Wet Chemistry-Derived Barrier Layers for Ceramic Superconductor Films

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INTRODUCTION

It is well established that substrate composition and orientation
play crucial roles in determining the properties of thin film ceramic
superconductors.[e.g.,1-4] The substrate can affect both the epitaxial
quality of the superconductor coating and interdiffusion between the
substrate and coating; these, in turn, affect superconducting
properties (e.g. transition temperature and critical current). Most
studies have indicated that, compared to preferred orientation of the
superconductor, diffusion from the substrate plays a dominant role.[e.g.,2]
Even in studies where film orientation has appeared to affect electrical
properties,[e.g.,5] the effects can be related to differences in coating
chemistry, rather than to anisotropy in the electrical properties. This
is not surprising since, in general, properties of polycrystalline
superconductors are limited more by grain boundary composition than by
crystallite orientation. Only in single crystal coatings would one
expect to see large anisotropies in the electrical properties.

The importance of substrate diffusion, rather than epitaxy, in thin film ceramic supeconductor has inspired many investigators to coat substrate with barrier layers, in the hope of effectively separating the coating from the diffusing substrate cations. ZrO_2, SiO_2, Ta_2O_5, LaF_3, MgO, VN, Ag, Au, (and some other compositions) have been tried.[e.g.,2,3,5,6] Many of these coatings, especially ZrO_2,[5] Ag,[7] and Au,[3] have resulted in significant improvements in the electrical properties of ceramic superconductor coatings. In general, these barrier layers have been used with superconductor coatings which are applied by vacuum deposition techniques, such as magnetron sputtering,[3] evaporation,[6] and electron beam evaporation.[2] As a result, the barrier layers have also been deposited using high vacuum processes. For chemically-derived superconducting coatings, however, the advantages in cost and versatility would be lost if the substrates had to be first coated with a barrier layer in a vacuum chamber. Hence, there is a need to develop barrier layers which can be deposited by more simple, versatile techniques, such as wet-chemical, or sol-gel, techniques.

Previously we reported preliminary results using a combination barrier layers of Ag on sol-gel derived ZrO_2 on sapphire.[7] This combination allowed superconducting $YBa_2Cu_3O_{7-x}$ films to be sputter-deposited on sapphire. Without the barrier layer, the films were not superconducting.

Presently, we are investigating a broader range of sol-gel barrier layers. These include Ta_2O_5, since it forms a nominally dense sol-gel coating at low temperatures (450-500 C)[8]; Y-stabilized ZrO_2 (YSZ), which is one of the preferred bulk substrate materials and which (without yttria stabilization) is a commonly used vacuum deposition barrier layer; $Y_2Cu_6O_9$, which may provide not only a barrier layer but also serve as a source of excess copper, which is often deficient after heat treatments; and $BaTiO_3$ and $SrTiO_3$, which are being studied because of the superiority of $SrTiO_3$ as a bulk substrate material. Each barrier layer is being studied with and without silver overcoats. We report

here synthesis procedures for two of these barrier layers ($Ta2O_5$ and Y-stabilized ZrO_2) as well as the effects of these barrier layers on coating adhesion, coating/substrate interdiffusion, and (preliminary) resistivity measurements for $YBa_2Cu_3O_{7-x}$ films sprayed from nitrate solutions onto barrier-coated sapphire substrates.

EXPERIMENTAL PROCEDURES

Barrier Layer Synthesis

The coating solutions were made from alkoxide precursors, as received from the vendor.[*] All solvents were purified by standard procedures before use. Single crystal sapphire slides, 90° cut[**] (1cm x1cm x1mm) were used as the substrate material. The slides were cleaned using the Huang process before coating. All samples were coated using a spin coater, 2000 rpm, for 20 sec.

