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HIGH TEMPERATURE SUPERCONDUCTING THIN FILMS PREPARED BY PULSED LASER DEPOSITION

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ABSTRACT

We have grown superconducting thin films on various substrates using a pulsed laser deposition (PLD) method. $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconducting thin films with the superconducting transition temperature ($T_{C\ offset}$) of 87K were grown on Si substrates using yittria-stabilized zirconia (YSZ) and CeO_2 double buffer layers. We have developed a large area pulsed laser deposition system. The system was designed to deposit up to 6 different materials on a large area substrate up to 7.5cm in diameter without breaking a vacuum. The preliminary runs of the deposition of YBCO superconducting thin films on $SrTiO_3$ substrate using this system showed a very uniform thickness profile over the entire substrate holder area. T_C of the deposited YBCO thin film, however, was scattered depending on the position and the highest value was 85K.

INTRODUCTION

Since high temperature superconducting material was discovered 10years ago, preparation of high quality superconducting thin films is one of the hottest research subject. Almost all deposition methods available including typical deposition methods, such as sputtering[1-3], evaporation[4-6], MOCVD[7] and new processes like pulsed laser deposition (PLD) method[8-10] were applied in preparation of oxide superconducting materials. Among those variety, PLD method has been known as the most successful one and has become a standard method in depositing various kinds of oxide superconducting materials. This is because it has many advantages like very high deposition rate, coincidence of chemical composition between the complex targets and deposited thin films, and the ability of processing in the high oxygen pressure. Some of disadvantages like small uniform deposition area and droplet (boulder) formation on the surface have been solved considerably now and recently the capability of PLD is expanded more to the fields of large-area deposition[11-13], and the layer-by-layer deposition (laser-MBE)[14-16].

The most frequently used superconducting materials in the thin film application is $YBa_2Cu_3O_{7-\delta}$ (YBCO). The high quality thin films of YBCO is now routinely obtained when the film is deposited on the single crystalline substrates like $SrTiO_3$. In the practical application to the electronics, we need to use a substrate which is cheaper than the single crystalline oxide and also it should be easy to obtain a high quality large area substrate. In this context, silicon is the best candidate substrate. Unfortunately, however, silicon is a bad substrate for the oxide superconductors from the materials point of view, because the lattice mismatch and the difference of the thermal expansion coefficients between Si and YBCO is considerably big, and more over it reacts with YBCO at the deposition temperature. Therefore, we need a suitable buffer layer between Si substrate and YBCO which can prevent the inter-diffusion and facilitate the epitaxial growth. Yttria stabilized zirconia (YSZ) and CeO_2 have been known as suitable buffer materials[17-19]. YSZ is stable at high temperature and has the similar structure and lattice parameters to Si. YBCO grows along c-axis on YSZ, but two types of in-plane alignment of YBCO are possible on YSZ and this introduces the high angle grain boundaries and degrades the critical current density of the thin film. In this work we have studied the growth orientation of YBCO films on Si substrates with the YSZ single buffer layer and the CeO_2/YSZ double buffer layer.

The research on the application of superconducting thin films to the electronic devices, such as superconducting quantum interference devices(SQUID), microwave devices for the mobile and satellite communications, digital and analog signal processing devices, has been progressed much and some of them are almost matured to be commercialized[20]. In the practical application, high quality large area thin films of which diameter is larger than 7.5cm(3 inch) are needed, especially in the field of the passive devices. Generally, it has been known to be difficult to deposit a large area with PLD method although this method gives high quality epitaxial thin film with very high growth rate. In this work, we developed a PLD system to deposit superconducting thin films on a large area substrate up to 7.5cm in diameter and YBCO thin films were deposited. The thickness and the critical temperature distributions over the entire substrate holder area were determined.

