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Systematic study of the growth-temperature dependence of structural disorder and superconductivity in $YBa_2Cu_3O_{7-\delta}$ thin films

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The growth-temperature dependence of the crystal structure and superconductivity of $YBa_2Cu_3O_{7-\delta}$ thin films has been investigated quantitatively for a series of sputter-deposited films prepared at substrate temperatures ranging from 593 to 726 °C. X-ray diffraction revealed that the reflection intensities of the films, especially $I(004)$, $I(005)$, and $I(006)$, change systematically with substrate temperature. Structure analyses suggested that there is a considerable degree of disorder between Y and Ba atoms in the structure of the thin films deposited at lower substrate temperatures. This degree of disorder decreases rapidly from 14 to 3 % (percentage of the Y site substituted by Ba atoms) with increase in the substrate temperatures up to 630 °C, and then decreases slowly to zero percent and remains zero even at higher substrate temperatures. Electrical-resistivity measurements showed that the superconducting transition temperatures of the thin films increase with increasing substrate temperature, in good agreement with the recovery of the disordered structure. The results indicate that there is an intrinsic relationship between the cation disorder and T_c, which are both strongly dependent on the growth temperature.

I. INTRODUCTION

There are numerous papers dealing with the dependence of the superconducting properties of $YBa_2Cu_3O_{7-\delta}$ thin films on deposition conditions, such as target composition, substrate material, substrate temperature, total and partial oxygen pressure, etc.[1-5] Among these conditions, substrate temperature is known as a dominant factor controlling T_c. Some authors have reported that thin films prepared at higher substrate temperatures exhibit better superconductivity,[3,4] and suggested that T_c suppression in the films prepared at lower substrate temperatures is due to a disordered arrrangement of cations, especially of Y and Ba. Alternatively, Matijasevic *et al.*[5] have mentioned the possibility of Y substitution by Ba atoms at lower oxygen pressure. However, without systematic investigation and further structure analyses of the thin films, there are still no substantial data supporting these suggestions.

In a paper published previously,[6] we dealt with the problem of oxygen deficiency in $YBa_2Cu_3O_{7-\delta}$ (YBCO) thin films. We observed that an YBCO thin film that was prepared at a low substrate temperature of 580 °C exhibited an expanded c lattice parameter and a different x-ray diffraction pattern from the standard one. Yet the abnormality in both the c length and x-ray intensity disappeared after heat treatment at 850 °C in flowing Ar–6% O_2 gas. The structures of this thin film before and after annealing were analyzed, and the results revealed that there is considerable disordering between Y and Ba atoms in the as-grown thin film, which was prepared at a relatively low substrate temperature.

Such disordering between cations seems likely to be a unique phenomenon that only occurs in thin films. Since thin films are prepared at substrate temperature 200–300 °C lower than that for bulk crystal growth, there is not sufficient mobility to attain the thermodynamically stable state. The structures of thin films could therefore be variable, depending on growth conditions like substrate temperature. For bulk samples, crystals grow at high temperature (above 900 °C in YBCO) and sufficient oxygen partial pressure, so that a thermodynamic equilibrium state is always reached during crystal growth. The $YBa_2Cu_3O_{7-\delta}$ phase is thought to be a line compound and to have no cation solid solution.[7] Although substitution of Ba by Y atoms at lower growth temperature has been reported by Iqbal *et al.*,[8] no Y substitution by Ba has been reported to our knowledge. Concerning disordering between Y and Ba, there was a report by Van Tendeloo *et al.*,[9] but the phenomenon has not been fully substantiated. This is understandable if one considers the large difference in the cationic radii [Y, 1.02 Å, Ba, 1.42 Å (Ref. 10)]. Therefore it seems difficult to observe and study ordering-disordering phenomena with bulk crystals, although it is believed that such studies would provide valuable information and additional understanding of these materials.

The present work is destined to make clear whether the growth temperature affects the crystal structure and superconductivity of the films, and, if it does so, then what is the mechanism. We prepared a series of thin films by controlling the substrate temperatures in the range from 593 to 726 °C. Subsequently, we carried out quantitative studies of the structural and superconducting properties of the thin films. Hereafter, we will give our data proving that cation disorder does exist in the structure of thin films prepared at lower substrate temperatures. Furthermore, we will verify that T_c is strongly dependent on the substrate temperature, in agreement with the change in

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the degree of disorder of the crystal structure. The relation between the disorder and the suppression of T_c will also be discussed.