Ta_2O_5 coatings were obtained from $Ta(OCH_2H_5)_5$ solutions. A 5 wt% $Ta(OCH_2H_5)_5$ solution in dry ethyl alcohol was prepared in a three-neck flask equipped with a nitrogen inlet, condenser, drying tube, and stirring and heating accessories. Water was added to this solution so as to maintain a 1:1.3 water to alkoxide ratio. The solution was stirred at room temperature for one hour, and then coated onto the sapphire substrates. To increase the thickness, this coating was heated at 80 C for 10 minutes, and then a second Ta_2O_5 layer was spun on. The dual coatings were finally fired for 4 hours at 950 C in air. Rutherford Backscattering (RBS) analysis showed the resulting coatings to be ~600 Å thick.

To prepare Y-stabilized ZrO_2 barrier layers, zirconium n-propoxide and anhydrous yttrium chloride were weighed into a three-neck flask, equipped as described above. The weight of components was adjusted in

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[*] Alfa Products, Danvers MA
[**] Saphikon Inc., Medford MA

such a way that ZrO_2 containing 9 wt% Y_2O_3 would be obtained. Dry isopropyl alcohol (30 ml) was added to this solution, and the resulting mixture was heated until a solution free from any solid particles was obtained. To hydrolize the alkoxide mixture, 1 mole % of the amount of water required for complete hydrolysis was added to one ml isopropyl alcohol. This hydrolysis solution was then added to the alkoxide solution and refluxed for about five hours. The solution was then spin coated onto the pre-cleaned sapphire substrates. A second coating was deposited after the first had been fired at 400 C in air for one hour. Then, the dual coating was given a final heat treatment at 900 C for four hours. RBS analysis showed the product coating to be ~800 Å thick; and x-ray diffraction analysis showed the coating to be a cubic crystalline phase.

Superconductor Coatings

Y-Ba-Cu-O films were sprayed onto the barrier layers using a nitrate solution technique which is described in detail elsewhere.[9] Basically, the process involves mixing nitrate solutions of the cations in the stoichiometric ratio (1:2:3 Y:Ba:Cu) and spraying this solution onto heated (170-190 C) substrates. The sprayed coatings were then given a complicated heat treatment, part of which involved heating at 925 C for 6 hours. The details of the spraying procedure and firing schedule, both important in obtaining good superconducting properties, are given in reference 9.

For 15 μm coatings sprayed on bulk YSZ substrates, a superconducting onset is obtained at 94 K, with a transition width of about 12 K (zero resistivity at 82 K). For thinner coatings, the onset temperature decreases and the transition width increases. It is apparent, therefore, that the extent of substrate poisoning can be very large - i.e., numbers of microns in extent - with the nitrate-derived coatings.

RESULTS AND DISCUSSION

Coating Adherence

For bulk YSZ substrates, the nitrate deposition technique formed very robust, well-adhering coatings. When the oxide barrier layers were added, the coatings became somewhat more fragile, and could be partially scraped off with a razor blade. In our previous work on sputtered films,[9] no such effect was observed with the sol-gel barrier layers. It is apparent that the complex chemical interactions at the coating/substrate interface make the nitrate-deposited coatings more sensitive to substrate chemistry than the vacuum deposited coatings. This difference was painfully evident when nitrate coatings were sprayed onto the silver coated barrier layers. Here, films could not be formed at all. The coatings coalesced into small islands, apparently the result of chemical attack of silver by nitric acid from the coating solution.

In some cases, the barrier layers could be used to enhance coatability. For example, the nitrate coatings did not adhere to unpolished polycrystalline Al_2O_3. With the addition of a $BaTiO_3$ barrier layer, however, adhering coatings could be formed. Hence, in addition to providing diffusion barriers, the sol-gel barrier layers can significantly affect coatability by changing the substrate chemistry and morphology, in both the positive and negative directions.

Substrate Diffusion

A representative SEM micrograph of the Ta_2O_5 coating (Figure 1a) shows a very smooth surface. Except for what seems to be cracking in the gold coating, there is no apparent structure (porosity) in the film down to at least 300 Å. The RBS spectrum of a fired Ta_2O_5 coating, Figure 2a, shows a very sharp Ta peak, indicating that there is very little interdiffusion between the Ta_2O_5 and Al_2O_3 during the 950 C

firing. Assuming the coating is dense, these RBS measurements correspond to a Ta_2O_5 coating thickness of about 600 Å. An Auger sputter depth profile of the same sample (Figure 3a) confirms the sharpness of the interface, but suggests a coating thickness of about 1500 Å, more than twice the RBS estimate. This discrepancy implies that, although coating shrinkage has long-since stopped by 950 C,[8] the Ta_2O_5 coating is not completely dense. For use as a barrier layer, this may have a significant negative effect.

