

HOMOEPITAXIAL GROWTH OF $\text{YBa}_2\text{Cu}_3\text{O}_7$ ON SINGLE CRYSTAL $\text{YBa}_2\text{Cu}_3\text{O}_x$ SUBSTRATES

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a- and *c*-axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) films were epitaxially grown on (100) and (001) YBCO single-crystal substrates, respectively, by metalorganic chemical vapor deposition under the same preparation conditions including substrate temperature. As a Ba precursor $\text{Ba}(\text{DPM})_2$ -2tetraen was adopted. This precursor increased a deposition rate for YBCO films to 50 nm/h at 140°C. The substrates were formed from a $14.5 \times 14.5 \times 13$ mm YBCO single crystal grown by a modified top-seeded crystal pulling method. Only a few surface atomic layers remained damaged after polishing and cleaning, which however did not affect the epitaxy of film growth. The crystallinity of the interface between an epilayer and substrate was much improved compared to that on usual perovskite substrates.

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1. Introduction

High T_c superconducting thin films have been successfully prepared by heteroepitaxial growth on oxide substrates such as MgO and SrTiO_3 . In heteroepitaxy the boundary between the film and substrate can have different structures depending on the nature of chemical bond, crystal lattice and lattice parameters. If there is a difference in the thermal expansion coefficients between an epilayer and substrate, the resulting strain affects lattice matching. In the case of the most familiar substrate SrTiO_3 *a*-axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ (YBCO) film is homogeneously strained to fit exactly the periodicity of the substrate, resulting in degradation of superconductivity [1].

The objective of this study is to elucidate influences of using conventional substrates on crystallinity and superconductivity of thin films. An analysis of the crystallographic nature and surface morphology of YBCO single-crystal substrates can help to make clear the advantages of homoepitaxial growth, where there is no misfit between lattice constants of the epilayer and substrate.

Homoepitaxy is a key technology for processing integrated circuits. In GaAs circuits, for example, the *n*-GaAs is homoepitaxially deposited on pure GaAs and formed into integrate circuits by ion implantation. Homoepitaxial growth is also

useful for forming a clean and flat surface. The surface of substrates that is mechanically and/or chemically polished usually shows roughening detectable by reflection high energy electron diffraction observations. In order to recover the flatness, the surface is covered with a buffer layer, which is a deposit of the same material as the substrate, followed by annealing.

Among the many remaining fabrication problems, a particularly difficult one is to get a defect-free superconducting film on an atomic scale, especially *c*-axis oriented films free from stacking faults originating from spiral growth and *a*-axis oriented films not composed of columnar grains. Homoepitaxy is expected to break through these difficulties.

2. Single crystal growth of $\text{YBa}_2\text{Cu}_3\text{O}_x$

YBCO is formed by a peritectic reaction from Y_2BaCuO_5 solid and BaO-CuO liquid. So it is impossible to directly grow it from a congruent melt. In the quasi-binary (Y_2BaCuO_5 vs. $3\text{BaCuO}_2 + 2\text{CuO}$) phase diagram the liquidus line near the peritectic reaction temperature is steep, which suggests that a reasonable growth rate is difficult to obtain, even if large supercooling could be applied to the system. Considering the characteristic features in the YBCO phase diagram mentioned above, a modified top-seeded crystal pulling method has been developed [2]. Figure 1 shows a schematic illustration of the method. BaO-CuO composite ($\text{Ba}/\text{Cu} = 3/5$) was put on the layer of Y_2BaCuO_5 powder in a crucible. A temperature gradient was provided in the solution to satisfy the condition that both the temperature at the melt surface is lower than the peritectic temperature

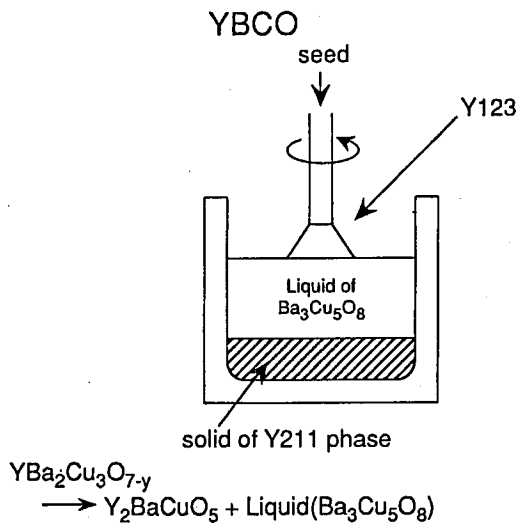


Fig. 1. Configuration of the solvent ($\text{Ba}_2\text{Cu}_5\text{O}_8$) and solute of Y_2BaCuO (Y211).

