we find that there is a strong minima at 0° and another at 23°, but not at 45°. (The corresponding NCSL parameters for these lattice matchings would be \( \sigma_{\text{YBCO}}/\sigma_{\text{MgO}}=4/25, 4/29, \) and 9/50, respectively, with NCSL lattice mismatches of 0.88%, 6.6%, and 6.4%, respectively.) Experimentally, we do not see any yttria misoriented by 23°, but we do observe it at 45°. For YBCO on yttria, we find a clear minima for the 45° alignment, as seen in the films, as well as weaker minima at 0° (cube-on-cube), 14°, and 21°, which we do not observe. (The corresponding NCSL parameters for these lattice matchings would be \( \sigma_{\text{YBCO}}/\sigma_{\text{MgO}}=8/1, 9/1, 41/5, \) and 29/4, respectively, with NCSL lattice mismatches of 1.4%, 7.3%, 2.6%, and 3.5%, respectively.) From the data and the results of the model, we believe the \( \phi \) scan in Fig. 1 can be explained by two types of microstructure in this sample. The first is where yttria is the initial phase growing on the MgO, and orients as cube-on-cube, and the YBCO that grows subsequently is misoriented by 45°. This type of microstructure is the predominant one in the sample. The second is where YBCO nucleates first on the MgO, growing as cube-on-cube, and the yttria that grows subsequently is misoriented by 45°. Careful study of the SAD images did show evidence of extra diffraction spots, which are most likely due to double diffraction. This would be consistent with the yttria and YBCO phases being on top or underneath each other.

Next, we turn to the composite sample on (110) MgO. As was discussed in Ref. 2, this sample was deposited in the same run as the composite sample on (100) MgO. However, XRD shows no yttria in the film, but instead indicates a-axis oriented Y-211 material. The sample was deposited, however, on top or underneath each other.

If we look at the \( \phi \) scans for peaks from MgO 240, YBCO 309 and Y-211 320, as in Fig. 3, we see that the YBCO is oriented with [100] YBCO \( || \) [001] MgO.
The Y-211 material is predominantly oriented as $[010]$ Y-211 $\parallel [001]$ MgO, with about 10% (by volume) of the Y-211 material oriented as $[010]$ Y-211 $\parallel [110]$ MgO, or a 90° misorientation. In Ref. 3, we predicted that the in-plane order of the (100) Y-211 material on the (110) MgO substrate would be $[010]$ Y-211 $\parallel [001]$ MgO and $[001]$ Y-211 $\parallel [110]$ MgO. This is what is seen for the bulk of the Y-211.

Figure 2 is a TEM BF image of the composite sample on (110) MgO, which clearly shows a two phase structure consisting of irregular-shaped, slightly faceted islands of average width 0.5 $\mu$m surrounded by a sea/matrix. Analysis of the SAD images shows the island phase to be c-axis oriented YBCO. Rotational spot splitting is also observed, which results from twinning within the islands of YBCO. The matrix phase is single phase a-axis oriented Y-211. SAD patterns from different parts of the sample had the same orientation, indicating the Y-211 grains are single domain over the region examined ($\approx 2\mu$m). Figure 3 shows a small amount of connectivity between the YBCO islands, but for the most part they are isolated. This result is consistent with the sample being insulating.