II. EXPERIMENTAL PROCEDURE

There are two methods applicable for the preparation of YBCO thin films in our laboratory. One is radiofrequency (rf) magnetron sputtering, and the other is molecular-beam epitaxy (MBE). Each method has its own advantages and is used according to the research purpose. In general, with the use of the MBE method, the T_c's of the films are relatively high (85–90 K), but the chemical compositions are extremely difficult to control. With rf sputtering, thin films might receive serious damage from the negative-ion bombardment during preparation, and exhibit relatively lower T_c's than those prepared using MBE, as reported in our previous paper.[6,11] On the other hand, with the use of rf sputtering, deposition conditions are easy to control to the same values. This limits the number of factors in the growth conditions needing to be considered and makes thin films of the same chemical composition available. Since the purpose of the present study is to investigate the growth-temperature dependence of crystal structure and T_c of YBCO thin films, it is definitely necessary to exclude the influence of all other factors but the substrate temperature on the structural and superconducting properties of the thin films. Also, it is extremely important to ensure that the thin films prepared at different growth temperatures have the same chemical composition. For the purpose, we chose the off-axis rf magnetron sputtering method to prepare thin films even though the T_c's might not be optimized.

The deposition conditions except substrate temperature for YBCO thin films were set the same for all the films as follows. A single target was used and the [Y]:[Ba]:[Cu] ratio of the target was 1.05:2.00:3.85. A polished MgO(001) single crystal ($10\times10\times0.5$ mm^3) was adopted as the substrate. The sputtering atmosphere was Ar–10% O_2 with the total pressure being controlled at about 2.0 Pa, and after the sputter deposition the films were cooled to room temperature in 1 kPa O_2. The power of the plasma was about 170 W. The films were sputtered at a rate of about 0.6 Å/s, and the thickness of the films was about 1500 Å.

Under the above conditions, a series of thin films was prepared with the electrical current supply to the substrate heater being controlled at values of 5.0, 5.2, 5.25, 5.5, 6.0, 6.5, and 6.8 A. The substrate temperatures were calibrated with a thermoelectric couple at exactly the same conditions as for the deposition, including sputtering atmosphere, plasma power, etc. The attachment between the thermoelectric couple and the substrate holder was made by silver paste, in almost the same manner as that between the MgO substrate and the substrate holder. We consider that the thermoelectric couple temperature thus measured could represent the substrate temperature, and in the present paper we regard the substrate temperature as the growth temperature of the films. Corresponding to each current value at which thin films were prepared, the substrate temperatures were measured to be 593, 608, 612, 633, 670, 705, and 726 °C. Depositions at temperatures lower or higher than this range were also tried. However, in our experiments, below the temperature of 593 °C, not only *c*-axis- but also *a*-axis-oriented films grow on the MgO substrate. This results in overlapping x-ray diffraction patterns and makes structure analyses difficult. On the other hand, at substrate temperatures higher than 726 °C, YBCO films fail to deposit homogeneously, or even decompose. For this reason, only thin films prepared in the temperature range of 593 to 726 °C were used for the present study.

Using these thin films, dependence of the chemical, crystallographic, and superconducting properties on the growth temperature was investigated with the following methods.

(1) The Rutherford backscattering (RBS) method was used to analyze the chemical composition of the thin films. The irradiation was 2.8 MeV He^{2+}.

(2) X-ray diffraction experiments were carried out on a JDX-3500 rotating-anode diffractometer. Graphite-monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) was used. The divergence slit was set at $\frac{1}{16}$° to ensure that the incident beam was completely diffracted by the thin film of limited size (10×10 mm^2) even at a very low 2θ angle. The diffraction intensities in the range $2\theta < 65°$ were collected in a 2θ-θ step-scan mode, with the step interval 0.01° and scan time at each step 0.2 s.

(3) Electrical resistivities were measured with the four-probe dc method. The current applied was 0.1 mA.

III. RESULTS AND DISCUSSION

A. Chemical compositions of the films

Figure 1 shows the results of the RBS composition analysis, where circles show the ratio [Ba]/[Y], and squares show [Cu]/([Y]+[Ba]) for films prepared at various substrate temperatures. The chemical compositions

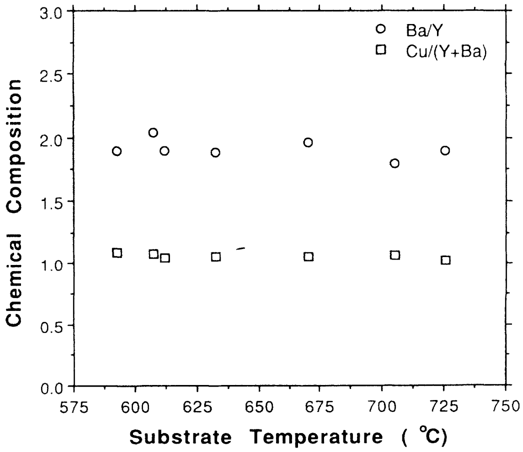

FIG. 1. Chemical compositions of the thin films prepared at different substrate temperatures. Circles and squares show atomic ratios of [Ba]/[Y] and [Cu]/([Y]+[Ba]), which were obtained using RBS analysis.