The RBS spectrum of the same Ta_2O_5 film after coating with the nitrate solution (1-2 μm) and firing (Figure 2b) shows an extension of the Ba peak, and especially of the Ta peak, indicating that interdiffusion between the superconductor and barrier coatings has taken place. The interdiffusion is more dramatically observed in Figure 3b, which is an Auger sputter depth profile of the same sample.[*] The barium has diffused into the substrate, leaving the bulk of the film deficient in Ba; the tantalum is evenly distributed throughout the bulk of the superconductor film; and, most importantly, the aluminium has diffused through almost the entire superconducting coating.

It is interesting that the sputter rate is significantly faster through the superconductor film than through the Ta_2O_5, suggesting that that the mechanical integrity of the nitrate-sprayed superconductor coating on a Ta_2O_5 barrier layer is rather poor. This is consistent with our observation of reduced adhesion for nitrate films on barrier layers.

An x-ray diffraction pattern of a fired nitrate coating on bulk YSZ is shown in Figure 4a. Only the superconducting, 1-2-3 phase is present. The diffraction pattern of a fired nitrate coating on a Ta_2O_5/sapphire substrate is shown in Figure 4b. In addition to the 1-2-3 material, impurity phases (Y_2BaCuO_5, $BaCuO_4$, and possibly others), as

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[*] The yttrium signal has been removed from Figure 3b. Its low concentration and the high noise at >1500eV made the Y signal difficult to interpret. Also, it must be recognized that the sensitivity factors used to calculate atomic concentrations are only approximate; the trends, however, are significant.

well as $BaCO_3$. The presence of phases other than the 1-2-3 is not surprising, in light of the extreme substrate / barrier layer / superconductor interdiffusion seen in the RBS and Auger results. The $BaCO_3$, however, is quite unexpected, since the barrier layers were fired to 950 C before coating with the nitrate solutions. We are currently investigating the reason for the carbonate formation.

An SEM micrograph of the YSZ coating (Figure 1b) shows that the YSZ coatings are also smooth and featureless, at least down to the 300 Å level. When coated with the nitrate solutions and fired, however, the XRD pattern (Figure 4c) shows the presence of the same impurity phases, including $BaCO_3$ as in the Ta_2O_5 barrier layer It is apparent that disruption of the 1:2:3 stoichiometry is just as severe with the YZS barrier coatings as with the Ta_2O_5 barrier coating.

This chemical interaction could be caused by incomplete densification before the nitrate coatings are applied, or by chemical attack of the superconductor during the rigorous heat-treatment to which the entire superconductor coating/barrier layer/substrate system is subject. Since YSZ is well established as one of the best (least reactive) substrates, it seems unlikely that the superconducting coating would severely attack these coating. Hence, there is strong indication that the YSZ coatings are not fully densified by the 900 C heat treatment, and that this relaxed porosity limits their effectiveness as barrier layers.

Resistivity versus temperature measurements were made for all nitrate-coated and fired barrier layers. Since the thickness of the superconductor coatings can vary by multiple microns across a sample, however, it is difficult to quantify the effects of the different barrier layers. Qualitatively, minor improvements in electrical properties (such as a slight increase in onset temperature) have been observed when sapphire substrates are coated with these barrier coatings.

SUMMARY

A variety of potential barrier layers has been successfully deposited on sapphire substrates using sol-gel methods. The barrier layers had a significant effect on the adhesion of nitrate-derived superconductor films. Their effectiveness as a diffusion barrier was rather minimal, however, most likely the result of incomplete densification before applying the superconductor coating. Nonetheless, the barriers made a qualitative improvement in the electrical properties of nitrate-coated sapphire substrates. Most importantly, it appears that successful implementation of wet-chemistry derived barrier layers will depend on precise characterization and control of the density of the coatings.

