Solid-state reactions in high-temperature superconductor-ceramic interfaces; Y-Ba-Cu-O on Al$_2$O$_3$ versus yttria-stabilized ZrO$_2$, and MgO

A. Fartash and Ivan K. Schuller

University of California, San Diego, Physics Department B-019, La Jolla, California 92093

J. Pearson

Materials Science Division, Building 223, Argonne National Laboratory, Argonne, Illinois 60439

We have prepared, using molecular-beam epitaxial techniques, superconducting Y-Ba-Cu-O films directly on Al$_2$O$_3$, yttria-stabilized ZrO$_2$ (YSZ), and MgO without buffer layers. The structure and stoichiometry of the films on Al$_2$O$_3$ are compared with those prepared on YSZ and MgO and found in large part determined by reactions with the substrates. The films on Al$_2$O$_3$ consist of textured Y$_2$Ba$_4$Cu$_8$O$_{20-x}$ with superconducting onset at 80 K and zero resistance at 69 K, whereas on YSZ and MgO, YBa$_2$Cu$_3$O$_{7-z}$ films are formed. Auger electron depth profile spectroscopy in conjunction with structural and transport studies suggest that copper is depleted from the region near the Al$_2$O$_3$ substrate.

I. INTRODUCTION

It is well known that high-T_c Y-Ba-Cu-O (YBCO) films react with their substrates during high-temperature processing.[1-4] It is important to understand the nature of these reactions, since in most cases they adversely affect the superconducting properties of the films. The present work compares the reactions of YBCO films on Al$_2$O$_3$ with respect to other important substrates. The main objective is to elucidate the differences, and clarify the specific interactions involved. Solid-state reactions between the films and their substrates result in changes in their structure and transport properties. These changes are easily measured and under controlled conditions, in conjunction with depth profiling techniques, are used to identify specific reactions. Although the results from standard depth profiling techniques are complicated to interpret[3,4] (due to preferential etching rates), if combined with a controlled preparation and test procedure they can be utilized to compare and clarify the physical changes that result from solid-state interactions at the film-substrate interface.

Al$_2$O$_3$ is a particularly important substrate because of its low cost, dielectric constant, and common industrial use. Unfortunately, the strong overlayer-substrate interaction has precluded the formation of high-quality YBCO films on Al$_2$O$_3$.[1,5,6] On the other hand, on perovskite substrates, such as SrTiO$_3$ and KTaO$_3$, high-quality YBCO films have been successfully prepared.[7,8] However, the high cost and dielectric loss make these substrates unattractive for future applications. The advantage of SrTiO$_3$, for example, over substrates such as Al$_2$O$_3$, YSZ, and MgO has been mainly due to its negligibly small overlayer-substrate interaction,[9] and for this reason it has been widely used for the production of high-quality YBCO films. To the best of our knowledge no conclusive work has emerged regarding the interaction between Al$_2$O$_3$ and YBCO and most efforts so far have focused on films with buffer layers.[5,10] For ZrO$_2$ a preferential Ba-Zr interaction has been found which produces barium zirconate, with the consequent degradation of superconducting properties of 1:2:3 YBCO films.[11] In the case of MgO, Mg substitution for Cu (or Ba) in the 1:2:3 YBCO lattice sites has been proposed to explain the low superconducting onset temperature of MBE-grown films.[1] The results reported for sputtered films confirm the doping by Mg.[12]