of the films are all found to be close to 1:2:3 stoichiometry, and no obvious substrate-temperature dependence of the chemical composition can be observed. The slight deviations of some films from the stoichiometry are suggested to be mostly caused by less surface smoothness or the relatively large thickness (about 1500 Å) of the films, which resulted in an irregular shape of the backscattered spectrum or a slight overlap of the spectrum, leading to decrease in the accuracy of the RBS composition analysis. In any case, it seems proper to consider that the chemical compositions of the thin films prepared by us do not depend on the substrate temperature in the range studied here. This means that all the phenomena observed in these films, which will be described hereafter, are not caused by chemical composition changes in the films.

B. Epitaxies and *c* lattice parameters

Figure 2 shows several typical x-ray diffraction patterns of the YBCO films prepared at different substrate temperatures. For clarity, the intensity of each pattern was normalized by its 005 reflection, and the horizontal axes (2θ) of each pattern were shifted about 1.0° from each other. It is obvious that films prepared at the temperature range of the present research are perfectly *c*-axis-oriented epitaxial films, except for one film prepared at the substrate temperature of 593 °C, where a small portion of *a*-axis-oriented grains appears along with the majority of the *c*-axis-oriented grains. In all the thin films, no reflection peak belonging to crystals other than $YBa_2Cu_3O_{7-\delta}$ was detected, indicating that there is no significant segregation of impurity materials composed of the excess Y, Ba, and Cu atoms.

By fitting individual *c* values calculated from 2θ Bragg angles of the $00l$ reflections as a function of $(1/\sin\theta+1/\theta)\cos^2\theta/2$ to reduce the evaluation error caused by the geometry of the sample setting inside the diffractometer, Fig. 3 was drawn to show the substrate-temperature dependence of the *c* lattice parameters of the as-grown thin films. It is obvious that the *c* lattice parameters expand considerably if the films are prepared at lower substrate temperatures. With increase of the substrate temperature, the *c* parameters decrease quickly in the range of 593 to 630 °C, and then decrease slowly at higher substrate temperatures. At the highest temperature of the present research range, the as-grown films showed the smallest *c* length, but still longer than 11.68 Å, the *c* value of bulk $YBa_2Cu_3O_{7-\delta}$ crystals. The expansion in *c* of the films prepared at higher temperatures is considered to come from crystallographic defects introduced with the lattice mismatch, deposition faults, etc. Oxygen deficiency is not the cause, as can be understood from the x-ray diffraction patterns of the as-grown and post-annealed films, in the way reported in a previous paper.[6]

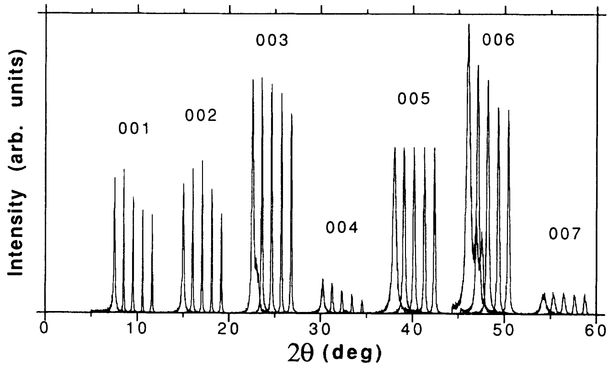

FIG. 2. Typical x-ray diffraction patterns of the as-grown thin films prepared at controlled substrate temperatures. 2θ values of the patterns were shifted 1° from each other for clarity, and intensities were normalized by their 005 reflections. The substrate temperatures of the films corresponding to the five patterns from left to right are 593, 608, 612, 633, and 705 °C, respectively.

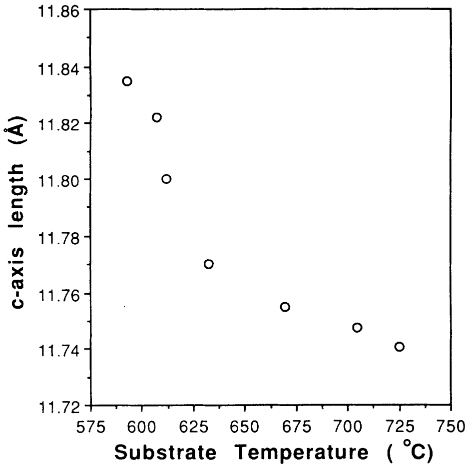

FIG. 3. Substrate-temperature dependence of the as-grown *c* lattice parameters of the films.

