New buffer layer for high-temperature superconducting ceramics on sapphire: $LaBa_2Cu_3O_y$/Ag bilayers

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We have grown highly oriented $LaBa_2Cu_3O_y$ (110)/Ag (111) bilayers on sapphire ($11\bar{2}0$). This structure constitutes a potentially excellent buffer layer for the growth of 1-2-3 ceramic oxides on sapphire substrates. This bilayer does not show superconductivity in resistive measurements. A $DyBa_2Cu_3O_y$ film grown on this bilayer also exhibited (110) orientation.

Sapphire (α-Al_2O_3) is a desirable substrate for the growth of superconducting thin films due to its low dielectric constant and the extensive interest on silicon on sapphire technology. Unfortunately there exists a strong chemical interaction between sapphire and $REBa_2Cu_3O_y$ (RE-123) ceramics[1-3] which complicates the growth of high-quality-thin-film ceramic superconductors. Several reports on the growth of RE-123 superconducting thin films on sapphire substrate with and without buffer layers[1-7] have shown that the quality of these films is inferior to that of films grown on other suitable substrates, e.g., $SrTiO_3$ and MgO. Witanachchi *et al.*[7] reported the growth of $YBa_2Cu_3O_y$ (Y-123) films on sapphire ($\bar{1}012$) using Ag buffer layers, but no structural information was reported for the Ag nor the Y-123 films.

Here we report the growth of $LaBa_2Cu_3O_y$ (La-123)/Ag bilayers on sapphire ($11\bar{2}0$) substrates and show them to be excellent buffer layers for the growth of RE-123 films on sapphire. This structure has the inherent advantages that it is well matched to other RE-123 films and that it provides an excellent diffusion barrier. Moreover, to our knowledge, this is the first time that well oriented non-*c*-textured 123 films are grown on sapphire. This is significantly important for electronics applications because of the short superconducting coherence length along the *c*-axis of 2–3 Å which makes non-*c*-textured 123 films preferable for Josephson and tunnel devices.

All fabrication processes were performed *in situ* using magnetron sputtering. The RE-123 stoichiometric ceramic targets were prepared from better than 99.9% pure La_2O_3, Dy_2O_3, $BaCO_3$, and CuO. The calcined powders were pressed into the proper shape and sintered in air at 935 °C for 3 h. The sputtering gas was a mixture of 10% oxygen/90% argon and either at 100 or 300 mTorr of total pressure. The deposition geometry was always with the substrate surface opposing the target (on-axis geometry) at a vertical distance of 1 in. The substrate was positioned above the edge of the target to avoid resputtering effect. The actual substrate temperature was calibrated against the holder temperature using a second thermocouple in different runs.

dc magnetron sputtering was used for the Ag deposition at typical rates of 20–50 Å/s. Either dc or rf magnetron sputtering was used to deposit RE-123 films with deposition rates in the range 0.4 to 1.0 Å/s. After the final deposition the chamber was immediately filled with 1 Torr of oxygen gas and the heater was turned off. Room temperature was reached in approximately 1 h. The structure of the films was investigated using Cu-K_α x-ray diffraction (XRD). Chemical composition of the films was determined from energy dispersive x-ray analysis (EDX) and electron probe micro analysis (EPMA) and found to be within 10% of the 123 composition. Electrical resistivity was measured using a conventional dc four-probe method.

The (111) preferential orientation of Ag on 90° cut sapphire with a weak Ag (200) XRD peak for substrate temperatures from 23 to 278 °C was reported by Khan *et al.*[8] Using pure argon as sputtering gas we found excellent ($11\bar{1}$) orientation at a substrate temperature of 450 °C on ($11\bar{2}0$) cut sapphire with these planes parallel within 0.5°. The in-plane structure was preferentially oriented with the Ag [101] parallel to the sapphire [0001]. Different Ag orientations were found on different sapphire orientations at the same substrate temperature; e.g., Ag grows (311) textured on ($01\bar{1}0$) sapphire and (110) textured on ($01\bar{1}2$) sapphire. For bilayer and trilayer depositions all Ag films were grown using 10% oxygen/90% argon as sputtering gas at 450 °C and resulted in pure Ag films with the same epitaxial orientation as films sputtered in pure argon although room temperature growth resulted in AgO films. This behavior is not surprising due to the thermodynamic instability of AgO at this high temperature.