II. EXPERIMENT

YBCO films (~ 0.5 μm thick) were deposited in a Riber molecular-beam epitaxy (MBE) apparatus with a starting pressure of 5×10^{-9} Torr. Substrates of Al$_2$O$_3$ (1120), YSZ (polycrystalline ZrO$_2$, yttria stabilized), and MgO (100) were placed together on a rotating Mo block heated to 550 °C to assure homogeneity. Yttrium was evaporated from a 10-kV Temescal electron-beam gun with rate control using electron emission spectroscopy (EIES) in a feedback mode. BaF$_2$ and Cu were evaporated from temperature-controlled Knudsen cells. Prior to film deposition the individual rates were calibrated from the thickness of a deposited layer on Al$_2$O$_3$ using a Tencor (alpha-step 200) profilometer. The procedures resulted in a speedy and reliable technique for calibration of YBCO films at desired overall average stoichiometries. In the first series of studies, the evaporation rates were adjusted to prepare films with a 5%–8% excess copper above the 123 stoichiometry. Partial oxidation was obtained by flowing high-purity oxygen into the chamber through a copper tube whose tip was ~ 15 cm away from the substrates. The chamber pressure was maintained at 2.5×10^{-6} Torr during the coevaporation. No special arrangements were made to enhance *in situ* oxidation of the films.

After deposition the samples were transferred into a quartz tube furnace, and post-annealed at 850 °C in wet oxygen for 1 h and at 550 °C in dry oxygen for 2 h. The furnace was cooled to room temperature at a rate of ~ 3 °C/min. The films were characterized using Cu$K\alpha$ x-ray diffraction, ion mill Auger electron spectroscopy (AES), and four-probe resistivity measurements. For the AES (~ 1.2 eV resolution) the films were ion milled using 3 keV argon ions.

III. RESULTS AND DISCUSSION

X-ray diffraction profile scans for representative films on Al_2O_3, YSZ, and MgO are shown in Fig. 1. The film on Al_2O_3 reveals a distinctly different structure from the c-axis oriented 123 structure formed on YSZ and MgO. Its structure corresponds to the Cu-rich 248 phase of the YBCO system with a negligibly small amount of 123 phase present (indicated by asterisks in the figure). The 248 phase is highly c-axis oriented; its diffraction peaks are indexed following the work of Marshall et al.,[13] and correspond to Bragg reflections from $(0,0,2n)$ planes. The small diffraction peaks on YSZ and MgO are due to impurity phases, and are pointed out by arrows with the 31.6° peak being common to both films. Although this peak cannot be unambiguously identified, in the light of the calibration it is likely to be due to interactions with the excess copper in the films. Similarly the additional impurity peak on MgO at 29.5° is also due to preferential interactions between copper and magnesium, and corresponds to the (011) reflection of Cu_2MgO_3.

Four lead resistivity versus temperature plots are shown in Fig. 2. The superconducting onset temperature ($\sim$80 K) of the film on Al_2O_3 is consistent with the transition temperature of the 248 phase[13] with the zero resistivity at 69 K. The normal state resistivity of this film is not linear, except over a short range from $\sim$135 to 80 K. The ratio of the
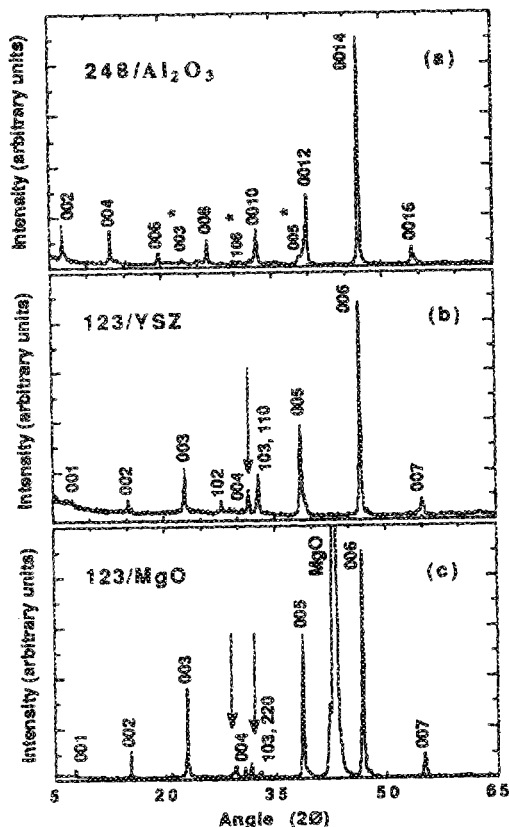

