JOURNAL OF MATERIALS SCIENCE 25 (1990) 2349–2352

Substrate/film interactions in thick films of YBaCuO on alumina

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The substrate–film interaction in thick films (>10 μm) of $YBa_2Cu_3O_{7-x}$ on alumina processed under normal conditions is investigated using electron-probe microanalysis. The formation of a mixture of barium aluminate and alumina over a thickness of about 2 μm in the interfacial region is established quantitatively using compositional mapping and point-count analysis across the substrate–film interface. Diffusion of aluminium into the film over several μm beyond the reaction layer is also observed. The variation of oxygen composition across the interface has been mapped. Leaching of oxygen from the 1-2-3 phase in the bulk is suggested as the reason for the observed decrease in $T_c(0)$ and increase in ΔT_c in films of $YBa_2Cu_3O_{7-x}$ on alumina.

1. Introduction

There has been a widespread interest in processing thick films (> 10 μm) of high-T_c superconductors such as $YBa_2Cu_3O_{7-x}$ (herein designated as YBaCuO) because of their potential application in microwave technology and microelectronics [1]. This has led to a number of investigations on preparing thick films of these superconductors on ceramic substrates such as $SrTiO_3$, MgO and alumina [2–12]. The transition temperature at which the resistance becomes zero, $T_c(0)$, is found to be the lowest (around 50 to 85 K) for alumina [2, 4, 9–12] and highest for $SrTiO_3$ (85 to 90 K) [4], with MgO [5] falling in between. Although better superconducting properties have been obtained in films on $SrTiO_3$ and MgO, these substrates are not as well suited for electronic applications as alumina. Therefore there is a need to investigate why thick films on alumina substrates have poor superconducting properties, so that improved processing techniques can be explored for circumventing the associated problems. The low $T_c(0)$ and the large superconducting transition width (ΔT_c) observed in the case of alumina substrates are ascribed to many factors associated with substrate–film interactions. Evidence about how the substrate–film interaction leads to a low $T_c(0)$ is not clearly substantiated, although interdiffusion of aluminium [2, 4, 9] and formation of barium aluminate [2] have been reported previously, as noted below. Some investigators [9] have suggested that the poor superconducting properties are due to the disruption of the YBaCuO phases by aluminium diffusion; however, evidence for this explanation is not conclusive. The observations of previous studies have been based on characterization techniques such as energy dispersive spectroscopy (EDS) [10], transmission electron microscopy (TEM) [11], secondary ion mass spectroscopy (SIMS) [4], auger electron spectroscopy (AES) [4], X-ray diffraction (XRD) [10], and Rutherford backscattering spectroscopy (RBS) [3, 4].

While the above studies indicate interdiffusion and reaction of aluminium and barium in the interface region, quantitative measures of the thicknesses of the interdiffusion layer and reaction layer are not available. An exception to this is the work of Sacchi *et al.* [2], who show, using EDS, the presence of aluminium and barium in the first 10 μm from the interface of a thick film (35 to 40 μm). The films studied by Sacchi *et al.* were, however, sintered at 980° C for 1 h, whereas normal sintering time for thick films (from precalcined powders) is more in the range of 6 to 15 min. The large sintering times used for these films are the probable cause of the observed large interdiffusion of aluminium and barium, which could then be seen using a relatively insensitive technique such as EDS.

The previous results indicate the interdiffusion of the metallic elements and the presence of barium aluminate in the film. However, quantitative estimates of reaction layer thicknesses and the variation of elemental concentrations (especially oxygen) across the films and substrates have not been possible in the above studies because of several difficulties in obtaining quantative results from the above techniques. For instance, EDS analysis is not very accurate because of its poor energy resolution, low peak-background ratios, and inability to detect light elements such as oxygen accurately. RBS is not reliable for films thicker than about 2 μm due to the overlap of signals from the various elements. Results obtained by TEM may be affected by sample preparation artefacts [13]. SIMS and AES are limited to surface analysis (depth of about 1 nm) and their results are also severely affected by sample charging. Among these techniques, XRD provides the best *qualitative* estimate of the phases present, but the quantitative analysis is affected by

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0022-2461/90 $03.00 + .12

factors such as orientation of the films, inability to detect small amounts of phases (e.g. $BaCuO_2$), and insensitivity to oxygen content. Quantitative information on reaction layer thicknesses and on elemental compositions across the interface is particularly useful for understanding the mechanisms of interfacial reactions and diffusion, and for devising methods to suppress them.

