Microstructure of superconducting $YBa_2Cu_3O_{7-\delta}$ thin films on Si and alumina substrates with buffer layers

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(Received 26 May 1989; accepted for publication 28 July 1989)

The microstructure of $YBa_2Cu_3O_{7-\delta}$ (YBCO) films grown on silicon and alumina substrates with yttria-stabilized zirconia (YSZ) buffer layers has been studied by transmission electron microscopy (TEM) and x-ray diffraction. The as-deposited films are not amorphous, but are in fact composed of small crystalline grains. The top surface of the post-annealed YBCO film consists mainly of the orthorhombic structure of YBCO with large grains. Other phases are present within the films and have been identified. The presence of a very thin interdiffused layer of $BaZrO_3$ between the YSZ and the YBCO has been shown by cross-sectional TEM.

I. INTRODUCTION

The use of materials with relatively low microwave dielectric losses such as silicon, alumina and sapphire as substrates for high-temperature superconductor thin films is becoming more common. Using these "difficult" substrates, much progress has recently been made towards understanding how different growth process parameters affect the quality of the resultant thin film. For example, the beneficial use of buffer layers as diffusion barriers between the thin film and the substrate has now been firmly established[1–9] and the use of relatively low process temperatures during oxygen annealing has resulted in higher-quality films (higher critical currents and temperatures).[6,10,11] High-temperature annealing changes the film composition[3] and promotes interdiffusion between the superconductor and the substrate. These anneals also produce cracks in the superconductor due to the different thermal expansion coefficients of the various materials. These effects drastically reduce the measured critical currents and temperatures for the films.

We have investigated the use of silicon and alumina as substrates for $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films,[1–3] deposited by single target rf diode sputtering. We have shown that the initial buffer layer film thickness is a major factor controlling its post-annealed preferred texture,[2,3] when deposited on silicon, and have improved the quality of our YBCO thin films by using buffer layers as diffusion barriers between the superconductor and the substrate.[1–3] We have also studied the compositional effects of sputtering pressure, rf input power, and post-deposition anneal temperature and duration.[3] We have thus obtained YBCO thin films with zero resistance ($\rho < 10^{-7}\ \Omega$ cm) temperatures as high as 63 and 73 K with alumina and silicon substrates, respectively. In this paper we focus on the microstructure of the films, studied by x-ray diffraction and transmission electron microscopy (TEM). We will present detailed TEM photographs of the top surface of the films. The as-deposited films are not amorphous, as usually reported by others, but are composed of small grains with tetragonal structure. We will show the importance of controlling post-anneal process parameters. The post-annealed films are composed of large grains of sizes between 100 and 200 nm. These grains are randomly oriented on silicon substrates and show evidence of *c*-axis orientation on alumina substrates. The top surface of the YBCO film is composed mainly of the orthorhombic phase of YBCO. Other phases are present within the films and have been identified by TEM and x ray. We will also show that the yttria-stabilized zirconia (YSZ) buffer layer indeed acts as a diffusion barrier between the superconductor and the substrate.

Cross-sectional TEM studies reveal large stress at the buffer layer-substrate interface and a very narrow interdiffused layer between the YSZ and the YBCO. We emphasize the result that this interdiffused zone has been measured to be approximately 30 nm thick and is composed of $BaZrO_3$. We believe that a quantitative measurement of the thickness of the interdiffused layer between YBCO and YSZ, as well as the clear cross-sectional TEM imaging of the substrate-buffer layer-superconductor interface has not yet been made in this system. This interdiffused layer is very thin compared to the thickness of both the YSZ and YBCO films, indicating that whilst interdiffusion processes are present, they are minimal. The successful growth of very thin (<200 nm) YBCO films on silicon by single target sputtering should be thus possible with the use of YSZ buffer layers.

