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Effect of Growth Temperature on Crystalline Structure of $YBa_2Cu_3O_{7-\delta}$ Thin Films Deposited by MOCVD Method Using a Vertical Reactor with a Flow Guide

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Abstract
Effect of growth temperature on crystalline structure of YBCO thin films have been studied by a MOCVD method using a vertical reactor with a flow guide. At growth temperature between 600°C and 675°C, the films are composed of a mixture of a-axis and c-axis oriented phases, while at growth temperature of 700°C or higher, the a-axis-oriented phase disappears. At these growth temperatures, only c-axis-oriented phases are existing on the films. Film grown at 680°C or higher have the composition of Y : Ba : Cu is 1 : 2 : 3, as confirmed from EDAX spectra. Films deposited at 700°C have critical temperature around 87.4 K.

Keywords : *Thin film YBCO, Growth temperature, Crystalline structure, MOCVD, vertical reactor, Flow guide*

Abstrak
Telah dikaji pengaruh temperatur penumbuhan terhadap struktur kristal film tipis YBCO yang dideposisi dengan metode MOCVD reaktor vertikal dengan menggunakan pemandu aliran gas. Pada temperatur antara 600°C sampai dengan 675°C, film yang terdeposisi tersusun atas campuran fase dengan orientasi pada sumbu-a dan sumbu-c, sedangkan pada temperatur 700°C atau di atasnya, fase dengan orientasi pada sumbu-a menghilang. Pada temperatur tersebut, yang nampak pada film hanya orientasi pada sumbu-c. Berdasarkan analisis spektrum EDAX, film YBCO yang ditumbuhkan pada temperatur 680°C atau di atasnya tersusun atas komposisi Y : Ba : Cu = 1 : 2 : 3. Film yang dideposisi pada temperatur 700°C bersifat superkonduktor dengan temperatur kritis sekitas 87,4 K.

Kata kunci : *Film tipis YBCO, temperatur penumbuhan, struktur kristal, MOCVD, reaktor vertikal, pemandu aliran.*

1. Introduction

Chemical vapor deposition (CVD) is a promising method for the preparation of high-quality epitaxial films of oxide superconductors for device application. It has capability of producing large-area films, and the possibility of low-temperature growth. The metalorganic chemical vapor deposition (MOCVD) has been used to grow thin film $YBa_2Cu_3O_{7-\delta}$ (YBCO) from single solution source[1)]. The grown layers are composed of a mixture of *a*-axis and *c*-axis oriented phase. However in the thin film (0.45 μm in thickness), *c*-axis is more dominant than *a*-axis oriented phase. On the contrary, in the thick film (3.5 μm in thickness) *a*-axis is more dominant than the *c*-axis.

Since the junction transport in superconductor devices is along the vertical direction, *a*-axis oriented films are suitable for such devices. The superconducting coherence length and the critical current density along the CuO_2 planes at these directions are the largest[2-4)]. One strong motivation for the development of *a*-axis epitaxial films has been the fabrication of all YBCO vertical tri-layer Josephson junction's device.

It is very difficult to grow the in plane aligned, *a*-axis oriented YBCO films. The growth of *a*-axis oriented YBCO films have been prepared by physical vapor deposition (PVD) such as sputtering and evaporation methods. Several approaches, such as low substrate temperature (Ts), template growth, growth with an appropriate buffer layer, and variation of the lattice match of the substrate to layer of films have been used to produce *a*-axis oriented films[4,5)].

Recently O. Martinez *et.al*[6)] have studied grain orientation and intergrain properties by micro-Raman spectroscopy in YBCO thin films deposited by pulse-laser-assisted method to estimate the epitaxial quality of the film. In this paper we report effect of growth temperature on crystalline structure of YBCO thin film deposited by a home-built vertical MOCVD on (100) MgO substrates, with a flow guide. The purpose of the flow guide is to obtain a high growth rate and better uniformity without using a rotated susceptor[7].

2. Experimental procedure

A vertical type MOCVD apparatus was used to prepare YBCO superconducting thin films. A cylindrical tube was used to guide the gas flow towards the susceptor. The tube was placed in the center of the reactor and the gas inlet is located at its end (Figure 1).