Electron probe microanalysis (EPMA) is a powerful technique [14] for very sensitive, highly accurate quantitative analyses (of even light elements such as oxygen) and could serve as a useful tool for studying substrate–film interactions in films. Quantitative compositional analyses [14–16] with standardization and matrix corrections and with full correction for dead time and background are possible at points selected on images obtained from backscattered electron (BSE) signals, which are sensitive to compositional differences. In addition, compositional mapping can be done with advanced imaging techniques and X-ray scans to produce images giving a lateral distribution of elements.

We present an analysis of interactions between YBaCuO films and alumina substrates using electron probe microanalysis. The extent of reaction of the film with the alumina substrate is investigated. The extent of diffusion of each species in the interface region is also obtained.

2. Experimental procedure

Thick films of $YBa_2Cu_3O_{7-x}$ were deposited on alumina substrates, using a suspension of precalcined powders mixed with an organic dispersant, and sintered at 980° C for 6 min in air followed by slow cooling in oxygen. The sintered films were annealed in oxygen at 600° C for 4 to 5 h. Additional details on the procedure have been presented elsewhere [17]. The thickness of the films was typically 50 to 80 μm as measured by electron microscopy. Films were mounted in cross-section and polished using alcohol or acetone as cleaning agent, as water attacks the superconductor chemically and changes its composition. It has been found [18] that acetone and alcohol do not affect the composition of YBaCuO as long as the films are exposed to them only for short periods of time. The epoxy-mounted films were coated with carbon to the same thickness as the coating on the standards used for quantitative microprobe analysis.

3. Results and discussion

EPMA has been used here both for quantitative point count analysis and compositional mapping. The compositional mapping indicates the extent of diffusion of various elements in the region of the interface. The mapping is obtained by recording the X-ray intensity over the scanned area for each constituent. The intensity matrices are then converted to compositional matrices and mapped over an area of 128 × 128 pixels. Each pixel stores the concentration of all the constituents.

The compositional mapping obtained in this work for the elements aluminium, yttrium, barium, copper and oxygen in the interface region is shown in Fig. 1. The brightness of the image within each frame in this figure is an indication of the mass fraction of the element in the region. It can be seen from Fig. 1 that yttrium does not diffuse into the substrate and that its concentration remains almost the same in the film. On the other hand, the X-ray map of barium indicates a noticeable barium-rich layer in the interface region (i.e. a bright band along the interface, indicating a higher concentration of barium than in the film). Similar variations of the concentrations of aluminium and oxygen are also seen at the interface. The above observations are confirmed by the EDS spectrum obtained from a backscattered image of the interface and shown in Fig. 2. Notice that Fig. 2 shows a 1 to 2 μm reaction layer containing barium and aluminium. The qualitative observation of the distribution of various elements from the X-ray maps near the substrate–film interface (Fig. 1) is confirmed by the quantitative point-count analysis across the interface shown in Fig. 3. The elemental compositions in the reaction layer can be computed from the data in Fig. 3, and correspond to the presence of a mixture of $BaAl_2O_4$ and Al_2O_3. The bulk of the film shows the

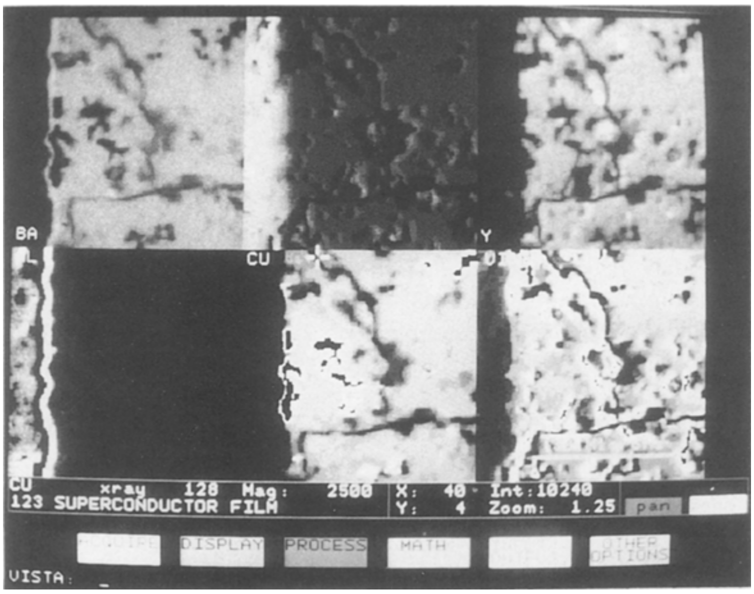


Figure 1 X-ray compositional maps obtained for various elements in the substrate–film interface region. Each frame corresponds to an X-ray map of one element. The original colour-coded photographs have been converted to black-and-white pictures. Starting from the top left and ending at the bottom right are X-ray maps for (i) barium, (ii) oxygen, (iii) yttrium, (iv) aluminium and (v) copper. The last frame is a digitized backscattered video image; the substrate is on the left in each frame.