II. EXPERIMENTAL DETAILS

rf diode sputtering, using 100% argon gas and without deliberately heating the substrates, was used for all the depositions. YSZ buffer layers, 3000–5000 Å thick, were sputtered at 25 mT from a 10% Y_2O_3/90% ZrO_2 (by weight) polished polycrystalline 5-cm-diam target.[2,3] YBCO targets were prepared by mixing the appropriate amounts of Y_2O_3, BaO and CuO powders, pressing the mixture into disks, and

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annealing the resultant target under an oxygen atmosphere. Superconducting films used in this work were sputtered at 90 mT argon pressure from a 5-cm-diam $YBa_{2.75}Cu_{3.45}$ oxide target in the case of depositions on silicon substrates and from a $YBa_{2.6}Cu_3$ target in the case of alumina substrates. The post-deposition anneal of the YBCO film (under an oxygen atmosphere) consisted of a ramp up at 2 °C/min with 1-h steps at 300, 400, 500, and 600 °C, a hold for 30 min at 810 °C, and a ramp down at 1 °C/min with the same steps as during the ramp-up.[3] After the anneal the films deposited on silicon had a $YBa_{2.1}Cu_{2.8}$ composition, as determined by energy-dispersive x-ray analysis (EDS), films deposited on alumina had a copper-deficient $YBa_2Cu_{2.4}$ composition. EDS measurements were performed in a CamScan Series 4 scanning electron microscope operating at 25 keV. Studies of film composition were done using a Princeton Gamma Tech System 4 x-ray analyzer using a bulk $YBa_2Cu_3O_{7-\delta}$ sample as a standard. Before every EDS measurement on unknown films, the standard was measured as an unknown to confirm the system's calibration.

X-ray diffraction measurements were obtained using a Rigaku θ-2θ diffractometer with Cu$K\alpha$ radiation. For TEM studies, performed using a Philips EM 420T analytical electron microscope at 120 keV, plane view samples were mechanically ground from the substrate side on emery paper using a lapping oil. For cross-sectional view samples, two thin films were imbedded in epoxy face to face and subsequently sliced using a wire saw. In both cases ion milling to electron transparency was performed with and without a cold stage. The crystallographic orientation of the film was determined using a combination of selected area diffraction (SAD) and microdiffraction patterns, as well as x-ray diffraction patterns.

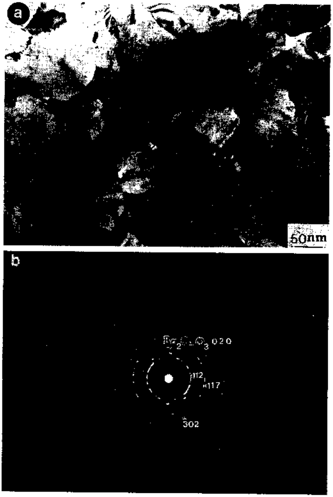

FIG. 1. (a) TEM plane view and (b) a representative SAD pattern of as-deposited Y-Ba-Cu-O on Si. The arrow denotes a twinned grain with orthorhombic structure.

III. RESULTS AND DISCUSSION

It is reported[12,13] that, when grown at low (<300 °C) substrate temperatures, as-deposited YBCO films appear to be amorphous by x-ray diffraction. Indeed, x-ray diffraction patterns of our as-deposited films show a featureless spectrum: These patterns do not exhibit peaks associated with any of the crystalline phases of YBCO. However, TEM plane views of the as-deposited YBCO films indicate that they are composed of small crystalline grains (60–120 nm) predominantly with the tetragonal $YBa_2Cu_3O_6$ structure (see Fig. 1). The identification of tetragonal YBCO was made by matching the observed d spacings to their known values. The tetragonal grains should not have twins since they formed directly. However, some grains do show twinning and hence are probably of the orthorhombic structure (arrow in Fig. 1). It should be noted however that Ba_2CuO_3 seems to be present as well, as observed in SAD patterns (see the extra reflections in Fig. 1). All these phases consist of grains that are small and randomly oriented and thus are thought to produce the featureless x-ray spectrum.