ACKNOWLEDGEMENTS

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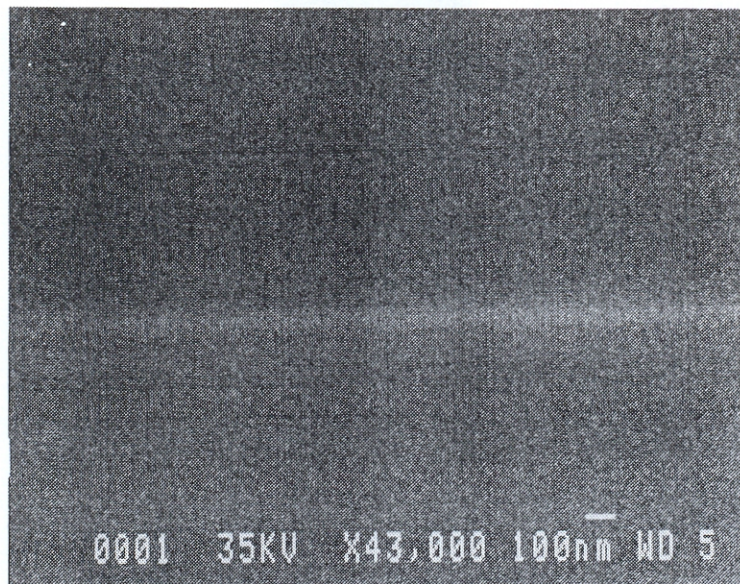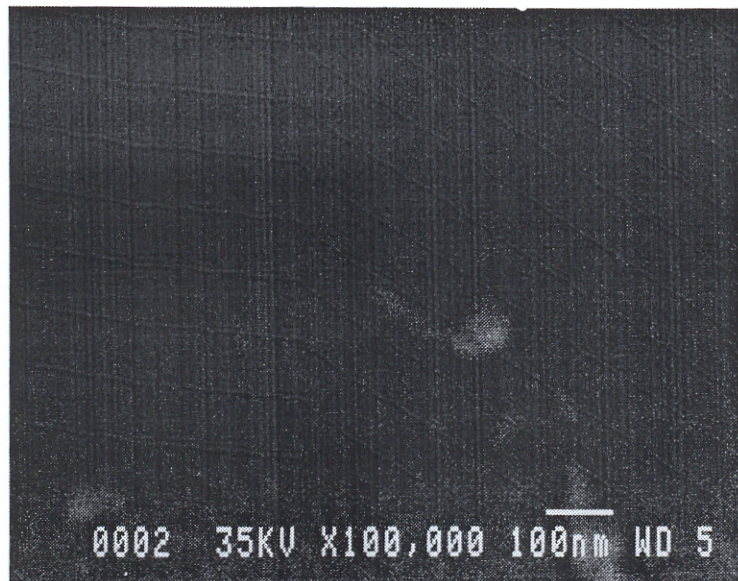