C. Crystal structures of the films

It is usual that, in thin films, the intensities of the reflections diffracted at very low 2θ Bragg angle have a large contribution from the matrix of the surface layers, owing to the effect of x-ray absorption. These reflections are also sensitive to the geometry of the sample setting inside the diffractometer. As a result, the intensities of these reflections are difficult to measure accurately. With increase in the 2θ Bragg angle, however, the influences of surface conditions and setting geometry on the reflection intensities become slighter. Thus an accurate measurement of the reflection intensities at high Bragg angles becomes possible and discussion of them is meaningful. Here, we concentrate our attention on the intensities of the 004, 005, 006, and 007 reflections. From Fig. 2, one can see that the intensities of the 004 and 006 reflections varied clearly and systematically among the films prepared at different substrate temperatures, while the 007 reflection changes very little.

To investigate the intensity changes quantitatively, we calculated the integrated intensity $I(00l)$ further by summing up the counts of all the scan steps of the reflection peaks after subtracting backgrounds. Figures 4(a) and 4(b) show the substrate-temperature dependence of the intensity ratios of the two most significantly varying reflections, $[I(004)/I(005)]\times 20$ and $I(006)/(005)$, respectively. It can be seen that both of the values decrease rapidly with increase in the substrate temperature up to 630 °C, and then remain almost constant in the temperature range higher than 630 °C.

Since all the thin films were prepared under the same sputtering conditions except substrate temperature, the intensity variations of the films must imply something important. According to our experience,[6,11] films prepared at an atmosphere of 2 Pa Ar–10 % O_2 gas and cooled in 1 kPa O_2 gas are usually fully oxygenated. This was verified by a supplementary experiment using a film prepared at a low substrate temperature of 608 °C. The film, whose $[I(004)/I(005)]\times 20$ and $I(006)/I(005)$ values are unusually large (2.70 and 1.86, respectively), was annealed at 640 °C for 30 min in flowing Ar–8% O_2 gas. A comparison of the diffraction patterns of the film before and after annealing showed no obvious intensity changes. This fact indicates that the abnormal as-grown diffraction pattern was not caused by oxygen deficiency, since the oxygen deficiency can be decreased by an annealing treatment at 400–650 °C, as reported in our previous papers.[6,11] Moreover, Ref. 6 demonstrated that the diffraction patterns of oxygen-deficient thin films behave in a totally different manner from the present case. That is, the values of $[I(004)/I(005)]\times 20$ and $I(006)/I(005)$ will decrease to less than 1.3 and 1.43, respectively, but not increase if oxygen deficiency is involved.

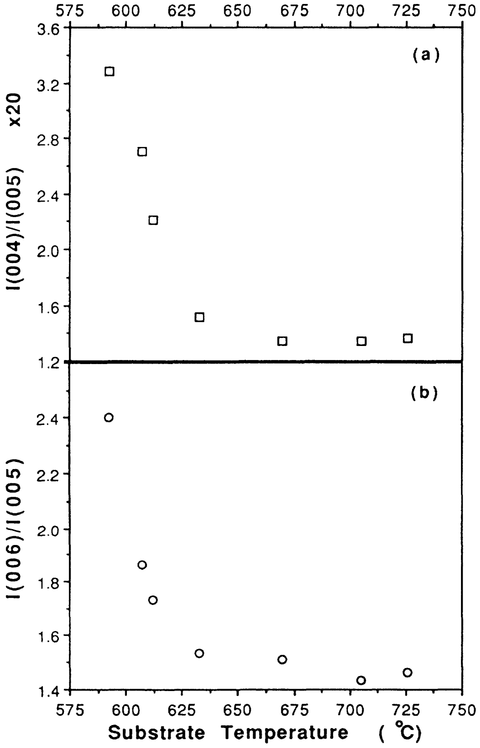

FIG. 4. Substrate-temperature dependence of ratios of the reflection intensities. (a) is for $I(004)/I(005)$, multiplied by 20, and (b) for $I(006)/I(005)$.

On the other hand, the RBS composition analysis showed that the chemical compositions of the films do not have any systematic variation with substrate temperature, implying that the intensity changes are not due to chemical-composition change in the films. This was also verified using several low-substrate-temperature-prepared films.[12] The films were annealed at 850 °C for 30 min in flowing Ar–8% O_2 gas at 1 atm. It is surprising that the diffraction patterns of the annealed films all changed to be just like those prepared at higher substrate temperatures, and showed no sign of impurity segregation. Since the as-grown thin films and the annealed thin films are the same, no chemical-composition change occurred during the annealing procedure. Therefore, the influence of the chemical composition can be totally excluded as a cause of the diffraction intensity changes shown in Figs. 2 and 4.