A minimum substrate temperature of ~500 °C is necessary to grow RE-123 films of RE = Sm, Dy, Y, Er, and Yb in our deposition system. The $LaBa_2Cu_3O_y$ crystal structure is formed at temperatures as low as 450 °C. Figures 1 and 2 show the XRD spectrum and temperature dependence of the resistivity of a La-123 film grown on polycrystalline yttria stabilized zirconia (YSZ) substrate at 450 °C. The two peaks from La-123 that are observed in Fig. 1 can be indexed either as the (100) and (200) reflections of (100) textured (*a*-textured) film or as the (003) and (006) reflections of (001) textured (*c*-textured) film with complete intermixing between La and Ba. (The latter means that our La-123 is no longer trilayer structure but is cubic.) We favor the *c*-textured hypothesis for the follow-

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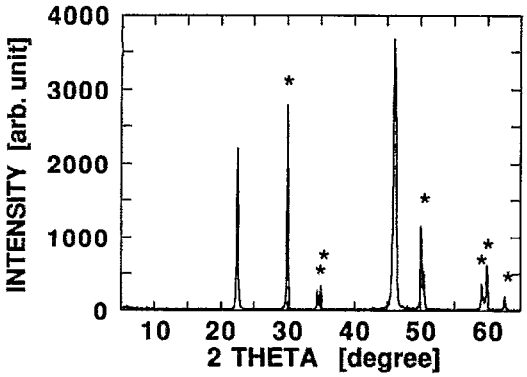

FIG. 1. XRD spectra of $LaBa_2Cu_3O_y$ film grown on a polycrystalline YSZ substrate at 450 °C. Asterisks show the reflection peaks of YSZ substrate.

ing reasons; (a) The $La_{1+x}Ba_{2-x}Cu_3O_y$ system[9] is known to have solid solution in the range $0 \leqslant x \leqslant 0.5$ with the excess La occupying Ba sites. It is also believed that La-Ba disorder exists even at $x = 0$, especially if the sample is prepared at low temperature. (b) All other RE-123 thin films fabricated by us on the same substrate exhibit c-texture dominant growth and superconductivity (except Pr-123). The resistivity of the La-123 film has semiconducting like temperature dependence and a high value which is not affected by oxygen annealing at a pressure of 1 atm at 300 °C for 12 h.

Figure 3 shows the XRD spectra of a Dy-123 (5000 Å)/ La-123 (1500 Å)/Ag (5000 Å) trilayer deposited on $(11\bar{2}0)$ sapphire. After the La-123/Ag bilayer deposition at 450 °C, the substrate temperature was increased to 530 °C and the Dy-123 layer was grown. This higher substrate temperature is necessary to form Dy-123 structure. Clearly the texture of 123 films is different from the La-123 film grown on polycrystalline YSZ. The peaks at $\approx 33°$ in Fig. 3 may be indexed as (110), (103), and (013) reflections. However, the presence of (013) and (103) textured phase implies that (0011) and (0013) reflections should be observed at $\approx 88.6°$ and $\approx 76.1°$ out of the perpendicular to the film. Since neither of these peaks were observed the 123 layers must be (110) textured. The high quality crystallographic orientation of these films is indicated by narrow full width at half maximum of rocking curves for Dy-123

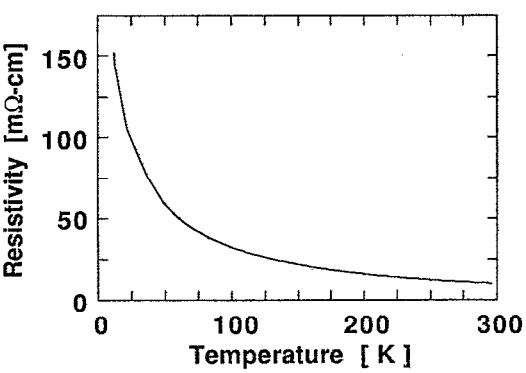

FIG. 2. Resistivity vs temperature curve of $LaBa_2Cu_3O_y$ film grown on polycrystalline YSZ substrate at 450 °C.

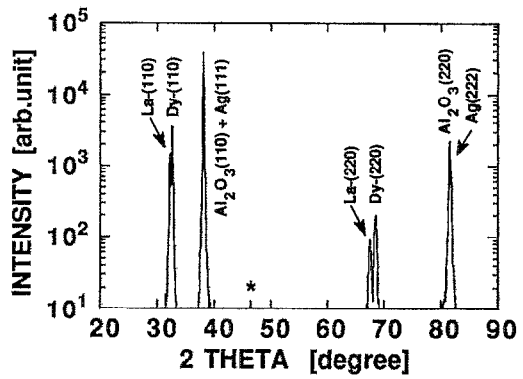

FIG. 3. XRD spectra of $DyBa_2Cu_3O_y/LaBa_2Cu_3O_y$/Ag trilayer on sapphire $(11\bar{2}0)$ substrate. The small reflection peak with an asterisk is (200), (020), or (006) peak of $LaBa_2Cu_3O_y$ or $DyBa_2Cu_3O_y$ films.

