Superconductivity and structure of a few-unit-cells-thick Bi-Sr-Ca-Cu-O ultrathin films

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Bi-Sr-Ca-Cu-O ultrathin films with thicknesses below 100 Å down to 10 Å have been deposited just on the (001) MgO substrate by single target rf magnetron sputtering. By elaborately controlled multistep annealing for extremely short times, remarkably high values of the zero-resistance transition temperature, $T_{c,0}$, 106, 88, and 84 K were obtained for 70-, 40-, and 20-Å-thick ultrathin films, respectively. A 10-Å-thick ultrathin film was almost insulating. Cross-sectional high-resolution transmission electron microscopy revealed that a 40-Å-thick ultrathin film with a $T_{c,0}$ of 88 K consisted of a set of half-unit-cell layers of the (2212) and (2223) phases. A 20-Å-thick ultrathin film consisted of a half-unit-cell layer of the (2212) phase. Thus, it was confirmed that in the Bi system the minimum unit for the occurrence of superconductivity is a half-unit-cell layer of the superconducting oxide crystal. Instead of the repeated use of thermal treatment at high temperatures, ion irradiation techniques combined with annealing at relatively low temperatures was useful to modify the crystal quality and related transport properties of our ultrathin films. [S0163-1829(98)09417-X]

I. INTRODUCTION

From both scientific and technological points of view, it is important to study how the superconducting transition temperature changes with the thickness of film substance, and also to examine the minimum thickness for the occurrence of superconducting states. In the case of high-temperature superconductors (HTS's), the dimensionality of HTS's has also been an interesting subject for understanding the mechanism of superconducting phenomena.

HTS ultrathin films, multilayers, or superlattices have been synthesized by means of atomic layer-by-layer growth techniques using magnetron sputtering,[1] pulsed laser ablation,[2] molecular-beam epitaxy,[3,4] and metal-organic chemical-vapor deposition.[5] In the Y system Terashima *et al.*[6] prepared a one-unit-cell thick layer of $YBa_2Cu_3O_7$ (YBCO) film by reactive evaporation. The film was covered and also buffered on the $SrTiO_3$ substrate with semiconducting $PrBa_2Cu_3O_7$ (PrBCO) layers. They have shown that superconductivity can occur in a one-unit-cell thick YBCO film in the absence of intercell couplings. In the Bi system, Li *et al.*[7] synthesized $Bi_2Sr_2CaCu_2O_8$ (BSCCO) (2212)/$Bi_2Sr_2CuO_6$ (2201) superlattices with alternating half-unit cells of the two compounds on heated MgO substrates by reactive magnetron sputtering. For the ten-unit multilayers they obtained T_c comparable to that of the bulk specimen. These experiments indicate that superconducting states are induced within one-unit-cell thick YBCO or BSCCO layers, with or without intercell couplings. The role of the semiconducting PrBCO layer or the metallic low-T_c (2201) layer is considered to optimize the doping level of carrier holes in the host materials.

However, there has been a naive question whether a few-unit-cells thick ''bare'' ultrathin films, neither buffered nor covered with other materials, should have T_c lower or equal to or even higher than the bulk T_c.[8]

In the present paper, we report the synthesis of a few-unit-cells thick BSCCO ultrathin films on the MgO (001) single-crystal substrate by magnetron sputtering. In spite of the large lattice mismatch with the MgO substrate, high-quality ultrathin films were successfully obtained by elaborately controlled multistep heat treatment that consisted of annealing for extremely short times followed by two-step cooling at different rates. For film thicknesses below 40–50 Å, however, it has become experimentally difficult to reproduce optimum annealing conditions for each sample.[9] The repeated use of thermal treatment at high temperatures is unfavorable because of inevitable evaporation of constituent atoms and chemical reaction with the substrate. Therefore, we use ion implantation techniques combined with annealing at relatively low temperatures to modify the crystal quality and related superconducting properties of ultrathin films.