EXPERIMENTAL PROCEDURE

Deposition of YBCO Thin Films on YSZ/Si and CeO_2/YSZ/Si Substrates

The CeO_2, YSZ and $YBa_2Cu3O_{7-\delta}$ targets were made from source powders, CeO_2, ZrO_2, Y_2O_3, and CuO with the stoichiometric ratios, Y : Ba : Cu=1 : 2 : 3 for YBCO and Y : Zr =1.8 : 8.2 for YSZ (10 mol% Y_2O_3). The mixture for YBCO was calcined in air at 900 ℃ for 12 hours. The calcined powder was reground and pressed into a 2.5 cm diameter pellet. The pellet was sintered at 950℃ in O_2 flow for 24h followed by the oxygen anneal at 500℃ in 1 atmospheric oxygen for 10 h. For the CeO_2 and YSZ target, the ground mixture was sintered at 1500℃ for 2h. These targets had high densities over 93%. All films were deposited by KrF mode excimer laser (Lumonics EX-700) with the wavelength of 248 nm and the laser energy fluencd on the target of 2 J/㎠. The substrate temperature and oxygen pressure during deposition were 810℃ and 0.4mtorr for YSZ, 810℃ and 200 mtorr for CeO_2 and 780℃ and 200 mtorrfor YBCO, respectively. The detail experimental procedures are described in elsewhere[21].

Design of the Large Area PLD System

Fig. 1 shows the schematic diagram of the system. Laser beam is focused to the rectangle of 2×2.5㎜^{2} on the rotating target of which diameter is 2.5㎝ or 5㎝ with the incident angle of 45°. In order to scan a wide area of the rotating (with 2 rpm) target uniformly, the focusing lens is moving up and down. The substrate holder made of stainless steel plate of 86㎜ in diameter is rotating with the speed of 1rpm in front of the heater. The heater was made of funnel shape gold coated stainless steel with a 1.2㎾ halogen lamp which is located at the focal point of the reflecting wall of the heater.

Deposition of YBCO Thin Film in the Large Area PLD System

YBCO thin film was deposited using KrF excimer laser(Lambda Physik COMPEX 205). The thickness variation and the critical temperature of thin films deposited with various conditions of laser energy fluence, and the distance between the centers of the plum and the substrate holder (off-set distance). The target-substrate distance, oxygen pressure and the substrate temperature were fixed at 4㎝, 200 mtorr and 750℃, respectively. The temperature distribution of the substrate holder during deposition was measured by the optical pyrometer(Minolta PR[630]. In order to measure the uniformity of the thickness of the deposited thin film, 3″ silicon wafer was used as a substrate and the thickness was measured by the optical interferometer after the selective etching of YBCO with dilute phosphorous acid solution.

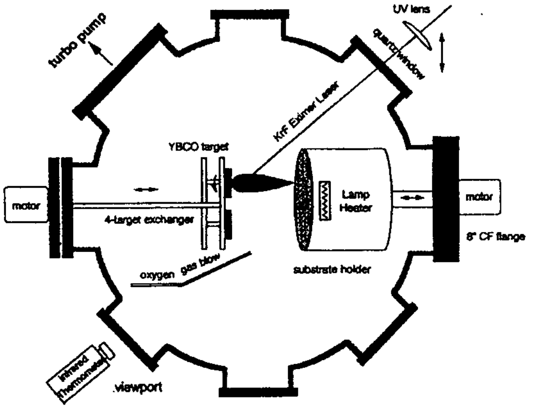


Fig. 1. Schematic diagram of the large area PLD system.

RESULTS AND DISCUSSION

Growth Orientation of YBCO Deposited on Si Substrate

Fig. 2(a) shows $\theta/2\theta$ scan of YBCO/YSZ bilayer on Si(100) substrate, and (b) shows the X-ray ϕ-scan of YBCO(103) peak. Only the (001) peaks of YBCO thin film are observed in $\theta/2\theta$ scan indicating that YBCO film is highly c-axis oriented. Fig. 2(b), overlap of the YBCO(103) and YSZ(202) peaks indicates YBCO[100] direction is parallel to YSZ[100] direction (YBCO[100]// YSZ [100], 0° rotation) and the separation of two peaks by 45° indicates YBCO[100] direction is parallel to YSZ[110] direction (YBCO [100]//YSZ[110], 45° rotation). The volume

