Epitaxial $YBa_2Cu_3O_y$ Thin Films Grown on Silicon With a Double Buffer of Eu_2CuO_4/YSZ

J. Gao, L. Kang, T. K. Li, Y. L. Cheung, and J. Yang

***Abstract*—We report a double buffer of Eu_2CuO_4 (ECO)/YSZ to improve the growth of $YBa_2Cu_3O_y$(YBCO) on Si wafer. The ECO buffer material possesses a very stable 214-T' structure. It has excellent structural and chemical compatibilities with YBCO and YSZ. Our study showed that the epitaxy and crystallinity of YBCO deposited on Si could be considerably enhanced by using such a double buffer of ECO/YSZ. The grown films were characterized by grazing incidence X-ray reflection, rocking curve, SEM, TEM, and surface profiler. It was also found that such a double buffer could lead to a very smooth surface in the YBCO layer.**

***Index Terms*—High temperature superconductors, materials processing, sputtering, superconducting films.**

I. INTRODUCTION

SILICON is the most widely used semiconductor in electronic industry. Highly epitaxial thin films of $YBa_2Cu_3O_y$ (YBCO) grown on Si wafer are of special interest for development of superconductor/semiconductor hybrid microelectronic devices and circuits. Attempts to make YBCO thin films directly on Si have not been successful as the severe reaction took place between Si and YBCO [1]. The reaction and interdiffusion lead to a serious degradation of superconductivity and crystallinity in the grown YBCO films.

It is well known that the substrates exerts an important influence at the early stage of film growth through the establishment of epitaxy, which in turns affecting the physical structure, surface morphology, and microstructure of the formed films. Crucial factors include the lattice match between the grown film and substrate, and bonding of the deposited atoms with the substrate. Other entries for a good substrate are well matched thermal expansion and chemical compatibility, flat surface, appropriate dielectric properties, stable crystal structure, etc. A substrate material fully satisfying these requirements has been seldom found. Thus the technique using a buffer layer has been widely applied. By using an intermediate buffer, the thermal strain in YBCO, which raises due to the difference in thermal expansion between YBCO and Si, could also be reduced. Hence the critical thickness above which severe cracking of the grown film ensues is increased. Various materials such as yttrium-stabilized ZrO_2 (YSZ) [2], CeO_2 [3], $SrTiO_3$ [4], MgO [5], $PrBa_2Cu_3O_y$ [6], and $SrBi_2Ta_2O_y$ [7], etc. have been employed as a buffer layer to separate YBCO film and Si substrate. To date the best results are achieved on the YSZ buffer.

However, the crystallinity and surface morphology of the YBCO films on YSZ buffered Si are still poor although a high transition temperature could be obtained. It is believed that the poor quality of YBCO is due to the large lattice mismatching between YBCO and YSZ. YBCO thin films grown directly on YSZ can have different orientations in a–b plane [8]. In addition, the initial epitaxy of YBCO on YSZ is often puzzled by the occurrence of an intermediate layer between YBCO and YSZ. Such an intermediate layer is mainly formed as $BaZrO_3$ below the substrate surface due to the diffusion of Ba into YSZ. The loss of Ba in the YBCO would result in imperfection and discontinuities in the initial grown film [9]. It has been also recognized by transmission electron microscopy (TEM) and *in-situ* resistance measurement that the initial growth of YBCO films on YSZ substrates showed clearly island formation [10]. There still remain lots to be improved.

In this paper we report a new double buffer of Eu_2CuO_4 (ECO)/YSZ for improving the growth of YBCO on silicon wafer. The ECO buffer material with a very stable 214-T' structure possesses an excellent structural and chemical compatibilities with YBCO and YSZ. Our study showed that the epitaxy and crystallinity of YBCO deposited on Si could be considerably enhanced by using such an ECO/YSZ buffer. It was also found that this double buffer could lead to a very smooth surface in the YBCO layer. The grown films were characterized by X-ray diffraction (XRD) and grazing incidence reflection, rocking curve, scanning electron microscopy (SEM), and TEM.

