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反應性 同時 蒸着法에 의한 As-grown $YBa_2Cu_3O_{7-X}$ 薄膜의 結晶 特性 및 表面形狀에 관한 硏究

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Crystalline Qualities and Surface Morphologies of As-Grown $YBa_2Cu_3O_{7-X}$ Thin Films on MgO(100) Substrate by Reactive Coevaporation Method

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Abstract The as-grown $YBa_2Cu_3O_{7-X}$ superconducting thin films on MgO(100) substrate have been prepared by a reactive coevaporation method. The superconducting transition temperature, surface morphology and crystalline quality were examined as a function of the substrate temperature ranging from 450℃ to 590℃. From the reflection high energy electron diffraction (RHEED) analysis, it was found the film consisted of almost amorphous phase with a halo pattern deposited at the substrate temperature of 450℃. The film deposited at the substrate temperature of 510℃ consisted of polycrystalline phase, showing a broad ring pattern. On the other hand, for the film deposited at 590℃, RHEED showed spotty pattern indicating that this film consisted of single crystal phase. It has rough film surface due to the surface outgrowth. The surface outgrowth increased as the substrate temperature increased from 510℃ to 590℃. The surface outgrowth may be due to the anisotropic growth rate. The highest transition temperature obtained in this study was Tc_{zero} of 83K with Tc_{onset} of 88K for the film deposited at 590℃ using activated RF oxygen plasma.

1. Introduction

Since the discovery of high-Tc oxide superconductors[1], the extensive efforts have been made on the development of high quality superconducting thin films for the application of electronic devices.

Recently, there have been many reports on the fabrication of the films and their superconducting properties, using a variety of techniques such as magnetron sputtering[2], laser ablation[3], reactive evaporation[4] and organometallic chemical vapor deposition[5]. For practical applications to electronic devices, it is desirable to deposit the as-grown superconducting films with the epitaxial single crystal under the condition of low substrate temperature and low oxygen partial pressure. However, it has been known that the superconducting transition temperature, the crystalline quality and the surface morphology are affected by the deposition temperature[6-7] and the oxidation[8]. In our previous paper[9], we reported the detailed fabrication process of the as-grown $YBa_2Cu_3O_{7-x}$(YBCO) thin films using reactive coevaporation method. In this paper, we are focusing on the crystalline quality and surface morphology as a function of the substrate temperature.

2. Experimental

The fabrication procedure of as-grown superconducting YBCO thin films was described in detail in our previous paper[10]. Briefly, the YBCO films were deposited on MgO(100) substrates using reactive coevaporation method with activated RF oxygen plasma. The source materials of Y_2O_3 and Cu were evaporated from electron beam guns, and Ba was evaporated from a knudsen cell. The deposition rate was about 40Å/min. The deposition pressure after introduction of oxygen into the chamber was maintained about 9.5×10^{-5} Torr. The film thickness and the deposition rate were monitored and controlled with three separated quartz crystal sensors located near the subtrate. The deposition rates of each source materials were effectively adjusted to achieve the stoichiometry. The substrate temperature was varied from 450℃ to 590℃ and measured by thermocouple attached to the surface of the MgO substrate. The film thickness after deposition was about 3000Å. After deposition, the as-grown films were cooled down at the same oxygen plasma conditions (the same pressure and RF power) as at the deposition. For the activated oxygen plasma, the bias coil with RF input power of 100W was introduced into the vacuum chamber. The deposition parameters of the as-grown YBCO films are listed in Table 1.

Figure 1 shows a schematic illustration of the reactive coevaporation system. The composition of the films was determined by inductively coupled plasma spectroscopy (ICP) and energy dispersive X-ray spectroscopy (EDXS). The crystal orientation and phases were analyzed by X-ray diffraction (XRD). For the investigation of crystal quality, the full width at half maximum (FWHM) of rocking curve was calcualted for a (005) reflection peak. The reflection high energy electron diffraction (RHEED) was also used under the in-situ condition to study the crystallinity of the films. The surface morphologies were studied by scanning electron microscopy (SEM). The critical temperature (Tc) was measured by a standard four probe method.

Table 1. Deposition parameters of the as-grown YBCO films by reactive coevaporation method.