Based on the above considerations, we suggest that the origin of the abnormality in the reflection intensities is structural change of the films and that the change could easily be recovered through heat treatment. Such a structural change is most probably of the ordered-disordered arrangement of the atoms in the structure. In YBCO thin films, it might occur among Cu, Y, and Ba atoms at four cation positions Cu(1), Cu(2), Y, and Ba, as shown in Fig. 5. Moreover, since the 1:2:3 stoichiometry was preserved in films prepared at different temperatures, only a mutual substitution of atoms seems likely. In a previously published paper,[6] we have reported the oxygen-content dependence of the structural parameters in YBCO thin films, and demonstrated that quantitative structure analyses of the thin films is possible if variables are limited. With the same considerations, to understand what the intensity variations mean, we carried out structure analyses on the seven films prepared at different substrate temperatures, using the structure factors of the films after applying Lorentz polarization and absorption corrections to the integrated intensities $I(00l)$ (the 001 reflection was ruled out for lack of accuracy).

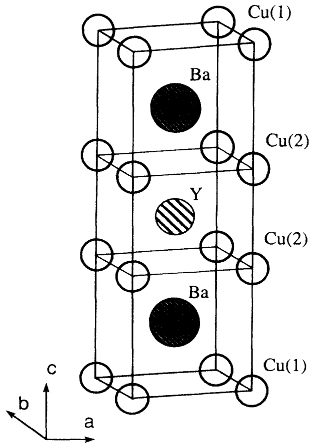

FIG. 5. Schematic structure of the orthorhombic phase of $YBa_2Cu_3O_{7-\delta}$.

The least-squares refinements[13] were carried out using various model structures assuming disordering among the three kinds of cations (Cu,Y,Ba) at four crystallographic sites [Cu(1),Cu(2),Y,Ba]. For convenience of the structure analyses, the slight deviations in the chemical compositions of the films from 1:2:3 stoichiometry were not considered. The results of the least-squares calculation told us that calculated structure factors based on a model of mutual substitution between Y and Ba atoms at Y and Ba sites fitted the observed structure factors best with the fewest variable parameters. To obtain a quantitative understanding of the disordering between Y and Ba atoms, we performed further calculations as follows. By imaging two typical model structures with ordered and completely disordered arrangements of Y and Ba atoms at the two crystallographic sites, the z positional parameters of Cu(2) and Ba sites in a partially disordered structure should be approximately given by

$$z(\text{site})=z_{\text{order}}(\text{site})-[G_{\text{order}}(\text{Ba})-G(\text{Ba})]S(\text{site}) ,$$

where

$$S(\text{site})=\frac{z_{\text{order}}(\text{site})-z_{\text{disorder}}(\text{site})}{G_{\text{order}}(\text{Ba})-G_{\text{disorder}}(\text{Ba})} ,$$

and z(site) is the z positional parameter of the Ba or Cu(2) site in the partially disordered structure, z_{order}(site) is the z positional parameter of the Ba or Cu(2) site in the ordered structure, z_{disorder}(site) is the z positional parameter of the Ba or Cu(2) site in the completely disordered structure, G(Ba) is the occupational parameter of the Ba atom at the Ba site in the partially disordered structure, G_{order}(Ba) is the occupational parameter of the Ba atom at the Ba site in the ordered structure, and G_{disorder}(Ba) is the occupational parameter of the Ba atom at the Ba site in the completely disordered structure.

Clearly, in the ordered structure, G_{order}(Ba) is 1.0, while in the completely disordered structure, G_{disorder}(Ba) must be 0.6667 for the chemical composition ([Y]:[Ba]=1:2) of the films. $z_{\text{order}}(\text{Ba}) = 0.1843$ and $z_{\text{order}}[\text{Cu}(2)]=0.3556$ were adopted according to Jorgenson *et al.*[14] With the increase in the degree of disorder, the difference between the Ba-containing cube and the Y-containing cube becomes less significant, and the z positional parameters of the Ba and Cu(2) sites decrease simultaneously. In the completely disordered structure, there will finally be no difference among the three cation-centered cubes. Therefore, z_{disorder}(Ba) and z_{disorder}[Cu(2)] must be 0.1667 and 0.3333, respectively. Model structures with different assumed G(Ba) and the calculated z(Ba) and z[Cu(2)] were used for the least-squares refinements. The temperature factors of the cations were constrained to 1.2, 2.0, 1.4, and 1.6 for Y, Ba, Cu(1), and Cu(2) sites, larger than those published for bulk crystals, considering the imperfections of the thin films compared to the bulk crystals. Other structural parameters were referred to the orthorhombic phase.[14] Only the scale factors were variable in the least-squares cycles.