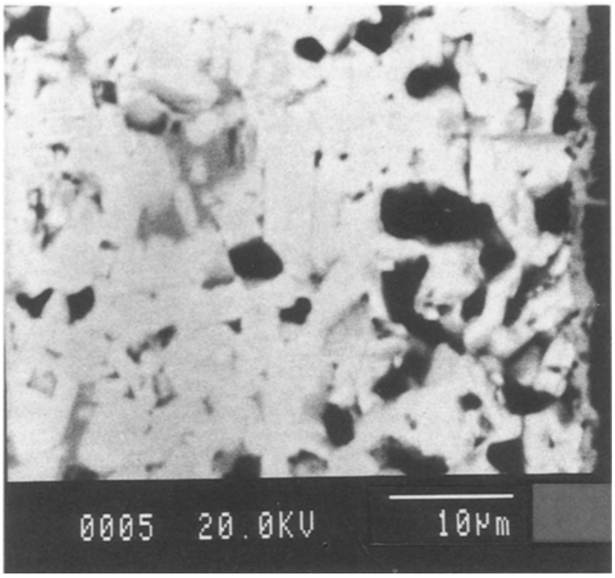


Figure 2 Backscattered electron image of a region containing the substrate–film interface.

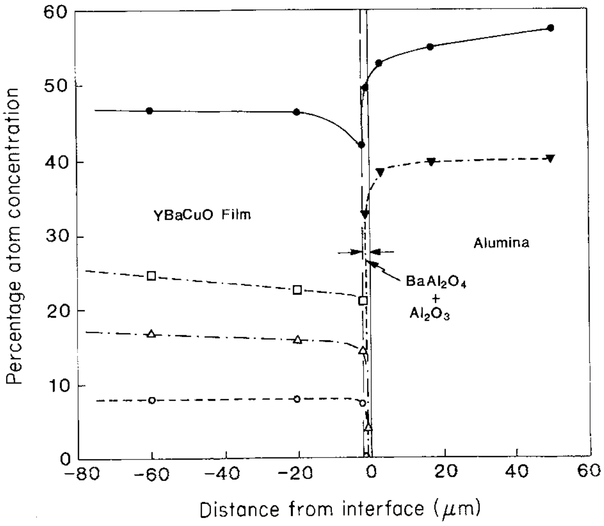


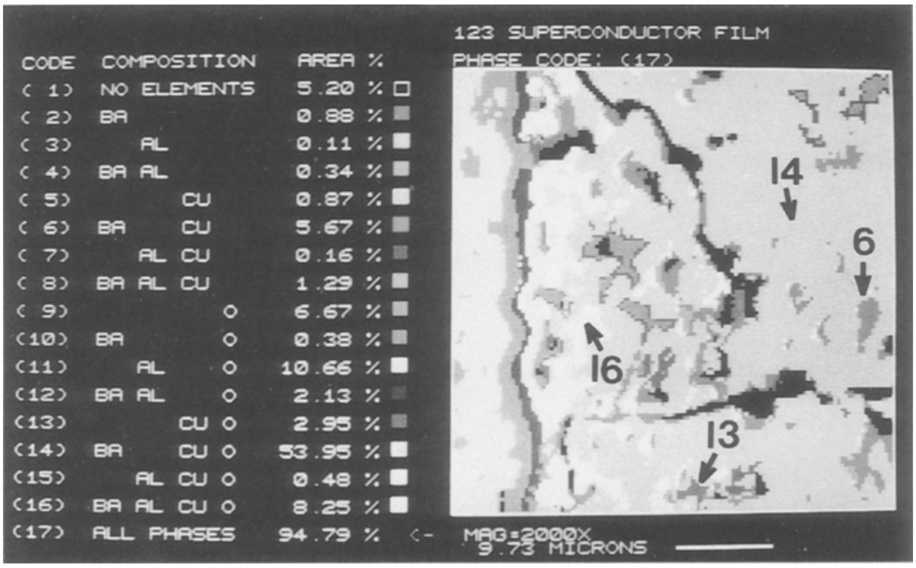
Figure 3 Distribution of various elements across the substrate–film interface. □, copper; △, barium; ○, yttrium; ●, oxygen; ▼, aluminium.

elements yttrium, barium and copper in the appropriate ratio of 1 : 2 : 3, indicating no major disruption of the YBaCuO (i.e. 1-2-3) phases in the bulk. The data in these figures indicate that the diffusion of barium from the bulk toward the interface does not lead to any major breakdown of the 1-2-3 phase in the bulk.

