Cubic Y–Ba–Cu–O thin films by high speed pulsed laser deposition


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Abstract

The crystal structure and properties of YBa2Cu3Ox (YBCO) thin films on LaSrGaO100 substrate have been investigated as a function of deposition rates in the range of 0.1–12.2 nm/s using different repetition rate of pulsed laser. At a given substrate temperature of 700°C, when the film was deposited at low deposition rate of 0.1 nm/s, c-axis oriented orthorhombic YBCO thin film growth was observed. However, at high deposition rate of 12.2 nm/s, cubic YBCO thin film growth was observed. This demonstrates that the shortening of interval time between the vapor pulses is important for the cubic YBCO thin film growth. The cubic YBCO thin film growth under high deposition rates was explained by the cation kinetics. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

As is known, the high-temperature superconducting YBa2Cu3Ox (YBCO) can be regarded as a perovskite-related structure based on ABO3 as shown in Fig. 1. Tetragonal YBCO structure is formed by three piled-up perovskite unit cells with Ba–Y–Ba order along c-axis direction (A1 site occupied by Y atom, A2 site occupied by Ba atom). Preferential oxygen occupation in CuO planes of tetragonal YBCO structure produces the orthorhombic YBCO structure. But, the random distribution of cation atoms over these three sub-lattices gives rise to the formation of a cubic YBCO structure with the chemical formula of Y0.33Ba0.67CuOx [1].

Among these structures, recently cubic YBCO have attracted much attention because it has the same perovskite-type crystal structure and stoichiometry as those of an orthorhombic YBCO. These unique features brought the cubic YBCO into a buffer layer [2–4] for a-axis oriented YBCO film growth [5–7] and a barrier layer in superconductor/nonsuperconductor (SNS) Josephson junctions. In the field of SNS Josephson junction fabrication, good reproducibility and performance is one of the important issues. Thus, cubic YBCO
interlayer which has the chemical compatibility and lattice matched with the YBCO superconducting electrode is considered to be most promising for its application of barrier layer in SNS edge type Josephson junctions [8–11].

Therefore, cubic YBCO thin film growth is a subject of increasing interest. However, in contrast to the considerable activities of orthorhombic YBCO thin film growth over 10 years, surprisingly little is known about the cubic YBCO thin film growth. Up to now, most of the cubic YBCO thin film growth has been done only at low substrate temperature of 550°C [1,2]. Although, at 650°C, a few nm-thick cubic YBCO seed layer was observed under a-axis oriented orthorhombic YBCO thin film on MgO and SrTiO₃ substrates [3,4], it has not been reported yet that a cubic YBCO thin film grows above 650°C.

All of the reports for cubic YBCO indicated that short surface migration length on the growing surface plays an important role for the cubic YBCO thin film growth. In general, the kinetic process of adatoms could be affected not only by the substrate temperature but also by the deposition rates [12]. By increasing the deposition rates of the atoms or molecules so much, the average distance over which the adatoms can travel before joining an existing island or meeting another adatoms can be greatly reduced, thus preventing the adatoms from finding energetically stable positions. Therefore, cubic YBCO thin film growth could be possible by increasing the deposition rates.

In this study, we will report on the growth of cubic YBCO thin film at high deposition rates. The ability to vary the deposition rates as independent is one of the principal features of pulsed laser deposition (PLD) compared to other physical vapor depositions such as sputtering technique. Thus, we have prepared cubic YBCO films by PLD operated at high pulse frequencies. We also show changes of structural and electrical properties of the YBCO thin films as a function of deposition rate.

2. Experimental procedure

All the YBCO thin films were deposited on LaSrGaO₄ (LSGO) (100) substrate using a PLD. The PLD system used in this work has been described elsewhere [5]. The 308 nm output from a XeCl excimer laser of 1 J/cm² was focused onto the rotating target at an incident angle of 45°. The deposition rate was controlled from 0.1 nm/s to 12.2 nm/s by varying the repetition rate in the range of 1 Hz to 100 Hz. During deposition, substrate temperature was fixed at 700°C and oxygen pressure was maintained at 100 mTorr. After deposition, the oxygen pressure increased to 500 Torr, and the substrate temperature was reduced to 470°C and then fixed for 1 h in order to allow a complete oxygenation of the film. The film thickness was 250 nm. The structure of the as-grown YBCO thin films was examined by X-ray diffractometer (XRD), Raman spectroscopy, and transmission electron microscopy (TEM). Resistance–temperature (R–T) characteristics were measured by a conventional four-probe method.