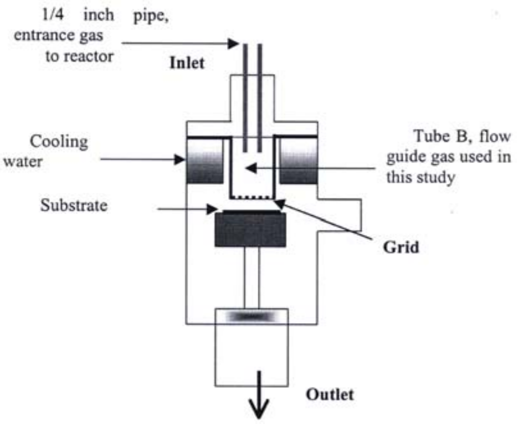

Figure 1. A schematic diagram of vertical MOCVD reaction chamber with a flow guide.

The MO sources were tris (2,2,6,6-tetramethyl-3,5-heptadionato) yttrium (III), bis (2,2,6,6-tetramethyl-3,5-heptadionato) barium hydrate, and bis (2,2,6,6-tetramethyl-3,5-heptadionato) copper (II). Each source was dissolved in tetrahydrofuran (THF) to a concentration of 0.5 mol/liter. The solution was placed in a stainless bubbler and its vapor was carried by argon gas to the reactor and mixed with oxygen gas at the entrance of the reactor. The Ar of the Y, Ba, and Cu sources and oxygen flow rates were maintained at 150 sccm, 250 sccm, 100 sccm and 190 sccm, respectively. The temperatures of the Y, Ba, and Cu sources were kept at 130, 240, and 140°C to ensure that the vapors do not solidify. The (100) oriented single-crystalline MgO were used as substrates. A molybdenum heater (U.S Thin Film Inc. USA) heated the substrates (10x10x0.5 mm3) and the YBCO films were deposited at a rate of 10-20 Å/min. The substrate temperatures were between 600°C and 750°C and after each deposition, the sample was cooled to 500°C at the rate of 15°C/min and post annealed at 1 atmosphere oxygen pressure for 90 minutes.

The crystalline quality of films were characterized by X-ray diffraction (XRD) using Cu-Kα (λ:1.54 Å) radiation. The elemental composition of the films was analyzed by electron dispersive X-rays (EDAX). Surface morphology and thickness of the films were observed by scanning electron microscope (SEM) and Dektak Sloan IIA profilometer. Electrical properties of deposited films were measured by four point-probe dc resistivity methods.

3. Results and Discussions

We have studied the effect of the growth temperature on the crystalline structure of YBCO films on MgO substrate. Figure 2 shows the XRD patterns of YBCO film grown on (100) MgO at 650°C and 700°C. The intensity of XRD peaks of the films grown at the growth temperature of 600°C is very weak and dominated by amorphous phase. The peaks is improved as the growth temperature is increased to 630°C. The peaks of (*h00*) and the peaks of (*00l*) planes are observed for the film grown at the substrate temperature of 630°C. The *a*-axis diffraction intensity of the film grown at *T*s = 650°C is increased and it is stronger than that of the film grown at *T*s = 630°C. This result is consistent with the view that the nucleation rate along *a*- or *b*-axis is faster than that of the *c*-axis[1]. However we found that the *a*-axis phase disappears for the film grown at 700°C or higher.

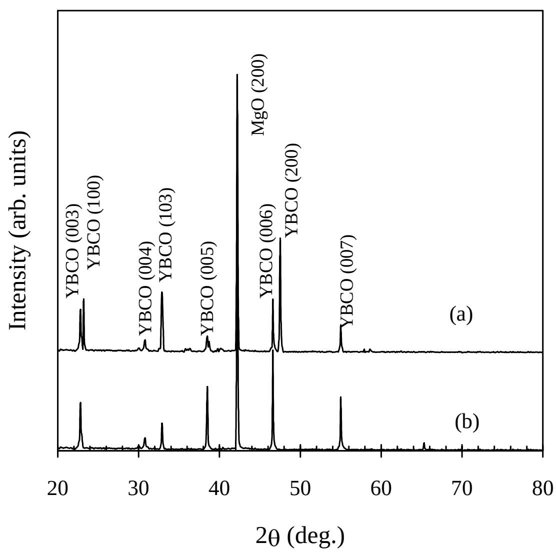

Figure 2. X-ray diffraction patterns of YBCO films grown on (100) MgO at (a) *T*s = 650°C and (b) *T*s = 700°C, and annealing temperature of 500°C. The carrier gas flow rates of Y, Ba, and Cu are 150 sccm, 250 sccm, and 100 sccm, respectively.