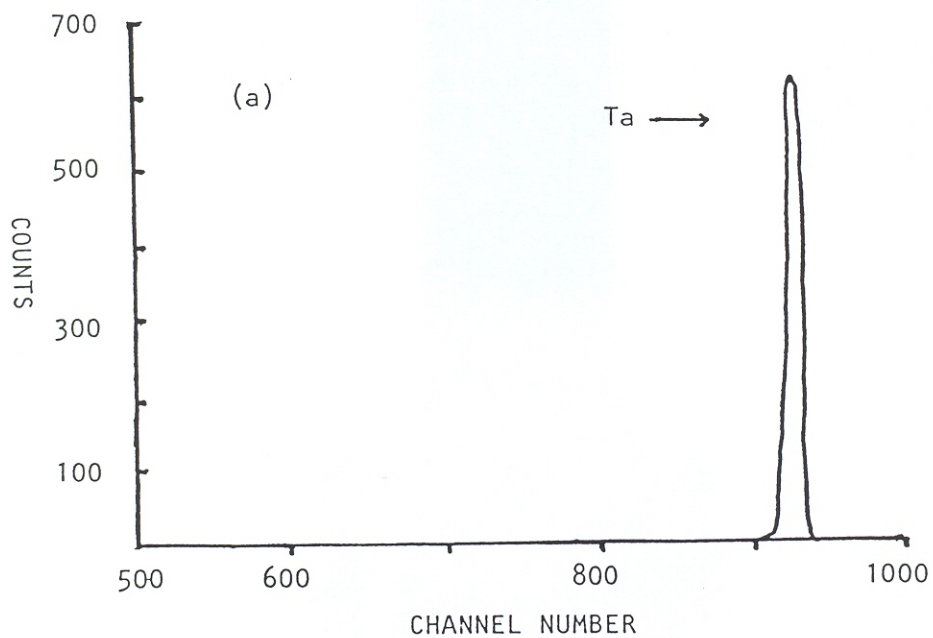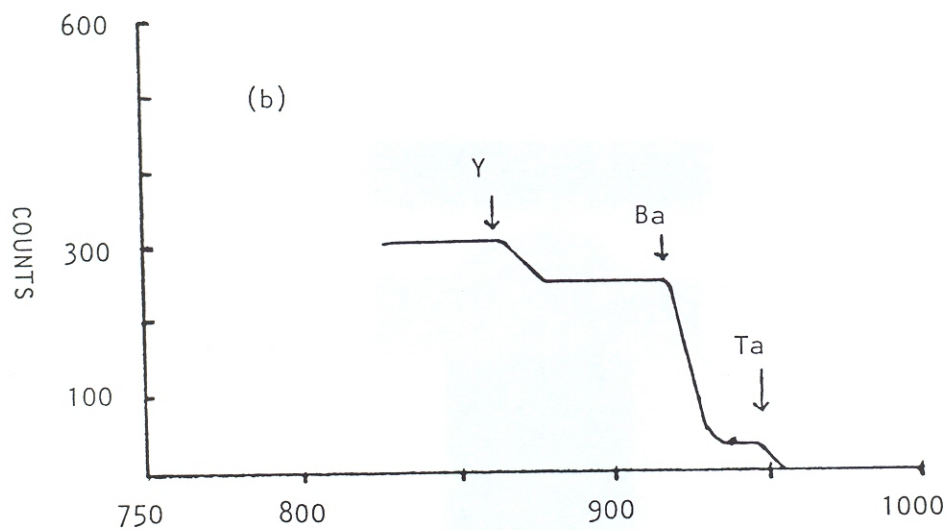Figure 1. SEM micrographs of barrier coatings, a) Ta_2O_5 and b) YSZ
on sapphire.

