Excellent buffer layer for growing high-quality Y–Ba–Cu–O thin films

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Eu_2CuO_4 (ECO) has been used as a buffer layer for growing of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films on $SrTiO_3(100)$ and Y-stabilized $ZrO_2(100)$ substrates. The epitaxy, crystallinity, and surface of YBCO thin films have been significantly improved by using ECO buffer layer as investigated by x-ray diffraction, rocking curves, scanning electron microscope, surface step profiler, and x-ray small-angle reflection. The best value of the full width at half-maximum of the YBCO(005) peak can be greatly reduced down to less than 0.1°. The scanning-electron-microscope photos indicate a very smooth surface for the YBCO thin films. The average roughness is less than 5 nm over a wide scanning region of 2000 μm. The results of x-ray small-angle reflection indicate a very clear and flat interface between YBCO and ECO layers. Meanwhile, the resistivity of ECO is about 20 times higher than that of $PrBa_2Cu_3O_y$ at the boiling point of liquid nitrogen. Our results suggest that ECO should be a good barrier candidate for fabricating high-T_c superconductor junctions.

I. INTRODUCTION

Compared with 123-phase compounds, the 214-phase compounds show higher stability in crystal structure and have no structural phase transition below the deposition temperature or when the oxygen content changes. On the other hand, the thin films of 214-phase compounds always show excellent crystallinity and very smooth surface. By using $La_{1.85}Sr_{0.15}CuO_4$ (LSCO) with 214-T-phase structure as a buffer layer, the growth of $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films on yttrium-stabilized ZrO_2 (YSZ) substrates can change from island-growth mode to the layer-by-layer one.[1] Nd_2CuO_4 (NCO) with 214-T′-phase structure had also been proved to significantly improve the initial epitaxy of YBCO thin films.[2] The in-plane lattice parameter of LSCO is $a \sim 3.79$ Å, and that of NCO is $a \sim 3.94$ Å. A compressive or an expansive stress could be arisen when YBCO thin film is grown on the LSCO or NCO buffer layer. The in-plane lattice parameter of Eu_2CuO_4 (ECO) ($a \sim 3.89$ Å) lies just between those of LSCO and NCO. Thus, we can compare the stress effects coming from different buffer layers on the superconducting properties of YBCO thin films. The lattice mismatch between ECO and YBCO is the smallest among the above-mentioned three 214 compounds, so the ECO could be a better buffer layer for the growth of high-T_c superconducting thin films. Besides, because ECO shows a semiconducting behavior, with high value of resistivity at low temperature, it could also be a good barrier for fabricating high-T_c Josephson junctions with high I_cR_n value. In this work, ECO thin films have been grown on $SrTiO_3$ (STO) (100) substrates by the magnetron radio-frequency (rf) sputtering method. The films were investigated by x-ray diffraction (XRD), rocking curves, scanning electron microscope (SEM), etc.

II. EXPERIMENTAL

YBCO thin films and ECO buffer layers were deposited on STO(100) and YSZ(100) substrates by an off-axis rf sputtering system.[3] The deposition temperature, referred hereafter to as the substrate temperature T_s, was measured by a k-type thermocouple inserted into the

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stainless substrate heater. The substrate was stuck on the heater by silver glue. The substrate temperature was 730 ~ 750 °C. The deposition gas was a mixture of argon and oxygen with different pressure ratios (P_{Ar}/P_{O2} ~ 3 to 4). The YBCO thin film and ECO buffer layer were grown by using the same deposition conditions. The XRD was performed on the Siemens D5000 x-ray diffractometer with Cu K_α radiation ($\lambda = 1.5405$ Å). The crystallinities of YBCO and ECO thin films were examined by measuring their rocking curves of (005) and (006) diffraction peaks respectively. The surface of YBCO thin films was characterized by a Dektak3ST surface step profiler and a Cambridge 440 SEM.

The temperature dependence of resistance was measured by a standard direct-current four-probe method using a closed-cycled cryogenerator. A platinum resistance thermometer was used to measure the temperature. The cooling rate was well controlled to be less than 1 K/min. A well-defined microbridge step (50 μm in width, 100 μm in length) was patterned by using the photolithography technique for determining the superconducting critical current of YBCO thin films. A 5-μV criterion was used to define the superconducting critical current I_c.

