Characterization of yttria-stabilized zirconium oxide buffer layers for high-temperature superconductor thin films

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We have employed transmission electron microscopy and x-ray diffraction to investigate the properties of yttria-stabilized zirconium oxide (YSZ) sputter deposited on silicon. It is shown that the as-deposited YSZ films are polycrystalline (grain size 7–20 nm) with microvoids between grains. Anneals of these films at temperatures of 800, 950, and 1100 °C for 1 h eliminate the microvoids and cause the grain size to increase from 20 to 50 nm at the higher anneal temperatures. Particular texture of the YSZ film is controlled by the details of the deposition conditions. Resistivity measurements of superconducting films deposited on silicon using these buffer layers are also presented.

INTRODUCTION

A number of workers have now reported the use of buffer layers to permit the deposition of thin films of high-temperature superconductors on substrates such as silicon, alumina, and sapphire.[1–4] It is likely that the use of buffer layers will make it possible to deposit thin superconducting films on a variety of substrates which by themselves are not suited for this application either due to a high degree of reaction with the superconductor or the lack of an appropriate lattice match. Yttria-stabilized zirconium oxide (YSZ) has been one of the buffer layer materials which has been employed both on silicon and alumina.[2–4] Recent work has also shown that it may be possible, by using certain deposition techniques, to obtain superconducting films on silicon without the use of buffer layers.[5,6] However, limiting the degree of reaction between substrate and superconductor is not the only role of the buffer layer. Morita and co-workers have shown that ZrO_2 may be grown epitaxially on silicon using vacuum evaporation with preferred orientations depending on the deposition conditions.[7] Thus, this buffer layer may aid in imposing particular orientation on the superconducting film.

In this paper we employ transmission electron microscopy (TEM) to examine the microstructural details of the YSZ films sputter deposited on (100) silicon and to analyze the crystallography of individual grains. X-ray diffraction was also employed to characterize the average texture of large areas of the buffer layer. Resistivity versus temperature measurements of superconducting films of $YBa_2Cu_3O_{6+x}$ deposited on silicon and employing the YSZ buffer layer are also presented.

EXPERIMENTAL DETAILS

rf diode sputtering from a single target was used to deposit the YSZ. Superconducting films were also deposited using rf diode sputtering from a single target in the same sputtering system. The sputtering system itself was constructed at CMU specifically for superconductor deposition. A small target to substrate spacing (approximately 1.5 cm) was employed so that high argon pressures (as high as 110 mTorr) could be used. It has been shown that the use of high argon pressure minimizes the degree of neutral oxygen resputtering and this along with details of the sputtering system are discussed in other publications.[8–10] For the deposition of the YSZ the argon pressure was 25 mTorr with a nominal input power of approximately 50 W. The YSZ target composition was 10% yttria by weight. The YSZ films studied were typically in the thickness range 5000–9000 Å. The superconductor was deposited using an argon pressure of 90 mTorr and the target employed was 25% rich in barium to improve the film stoichiometry. In both cases the substrate was not deliberately heated.

Transmission electron microscopy was carried out using a Philips EM 420T electron microscope operating at 120 kV. For the TEM studies plan view samples were removed from the substrate by mechanical thinning after which they were mounted onto molybdenum grids and ion (Ar^+) beam milled. X-ray diffraction measurements were performed using a Rigaku θ–2θ diffractometer with Cu$K\alpha$ radiation. Films of YSZ were studied as-deposited as well as after anneals at 800, 950, and 1100 °C under an oxygen ambient. The anneals of both the YSZ and superconducting film consisted of a ramp up at a rate of 30 °C per min, 1 h at the desired temperature, followed by a ramp down at 2 °C per min to room temperature.

RESULTS AND DISCUSSION

Figure 1 is a typical (a) bright- and (b) dark-field TEM micrograph of the as-deposited YSZ film as well as (c) selected area diffraction (SAD) and (d) convergent beam electron diffraction (CBED) patterns. In this instance, the YSZ films are composed of small crystalline grains with microvoids (arrow) between the grains; the grain size is in the range of 7–20 nm. The formation of crystalline phases can be confirmed by the SAD pattern in Fig. 1(c) since we do not observe any evidence of amorphous halo rings in this pattern. The SAD pattern also indicates that the films consist primarily of the tetragonal YSZ phase and are nearly ran-

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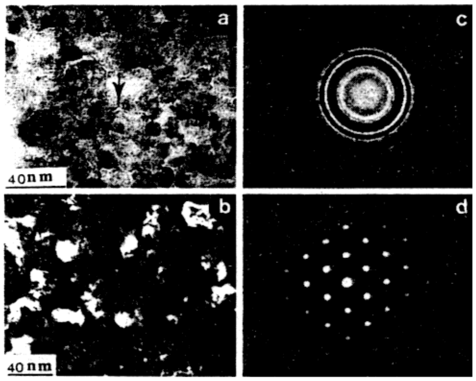

FIG. 1. (a) TEM bright-field and (b) dark-field images of as-deposited YSZ film on silicon. In (c) and (d) are presented the SAD and CBED patterns for this film with (d) oriented in the [110] direction.

domly oriented. The CBED pattern is for a [110]-oriented grain.