II. EXPERIMENTAL PROCEDURES

Bi-Sr-Ca-Cu-O ultrathin films of thicknesses 70, 40, 20, and 10 Å were deposited on (001) MgO substrates by rf magnetron sputtering using a modified single target.[10] The target material used was $Bi_{2.3}Sr_{2.0}Ca_{2.0}Cu_{3.5}O_x$ powders in nominal composition. The MgO substrate surface was mechanically polished within an accuracy of $\pm 0.3°$ from (001) orientation. The deposition rate was approximately 0.4 Å/s. During the deposition the substrate was not heated. In the as-deposited state, films were amorphous, and were annealed to induce superconductivity by precisely controlled thermal treatment. Electrical resistivity of thin films was carried out by a four-point probe method using silver paste contacts. The crystal structure and the surface morphology of specimens were studied by x-ray diffraction (XRD) and scanning electron microscopy (SEM). The film thickness and atomic structure were examined by cross-sectional high-resolution transmission electron microscopy (JEOL-4000EX). Irradiation of 100-keV Ar ions was carried out at low temperatures, 10–20 K, using a closed-cycle He gas refrigerator.

III. RESULTS AND DISCUSSION

A. Heat treatments of ultrathin films

In ultrathin films below several tens of nanometers, any small amounts of constituent atoms that evaporate and any

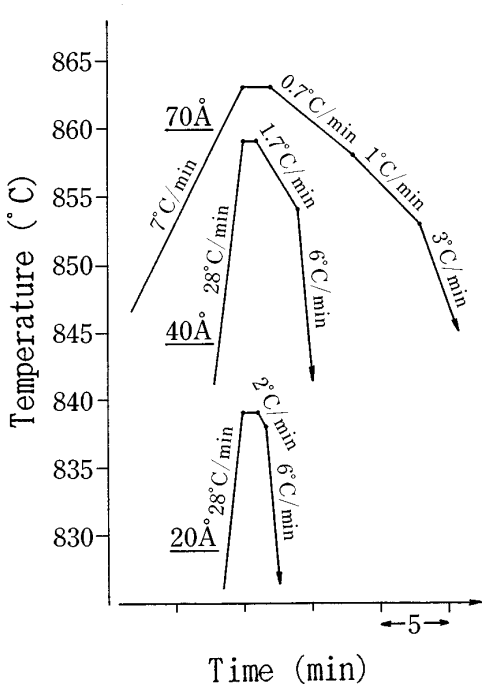

FIG. 1. Heat-treatment programs for preparation of the Bi system superconducting ultrathin films.

slight chemical reactions during heat treatments should cause serious deviations from the initial state of ultrathin films, deteriorating their superconducting properties. Therefore, it has been considered that it may be essentially difficult to establish optimum heat treatments for ultrathin films.

In view of these facts, we have tried to minimize compositional and structural changes in ultrathin films by lowering annealing temperature and shortening annealing time.[11] After elaborate experiments, we have developed a specific heat treatment program for ultrathin films, as shown in Fig. 1. It was found that a slow rate of the initial cooling for a few minutes, and a faster rate of the subsequent cooling were necessary to enhance the growth of superconducting phases and to improve the coherency of the interface between the superconducting phases. The annealing temperature, normally 875 °C, gradually decreased to 863, 859, and 839 °C with decreasing film thickness 70, 40, and 20 Å. Furthermore, duration at these high temperatures drastically decreased from several tens of hours to a few minutes.

The realization and availability of such heat treatments for oxide materials with low thermal conductivity suggests that the film temperature reaches a prescribed value in a sufficiently short time, and the temperature gradient across the film thickness should be sufficiently small, when the film thickness is extremely small. During annealing for extremely short times at relatively low temperatures, good-quality ultrathin crystals can grow epitaxially on the MgO substrate under a strong interaction between deposited atoms and the (001) MgO substrate surface. Furthermore, in the case of ultrathin films, excess impurity atoms can easily diffuse out towards the external surface and form the surface oxides. Thus, excess atoms, if any, would not worsen the crystal structure and transport property of ultrathin films.

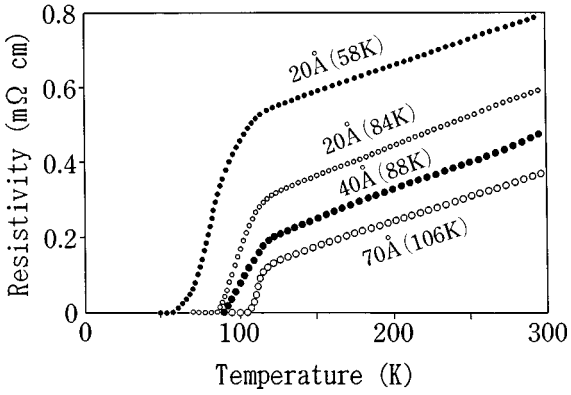

FIG. 2. Resistivity-temperature curves for 70-, 40-, and 20-Å-thick ultrathin films.