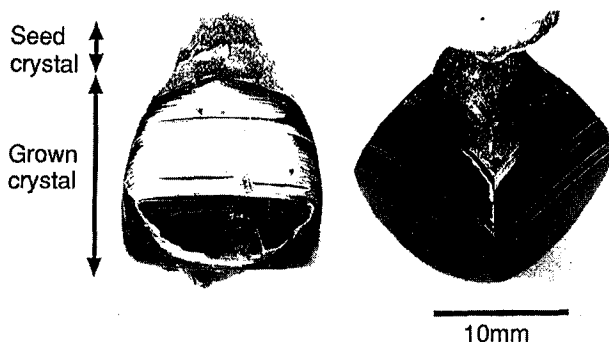


Fig. 2. YBCO single crystal grown by a top-seeded crystal pulling method.

($T_p = 1010^\circ\text{C}$) of YBCO and that the temperature at the bottom of the solution is higher than T_p . Y_2BaCuO_5 solid exists at the bottom of the crucible as a source of the solute. If the melt near the surface is supersaturated with Y, then a YBCO single crystal can be grown around the surface. In this method, the transport of the solute from the bottom of the crucible to the growing crystal is dominated by convections in the solution. The seed crystal was a YBCO single crystal prepared separately. A sintered Y_2O_3 crucible was used in order to avoid contamination of the melt from the crucible. The crystal was grown with a rotation rate of 120 rpm, which is rather fast to enhance the convection in the solution. A typical pulling rate was about 0.1–0.5 mm/h. Figure 2 shows a $14.5 \times 14.5 \times 13$ mm crystal grown for 214 h along the c -axis. The square shape in the plane perpendicular to the c -axis reflects the symmetry of the c -plane suggesting a strongly faceted nature of the crystal.

3. $\text{YBa}_2\text{Cu}_3\text{O}_x$ substrate

A YBCO single crystal was sliced into (001) platelets of 0.8 mm thickness within a deviation of 1.0° from the (001) axis. The {100} and {010} facets were used to orient the crystals. The as-sliced plates were polished with aluminum oxide powder and then with colloidal silica solution. The process was free from water throughout.

The single crystal substrates were examined by several methods [3]. X-ray topography showed that the substrates are composed of mm-size grains tilted by a small angle from each other. The overall crystallinity was good enough to split the (005) diffraction peak into $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks in the θ – 2θ scan. The full width at half maximum of the rocking curve through the (005) peak is 0.1 degrees. The crystallinity of YBCO substrates was also investigated using Rutherford backscattering spectrometry (RBS) in the channeling mode. A minimum yield of 1.8% was measured as shown in Fig. 3, demonstrating that the quality of the surface of these YBCO substrates is as well as SrTiO_3 substrates [4]. For (100) YBCO substrates, the value of a minimum yield is larger than (001) substrates ranging from 3 to 4%.

The surface morphology was evaluated using atomic force microscopy (AFM). The AFM image of YBCO substrate vicinally polished from the [001] direction by

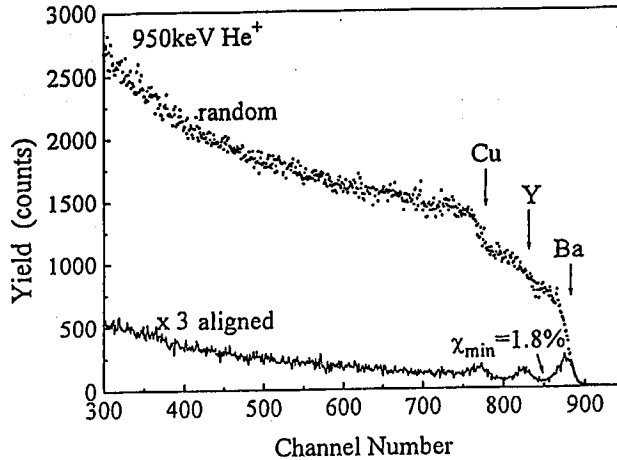


Fig. 3. RBS channeling and random spectra for $\text{YBa}_2\text{Cu}_3\text{O}_x$ observed using 950 eV He^{2+} beams, (001) substrate.