It should be noted that the x-ray diffraction measurements of the as-deposited films (not shown here) are in agreement with the TEM observations described above. The formation of microvoids at the grain boundaries is not unexpected since the argon pressure used during deposition is high enough to produce microvoids.[11,12] When the film is annealed at 800 °C, the grain size increases from 10 to 25 nm and most of the microvoids disappear. The disappearance of the microvoids is probably due to the grain growth. A similar observation has been made on the film annealed at 900 °C.

Figure 2 is a bright-field image (a) of the YSZ film annealed at 1100 °C together with its SAD pattern (b) and CBED patterns [(c) and (d)]. In this case the grain size is in the range 20–50 nm with some grains substantially larger. There is no evidence for microvoids as observed in the films annealed at lower temperatures. The SAD pattern shows a combination of the tetragonal and monoclinic structures although the tetragonal structure is predominant. This is confirmed by the CBED patterns on individual grains [see Figs. 2(c) and 2(d)]. Figure 2(c) shows the CBED pattern for a [110]-oriented grain while in 2(d) the pattern for a [001]-oriented grain is presented. The observation of monoclinic structure is infrequent although larger grains are usually monoclinic. For the grain size in the range of 80–100 nm the *d* spacings for the SAD pattern and CBED patterns reveal values of 2.84, 2.45, 2.33, and 2.11 Å which match well with the monoclinic structure obtained from x-ray diffraction literature.

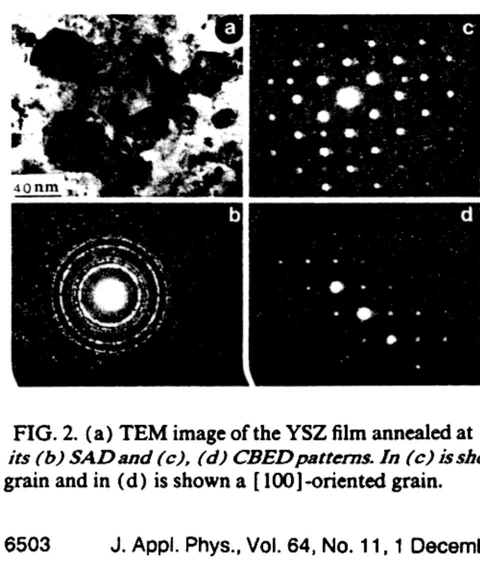

FIG. 2. (a) TEM image of the YSZ film annealed at 1100 °C together with *its (b) SAD and (c), (d) CBED patterns. In (c) is shown a [110]-oriented* grain and in (d) is shown a [100]-oriented grain.

The observation of monoclinic structure at larger grain size is consistent with other results.[13] Similarly it has been reported that a mixture of monoclinic and tetragonal structure are present in ZrO_2 annealed below 800 °C but only the tetragonal structure is produced above 800 °C.[6] It thus appears that annealing temperature and grain size are major causes for the stabilization of the metastable tetragonal ZrO_2 at room temperature and not yttria content alone.

In Fig. 3 is presented an x-ray diffraction pattern for a YSZ film (approximately 0.6 μm thick) deposited on silicon and annealed for 1 h at 1100 °C under an oxygen ambient. The peaks are labeled according to the cubic system for the tetragonal phase. This pattern alone is not sufficient to distinguish between the cubic and tetragonal YSZ phase but our identification is based rather on both the x-ray and electron diffraction results. The integrated intensity ratio of the (111) to (220) reflection would be 100/35 for a random powder sample as obtained from x-ray diffraction files. In Fig. 3 the estimated integrated intensity (FWHM times peak height) ratio of the diffraction peak associated with the (111) planes to the (220) reflection is about 100/27. While this is in approximate agreement with the intensity ratio expected for a random powder sample the absence of the (200) reflection, for example, indicates that this film has primarily (111) and (220) texture. In Fig. 4 is presented the x-ray diffraction spectrum for a YSZ film (approximately 0.9 μm thick) deposited on silicon and annealed at 1100 °C for 4 h. We see that the ratio of the (111) to (220) reflection is 100/183. We therefore conclude that this film is primarily textured with the (110) planes parallel to the silicon surface. We also observe the appearance of the (200) reflection which was not observed in Fig. 3. The intensity ratio of the (111) to (200) reflection in Fig. 4 is 100/62. This ratio

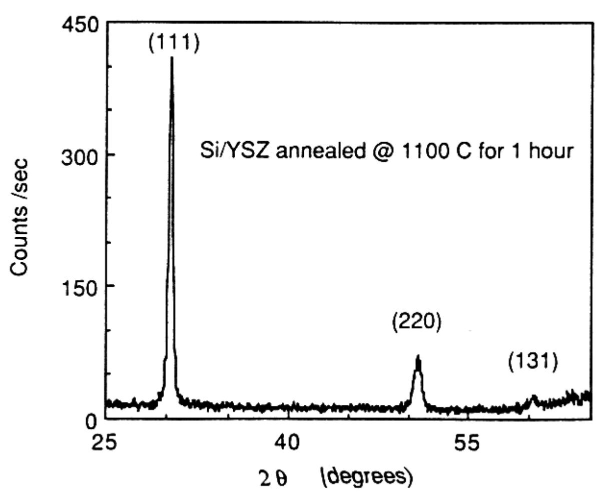

FIG. 3. X-ray diffraction pattern for a YSZ film deposited on silicon and *annealed at 1100 °C for 1 h. The peaks are labeled according to the cubic* system for the tetragonal phase.