Figure 6 shows two typical results of the structure refinements, where open circles are those of the film prepared at a low substrate temperature (593 °C), and solid circles are those of the film prepared at a high substrate temperature (705 °C). In the figure, the horizontal axis represents the degree of disorder of the Y site, i.e., the percentage of the Y site substituted by Ba atoms. The vertical axis is R, a factor showing the consistency between the observed structure factors and the calculated ones based on the model structure used in the least-squares refinements. From the figure, one can see that, for the film prepared at low temperature, a model structure with 14% disorder (i.e., 14% of Y atoms in Y site being substituted by Ba, and 7% of Ba in two Ba sites being substituted by Y atoms) shows the smallest R factor. For the high-temperature-prepared thin film, the R factor exhibits the smallest value in the model with the degree of disorder near zero.

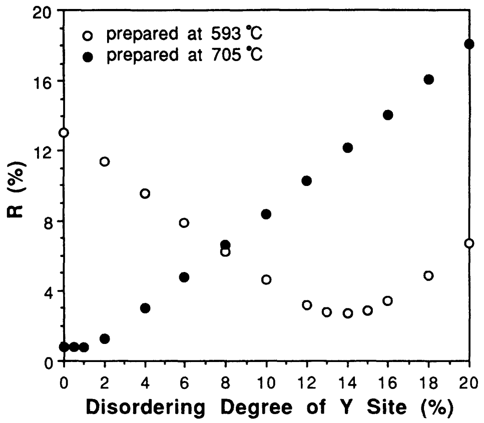

FIG. 6. Results of structure analyses of two typical films prepared at 593 °C (open circles) and 705 °C (solid circles).

Similarly, using this ordering-disordering model between Y and Ba atoms, structure analyses were performed for the seven thin films prepared at different substrate temperatures. Figure 7 shows the substrate-temperature dependence of the degree of disorder of the Y site in the films. We see that, along the increase in the

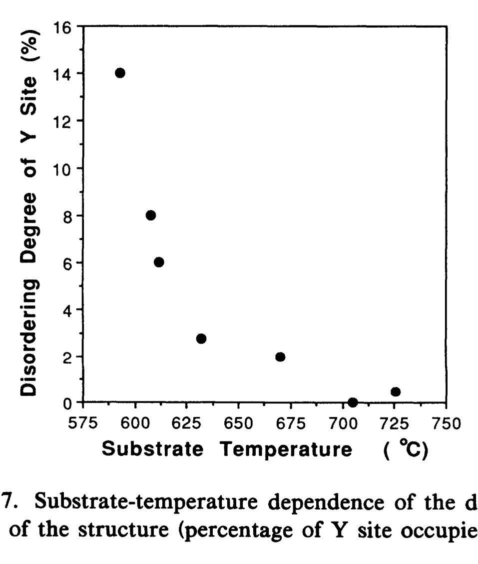

FIG. 7. Substrate-temperature dependence of the degree of disorder of the structure (percentage of Y site occupied by Ba atoms).

substrate temperatures from 593 to 630 °C, the degree of disorder of Y and Ba atoms decreases rapidly from 14% to about 3%. In the higher-temperature area, it decreases slowly and finally falls to zero.

As mentioned previously, disordering between Y and Ba atoms has not been reported in $YBa_2Cu_3O_{7-\delta}$ bulk samples. However, the phenomenon itself seems quite intuitive and reasonable, if we consider the mechanism of thin-film preparation. According to recent research using reflection high-energy electron diffraction[15] (RHEED) and scanning tunneling microscopy[16] (STM), the *c*-axis-oriented films grow by a terraced-island growth mechanism, and the step heights of the flat terrace are one unit or multiples of the *c*-axis length. This suggests that, to form an ordered structure in YBCO thin films, not only surface diffusion, but also diffusion of the cations along the growth direction within one unit-cell length is necessary.