II. EXPERIMENT

Both YBCO thin film and ECO/YSZ buffer layer were deposited on Si (100) single crystal wafer by pulse laser deposition (PLD) [11]. The background pressure of the chamber was below 3×10^{-6} mbar. The distance between the substrate and the target was typically 6 cm. An excimer laser with wavelength of 308 nm was used with the laser pulse energy ~300 mJ and repetition rate of 5 Hz, respectively. The laser beam was focused by a lens onto the target with a beam density ~4 J/cm^2. The Si substrate was stuck on the heater by silver paste. The substrate temperature was 730–780°C, which was measured by a k-type thermocouple inserted into the stainless substrate heater. The deposition gas was a mixture of argon and oxygen with different pressure ratios $(P_{\rm Ar}/P_{\rm O_2} \sim 3\text{–}4)$. XRD was performed

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J. Gao, T. K. Li, and Y. L. Cheung are with the Department of Physics, The University of Hong Kong, Hong Kong (e-mail: jugao@hku.hk).

L. Kang is with the Department of Physics, The University of Hong Kong, Hong Kong, on leave from Nanjing University, Nanjing, China.

J. Yang is with Superconducting Material Research Center, Beijing General Research Institute for Nonferrous Metals, Beijing 100088, China.

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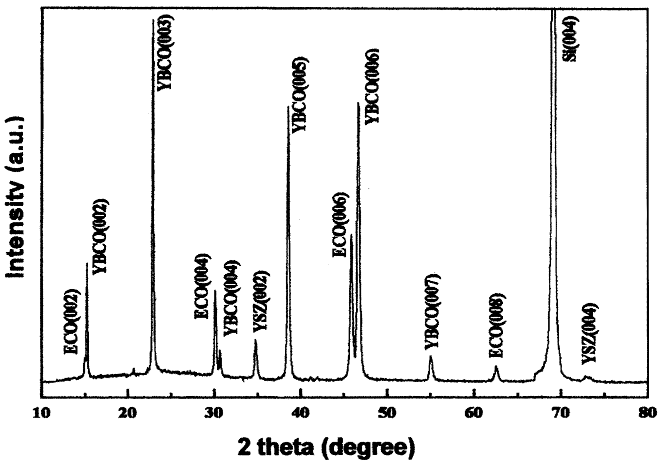

Fig. 1. Typical RDX spectra for YBCO grown on Si with a double buffer of ECO/YSZ.

on the Siemens D5000 x-ray diffractometer with CuKα radiation ($\lambda = 1.5405$ Å). The crystallinity of YBCO, ECO, and YSZ layers was examined by measuring their rocking curves of (005), (004), and (002) diffraction peaks respectively. The surface smoothness of the grown films was characterized by a Dektak^3ST surface step profiler and a Cambridge 440 scanning electron microscope (SEM).

The temperature dependence of resistance was measured by a standard DC four-probe method using a closed-cycled cryostat. 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 (50 μm in width, 100 μm in length) was patterned by using photolithography technique for determining the critical current of YBCO thin films.

III. Results and Discussions

The ECO material has a stable tetragonal structure with lattice constants $a = 3.90$Å and $c = 11.93$ Å, matching well with that of YBCO ($a = 3.82$ Å and $b = 3.89$ Å). A pure ECO film behaves as a semiconductor with resistivity $\sim$ 200 m$\Omega \cdot$cm at 77 K. It is chemically compatible with YBCO and YSZ. No intermediate layer can be formed at the interface between ECO and YSZ. As $EuBa_2Cu_3O_y$ is also a high-T_c superconductor with a $T_c \sim 90$ K, the diffusion of Eu into YBCO, if takes place, will not degrade the superconductivity of the grown films. Another important reason we use this material as a buffer is that the film surface of ECO is very flat and smooth. Outgrowths or other surface defects, which are typical for the thin films made of 1–2–3 materials, can be hardly found on the ECO films. Also, worthy to mention is the deposition conditions for growing ECO layers are almost the same as we used to grow YBCO thin films. It will make the deposition process simple and easy.

XRD has been performed on a large number of samples to examine the phase structure formed in grown films. The diffraction spectra always reveal a coherent orientation of YBCO, ECO, and YSZ layers with the c-axis orientation. A typical XRD spectrum for an YBCO film grown on ECO/YSZ double buffered Si is presented in Fig. 1. From the XRD pattern, only (001) peaks for grown layers were observed. No reflections due to random crystallographic orientation or secondary phases could be observed. Fig. 2 shows the rocking curves of the YBCO, ECO, and YSZ layers, respectively. The rocking curves indicate very small values of the full width at half maximum (FWHM), 0.14° for YBCO, 0.12° for ECO and 0.11° for YSZ. Small FWHM values result from excellent crystallinity of YBCO thin film and ECO/YSZ buffer layer. In comparison, the FWHM value for YBCO films grown on YSZ buffered Si substrate without the ECO layer is ~0.36°. It is found that the FWHM value for the YBCO thin films with an ECO/YSZ double buffer is remarkably smaller than that without the ECO layer, indicating that the use of additional ECO layer can significantly improve the crystallinity of YBCO thin films.