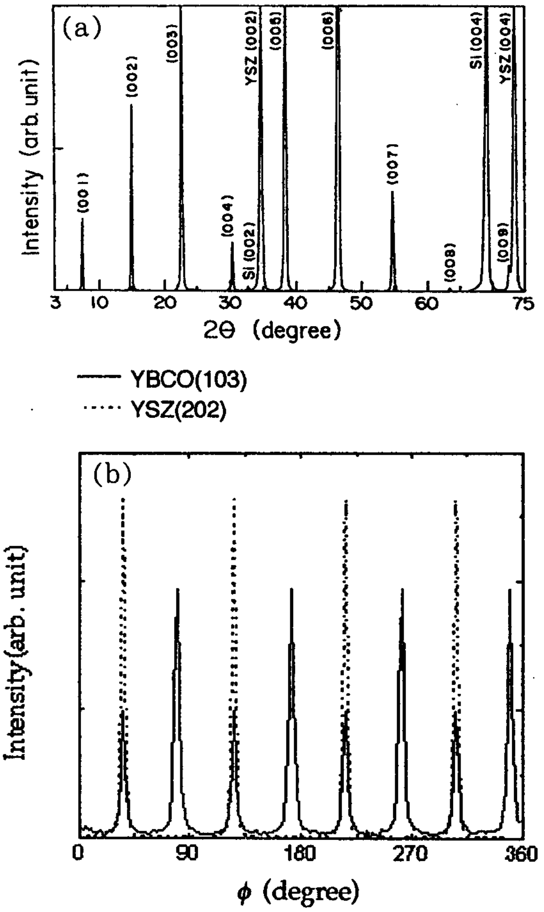


Fig. 2. (a) XRD pattern of YBCO/YSZ bilayer on silicon substrate, (b) X-ray ϕ-scan of YBCO(103) (solid line) and YSZ(202) (dotted line)peaks.

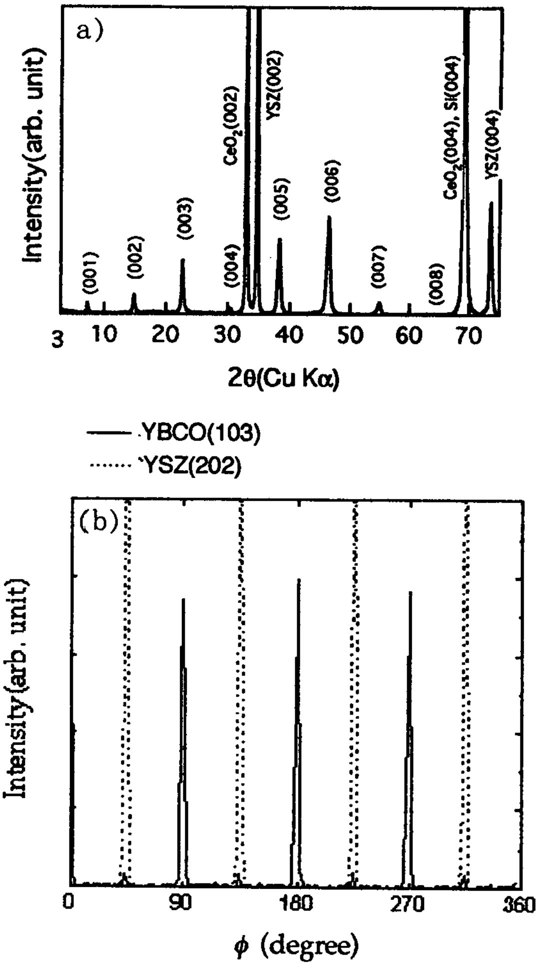


Fig. 3. (a) XRD pattern of YBCO/CeO_2/YSZ trilayer on silicon substrate, (b) X-ray ϕ-scan of 100 nm thick YBCO deposited on CeO_2(50 nm)/YSZ/Si substrate.