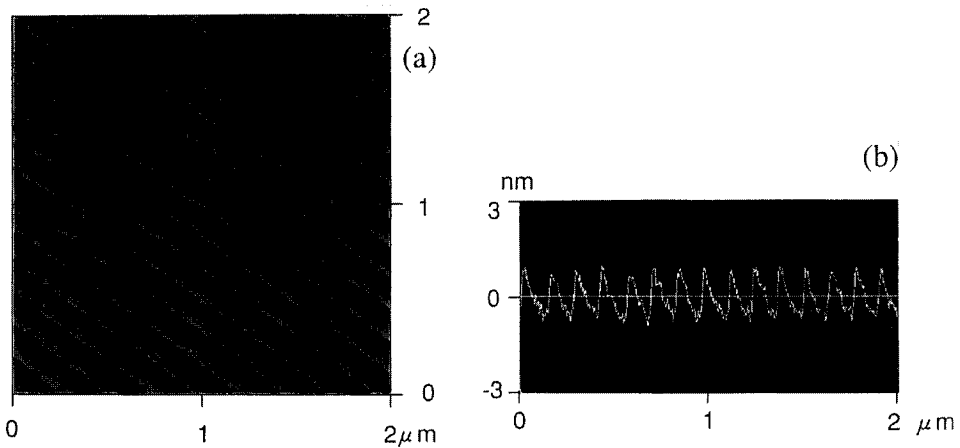


Fig. 4. (a) AFM images of 0.5° vicinally polished YBCO (001) substrate surface. (b) Line scan profile showing a peak to valley roughness height of 1.2 nm and 140 nm horizontal separation.

0.5° shows an atomically flat surface (Fig. 4). As seen in the line scan, there is a periodic feature with a peak to valley height of 1.2 nm (unit cell height of YBCO) and terrace width of 140 nm, which corresponds to the vicinal tilting from the (001) plane. The surfaces of (100) YBCO substrate showed no terrace-like features and had an average root mean square roughness of 0.15 nm.

In order to evaluate the chemical stability, the chemical state of Ba, which is the most active element composing YBCO, was examined using angle-resolved X-ray photoelectron spectroscopy (ARXPS). Figure 5 shows the ARXPS spectra

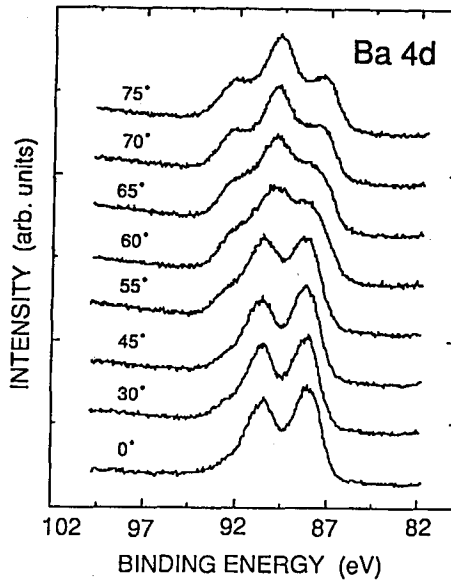


Fig. 5. ARXPS spectra of the Ba 4d core levels of YBCO (001) substrate. As the electron escape angle increases, the analyzing depth decreases from about 8 atomic layers to the surface.

of Ba 4d level observed for various electron escape angles. As the angle increases, a greater contribution to the spectrum comes from electrons emitted from the surface region. The Ba $4d_{7/2}$ peak at 93 eV, which is attributed to a Ba compound like $BaCO_3$ and $Ba(OH)_2$, becomes evident at angles larger than 60° corresponding to several atomic layers or less, depth from the surface.