For the composite sample on (110) MgO, we used Eq. 1 to model the matching of Y-211 (100) to MgO (110) using for Y-211 lattice parameters $b=12.16 \pm 0.04\,\text{Å}$ and $c=5.656 \pm 0.002\,\text{Å}$ (measured for this sample). We find the strongest minima for the predominant orientation of $[010]$ Y-211 $\parallel [001]$ MgO, but the 90° orientation $[010]$ Y-211 $\parallel [110]$ MgO also has a strong minima. There is also a weak minima for 45° oriented material. (The corresponding NCSL parameters for these lattice matchings would be $(k,l)_{Y-211} / (k,l)_{MgO} = (1,0) / (3,0)$, $(0,3) / (4,0)$, and $(1,1) / (1,2)$, respectively, with NCSL lattice mismatches of 1.4%, 0.92%, and 6.1%, respectively.) For the case of Y-211 (100) to YBCO (001), we find the best match at a 45° misorientation, and weaker minima for either Y-211 [010] or [001] YBCO [100]. (The corresponding NCSL parameters for these lattice matchings would be $(k,l)_{Y-211} / (k,l)_{YBCO} = (0,1) / (1,1)$, and $(0,2) / (0,3)$, respectively, with NCSL lattice mismatches of 5.1%, and 0.77%, respectively.) Since we did not observe the 45° misorientation in the x-ray scans, we conclude that the Y-211 and YBCO phases grow on the (110) MgO substrate, unlike the case for a composite sample on (100) MgO with YBCO and yttria, where the evidence is that the bulk of the YBCO grains grow on yttria, not on the (100) MgO.

IV. DISCUSSION

One of the major motivations for this work was to understand why different phases form on (100) MgO than (110) MgO substrates for composite samples. The in-plane ordering we observe suggests that phase formation is driven by lattice matching to the substrate. However, if we use Eq. 1 to predict how yttria or Y-211 will grow on the two orientations of MgO, the results do not agree with our XRD studies. For (001) yttria, the model predicts a lower strain for growth on (100) MgO compared to (110) MgO. For a-axis oriented Y-211, the model also predicts a lower strain for growth on (100) MgO, not (110) MgO, with an in-plane orientation at 45°. These results suggest that if substrate lattice matching is driving the formation of Y-211 on (110) MgO, then Y-211 should also form on (100) MgO. Our studies show otherwise.

Another approach to understanding the growth of Y-211 on (110) MgO is to assume it is controlled by the bulk phase diagram for the Y-Ba-Cu-O system. We would estimate from the location of the composite sample on (110) MgO in the Y-Ba-Cu-O phase diagram (in Ref. 2) that there should be 49% YBCO, 39% Y-211 and 12% CuO by volume. However, from Fig. 4 we find that the volume fraction of YBCO is only 35%, and neither XRD or TEM shows the presence of CuO in the films. Clearly the growth mechanism on (110) MgO is not fully understood.

V. CONCLUSIONS

We have seen by both XRD and TEM that composite films of YBCO and yttria exhibit a great deal of in-plane orientation. We have successfully verified the prediction in Ref. 3 that composites grown on (110) MgO have a-axis oriented Y-211 present with a predominant in-plane orientation of $[010]$ Y-211 $\parallel [001]$ MgO, but some fraction of the Y-211 phase is oriented at 90° to this. The composites on (001) MgO show in-plane orientations that indicate two types of microstructure, either yttria on YBCO or YBCO on yttria. The sizes of the YBCO grains are $\approx 1\,\mu$m for the composites on (100) MgO, while on (110) MgO YBCO forms oblong islands of up to several microns in length. Our attempts at studying the lattice matching using a modified near coincidence site lattice model did show that we could understand the observed in-plane orientations, but could not explain the occurrence of different phases growing on (100) and (110) MgO.

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FIG. 1. X-ray intensity (log scale) versus $\phi$ for diffraction along the yttria 226, YBa$_2$Cu$_3$O$_{7-\delta}$ 309 and the MgO 402 peaks for the composite sample grown on (100) MgO. The curves are offset for clarity.

FIG. 2. Bright field plan view TEM images for the composite sample grown on (100) MgO showing YBCO grain structure with yttria at the grain boundaries. The darker faceted islands are the YBCO phase, with the yttria phase showing up as white in the grain boundaries.

FIG. 3. X-ray intensity (log scale) versus $\phi$ for diffraction along the Y$_2$BaCuO$_5$ 320, YBa$_2$Cu$_3$O$_{7-\delta}$ 309 and the MgO 240 peaks for the composite sample grown on (110) MgO. The curves are offset for clarity.

FIG. 4. Bright field plan view TEM image for the composite sample grown on (110) MgO showing the morphology of the sample at low magnification. The lighter region is the Y-211 phase, with the YBCO phase in oblong islands.
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