Figure 3 shows the diffraction intensity ratio of YBCO (100) to YBCO (600) or *I* (100)/ *I* (006) as a function of the substrate temperature. For growth temperatures higher than 675°C, the value of *I* (100)/ *I* (006) are very low because the *c*-axis orientation is dominant. On the other hand, at growth temperature between 630°C and 650°C, the value of *I* (100)/ *I* (006) increases as the temperature increases, which means the *a*-axis orientation becomes more dominant. As the substrate temperature is increased above 675°C, the ratio decreases. We consider that the increasing growth temperature up to 675°C is easier to deposit of *c*-axis orientation, because the nucleation in *c*-plane is stronger than the *a*-*b* plane[4)].

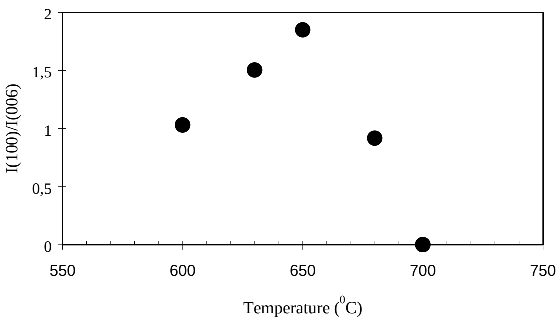

Figure 3. Dependence of intensity ratio (I(100)/I (006)) on substrate temperature for the YBCO films deposited on (100) MgO.

Figures 4(a) and 4(b) show the surface morphology of the YBCO films grown at 650°C and 700°C, respectively. The SEM images show several structures, and the surface morphologies are not smooth. The surface morphology of the YBCO film grown at 650°C formed needle-shaped grains which, by using the XRD pattern indicates that the film is dominated by *a*-axis orientation. On the contrary at growth temperature 700°C the grains size relatively large, this fact indicates that the film is dominated by *c*-axis orientation. The composition of films does not depend on substrate temperature and the analyzed value of the elemental composition from EDAX spectra is shown in Table 1.

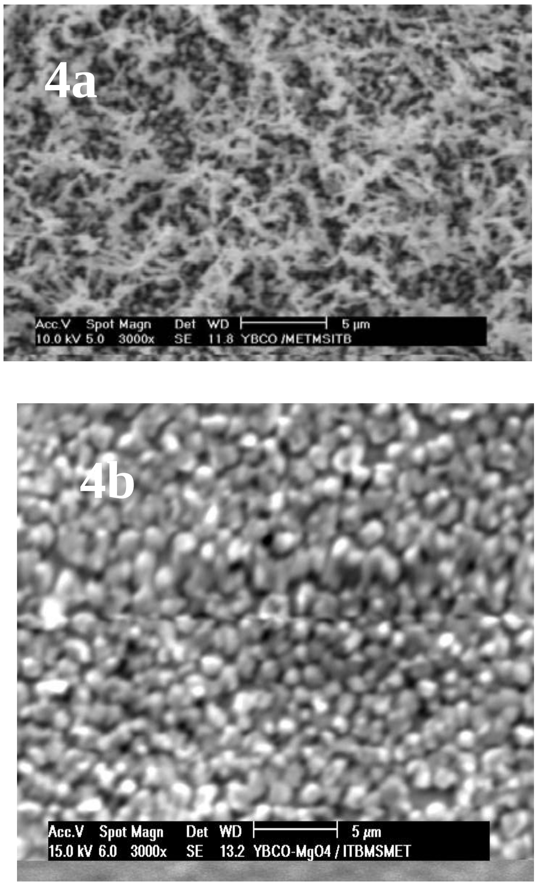

Figure 4. Surface photograph of scanning electron microscope (SEM) of sample (a) *T*s = 650°C, and (b) *T*s = 700°C.