4. Homoepitaxial growth of YBCO films

The YBCO films were made by metalorganic chemical vapor deposition (MOCVD) on (100) YBCO and 2.0° off-cut (001) substrates [5]. We used a conventional system with a horizontal, cold-wall reactor, substrate susceptor put in an rf heating coil and an oven containing vaporizers and transfer tubes. The precursors are $Y(DPM)_3$, $Ba(DPM)_2$ -2tetraen and $Cu(DPM)_2$. $Ba(DPM)_2$ -2tetraen has high volatility and a low melting temperature, below room temperature. When we consider that the conventional precursor, $Ba(DPM)_2$, had restricted the deposition rate of YBCO films owing to its low volatility, this new precursor has advanced the MOCVD method towards practical processing of films. The temperature dependence of the deposition rate of Ba oxide is shown in Fig. 6 for $Ba(DPM)_2$ and $Ba(DPM)_2$ -2tetraen. The $Ba(DPM)_2$ -2tetraen made it possible to prepare YBCO films at a deposition rate of 50 nm/h at $140^\circ C$, which is seven times faster than that of $Ba(DPM)_2$ at $187^\circ C$. We deposited films at a susceptor temperature of $800^\circ C$ for both substrates.

The crystallinity of the homoepitaxial YBCO films was investigated by transmission electron microscopy (TEM). Figure 7 shows cross-sectional TEM images

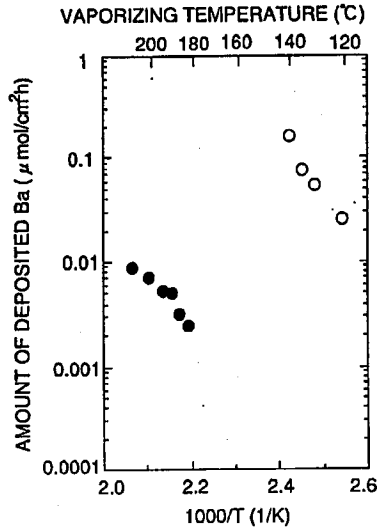


Fig. 6. Vaporizing temperature vs. deposition rate of Ba oxide for Ba(DPM)₂ (open circle) and Ba(DPM)₂-2tetraen (closed circle) precursors.

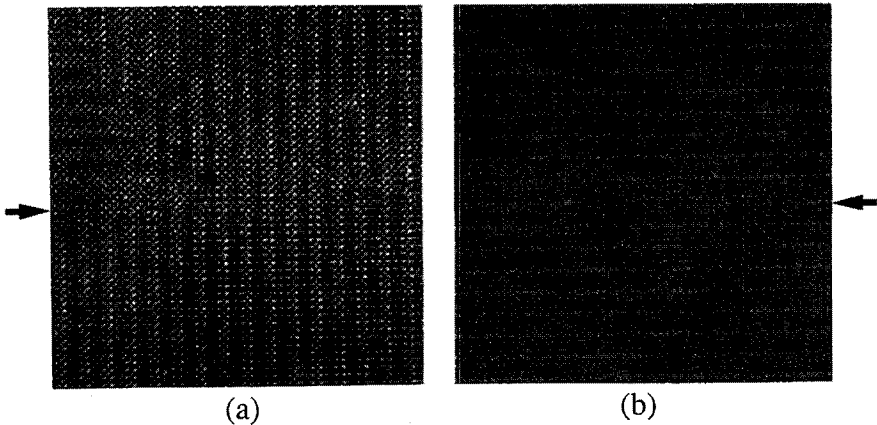


Fig. 7. Cross-sectional TEM images to the interface of YBCO films homoepitaxially grown on (100) substrate (a) and on (001) substrate (b). The arrow shows the interface between the film and substrate.

of the interface between the epilayer and substrate. On the (100) substrates, we achieved epitaxial growth of *a*-axis oriented films (Fig. 7a). There are no disordered layers at the interface, although they are often observed when YBCO is deposited on usual perovskite substrates. However, *c*-axis oriented grains did nucleate at sites where there exists some degradation on the substrate surface. *c*-axis oriented films grew on (001) substrates, (Fig. 7b). Epitaxy is so good that it is difficult to locate the interface in the picture. A stacking fault appears at steps with a subunit cell height on the substrate surface.

The YBCO films deposited by sputtering on YBCO substrates show poor epitaxy compared with those prepared by MOCVD, which suggests that film processing near thermal equilibrium is preferable for homoepitaxial growth [6].

5. Summary

Large YBCO single crystals were grown by the modified top-seeded crystal pulling method and then successfully formed into substrates. Epitaxial growth of a - and c -axis oriented YBCO films was achieved on (100) and (001) YBCO substrates, respectively, using the MOCVD method. The films show a defect-free interface between an epilayer and substrate. The technology of homoepitaxial growth will further advance the processing for high T_c superconductor devices.

Acknowledgments

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