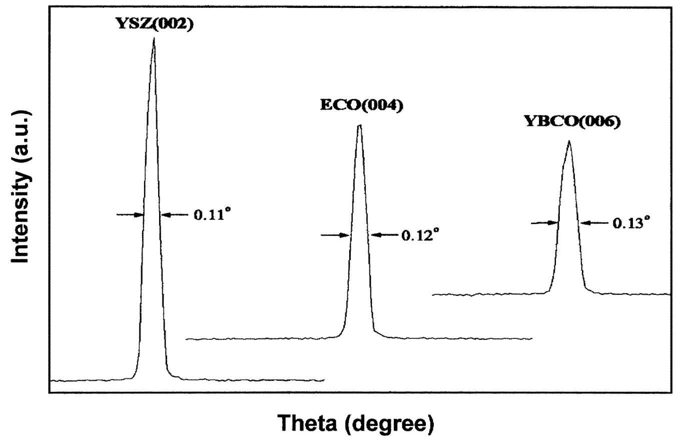

Fig. 2. Comparison of the rocking curves for the YBCO, ECO, and YSZ layers.

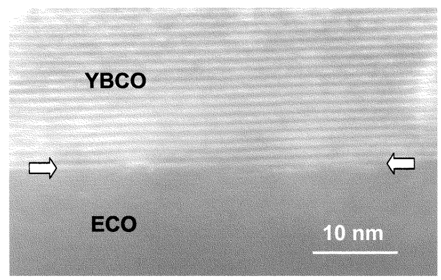

Fig. 3. Cross sectional TEM image of the interface between YBCO and ECO.

It has been known that two different in-plane orientations can exist between YBCO and YSZ due to their large lattice mismatching [8]. To determine the in-plane orientations of our films, ϕ-scan measurements were carried out. The ϕ-scans of the YBCO film and ECO buffer layer indicate in-plane single orientation with four-fold symmetry, which characterize the achievement of heteroepitaxial growth of the YBCO film. The in plane epitaxy relationship between layers was found as YBCO $[100]//\mathrm{ECO}[100]//\mathrm{YSZ}[110]$.

By using the ECO/YSZ double buffer, full superconducting transitions with $T_{c,\mathrm{zero}} \geq 90$ K can be obtained readily. The critical current density at 77 K was found ~5–8$\times 10^5$ A/cm^2, which is reasonable for YBCO films grown on Si. Indeed, the superconducting properties in these YBCO films grown on buffered Si substrates are found being much better and stable in comparing with YBCO films on Si substrate with a single YSZ buffer.

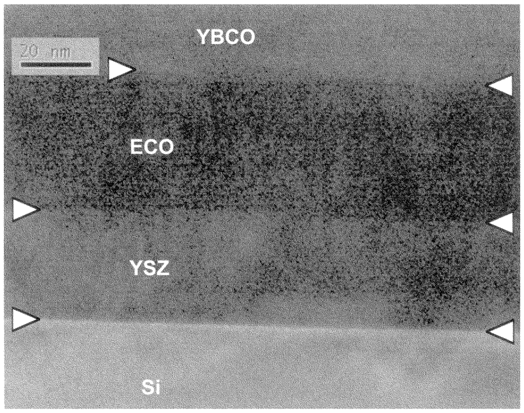

Fig. 4. TEM photograph with a low magnification shows the interface between YSZ and Si. A SiO_2 intermediate layer of 5 nm is formed.

The interfaces between layers were studied by using TEM. A cross sectional TEM image of the YBCO/ECO interface is shown in Fig. 3. An atomically sharp interface is clearly seen. The layer thickness found from TEM image agree well with that estimated from the deposition time. All layers are rather uniform and single crystal like. Moreover, the strain effects due to lattice mismatch are not likely appear as the TEM image shows a sharp contrast for each layer. The high resolution TEM image demonstrates a highly epitaxy of YBCO obtained on Si wafer with an ECO/YSZ double buffer.