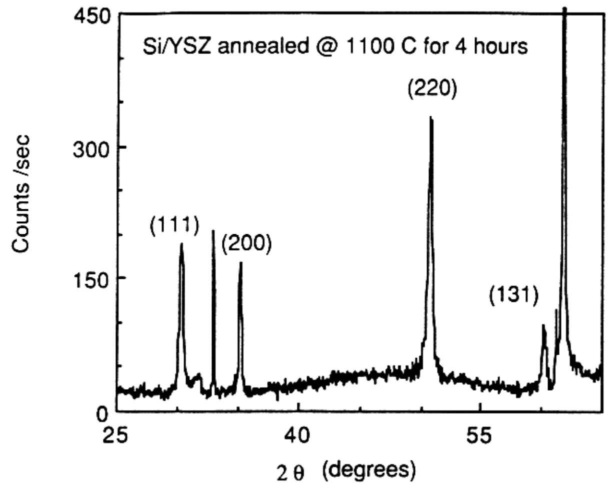

FIG. 4. X-ray diffraction pattern for a YSZ film deposited on silicon and annealed at 1100 °C for 4 h. The peaks are labeled according to the cubic system for the tetragonal phase. The peak at about 33° corresponds to the (200) forbidden reflection of the silicon while the peak at about 62° corresponds to the (400) $K\beta$ reflection from the silicon.

would be expected to be 100/25 for a random powder sample. In Fig. 4 the peak at ~33° corresponds to the forbidden (200) reflection from the silicon substrate while the peak at ~62° corresponds to the (400) $K\beta$ reflection from the silicon substrate. It is our observation that we consistently obtain an x-ray diffraction spectrum similar to that of Fig. 3 when the YSZ film is about 0.5 μm thick and independent of annealing conditions (anneal time, cooling rate) at 1100 °C. We obtain an x-ray diffraction pattern similar to that of Fig. 4 when the YSZ film is about 1.0 μm thick. Thus, thickness appears to be controlling the texture of the YSZ film.

Finally in Fig. 5 is presented a resistivity versus temperature plot for a superconducting film deposited on silicon with a YSZ buffer layer annealed at 1100 °C for 1 h. This film was approximately 1.4 μm thick at the center of a 2-in.-diam wafer and was annealed at 800 °C for 10 min in an oxygen ambient after deposition. An onset of the resistive transition is observed at 95 K and zero resistance ($\rho < 10^{-7}\ \Omega$ cm) is achieved at 43 K (the highest zero-resistance state we have obtained to date is at 51 K). The breadth of the transition, the semiconducting behavior observed above T_C, and the fact that the values of the resistivity are larger than the corresponding bulk values indicate that our films are probably not stoichiometric. Compositional and structural studies of these films are currently in progress.

CONCLUSIONS

In conclusion we have shown that yttria-stabilized zirconium oxide may be sputter deposited on silicon and a polycrystalline film with texture can be obtained. The texture obtained has been shown to be a function of the details of the

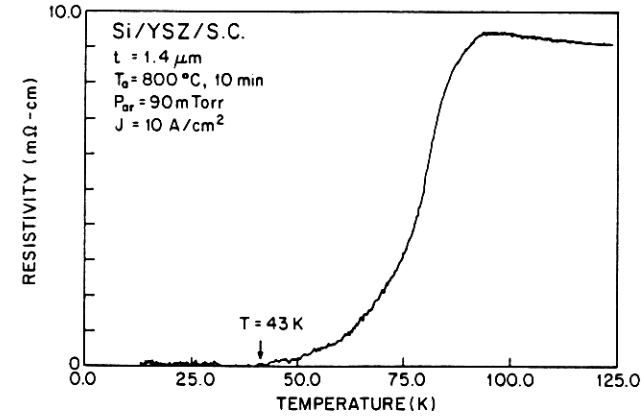

FIG. 5. Resistivity vs temperature plot for a superconducting film deposited on YSZ-coated silicon. The measurement was made in a four-point van der Pauw configuration using indium contacts.

processing conditions employed. The YSZ films not only decrease the degree of substrate superconductor reaction, resulting in sharper transitions as has already been shown,[1,4,14] but may, given the texture of the buffer layer, impose a texture on the superconducting film. The ability to texture the superconductor on substrates such as silicon is important if one is to fabricate superconductors with high current densities on these materials.

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