Table 1. The elemental composition of YBCO thin filmsby EDAX spectra

Samples (*T*a = 500 °C)	Y	Ba	Cu
(a) *T*s = 630 °C	1.1	1.6	3.2
(b) *T*s = 650 °C	1.1	1.5	3.3
(c) *T*s = 680 °C	1.2	1.8	3.1
(d) *T*s = 700 °C	1.2	1.8	3.1
S. Matsuno[1] *T*s = 700 °C	1.1	1.6	2.2

Figures 5 shows resistivity versus temperature curves of the samples grown at *T*s = 650°C and 700°C. Each samples was post annealed at 500°C under oxygen atmosphere. Only sample grown at 650°C or higher show the superconducting properties. The electrical properties are usually represented by critical temperature (*T*c, onset) and zero resistivity critical temperature (*T*c, zero). The *T*c, onset for YBCO thins films grown at 650°C and 700°C is 89.6 K and 91 K, respectively, and the *T*c, zero is 78.6 K and 87.4 K, respectively. In general, the (Tc, onset) increases as the growth temperature is increased. The Tc, onset and Tc, zero obtained from this experiment is comparable to those previously reported by other workers[1-3].

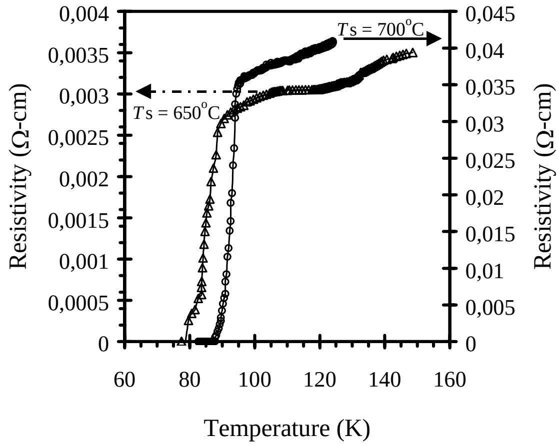

Figure 5. Resistivity as function of temperature for YBCO films grown on (100) MgO at Ts = 650°C and Ts = 700°C.

4. Conclusion

YBCO thin films were prepared by home-built vertical MOCVD reactors with the flow guide at growth temperature varied between 600°C and 750°C. Stoichiometry YBCO was obtained at the substrate temperatures between 650°C and 700°C. Crystal orientations of the films grown at the substrate temperatures between 630°C and 675°C are composed a mixture of *a*-axis and *c*-axis oriented phases. Superconducting films were obtained for films grown at Ts = 650°C or higher, with Tc, onset = 91 K and Tc, zero = 87.4 K for film grown at 700°C.

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References

1. S. Matsuno, F. Uchikawa, S. Utsunomiya, and S. Nakabayashi, *Appl. Phys. Lett*. **60** (1992) 2427.
2. H. Zama, T. Miyake, T. Hattori, and S. Oda, *Jpn. J. Appl. Phys*. **31** (1992) 3839.
3. R. Singh, J. T. C. Ng, R. K. Singh, F. Qian, N. J. Hsu, and D. J. Krueger, IEEE Trans. On *Appl. Supercond*. **3** (1993) 1.
4. Y. Yoshida, Y. Ito, H. Nagai, Y. Takai, and I. Hirabayashi, *Jpn. J. Appl. Phys*. **36** (1997) 852.
5. W. Ito, A. Oishi, S. Mahajan, Y. Yoshida, and T. Morishita, *J. Mater. Res*. **10** (1995) 803.
6. O. Martinez, J. Jimenez, D. Chambonnet, and C. Belouet, *Journal of Materials Reearch* **15** (5) (2000) 1069.
7. Eko H. Sujiono, P. Arifin, and M. Barmawi, Ext. Abst. 10th Int. Conf. Metalorganic vapor phase epitaxy (ICMOVPE 2000), Sapporo, Japan, 2000, p. 245.