FIG. 2. Resistivity vs temperature data of c-axis oriented samples of (a) $Y_2Ba_4Cu_8O_{20-x}$ on Al_2O_3 (the linear portion above the superconductive onset is a guide to the eye), (b) $YBa_2Cu_3O_{7-z}$ on YSZ, and (c) $YBa_2Cu_3O_{7-z}$ on MgO.

intercept of the linear portion to that at 300 K is 14%, close to the value obtained by Berkeley et al. ($\sim$8%),[14] but in contrast with the work of the Char et al.[15] reporting a negative zero temperature intercept. To explain their result the Stanford group has proposed a nonlinear scattering mechanism with a characteristic temperature above room temperature such that at low temperatures it is approximately linear with a negative intercept. The room-temperature resistivity of our sample is $\sim$20% lower than the intercept of its linear portion. This behavior cannot be due to the presence of small amounts of 123 impurity since as reported[15] the resistivity of 123 is linear. The nonlinearity may be caused by spatial changes in the film stoichiometry due to chemical interactions between the film and substrate. On $SrTiO_3$, for which overlayer-substrate interaction is minimal, the room-temperature resistivity of 248 films of the Stanford group is an order of magnitude smaller than the film shown in Fig. 2(a). It is known that Al dopes $YBa_2Cu_3O_{7-z}$,[16] and for small amounts ($\sim$1%) strongly depresses T_c. Regarding $Y_2Ba_4Cu_8O_{20-x}$, to our knowledge no work has been published. But the absence of any significant reduction of the superconducting onset temperature of the film from its bulk value is suggestive that either Al doping does not occur or it has little influence on the T_c of the 248 material. In any event, the nonlinear temperature dependence is an outcome of film-substrate interaction, since for films on $SrTiO_3$ such behavior does not exist.

The 123 films on YSZ and MgO are both metallic in their normal states (Fig. 2). The superconducting onset temperature of the 123 film on YSZ is 92 K, consistent with

FIG. 1. Cu$K\alpha$ x-ray diffraction pattern of samples: (a) $Y_2Ba_4Cu_8O_{20-x}$ on 1120 oriented Al_2O_3 substrate, the peaks corresponding to the 123 phase are indicated by asterisks; (b) $YBa_2Cu_3O_{7-z}$ on polycrystalline YSZ substrate, the arrow at 31.6° indicates an impurity peak; and (c) $YBa_2Cu_3O_{7-z}$ on 100-oriented MgO substrate, the arrows at 29.5° and 31.6° indicate impurity peaks.

the expected value for this phase,[17] with a transition width of 7 K. On MgO the superconducting onset temperature is depressed to 79 K, with a slightly resistive transition to the final superconducting state at 63 K. This behavior suggests that this film is most likely doped with Mg.

In the light of distinct structures formed on different substrates the comparison of AES plots can provide valuable information regarding distinct features of film-substrate interactions. AES plots of metal constituents of representative films are shown in Fig. 3. On Al_2O_3 the behaviors of Cu, Ba, and O are clearly different from that on YSZ and MgO. The intensity of Cu is higher on Al_2O_3 as expected from its stoichiometry. Both Ba and O reveal anomalous features that are not present on YSZ and MgO. The increase of their intensities at the Al_2O_3 interface indicates either a buildup of these materials or some other abrupt change in composition that strongly affects their etching rates. It is also interesting to note that in this region Cu has a smaller intensity than Ba, whereas on YSZ and MgO their intensities both vary in tandem. In combination with distinct structural and transport properties the most consistent model that emerges suggests

that copper is depleted from the Al_2O_3 interface. The possible cause for this behavior is due to preferential interactions. There is a strong possibility that a Ba-O-rich layer is formed that rejects copper from the Al_2O_3 interface.