3. Results and discussion

Fig. 2 shows the θ–2θ scans of XRD with CuKα radiation for a series of the YBCO thin films deposited on LSGO (100) substrates at different deposition rates. The crystal structure of YBCO thin films was strongly affected by the deposition rates. For the
Fig. 2. X-ray diffraction patterns for the YBCO thin films deposited at 700°C with different deposition rates of (a) 0.10 nm/s, (b) 0.65 nm/s, (c) 2.6 nm/s, (d) 6.50 nm/s and (e) 12.2 nm/s.

case of YBCO thin film deposited at low rate of 0.1 nm/s, only the (00l) peaks indicating the formation of c-axis oriented orthorhombic YBCO thin film were dominant. However, with increasing the deposition rate into 2.3 nm/s, the diffraction peak at 2θ = 23.2° (23.2° peak) became strong. At 12.2 nm/s deposition rates (Fig. 2e), the 23.2° peak and the (200) LSGO peak were dominant. (100) LSGO diffraction peak was not observed because of the very low value of the relative intensity ratio, I(100)/I(200) ~ 10^-3. According to the diffraction spectrum of LSGO (JCPDS file number 24-1208), (100) LSGO diffraction peak was forbidden. The quite weak (005) diffraction, however, indicates the remaining of c-axis oriented orthorhombic phase. The lattice parameter of YBCO thin film determined from 23.2° peak was 0.389 nm which was consistent with that of lattice constant along the b-axis direction of orthorhombic phase [13] or a lattice constant of cubic phase. However, the θ–2θ diffraction analysis does not provide further information about the phase. Therefore, we could not distinguish whether the 23.2° peak was resulted from b-axis oriented orthorhombic phase or cubic one.

The phase identification of YBCO thin film deposited at high deposition rates was carried out by Raman spectrum analysis. Fig. 3 shows the Raman spectra of YBCO thin films deposited on LSGO (100) substrates with different deposition temperature and rates. The characteristic lines of the Raman spectra for the orthorhombic YBCO occur at 118, 150, 340, 435 and 500 cm⁻¹ corresponding to the vibrations along the c-axis of Ba, Cu, planar oxygen in CuO₂ plane (out of phase), planar oxygen in CuO₂ plane (in-phase) and apical oxygen, respectively. Among these phonons, special interesting modes for the determination of the crystal structure are the 340 and 500 cm⁻¹ because these are characteristic peaks of the c-axis and a-axis oriented orthorhombic YBCO thin film structures, respectively.

Fig. 3. Raman spectra of the YBCO thin films deposited at (a) 800°C, 0.10 nm/s, (b) 700°C, 0.10 nm/s, (c) 650°C, 0.1 nm/s and (d) 700°C, 12.2 nm/s.
The 500 cm\(^{-1}\) peak is very weak and 340 cm\(^{-1}\) peak is strong for the c-axis oriented orthorhombic YBCO thin film, and it is reversed for the a-axis oriented orthorhombic YBCO thin film. Fig. 3a shows the typical Raman spectrum of fully oxygenated c-axis oriented orthorhombic YBCO thin film deposited at 800°C using a deposition rate of 0.1 nm/s. Otherwise, in Fig. 3b, as the substrate temperature decrease from 800°C to 700°C, a new peak observed at 570 cm\(^{-1}\). The appearance of the additional phonon peak at 570 cm\(^{-1}\) in the Raman spectrum is closely related to the oxygen disorder in YBCO thin film [14]. Fig. 3c shows the typical Raman spectrum of the a-axis oriented orthorhombic YBCO thin film deposited on a PBCO template layer [6]. The 500 cm\(^{-1}\) peak, the strongest feature of which the c-axis lies parallel to the substrate surface, is very strong. On the other hand, Raman spectrum of YBCO films deposited at 12.2 nm/s was substantially different from that of orthorhombic YBCO thin films. Important feature to note in Fig. 3d is the extinction of the 340 and 500 cm\(^{-1}\) peaks and appearance of the strong band centered at 550 cm\(^{-1}\). This result clearly indicates that an existence of pronounced cation disorder in YBCO crystal structure. Therefore, we found that the cubic YBCO films grew by the high speed PLD process, instead of a-axis oriented orthorhombic YBCO films.

In order to confirm clearly the cubic phase of the films grown at high deposition rates, the microstructure of the film was observed by high-resolution TEM. Fig. 4 shows a cross-sectional TEM image of the YBCO thin film deposited at 12.2 nm/s. A c-axis oriented orthorhombic was observed near the substrate surface. However the layered CuO chains do not propagate to long distances. This means that the formation of c-axis oriented orthorhombic YBCO domains was disrupted by the arrival of some unwanted cations. We thought that the weak (005) peak of the XRD patterns was attributed to this domains. A similar result has also been reported in Ref. [1]. Meanwhile, on top of the c-axis oriented orthorhombic layer, simple square contrast image which is the inset image in Fig. 4 was observed, and we could not observe the layered lattice image peculiar to orthorhombic YBCO structure. It is clear from this cubic lattice image that the top area of the YBCO thin film has a cubic YBCO structure [1,15]. Even though the possibility that this image is taken along the in-plane [001] direction of large a-axis oriented orthorhombic domain may exist, the clear difference in Raman spectra between the YBCO thin film deposited at high rate and the a-axis oriented orthorhombic YBCO films as shown in Fig. 3, convinced that the cubic lattice image was not an a-axis oriented orthorhombic domain.