At lower temperature, YBCO films tend to grow in *a*-axis orientation, as reported by many authors. This is natural since, in such a case, all the cation sites are exposed to the surface and only surface migration is necessary to form an ordered structure. The activation energy for the surface migration should be smaller than for three-dimensional bulk diffusion. At higher temperature, the *c*-axis-oriented film grows predominantly, because it has less surface energy than the *a*-axis-oriented film, as can be understood from the terraced-island growth of the *c*-axis-oriented film. However, in the lower temperature range of this *c*-axis-oriented growth, some Y and Ba atoms might occupy irregular positions since both ions form the perovskite structure with Cu ions in the YBCO structure, in spite of the relatively large difference between the Y and Ba cationic radii and different valence (+3 and +2). To change their irregular positions, some excess activation energy and vacancies through which cations migrate to their regular positions would be needed. But the energy necessary to activate such migration could not be supplied at these lower substrate temperatures, as verified in our post annealing experiments.[12] The disordered arrangements are therefore frozen into the structure during growth. As a result, at relatively lower growth temperature, a considerable amount of mislocation of Y and Ba atoms (or degree of disorder) exists in thin films. With increase in substrate temperature, the rate of migration increases, leading to a rapid decrease in the degree of disorder. At higher substrate temperatures (here, above 630 °C), the mobility of the atoms might be sufficient to form films in a nearly completely ordered structure.

It is worth indicating that disordering between Y and Ba atoms may destroy the local charge balance (although the total cation charge balance was kept for the thin films) and make the YBCO structure unstable. This might account for the fact that only partial disordering (maximum about 14%) was observed in the films used for the present research. In addition to the influence on local electronic properties of the structure, disordering might also simultaneously create a certain density of defects in the crystal, and influence the texture of the thin films. As can be seen from Fig. 2, there is some broadening of the x-ray diffraction profiles in the films prepared at lower temperatures. The peak broadening, reflecting information about grain size and lattice strain along the deposition direction, i.e., the *c* axis, is consistent with increasing amounts of defects accompanying structure disorder. Another significant influence of disorder on crystallographic defects is serious expansion in the *c* lattice parameter, as could be observed from Fig. 3. The details of the growth-temperature dependence of morphology of the thin films will be discussed in a separate paper.[12]

D. Superconductivity

Figure 8 shows the results of electrical-resistivity measurements, with open circles and solid circles representing onset and zero point of the critical temperatures, respectively. It can be seen that critical temperatures, especially zero-point temperatures, depend strongly on the substrate temperature. At temperatures lower than 630 °C, T_c increases quickly with increase in substrate temperature. However, at higher temperatures, T_c increases very slightly and finally saturates at a certain value.

As introduced in the experimental section, to obtain thin films of the same chemical composition and limit the number of factors to be considered in the present study, we prepared all the thin films using the sputtering method under the same deposition conditions except for the substrate temperature. Owing to the details of the sputtering mechanism itself, thin films might receive serious damage from the negative-ion bombardment during preparation. As a result, the T_c's of the films are relatively lower than those prepared using MBE, as reported in our previous paper.[6,11] Although the T_c's of the present films are not so high in general, the dependence of T_c on growth temperature, as shown in Fig. 8, is clear enough to show the intrinsic relationship of the two parameters.

Furthermore, if one compares the temperature dependences of the structural and superconducting properties

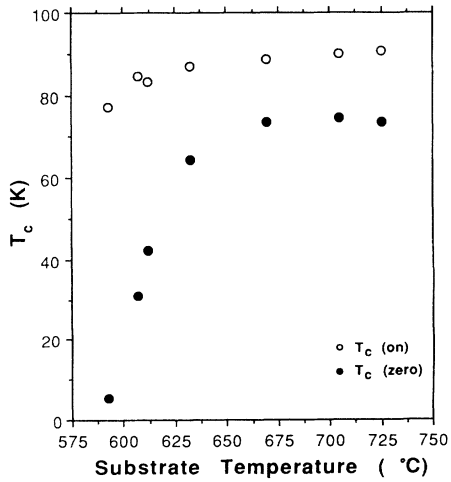

FIG. 8. Substrate-temperature dependence of T_c with open circles and solid circles representing onset and zero-point critical temperatures, respectively.

of the films, which were shown in Figs. 7 and 8, one can see that the degree of disorder and T_c vary simultaneously with the substrate temperature. Such a relationship among structure, T_c, and growth temperature seems also to exist in thin films prepared using other methods, at least the MBE method. There is an interesting experiment where, during a deposition procedure using MBE, the MgO(100) substrate attached to the holder by silver paste accidentally became partially detached from the holder. This means that the substrate temperature of the film changed continuously from one side to the other during deposition. Structure analyses of this film indicated that the degree of disorder of the structure is position dependent, and electrical-resistivity measurements revealed that the T_c is also position dependent. Although a quantitative understanding of the relationship has not been reached due to the difficulty in calibrating substrate temperatures in this case, the variations of the disordering degree and T_c with substrate temperature are similar to those observed in the sputter-deposited films. Results of studies on these films indicate that there is an intrinsic relationship between the cationic disorder of the structure and the T_c value in YBCO films.