III. RESULTS AND DISCUSSION

The XRD pattern for single ECO layer indicates highly *c*-axis oriented and excellent crystallinity. Only (00*l*) ($l = 2n$) diffraction peaks for ECO were observed. The rocking curves indicate very small value of the full width at half-maximum (FWHM), typically smaller than 0.15°. This value even is smaller than that of (005) with lower 2θ value (approximately 38.5°) for YBCO. Unlike 123-phase thin films, ECO thin film exhibits a very smooth surface without outgrowth. That could be attributed to its high structural stability.

The ECO thin film exhibits a semiconducting behavior. Figure 1 shows the temperature dependences of the resistivities of ECO and $PrBa_2Cu_3O_y$ (PBCO) thin films. It is seen that the resistivity of ECO is much higher than that of PBCO, especially at lower temperature. For example, at 77 K, the resistivities for ECO and PBCO are 140 and 7 mΩ cm, respectively. Besides, the increasing rate of the resistivity with temperature for ECO thin film is also remarkably larger than that of PBCO. PBCO has been widely used as a buffer layer and a barrier material for high-T_c junctions. However, it has several drawbacks, such as poor surface, structural instability, chemical interdiffusion, and relatively low resisitivity. ECO could be superior to PBCO for the applications as a buffer layer or a barrier material.

By using ECO as a buffer layer, YBCO thin films have been grown on STO and YSZ substrates. Figure 2 shows the XRD pattern for two typical YBCO thin films with an ECO buffer layer on STO(100) and YSZ(100) substrates. From the XRD patterns, only (00*l*) peaks for YBCO thin film and (*002l*) peaks for the ECO buffer layer were observed. It is suggested that the YBCO thin film and ECO buffer layer were grown along the *c*-axis orientation. The rocking curves of the (005) peak for the YBCO thin film and the (006) peak for the ECO buffer layer were measured respectively. Both rocking curves indicate very small values of the FWHM, smaller than 0.10° for both YBCO thin film and ECO buffer layer on STO and YSZ substrates. Small FWHM values result from excellent crystallinities of YBCO thin film and the ECO buffer layer. For the sake of comparison, we show the rocking curves for the YBCO thin films with ECO buffer layer on STO and YSZ substrates in Fig. 3. It is found that the FWHM value for the YBCO thin film on YSZ is slightly smaller than that on STO, indicating

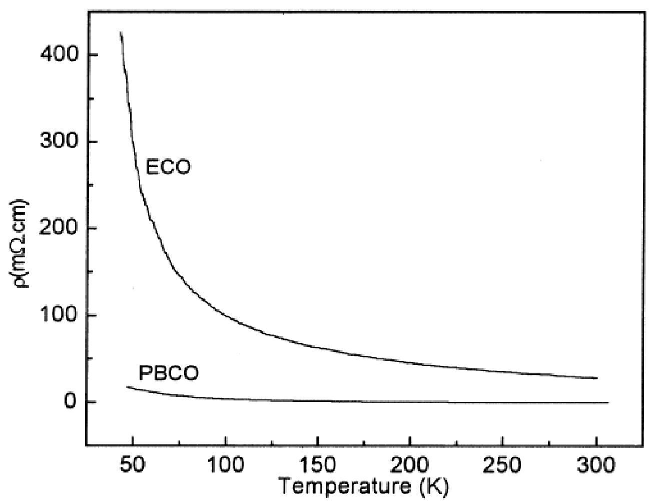

FIG. 1. Temperature dependences of the resistivities of ECO and PBCO thin films.

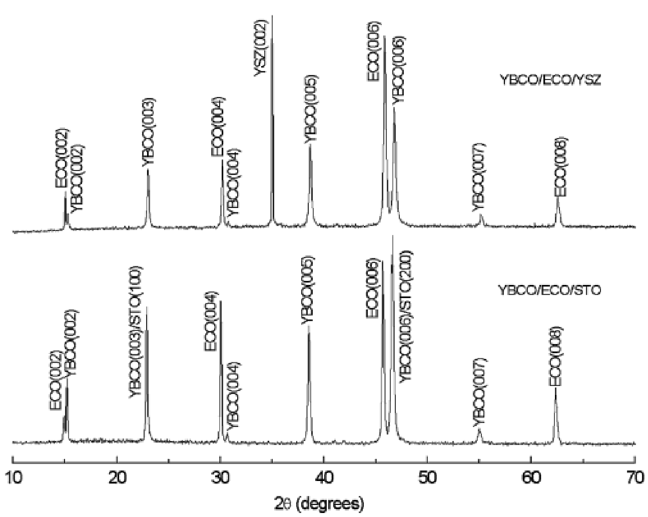

FIG. 2. XRD patterns for two typical YBCO thin films with ECO buffer layer on STO(100) and YSZ(100) substrates.