	Parameters
Substrate & Size	MgO(100)
	100㎜ in length & width
Substrate Temp.	0.5㎜ in thickness
Deposition Rate	450℃ − 590℃
Film Thickness	about 30Å/min
Deposition Pressure	about 3000Å
RF Power, Input	9.5×10^{-5} Torr
	100 Watt

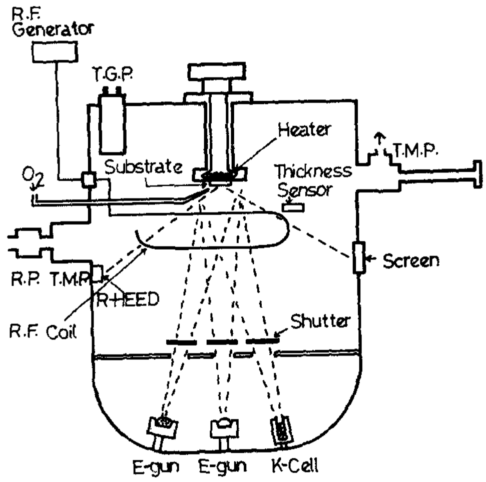

Fig. 1. A schematic illustration of the reactive coevaporation system.

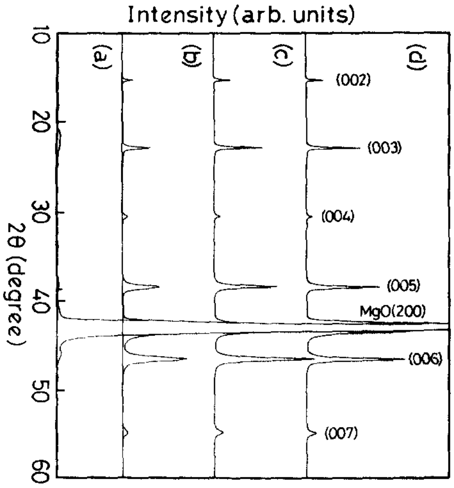

Fig. 2. XRD patterns of the as-grown YBCO films on MgO(100) substrate deposited at various substrate temperature of (a) 450℃ (b) 510℃ (c) 550℃ and (d) 590℃.

3. Results and Discussion

Figure 2 shows the XRD patterns of the as-grown YBCO films on MgO(100) substrate deposited at substrate temperatures 450℃, 510℃, 550℃ and 590℃ with activated RF oxygen plasma. The XRD analysis for the film deposited at substrate temperature of 450℃ showed halo diffraction pattern, suggesting that the film is amorphous phase. In contrast, for the films deposited at substrate temperatures above 510℃, the XRD patterns exhibited preferentially c-axis oriented phase perpendicular to the film surface, which were indexed as (00 ℓ) lines (ℓ =2-7). Other reflection peak was not found. The intensity of the XRD peaks increased as the substrate temperature increased from 510℃ to 590℃. The diffraction pattern for the film deposited at the substrate temperature of 510℃ has an intensity being about half of that for the film deposited at 590℃. The value of FWHM of the film as-grwon at 510℃ was about 1.92°, whereas about 0.7° for the film deposited at 590℃. This decrease of FWHM of rocking curves suggests that the crystalline quality was improved as the substrate temperature increased.

Figure 3 shows the typical SEM images and the RHEED patterns of the films as-grown at various substrate temperatures of 450℃, 510℃, 550℃ and 590℃. The as-grown films have a mirror-like black surface. For the film deposited at the substrate temperature of 450℃, it was observed from the SEM micrograph that the film surface was smooth without surface outgrowths. The RHEED observation shows halo-like pattern, suggesting that the film is almost amorphous phase which is well agreed with the observation made in XRD analysis. As can be seen in the SEM micrographs, the surface outgrowth was observed on 510℃. The surface outgrowth increased as the substrate temperature increased, leading to the degradation of the smoothness of the film surface. Clemens et. al.[11] reported that the roughness of the superconducting films originates from the anisotropic crystal growth rate between a-b and c axes. For the film deposited at the substrate temperature of 510℃, the RHEED photograph shows a broad ring pattern, indicating that the film deposited at 510℃ is a polycrystalline. The polycrystalline phase formed in this film is due to the low deposition temperature.

In contrast, for the film deposited at 590℃, the RHEED shows spotty pattern, indicating that this film has a single crystalline nature with rough film surface. This RHEED pattern is different from that of single crystal film with smooth surface, in which the RHEED shows sharp streak pattern[12]. From the SEM and RHEED obervation, it was found that the initial crystallization and the surface outgrowth occurred at the substrate temperature of above 510℃ and the higher substrate temperature of about 590℃ was required in order to get single crystal film with c-axis preferred orientation using reactive coevaporation method.