fraction of 45° rotated portion obtained by calculating the area of each peak was about 70%. The introduction of CeO_2 layer between YSZ and YBCO reduces the 0° rotation portion. Fig. 3 shows the X-ray $\theta/2\theta$ scan and ϕ-scan of 100 nm thick YBCO thin film on the YSZ/Si substrate with 50 nm thick CeO_2 layer between YBCO and YSZ. Fig. 3(a) shows that c-axis oriented YBCO thin film was afraction of 45° rotation portion became muchlso grown on the CeO_2/YSZ double buffer layer, but in Fig. 3(b) the volume higher if compared with Fig. 2(b). The volume fraction of 45° rotation portion is higher than 97%, which means that the in-plane epitaxy was improved very much by introducing CeO_2 layer.

Fig. 4 shows the 0° rotation and 45° rotationi using Cu-O plane of YBCO and (100) planes of YSZ and CeO_2 schematically. As shown in the figure, the interface of 45° rotation is more stable than that of 0° rotation due to the direct matching of all atoms

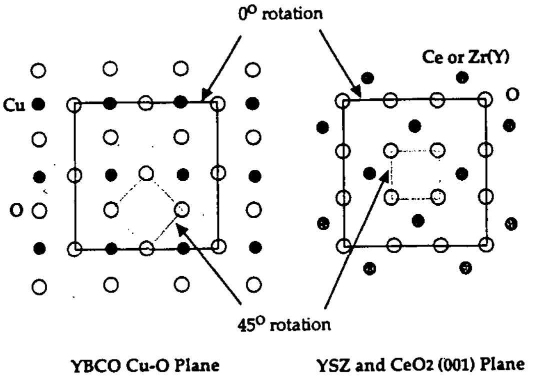


Fig. 4. Matching of YBCO Cu-O plane with YSZ or CeO_2 plane.

in oxygen sublattice. In the YBCO/YSZ system, however, considerable amount of 0° rotated grains grow together with 45° rotated grains, because the lattice misfits between YBCO and YSZ are$<0.2\%$ and 6% for 0° rotation and 45° rotation, respectively. On the other hand, in the YBCO/CeO_2/YSZ system, the misfits between YBCO and CeO_2 are changed to 4.9% and 1% for 0° rotation and 45° rotation, respectively. And hence, 45° rotated growth is prevailing.

Deposition of Large Area YBCO Thin Films

Fig. 5 shows the temperature distribution of the substrate holder (the diameter of the heated area was 86 mm). With the oxygen pressure of 200mtorr, the temperature deviated by ±1℃ in the circle of 25mm in diameter, -16℃ in 50mm, and -40℃ in 75mm from 750℃ at the center. In order to deposit the uniform large area film with a small target, the position of the rotating substrate holder was adjusted so that the center of the plum reached 15cm apart from the center of the holder. Fig. 6 shows the thickness variation of the YBCO thin film deposited on a 3inch

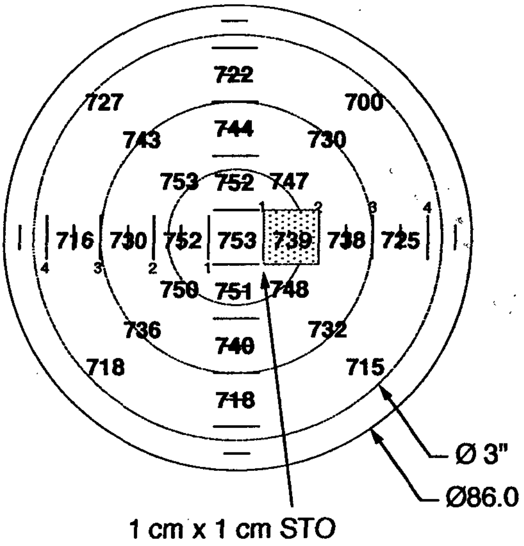
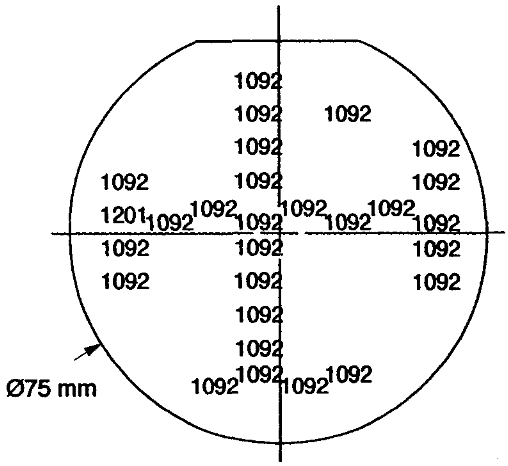