that by using ECO buffer layer, improvement of the crystallinity of YBCO thin film on YSZ is better than that on STO. That is consistent with the results of the x-ray small-angle reflection experiment.

The surface roughness and morphology of YBCO thin films was characterized by a surface step profiler and an SEM. The best vertical resolutions of the surface step profiler are 1 Å for the measuring range of 65 kÅ. Considering the flatness of the substrate, we first measured the average roughness of the YBCO thin film on the STO or YSZ substrate for ten times at random places, and got a mean value of the average roughness for the YBCO thin film on the STO or YSZ substrate, and then removed the YBCO thin film and ECO buffer layer from the STO or YSZ substrate by acid etching and cleaned the substrate to get another mean value of the average roughness for the raw substrate. The used acid is phosphoric acid (H_3PO_4). It does little damage to STO or YSZ substrate. In fact, most of the substrates were used repeatedly. Thus, we just ignored the effect of acid etching on the surface of substrates. The difference of the mean values of the average roughnesses for the YBCO thin film on the substrate and for the raw STO or YSZ substrate was defined as the average roughness of the YBCO thin film. The average roughness of YBCO thin films on both STO and YSZ over a wide scanning region of 2000 μm is less than 5 nm.

The YBCO thin films on STO and YSZ substrates both show excellent surface morphologies. Figure 4 shows the SEM surface morphology photos for the YBCO thin films without [Fig. 4(a)] and with [Fig. 4(b)] ECO buffer layer on YSZ substrate. The thickness of YBCO thin film is approximately 160 nm, and the thickness of ECO buffer layer is approximately 40 nm. It can be seen that YBCO thin film grown directly on YSZ substrate shows poor surface morphology. Many small outgrowths were observed, which are typical surface features for 123-phase thin films. By using the ECO buffer layer, the outgrowth was totally eliminated. The YBCO thin film with ECO buffer layer has an extremely smooth surface. The average roughness is less than 5 nm measured by a surface step profiler. Such a smooth surface could result from the layer-by-layer growth mechanism. It has been reported that the growth of YBCO thin film on YSZ substrates can change from island formation to layer-by-layer growth by using $La_{1.85}Sr_{0.15}CuO_4$ as a buffer layer.[1]

We have studied three compounds with 214-phase structure, i.e., $La_{1.85}Sr_{0.15}CuO_4$,[1] Nd_2CuO_4,[2] and Eu_2CuO_4 as buffer layers for the growth of YBCO thin films. All of them show good surface and crystallinity, and greatly improve the film quality of YBCO thin films. However, the currently used buffer layers of the doped 123-phase compounds, such as Ca-doped $PrBa_2Cu_3O_y$[4] and Nb-doped $YBa_2Cu_3O_y$[5] often cause poor surface

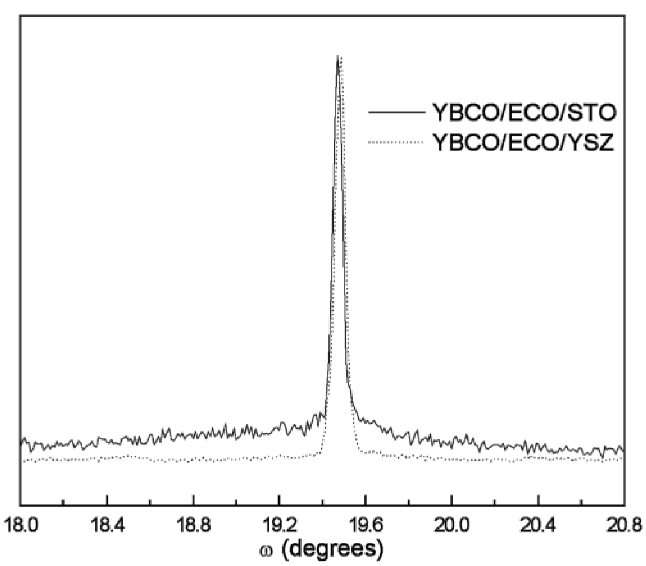

FIG. 3. Rocking curves for (005) peaks of YBCO thin films with ECO buffer layer on STO and YSZ substrates.