The critical temperature T_c is known to depend strongly on the hole carrier density, which can be varied by charge compensation or oxygen nonstoichiometry.[17] In the present research, 1:2:3 stoichiometry was preserved in all the films prepared at different substrate tempeatures, which crystallized in the structures with different degrees of disorder. Therefore, T_c suppression related to a change in hole carrier density due to charge compensation is unlikely. Similarly, change in oxygen content also seems unlikely because of the balance in the total cation charge. However, even if the total cation charge balance was kept, the local charge balance of the Y- and Ba-containing units might be destroyed by substitution between Y and Ba, which are different in valence. This may change the maximum oxygen content in $YBa_2Cu_3O_{7-\delta}$, leading to a change in hole carrier density and depressing T_c. The reported lower T_c and larger oxygen content in $LaBa_2Cu_3O_{7-\delta}$,[18] where La and Ba are considered partially disordered, might be another fact supporting the above suggestion. The change in oxygen content accompanying the Y-Ba substitution, if it exists, could not be recovered easily through heat treatment at temperatures around or lower than 600 °C, as in ordered YBCO thin films.[4,6]

Besides hole carrier density, T_c also depends on local electronic properties, as illustrated by Miceli *et al.*[19] for the oxides $YBa_2Cu_{3-x}Co_xO_{7-\delta}$. As described in the previous section, in the structure of YBCO, structural disorder results in a decrease in size of the Ba-containing cube and increase in size of the Y-containing cube. The structural parameters including bond lengths of Cu(1)-O and Cu(2)-O must then vary with the structural disorder. In addition to the possible change in oxygen content due to destruction in local charge balance, such a structural change would also certainly cause a change in the local electronic properties, especially to modify the hybridization of the Cu orbitals, resulting in the depression in T_c.

The other possibility is that not the structural disorder itself, but the defects accompanying the structural disorder, affect T_c. Since cation disorder would certainly create a density of defects in the crystal, as can be understood from the observed expansion in *c* lattice parameters, crystallographic defects could also be considered as a candidate for depressing T_c. However, it is not clear what kind of defects exist and how the defects would locally modulate the superconducting order parameter and depress T_c.

T_c suppression has been observed by Shaw *et al.*[20] in high-density sintered $YBa_2Cu_3O_{7-\delta}$ bulk materials. They attributed the reduced T_c to carbon retention of about 1 wt % in the structure in a barium-carbonate-like configuration. However, this seems unlikely to be true in the thin films prepared by us. From thermodynamic considerations, at least 0.4 Pa partial pressure of CO_2 is required to form $BaCO_3$ at 600 °C, but in our experiment the films were deposited in an atmosphere of 2.0 Pa $Ar-10\%\ O_2$. It is hard to consider that there is 0.4 Pa contamination of CO_2 to compose barium carbonate in the thin films which would play an important role in depressing T_c. It should also be noted that in thin films prepared using MBE, where the films were deposited in an oxygen partial pressure of 10^{-2} Pa, the relation among substrate temperature, structural disorder, and T_c also exists. Moreover, the remarkable variations observed in x-ray diffraction intensities of thin films prepared at lower substrate temperatures could not be explained by about 1 wt % carbon retention in the structure.

It should be added here that, in the present study, thin films prepared at lower substrate temperatures decreased their T_c very quickly with the passing of time, while those prepared at higher temperatures keep their T_c's even after long storage (longer than six months) in air. This may be associated with the large amounts of defects introduced with the cation disorder in these low-temperature-prepared films. Such thin films of poor degree of structural order and low T_c, prepared at lower substrate temperatures, can be improved in both structure and T_c through an annealing treatment at high temperature, as will be detailed in a later publication.[12]

IV. CONCLUSIONS

Through a systematic investigation of a series of YBCO thin films with the approximate 1:2:3 chemical stoichiometry, which were prepared at the same deposition parameters except growth temperature, two overall conclusions can be drawn as follows.

First, the crystal structure of the YBCO thin films depends on the growth temperature. At lower temperature, the mobility of the cations might not be high enough to make them reach their regular positions, resulting in the freezing of a considerable degree of disorder between Y and Ba atoms. With increasing growth temperature from 593 to 630 °C, the mobility of the atoms increases exponentially, leading to a rapid decrease in the degree of disorder. At higher growth temperatures, there is enough mobility of atoms to form a completely ordered structure.

Second, the superconducting transition temperatures of the thin films depend on the growth temperature. With increasing growth temperature, T_c increases from a very low value to an optimized value, responding to the recovery of the disordered structure. Although the mechanism depressing T_c is not clear yet, it is undoubtedly the structural disorder itself, or defects accompanying the freezing of cation disordering, that depresses T_c. The depression of zero-point T_c is particularly serious in YBCO thin films.

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