Based on this model the migration of copper away from substrate changes the film stoichiometry in the rest of the film with a consequent copper enrichment which gives rise to a 248 stoichiometry. Similar observations regarding Cu and Ba reactions with Al_2O_3 have been recently reported by Asano et al.[18] for YBCO spray-coated Si wafers with thick Al buffer layers. After annealing their wafer in oxygen at 950 °C for 5 h, XPS studies revealed that the oxidized Al buffer layer inhibits the precipitation of Cu at the interface. In addition, a significant amount of Ba was found in both the oxidized Al and Si substrate.

To further confirm the above observations we coevaporated YBCO films without excess copper and the same thickness ($\sim 0.5\ \mu m$) as discussed above. This was done to produce pure 123 films on YSZ and MgO, without impurity peaks in their x-ray diffraction profiles. As expected, the film on Al_2O_3, due to smaller amount of copper, consisted of 123 and 248 mixed phases. Further support comes from studies on YBCO films prepared on Al_2O_3 which show rising values of T_c with increasing film thickness.[10] In the light of interactions described above, it is therefore clear that thinner films are more susceptible to changes of their stoichiometry and degradation of their superconducting properties by preferential diffusion and reactions.

SUMMARY

We have shown that depending on the substrate distinct structures of YBCO films can be produced under identical conditions: 248 on Al_2O_3 and 123 on YSZ and MgO. These findings, in conjunction with AES studies, have enabled us to establish the significant features of interactions between YBCO and Al_2O_3. In the overlayer-substrate interface copper is preferentially depleted and a material most likely rich in barium and oxygen is formed. The present observations highlight the importance of film-substrate interactions which can significantly alter the film stoichiometry, and show that chemical reactions at the substrate interface play a more significant role than other factors such as epitaxial match. The production of thin YBCO films must take into account the important reactions involved. Using these facts we have produced YBCO films on Al_2O_3 and YSZ fully superconducting at 69 and 85 K, respectively.

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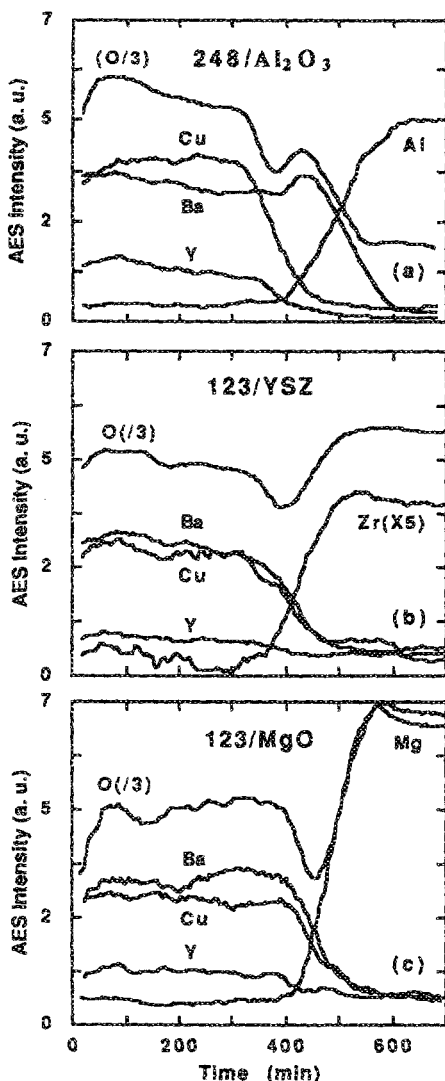
FIG. 3. Ion mill AES intensity of Y, Ba, Cu, and O for (a) $Y_2Ba_4Cu_8O_{20-x}$ on Al_2O_3, (b) $YBa_2Cu_3O_{7-z}$ on YSZ, (c) $YBa_2Cu_3O_{7-z}$ on MgO.

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