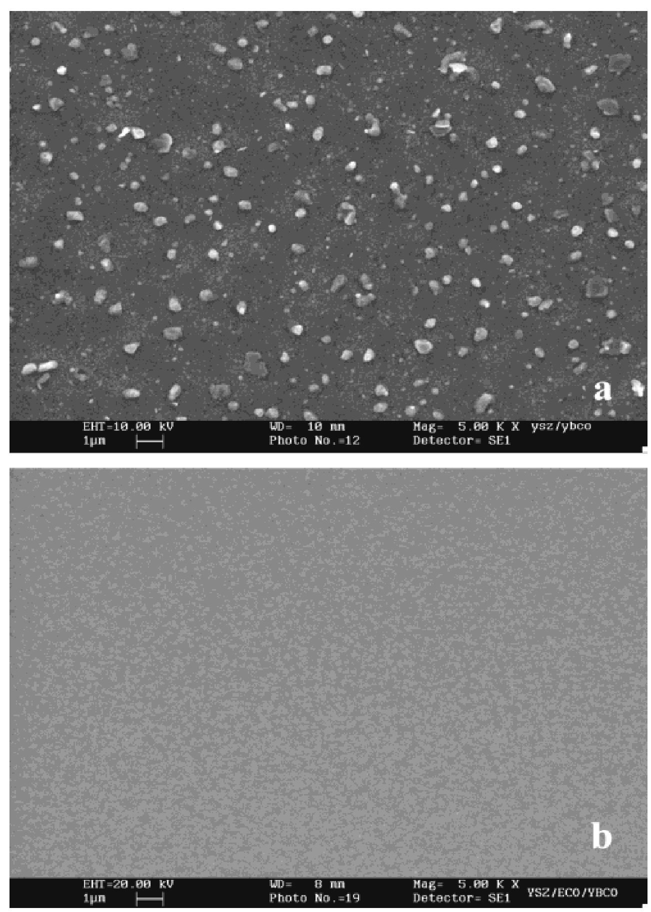

FIG. 4. The SEM surface morphology photos for the YBCO thin films (a) without and (b) with ECO buffer layer. The thickness of YBCO thin film is approximately 160 nm, and the thickness of the ECO buffer layer is approximately 40 nm.

morphology and crystallinity. This is because the outgrowths are easily formed for the 123-phase compounds. In general, a good buffer layer for growing high-T_c superconducting thin films should have a stable crystal having good lattice matching with the superconducting material. The buffer layer will not react with the grown superconducting thin films and has no significant interdiffusion. Also a good buffer layer should present a very smooth surface without outgrowths or other surface structures. Combining all above requirements, we can conclude that the 214-phase compounds are good buffer materials for growing high-T_c superconducting thin films.

TABLE I. Fitting results of the x-ray small-angle reflection profiles for YBCO thin films with and without ECO buffer layer on STO and YSZ substrates.

Sample[a]	Sublayer	Atomic density ($Å^{-3}$)	Thickness (±2 Å)	Root mean square of roughness (±2 Å)
A	YBCO	0.072	295	$\sigma_{air/YBCO} = 29$
	ECO	0.074	345	$\sigma_{YBCO/ECO} = 10$
	STO	0.082	⋯	$\sigma_{ECO/STO} = 3$
B	YBCO	0.075	290	$\sigma_{air/YBCO} = 18$
	YBCO	0.060	15	$\sigma_{YBCO/YBCO} = 4$
	STO	0.082	⋯	$\sigma_{YBCO/STO} = 5$
C	YBCO	0.075	255	$\sigma_{air/YBCO} = 23$
	YBCO	0.071	15	$\sigma_{YBCO/YBCO} = 3$
	ECO	0.075	408	$\sigma_{YBCO/ECO} = 6$
	YSZ	0.088	⋯	$\sigma_{ECO/YSZ} = 3$
D	YBCO	0.075	400	$\sigma_{air/YBCO} = 53$
	$BaZrO_3$	0.070	65	$\sigma_{YBCO/BZO} = 21$
	YSZ	0.087	⋯	$\sigma_{BZO/YSZ} = 5$

[a]Sample A, YBCO(500 Å)/ECO(500 Å)/STO; Sample B, YBCO(500 Å)/STO; Sample C, YBCO(500 Å)/ECO(750 Å)/YSZ; Sample D, YBCO(500 Å)/YSZ.