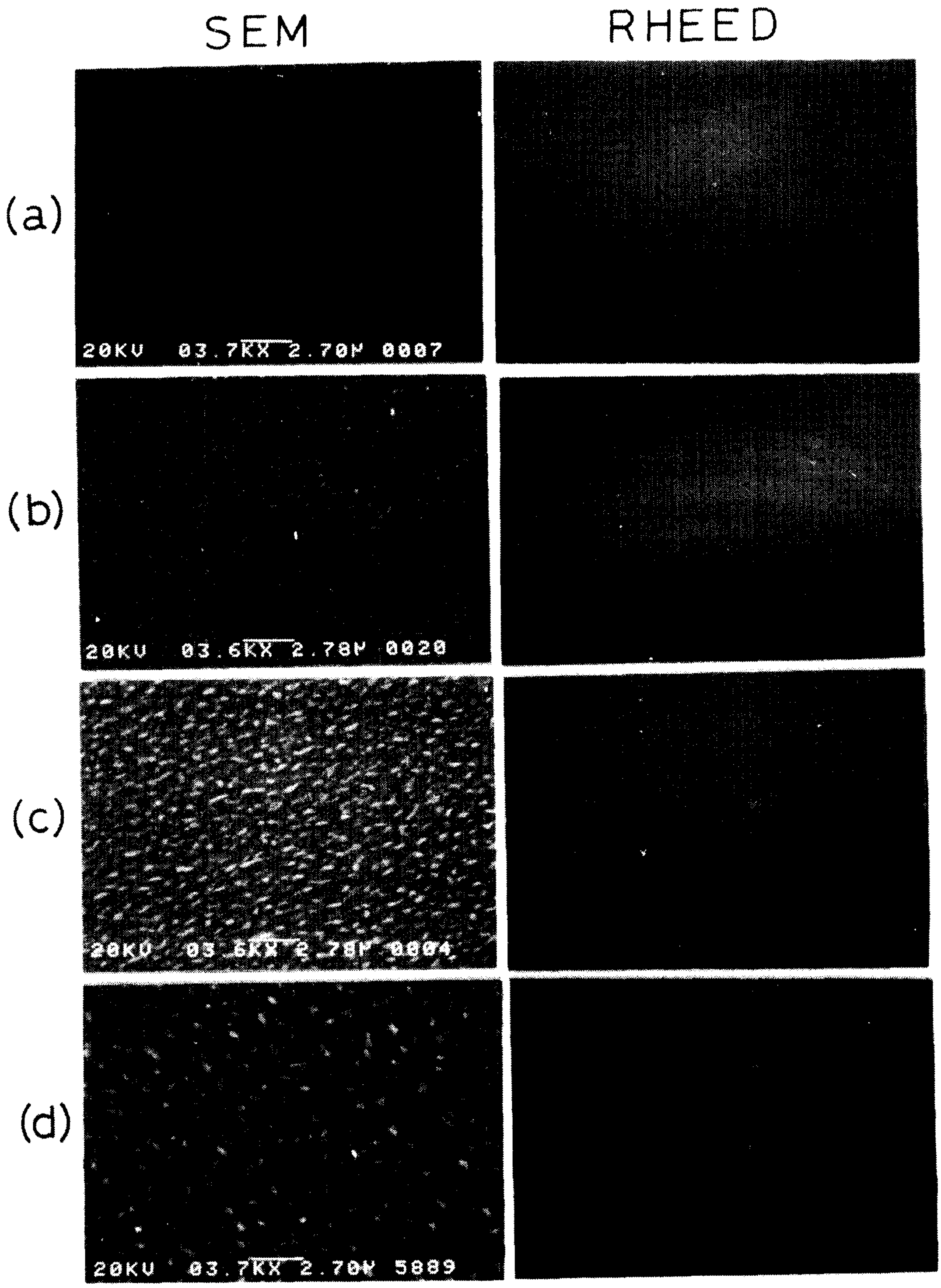

Fig. 3. SEM micrographs and RHEED patterns of the as grown films on MgO(11) substrate deposited at the substrate temperature of (a) 450℃ (b) 510℃ (c) 550℃ and (d) 590℃. The incident direction of the electron beam was ⟨110⟩ and ⟨100⟩ of the substrate for the sample (c) and (d), respectively.

Table 2. Tc_{zero} and FWHM of rocking curve for the as-grwon YBCO films on MgO(100) substrate together with the transition width(△Tc), normal state resistivity (ρ250, ρ100) and resistivity ratio(R250/R100) as a function of the substrate temperature.

Sample No.	Substrate Temp.(℃)	Tc_{zero} (K)	△Tc (K)	ρ100 ($\mu\Omega$cm)	ρ250	R250/R100	FWHM of rocking curve (deg.)
(a)	450	<4.2	–	15525	8438	0.54	–
(b)	510	57	23	723	866	1.20	1.92
(c)	550	78	9	381	656	1.72	0.89
(d)	590	83	5	279	504	1.81	0.7

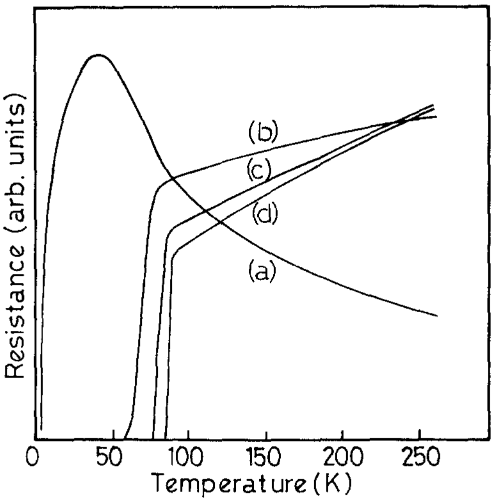

Fig. 4. Resistivity versus temperature characteristics for the as-grown films on MgO(100) substrate deposited at various substrate temperature of (a) 450℃ (b) 510℃ (c) 550℃ and (d) 590℃.