The TEM micrograph also revealed that an amorphous layer ~5 nm, probably in the form of SiO_2, was formed between YSZ and Si (Fig. 4). Such an oxide intermediate layer was found on all samples used for TEM study. It is known that the Si surface most often has a native silicon oxide that needs to be removed before deposition of any subsequent layer in order to enforce an epitaxial growth. In our process, HF acid was used to remove such a native oxide layer. But even when this native oxide is removed, an amorphous silicon oxide is frequently observed at the interface between YSZ and Si [12]. Since the epitaxy of ECO layer is still remain, this oxide intermediate layer should be formed after initial epitaxy has been established through oxygen diffusion from YSZ into Si. This oxide may be beneficial for relieving the thermal stresses that occur during cooling.

The interfaces between layers were further characterized by the small angle reflection of x-ray, which is known being sensitive to the change of chemical compositions in multilayer structures. The obtained reflection profile of YBCO films with the ECO/YSZ double buffer consists of many reflection peaks. Both interfaces of ECO/YSZ and YBCO/ECO are very sharp and smooth. No intermediate layer was observed. The mean surface roughness for the ECO/YSZ and the YBCO/ECO interfaces are 5 Å and 8 Å, respectively, which demonstrating very sharp and clear interfaces. In contrast, only one peak was observed for the YBCO film on YSZ/Si. Also, an intermediate layer was found, indicating that a chemical reaction takes place between YBCO and YSZ.

A very desirable feature for applying the ECO buffer is that it can enforce a very good surface morphology. In contrast to thin films of 1–2–3 compounds, films with the 214-T' structure always reveal a very smooth and stable surface. We have studied three compounds with 214-phase structure, i.e., Nd_2CuO_4, $La_{1.85}Sr_{0.15}CuO_4$, and ECO as buffer layers for the growth of YBCO thin films on reactive substrates. All of them show a smooth surface and good crystallinity, as well as greatly improved quality of YBCO thin films [9], [13], [14]. Among these 214 materials, the lattice match between ECO and YBCO is the least thus it was selected for this work. The surface morphology and average roughness of our samples were studied by using SEM, AFM, and surface profiler. Fig. 5 shows a SEM image of a typical surface of YBCO film on ECO/YSZ/Si. The grown film is very flat and smooth over a large area. No observable particles and surface structures can be found. The average roughness of the film surface was evaluated with a large scanning length of 2 mm, which is the maximum scan length could be obtained on our profiler. After the measurement, the samples were etched away using acid and the same scanning procedure was performed to examine the roughness of the substrate. For most YBCO films the average roughness was found less than 5 nm within 2 mm range, whereas the Si substrate roughness is about 2 nm. Such a very small value implies an extremely smooth film surface, demonstrating advantages of the ECO/YSZ double buffer.

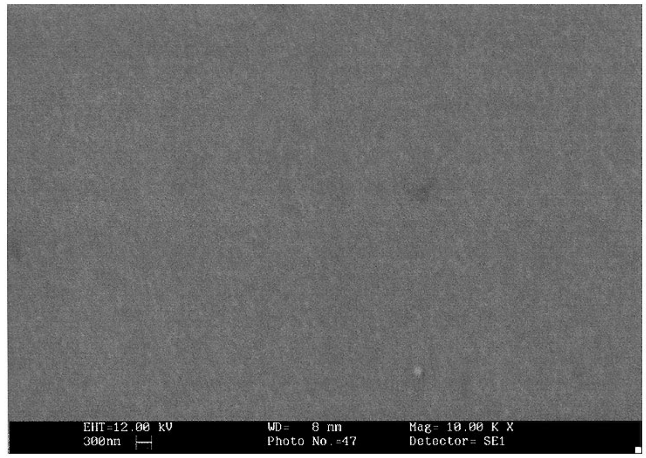

Fig. 5. SEM image of a film surface of YBCO grown on Si with an ECO/YSZ double buffer.

IV. Conclusion

Highly epitaxial YBCO thin films have been successfully obtained on silicon wafers with a double buffer of ECO/YSZ. These films showed good crystallinity and single in-plane orientation. High transition temperatures ~90 K could be readily obtained. TEM studies revealed that the epitaxy remains through all layers although an oxide intermediate layer was found at the YSZ/Si interface. It seems that such an oxide layer was formed after the epitaxy of YSZ established due to the diffusion of oxygen. A superior feature to use such an ECO/YSZ double buffer is the very smooth film surface of YBCO. These films could be of potential for many applications.

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