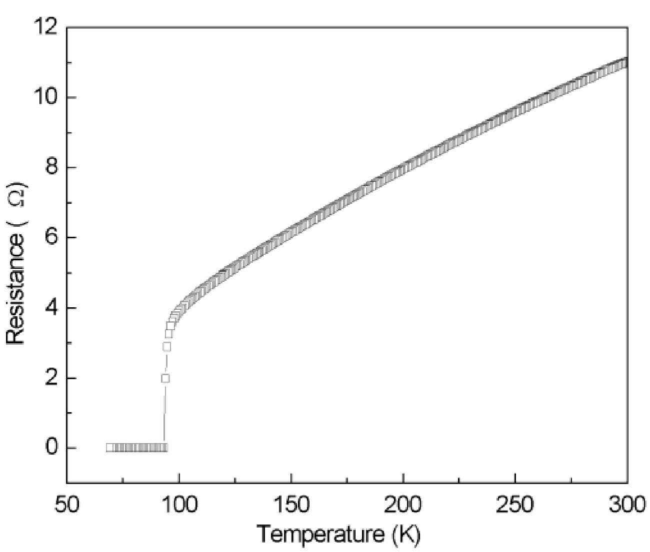

FIG. 5. The temperature dependence of the resistance for YBCO thin film (2000 Å) with ECO buffer layer (1000 Å) on YSZ substrate. Its zero-resistance transition temperature (T_{c0}) is 92 K.

The interfaces of ECO/STO(YSZ) and YBCO/ECO were investigated by the x-ray small-angle reflection experiment. Table I gives the fitting results of the x-ray small-angle reflection profiles for YBCO thin films with and without ECO buffer layer on STO and YSZ substrates. Detailed results will be reported elsewhere. For the thin film of YBCO growth directly on YSZ, an intermediate layer of $BaZrO_3$ was found. This $BaZrO_3$ layer normally causes poor crystallinity and degrades the superconductivity of YBCO thin film in the early growing stage. By using the ECO buffer layer, the $BaZrO_3$ intermediate layer was avoided. The interfaces of ECO/YSZ and YBCO/ECO are very clear and smooth. The values of the mean roughness are 3 and 6 Å, respectively. For YBCO thin film with ECO buffer on STO substrate, the mean roughness for the ECO/STO and the YBCO/ECO interfaces are 3 and 10 Å, respectively. Detailed interface characterizations by the transmission electron microscope and x-ray small-angle reflection are currently under study.

The YBCO thin films with the ECO buffer layers exhibit the higher zero-resistance superconducting transition temperature T_{c0}, normally higher than 87 K. The highest T_{c0} was 92 K for YBCO thin film (2000 Å) with ECO buffer layer (1000 Å) on YSZ substrate. (See Fig. 5). The superconducting critical current density was measured across a bridge with a width of 50 μm. The critical current density at 77 K under zero field is $2 \sim 4 \times 10^6$ A/cm^2, which is close to the reported value for YBCO thin films on STO substrates with La_2CuO_4 as buffer layers.[6] For YBCO thin films thicker than 1000 Å, we did not observe different effects of STO and YSZ substrates on the superconducting properties of YBCO thin film.

IV. CONCLUSIONS

ECO has been used as a buffer layer for growing YBCO thin films on STO and YSZ substrates. The epitaxy, crystallinity, and surface of YBCO thin films have been significantly improved by using an ECO buffer layer as shown by the results as investigated by XRD, rocking curves, SEM, surface step profiler, and x-ray small-angle reflection. The best value of the FWHM of the YBCO(005) peak can be greatly reduced down to less than 0.1°. The average roughness is less than 5 nm in the region of 2000 μm. The results of x-ray small-angle reflection indicate a very clear and flat interface between YBCO and ECO layers. Our results suggest that ECO should be a good barrier candidate for fabricating high-T_c superconductor junctions.

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