Figure 2. RBS spectra of a) Ta_2O_5 barrier coating on sapphire, and b) superconductor coating on Ta_2O_5 on sapphire, after heat treatment.
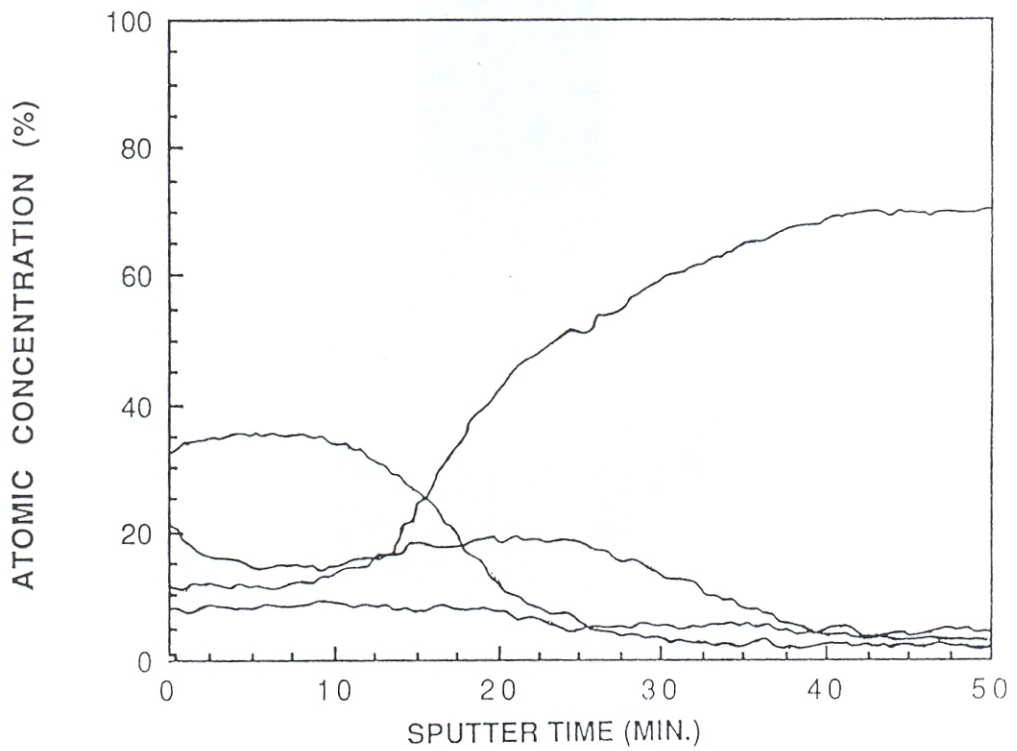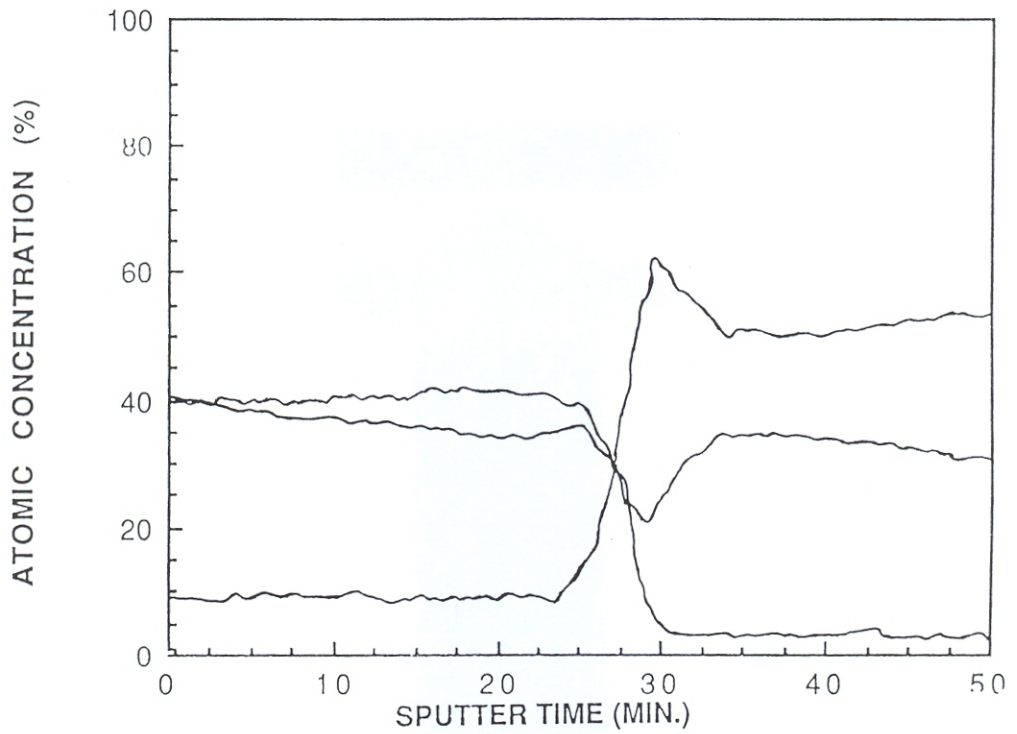
Figure 3. Auger sputter depth profiles of a) Ta_2O_5 barrier coating