The oxygen–yttrium concentration in the film is found to be 6.0 (Fig. 3), which is less than expected (6.5 to 7.0) after oxygen annealing during the fabrication of the film. However, there are uncertainties involved in the determination of oxygen concentration due to interference from carbon, thus the actual oxygen concentration could be higher. Even though the quantitative analysis was done with special attention to standardization and other corrections for matrix and background, the interference from a significant carbon count (either from coating, epoxy or even the film) of about 1 to 5 wt % could affect the calculated oxygen concentrations in spite of careful compensation for carbon interference.

The previous observations concerning the absence of major phase decompositions in the bulk of the film do not, however, preclude leaching of oxygen from the bulk due to interfacial reactions. The oxygen concentration profile shown in Fig. 3, in fact, indicates diffusion of oxygen from the bulk of the film. Further, compositional analysis (Fig. 4), which shows combinations of elements (phases) present in the region, indicates the diffusion of aluminium, white regions, labelled '16' on the figure, away from the reaction layer and toward the bulk of the film. It is possible that diffusion of oxygen from the bulk of the film takes place towards regions showing the presence of aluminium. Consequently, oxygen would also have a tendency to diffuse from the film towards the interface and react with barium and aluminium to form barium aluminate.

Based on the resistivity against temperature behaviour in bulk specimens, it is reasonable to expect that as long as the superconducting phase in the film is in sufficient quantity to form a percolating network, the presence of impurity phases cannot be responsible for lowering $T_c(0)$ and for increasing ΔT_c substantially (20 to 30 K). Since the bulk of the film shows the appropriate stoichiometric ratio in the



CODE	COMPOSITION	AREA %	
(1)	NO ELEMENTS	5.20 %	□
(2)	BA	0.88 %	■
(3)	AL	0.11 %	■
(4)	BA AL	0.34 %	■
(5)	CU	0.87 %	■
(6)	BA CU	5.67 %	■
(7)	AL CU	0.16 %	■
(8)	BA AL CU	1.29 %	■
(9)	O	6.67 %	■
(10)	BA O	0.38 %	■
(11)	AL O	10.66 %	■
(12)	BA AL O	2.13 %	■
(13)	CU O	2.95 %	■
(14)	BA CU O	53.95 %	■
(15)	AL CU O	0.48 %	■
(16)	BA AL CU O	8.25 %	■
(17)	ALL PHASES	94.79 %	<-

Figure 4 Phase compositional map obtained from elemental composition map (Fig. 1). Each phase is numbered. Copper oxide (13) and barium cuprate (6) are seen in addition to the 1–2–3 phase (14) and 1–2–3 phase mixed with aluminium (16) in the film. The original colour-coded photographs have been converted to black-and-white pictures. (Yttrium is not included in the phase composition because combinations of only four elements were possible for display.)

metallic elements, there must be some other factor for the observed decrease in $T_c(0)$ and increase in ΔT_c. Our supposition is that aluminium interdiffusion does not disrupt the concentrations of barium, yttrium and copper beyond the reaction layer (1 to 2 μm); however, the presence of aluminium over a substantial thickness near the reaction layer could increase the diffusion of oxygen from the unreacted 1-2-3 phases towards the aluminium-rich regions, thus leading to a reduction of oxygen content in the unreacted 1-2-3 phases. This reduction of oxygen content in the bulk (and the possible variation of oxygen stoichiometry within the bulk) would increase ΔT_c and decrease $T_c(0)$. These results imply that under normal processing (sintering and annealing) conditions for films of YBaCuO on alumina, there is a tendency for formation of a reaction layer of about 1 to 2 μm thickness which would lead to loss of superconductivity in films of thickness in this range.

4. Summary

In summary, the results of EPMA indicate the presence of a reaction layer of about 1 to 2 μm thickness containing barium aluminate in films of YBaCuO deposited on alumina substrates. The diffusion distance of aluminium into the film is seen to be of the order of several μm. No major disruption of the YBaCuO phases (in the bulk) due to aluminium diffusion is observed. However, aluminium diffusion may lead to oxygen depletion from the surrounding 1-2-3 regions, thus leading to poor superconducting properties of the fabricated films. A comprehensive test of the effects of various sintering and annealing conditions of the extent of reaction and the diffusion of various species is needed for devising methods to improve the electrical properties of thin and thick films of the superconductors.

Acknowledgements

This work was supported by the Texas Center for Superconductivity at the University of Houston (TCSUH) and the State of Texas (through its Advanced Technology and Research Program).

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Received 16 January
and accepted 20 June 1989