A typical resistivity-versus-temperature curve of the as-deposited films follows semiconducting behavior. Even though we do not deliberately heat the substrates during the deposition, temperature measurements using a thermocouple resting on top of the substrate have shown that heating due to the argon plasma raises the substrate temperature to 100–500 °C, depending on power levels used. This could account for our microscopic observations. We note that localized heating during specimen preparation for TEM by ion milling without a cold stage could in principle cause crystallization from the amorphous phase. We do not believe this to be the case because we observe small crystalline grains on as-deposited samples which have been prepared by cold stage ion milling. The presence of two phases (i.e., $YBa_2Cu_3O_6$ and Ba_2CuO_3) is not surprising since we used an $YBa_{2.75}Cu_{3.45}$ off-stoichiometric target.

Figures 2 and 3 are TEM micrographs and electron diffraction patterns of annealed YBCO films. In general the films contain copious twins and show a zero-resistance ($\rho < 10^{-7}$ Ω cm) temperature $T_c \approx 60$–75 K. We have observed untwinned grains infrequently, even after post-deposition annealing. Figure 2 shows a TEM micrograph (a) as well as SAD (b) and microdiffraction (c) patterns of these un-twinned grains. Their size (70–110 nm) is generally smaller than that of the twinned grains. We identify them by TEM microdiffraction patterns as Y-absent grains of Ba_2CuO_3 with the orthorhombic structure ($a = 1.296\,55$ nm, $b = 0.410\,07$ nm, $c = 0.390\,69$ nm).[14] We have also observed this phase in our x-ray spectra.

Figure 3 shows typical bright-field micrographs of the annealed YBCO film near the top surface, on Si (a) and

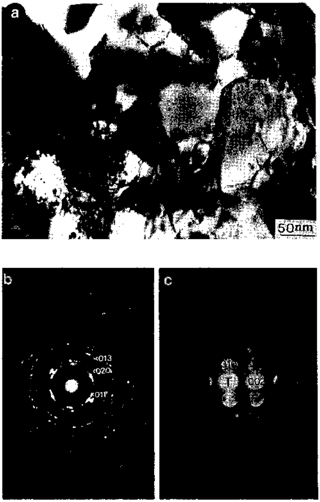

FIG. 2. (a) TEM micrograph, (b) SAD, and (c) microdiffraction ([1$\bar{3}$0] zone axis) patterns of Ba_2CuO_3.

Al_2O_3 (b) substrates, together with their microdiffraction patterns (c) and (d). The films are composed of equiaxed and platelet grains of size 100–200 nm. Smaller grains (size less than 70 nm) do not reveal any twinning [arrow A in Fig. 3(a)], consistent with previous observations.[15] Larger grains show the presence of numerous narrow twins. The width of the twins is approximately 10 nm which is rather narrow when compared to values typical of the bulk material. These narrower twin widths have also been observed in smaller grains in bulk YBCO alloy.[15] Thus, the narrowness of the twin width is likely to be due to a grain size effect but not to the lattice mismatch between the superconductor film and the substrate[16] since the lattice mismatch would not affect the top layers of the YBCO films, as will be discussed below with respect to Fig. 4. The nonsuperconducting tetragonal phase of YBCO does not have twins, suggesting that the top surface is comprised of the YBCO orthorhombic structure. In general the microstructural characteristics of the films on silicon and alumina substrates are quite similar. However, the SAD and microdiffraction patterns [see Fig. 3(c)] reveal that many of the grains on the alumina substrate are beginning to be c-axis textured normal to the film plane; while the grains on the Si substrate are observed to be randomly oriented. This could be due to the difference in substrate lattice parameters. This is consistent with x-ray results in that the observed $(00l)$ peaks are relatively stronger in the case of alumina substrates.