on sapphire, and b) superconductor coating on Ta_2O_5 on sapphire, after heat treatment.
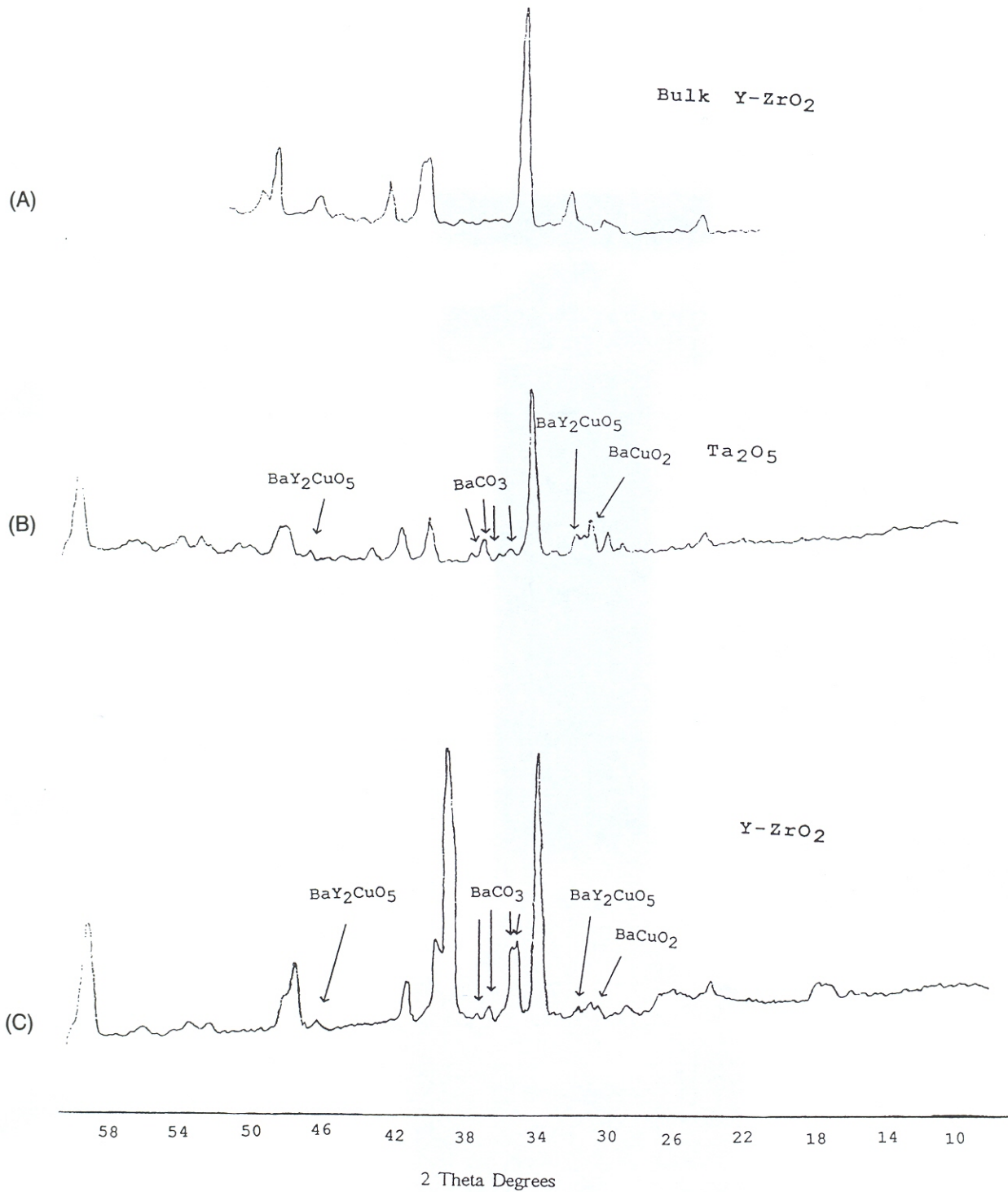
Figure 4. X-ray diffraction patterns of superconductor coatings on a) bulk YSZ, b) Ta$_2$O$_5$ barrier coating on sapphire, and c) YSZ barrier coating on sapphire.