According to the ICP analysis, the composition of metallic elements of the films was almost consistent with the stoichiometric 1 : 2 : 3 regardless of the substrate temperature.

Fig. 4. shows the resistivity versus temperature curves for the as-grown YBCO films on MgO(100) substrates deposited at the substrate temperatures of 450℃, 510℃, 550℃ and 590℃. The Tc's of the as-grown films were affected strongly by the substrate temperature. The as-grown film deposited at the substrate temperature of 590℃ with activated RF oxygen plasma shows Tc_{zero} of 83K with the onset temperature of 88K. The Tc_{zero} was not observed above 4.2K at the substrate temperature of 450℃, although the resistivity was decreased below 40K. The Tc_{zero} and the FWHM of rocking curve for the as-grown YBCO films were summarized in Table 2 together with transition width (△Tc), normal state resistivity (ρ250K, ρ100K) and resistivity ratio (R250K/R100K) as a function of the substrate temperature.

4. Conclusions

We investigated the crystalline quality and the surface morphology of the as-grown YBCO thin films on MgO(100) prepared by the reactive coevaporation method. The surface morphology, crystalline quality and Tc were strongly affected by the substrate temperature. At the substrate temperature 450℃, it was found from the RHEED analyses that the as-grown film was almost amorphous phase with a halo-like pattern. When the films were deposited at 510℃, the RHEED showed a ring pattern, indicating that this film has a polycrystalline which may be due to the low substrate temperature. However, at the substrate temperature of 590℃, the RHEED showed spotty pattern indicating that the film is single crystalline nature with rough film surface. The surface outgrowths were observed at the substrate temperatures above 510℃. These surface outgrowths may be caused by the anisotropic crystal growth rate during deposition.

From the SEM and RHEED analyses, we found that the initial crystallization and surface outgrowths occurred at the substrate temperature of around 510℃ and the high temperature of about 590℃ was needed in order to get single crystal films with the c-axis preferred orientation. The Tc_{zero} for the film deposited at 590℃ under the activated RF oxygen plasma was 83K with Tc_{onset} of 88K.

References

1) C.W. Chu, P.H. Horr, R.L. Meng, L. Gao, Z.J. Huang and Y.Q. Wang : Phys. Rev. Lett. **58**, 405(1987).
2) Y. Emoto, T. Murakami, M. Suzuki and K Moriwaki : Jpn. J. Appl. Phys. **26**, L1248 (1987).
3) G.K. Wehner, Y.H. Kim and A.M. Goldman : Appl. Phys. Lett. **52**, 1187 (1988).
4) T. Terashima, K. Iijima, K. Yamato, Y. Bando and H. Mazaki : Jpn. J. Appl. Phys. **27**, L91(1988).
5) H. Yamane, H. Masumoto, T. Hirai, H. Iwasaki, K. Watanabe, N. Kobayasi, Y. Muto and H. Kurosawa : Appl. Phys. Lett.**53**, 1548(1988).
6) T. Arikawa, H. Itozaki, K. Harada, K. Higaki, S. Tanaka and S. Yazu : Jpn. J. Appl. Phys.**29**, L2199(1990).
7) H. Asano, M. Asahi O. Michikami : Jpn. J. Appl. Phys.**28**, L981(1989).
8) M. Matsumoto, H. Akoh and S. Tanaka : J. Appl. Phys.**66**(8), 3907(1989).
9) H.J. Chang, Y. Watanabe, Y. Doshida, K. Shimizu, Y. Okamoto, R. Akihama and J. T. Song : Jpn.J.Appl.phys.**29**, L2207(1990).
10) Y. Doshida, H.J. Chang, Y. watanabe, K. Shimizu, Y. Okamoto, R. Akihama and J. T. Song : Crygenic Eng.**26**, 47(1991).
11) B.M. Clemens, C.W. Nieh, J.A. Kittle, W. L. Johnson, J.Y. Josefowicz and A.T. Hunter : Appl.Phys.Lett.**53**, 1871(1988).
12) Y. Bando, T. Terashima, K. Iijima, K. Yamamoto, K. Hirata, T. Takada, K. Kamigaki and H. Terauchi ; Thin Solid Films, **181**, 147(1989).