We have found that the critical temperature T_c of the annealed YBCO films depends strongly on the annealing temperature and cycle, in agreement with other results[5]; high T_c grains with a and b axes in the film plane were obtained at 900 °C. This is consistent with other results where the growth rate of c-axis oriented grains is fastest at 900 °C,[17] and for a and b axis orientation at 850 °C.[18] Rounded precipitates frequently form within high T_c grains in both specimens [arrow B in Figs. 3(a) and 3(b)]. These precipitates formed during the post-deposition anneal since no precipitates within the grains of the as-deposited films have been observed. The microdiffraction patterns of the precipitates observed in the post-annealed films [see, for example, Fig. 3(d), which is representative of many such patterns] are consistent with the $BaCuY_2O_5$ orthorhombic structure[19]

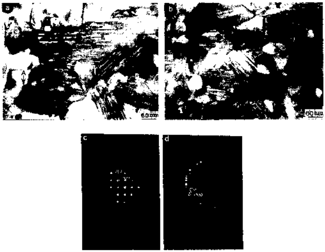

FIG. 3. Bright-field image of annealed YBCO on (a) silicon and (b) alumina. The arrow (A) shows an untwinned grain of size less than 70 nm. The arrow (B) shows a $BaCuY_2O_5$ precipitate, the microdiffraction pattern (near [001] zone axis) of which is shown in (d). (c) is the microdiffraction pattern of YBCO on Al_2O_3 ([001] zone axis).

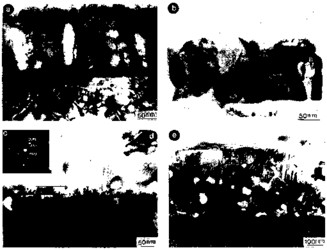

FIG. 4. Cross-sectional TEM view of Al_2O_3/YSZ/YBCO. Arrows in (a) and (b) show equiaxial and columnar YSZ buffer layer grains. (c) and (d) Thin ($\simeq 30$ nm) interdiffused $BaZrO_3$ layer between the YBCO and the YSZ.

($a = 0.713\ 19$ nm, $b = 1.218\ 02$ nm, $c = 0.565\ 93$ nm). This is inconsistent with other work in which similar precipitates have been identified as Y_2O_3 and CuO,[20] as well as $Cu_2Y_2O_5$.[5] The observation of this $BaCuY_2O_5$ phase could be explained by the fact that the post-annealed film compositions ($YBa_{2.1}Cu_{2.8}O_x$ on silicon and $YBa_2Cu_{2.4}O_x$ on alumina) are Y and Ba rich and Cu poor with respect to (1,2,3) stoichiometry. The dependence of T_c on the annealing process parameters is also seen in x-ray diffraction patterns (not shown here) which, for films with $T_c < 50$ K, show peaks associated with $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$, and Ba_2CuO_3.

Figure 4 shows a cross-sectional view of a YBCO film deposited on YSZ-coated alumina. The interface between the substrate and the buffer layer appears to be highly stressed since tangled dislocations can be seen near the interface [Fig. 4(a)]. The formation of dislocations is expected to accommodate the high stress caused by the difference in the thermal expansion coefficients between Al_2O_3 (7.5×10^{-6}/°C) and YSZ (10^{-5}/°C). The YSZ layer contains a combination of equiaxed and elongated grains perpendicular to the film plane. We expect[2] that the as-deposited buffer layer is composed of columnar grains; during the post-deposition anneal of the YSZ film, the grain size increases through the destruction of some of these columnar grains. Left behind are equiaxed grains and undestroyed columnar grains [see arrows in Figs. 4(a) and 4(b)]. It is now well known that interdiffusion processes between YBCO films and substrates (especially Si) during post deposition anneals seriously deteriorate the superconducting properties of the resultant film. As mentioned above, interdiffusion can be minimized by the use of buffer layers such as YSZ and MgO as diffusion barriers between the superconductor and the substrate. However, as can be seen in Fig. 4(d), a thin ($\simeq 30$ nm) region of interdiffused layer is present between the YBCO and the YSZ. Even though it is very thin, this interdiffused layer is extended in the plane of the interface. It consists of very small (< 10 nm) columnarlike grains. These observations are consistent with other results obtained by elemental depth analysis[6,21] and TEM.[22] The diffraction pattern from this layer is consistent with it being composed of the $BaZrO_3$ phase [Fig. 4(c)] as also reported by others.[22,23] The presence of $BaZrO_3$ has also been seen in TEM studies of annealed pellets of mixed YBCO/ZrO_2.[24] Previous studies of the interdiffusion of YBCO and various substrate materials have not shown clear photographs of the interface[4,9,11,25]; the interdiffused layer thickness is an important result which can place a lower limit on the YBCO film thickness that could in principle be grown on silicon and alumina, and has only been measured once.[9] In the YBCO film, randomly oriented small and equiaxed grains, which are twin-free, are present at the top of the newly formed $BaZrO_3$ layer. These grains may be Ba deficient $BaCuY_2O_5$ since Ba would diffuse from the YBCO film into the buffer layer in order to form barium zirconate. This is consistent with our previous composition measurements[3] which have shown that films post-annealed at higher temperatures (800–850 °C) tend to be Ba-deficient with respect to unannealed films or films annealed at lower temperatures, suggesting a superconductor-buffer layer interaction. Careful examination of YBCO grains very close to the interface suggests that there is no one to one correspondence between grains of YBCO and grains of $BaZrO_3$. It may be thus inferred that the orientation of the YBCO grains is not correlated with the orientation of the buffer layer. As the superconductor film thickness increases, the grain size increases with some grains and platelets containing twins with their c axis normal to the film plane. This indicates that nucleation and growth of c-axis oriented grains is occurring on top of a certain thickness of randomly oriented grains, as suggested by others.[23] Thus we may conclude that nucleation and growth kinetics of differently oriented grains are dependent upon growth temperature, and determine the final film texture,[26] and that a minimum thickness (of the order of 300 Å) of YBCO is necessary in order to obtain a fully superconducting thin film.