Fig. 5. Temperature profile of the substrate holder of 86m in diameter.

silicon wafer. The uniformity of the thickness was very good through the whole area. We used laser fluency of 1.7 J/cm² and the deposition rate was about 5.5 nm/min. In order to check the deviation of superconducting property, we deposited YBCO thin film on 4 $SrTiO_3$ substrates of 10mm×10mm which were placed side by side 1mm apart from one another from the center. Fig. 7 shows the resistivity-temperature curves of YBCO films depending on the distance from the center. The critical temperature(T_C) was 80K at the center and in creased to 85K at the position of 11±5mm apart form the center and was 83K at the position of 22±5mm apart form the center. We speculate that T_C at the center is somewhat lower than the neighbor site because the central part was mainly deposited by the edge of the plum because the offset distance was 15mm. The film deposited on the substrate placed at 33±5mm did not show the



precision ± 100 Å

Fig. 6. Typical homogeneity of thin film thickness of YBCO deposited on 3 inch silicon wafer.

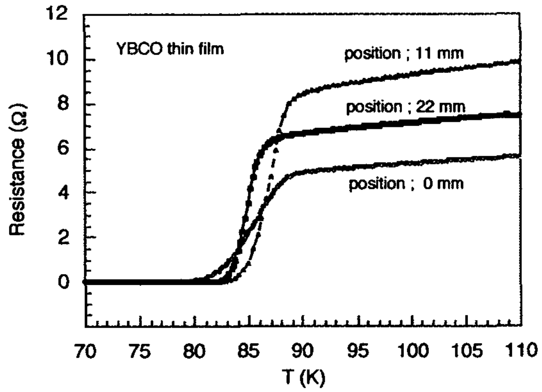


Fig. 7. R-T curves of YBCO thin films deposited on $SrTiO_3$ at the different position of the 3 inch rotating substrate holder.

superconductivity above 50 K, probably because the temperature of the substrate was too low to form a good superconducting phase at this site. The temperature at this point was about 710℃. In our deposition condition, YBCO thin film with Tc higher than 85 K was obtained in the temperature range of 720-820℃ [21].

CONCLUSIONS

YBCO superconducting thin films were prepared on YSZ buffered and CeO_2/YSZ buffered silicon substrates by PLD. All YBCO films were highly oriented along c-axis perpendicular to the substrate surface. YBCO film grown on a YSZ single layer buffered Si substrate had two different in-plane orientations: YBCO<100>//Si<110> and YBCO <110>//Si<110> with the volume fraction of 0° rotated grains was about 30%. By using CeO_2/YSZ double buffer layer, it was possible to reduce the volume fraction of 0° rotated grains to less than 3%. This is because the lattice matching of 45° rotation between YBCO and CeO_2 is much better than that between YBCO and YSZ.

We developed a PLD system to deposit YBCO thin films on a substrate with 7.5㎝ in diameter. It was possible to deposit YBCO thin films on 3 inch silicon substrate with very uniform thickness. The T_C however, was low with the maximum 85 K and scatters much depending on the site. Further optimization is under investigation to obtain a high quality large area thin film with uniform and higher T_C.

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