On the other hand, Wu et al. [16] reported the successful synthesis of c-axis oriented orthorhombic YBCO thin films by PLD with deposition rates up to 14.5 nm/s. This report seems to contradict our result. We suspect that the difference with the results from Wu et al. is due to the application of a lower substrate temperature than used by Wu et al. Hence, deposition rate which is high at 700°C in the present study may be considered low at a substrate temperature of 750°C.
The $R$–$T$ characteristics for the series of YBCO thin films with different deposition rates grown on LSGO (100) substrates are shown in Fig. 5. As the deposition rate increased, the normal state resistance increased and a tail developed in the resistance. The YBCO thin films deposited at 0.1 nm/s exhibited a metallic behavior with a zero-resistance temperature ($T_{c,0}$) of 80 K. For YBCO thin films deposited at 6.50 nm/s, the temperature dependence of the resistance was semiconducting and $T_{c,0}$ was not observed. Moreover, the normal state resistance increased remarkably. Considering the structural change of YBCO thin film as described above, we can understand that the deterioration of superconductivity in the YBCO thin films prepared at high deposition rates is due to the cubic phase formation.

The remarkable differences in crystal structures of YBCO thin films deposited at high deposition rates were explained by considering the kinetics of adatoms. Generally, the growth process of a solid film from the vapor phase proceeds via the impingement of vapor atoms onto the substrate followed by surface diffusion to stable lattice sites. During the surface migration of adatoms, they interact with each other and form clusters or attach to a growing crystallite. In PLD process, two concepts of the deposition rates need to be considered, i.e., instantaneous and average deposition rates. Since the PLD occurs in a pulsed mode, whereby with each pulse there is a high instantaneous deposition rate. If the laser energy density is kept constant, the instantaneous deposition rate is not changed. But by varying the repetition rate, which we have done in this study, the average deposition rate can be controlled. If we consider that the first vapor pulse is incident on the substrate surface, there is a high density of clusters that are of much smaller dimension than those that would be stable for much lower instantaneous deposition rates. These smaller clusters are not stable once the vapor pulse has decayed. Therefore, these small clusters will tend to dissociate into mobile species that will nucleate new clusters with a larger dimension during the time of no vapor pulse arrival. The next pulse will initiate the same sequence with some of the mobile adatoms being added to the existing clusters. Therefore, the interval time between the vapor pulses will influence the domain size. And the interval time can be easily controlled by changing the repetition rate.

For simplicity, we considered only the Y and Ba cation kinetics [17,18]. At low deposition rate (0.1 nm/s) which has a long interval time, adatoms are allowed sufficient time to migrate to some of the local free energy minimum, thus, very large $c$-axis oriented orthorhombic YBCO domains with long-range ordering of Y and Ba atoms will be formed. However, at high deposition rate (12.2 nm/s) which has very short interval time, the encounter probability between migrating adatoms on substrate surface is very high. Therefore, very small $c$-axis oriented orthorhombic YBCO domains with short-range ordering of Y and Ba atoms will be formed, which eventually lead to cubic YBCO thin film structure by suggested Linzen et al. [19].

4. Conclusions

We have investigated the influence of the deposition rates on the in-situ YBCO thin film growth on LSGO (100) substrates by using PLD technique. The deposition rate was varied in the range of 0.1–12.2 nm/s by controlling the repetition rate of pulsed...
laser in the range of 1–100 Hz. At 700°C substrate temperature, as the deposition rate increases from 0.1 nm/s to 12.2 nm/s, the c-axis oriented orthorhombic YBCO thin film growth changed to cubic YBCO thin film growth. The presence of cubic YBCO at high deposition rate suggests that very small orthorhombic YBCO domain could be responsible for the cubic YBCO thin film formation. Because of the deposition rates, the interval time between the vapor pulses influences the orthorhombic YBCO domain size. We propose that the high deposition rate as well as the low temperature is also effective for the cubic YBCO thin film growth. Finally, we would like to mention that the results obtained in this study are expected to provide a more convenient fabrication process of the SNS Josephson junctions consisted of all YBCO thin films.

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References