III. CONCLUSIONS

In summary, we have studied in detail, by x-ray diffraction and TEM, the microstructure of YBCO films grown on silicon and alumina substrates with YSZ buffer layers. As-deposited films are not amorphous as is usually the case, and we believe that this is due to rf heating of the substrate. The films are composed of small grains (60–120 nm) with most probably tetragonal $YBa_2Cu_3O_6$ structure. The post-annealed films are cracked. Large grains (100–200 nm), some of which are twinned, are visible in TEM micrographs. The films are randomly oriented on silicon substrates and show the beginning of c-axis orientation on alumina substrates. The top surface of the YBCO film is composed mainly of the orthorhombic structure of YBCO. Other phases are present within the films and have been identified as $BaCuY_2O_5$, $YBa_2Cu_3O_6$, and Ba_2CuO_3. The YSZ buffer layers indeed act as diffusion barrier between the superconductor and the substrate. Cross-sectional TEM studies reveal evidence of large stresses at the buffer layer-substrate interface, mainly due to the difference in thermal expansion coefficients of the various materials. The presence of a very small interdiffused layer between the YSZ and the YBCO has also been shown: We have presented clear cross-sectional TEM photographs showing the substrate-buffer layer-superconductor interface. The interdiffused layer is very sharp and localized and its thickness was readily measured. This interdiffused zone is approximately 30 nm thick and is composed of $BaZrO_3$. Our measurements show that the thickness of the $BaZrO_3$ layer is much smaller than the YSZ and YBCO thickness, suggesting that very thin superconducting films of YBCO could be formed by sputtering on YSZ-coated silicon. Interdiffused layers with thickness of this magnitude have been reported by others[9] and "ultrathin" films of YBCO ($t = 300$ Å) have been successfully grown on $SrTiO_3$ by other techniques,[27] with faulted single-crystalline structure.[28] Our work has shown the importance of using anneal temperatures as low as possible to reduce thermal effects which produce mechanical stress in the film and promote the growth of undesired, nonsuperconducting phases and has introduced barium zirconate as a possible candidate for a buffer layer as a thin diffusion barrier between YBCO and technologically important substrates such as silicon and alumina. Reactive sputtering with relatively low-temperature substrate heating is also an attractive alternative to the post-deposition anneal method and we are furthering our efforts in that direction.

ACKNOWLEDGMENTS

The authors gratefully acknowledge technical assistance from N. T. Nuhfer and K. Zuroski. This work was supported in part by National Science Foundation Grant Nos. MSM-8717200 and DMR-8613386.

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