(220), La-123 (220), and Ag (222) peaks of $\approx 0.6°$, $\approx 0.6°$, and $\approx 0.3°$, respectively. These rocking curve scans also indicated that (110) planes of Dy- and La-123 films are parallel to Ag(111) plane and sapphire $(11\bar{2}0)$ plane, and not parallel to substrate surface, showing the epitaxial nature of this system. The superconducting properties of Dy-123/La-123/Ag trilayer are still under investigation and will be reported separately. La-123/Ag bilayers on sapphire are not superconducting down to 10 K.

Figure 4 shows XRD spectra of a Ag (5000 Å)/La-123 (5000 Å)/Ag (5000 Å) trilayer deposited on $(11\bar{2}0)$ sapphire at 450 °C. The almost perfect La-123 (110)/Ag (111) texture exhibits a weak reflection peak at 46.3° indexed as La-123 (006) and a trace of Ag (200) reflection $\sim 10\,000$ times weaker than the Ag (111) reflection. These results show that the La-123 (110)/Ag (111) is also a good candidate for an artificially multilayered material.

Only a very narrow window of temperature exists for the growth of highly textured La-123 (110) on Ag (111)/sapphire $(11\bar{2}0)$. Figure 5 shows the XRD spectra of a La-123 (560 °C)/Ag (450 °C) bilayer on sapphire. Although at this substrate temperature La-123 layer has (001) preferential orientation, other orientation peaks are also observed. The existance of the (001) and (002)

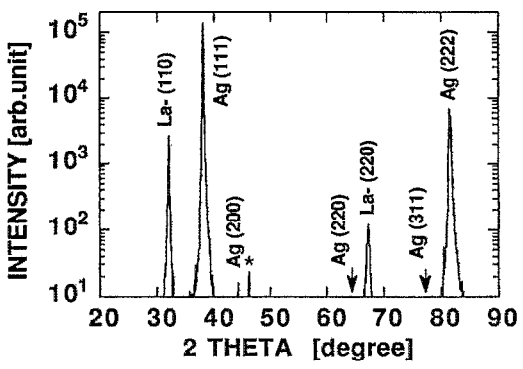

FIG. 4. XRD spectra of $Ag/LaBa_2Cu_3O_y$/Ag trilayer on sapphire $(11\bar{2}0)$. The reflection peak with an asterisk is $LaBa_2Cu_3O_y$ (200), (020), or (006) peak. A small Ag (200) peak is also observed; the expected peak positions for the Ag (220) and (311) are also shown with arrows.

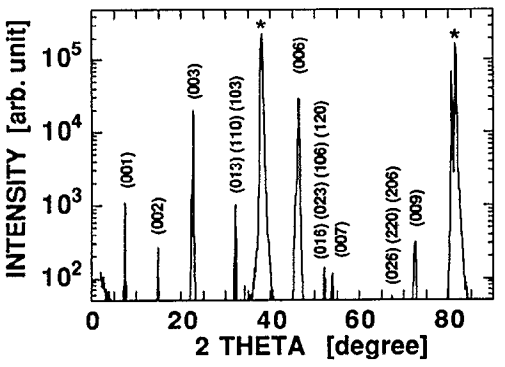

FIG. 5. XRD spectra of $LaBa_2Cu_3O_y$/Ag bilayer on sapphire ($11\bar{2}0$) with $LaBa_2Cu_3O_y$ layer deposited at a substrate temperature of 560 °C. Asterisks show the peaks of Ag layer and sapphire substrate.

peaks indicate that this La-123 layer does not have complete intermixing between the La and Ba sites, nevertheless, it is not superconducting. Our hypothesis is that there still exists a big amount of A-site cation disorder in this material. At this and higher growth temperatures of La-123 the resultant film is rough maybe due to the Ag surface roughness. However, in the Dy-123/La-123/Ag trilayer system the growth of Dy-123 film at higher temperature, e.g., 700 °C, on 450 °C grown La-123/Ag bilayer does not exhibit this roughness presenting very smooth surface morphology with (110) orientation.

In summary, we fabricated $LaBa_2Cu_3O_y$/Ag bilayers on sapphire ($11\bar{2}0$) substrate and showed they are potentially excellent buffer layers for 123 film growth on sapphire. The $LaBa_2Cu_3O_y$ layer on Ag layer shows excellent (110) texture at a deposition temperature of 450 °C and (001) preferred orientation at a deposition temperature of 560 °C. All $LaBa_2Cu_3O_y$ layers in this study were not superconducting. A $DyBa_2Cu_3O_y$ film on (110) $LaBa_2Cu_3O_y$ also presented (110) orientation.

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