B. Resistivity-temperature curves and structural analysis

Figure 2 shows typical resistivity-temperature curves for ultrathin films with thicknesses of 70, 40, and 20 Å. Remarkably high values of $T_{c,0}$, i.e., 106, 88, and 84 K, were obtained for 70-, 40-, and 20-Å-thick ultrathin films, respectively. To our best knowledge the $T_{c,0}$ of 106 K is the highest for 70-Å-thick films of the Bi system. It should be noted that the onset of the superconducting transition, $T_{c,\text{onset}}$ is located around 110 K, indicating the formation of the (2223) phase even in these ultrathin films. At a film thickness of 10 Å the ultrathin film was found to be almost insulating.

Figure 3 presents XRD patterns for these ultrathin films. For film thicknesses below 70 Å, it was found that the x-ray reflection lines became broader and their peak positions shifted significantly, as expected from the size effect of x-ray diffraction from a layered modulated structure. For example, except for the $(00\bar{1}2)$ lines, the (002), $(00\bar{1}0)$, and $(00\bar{1}4)$

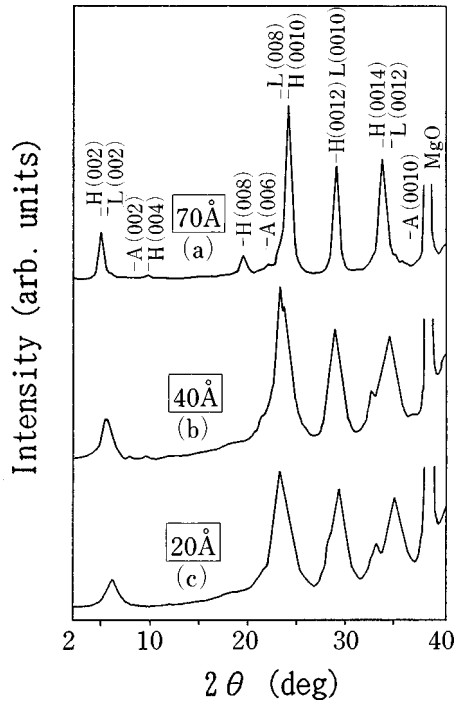

FIG. 3. XRD patterns for 70-, 40-, and 20-Å-thick ultrathin films.

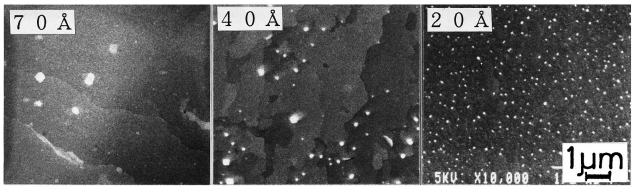

FIG. 4. SEM images for the surfaces of 70-, 40-, and 20-Å-thick ultrathin films.

lines of the (2223) phase shifted toward the (002), $(00\overline{1}0)$, and $(00\overline{1}2)$ lines of the (2212) phase, respectively. As a result, we cannot simply distinguish between the (2223) and the (2212) lines and some of the low-T_c (2212) lines become asymmetrical, as seen in the figure. Nevertheless, the film was identified to be of mixed-phase film of the low-T_c (2212) and the high-T_c (2223) phases.

Figure 4 shows SEM images of the surfaces of these ultrathin films. For a film thickness of 70 Å, we observe a directional array of thin crystals with very fine steps like ''fish scales.'' Atomic force microscopy studies have shown that most steps have the height of one-unit-cell thickness of the Bi system. As the film thickness was decreased, the step density decreased with only occasional steps. At a film thickness of 20 Å, the film surface was very smooth except for the presence of small oxide particles of approximately 10 Å in diameter.

In the present study the film thickness described above was estimated from the interpolated relationship between film thickness and deposition time. Thus, we examined the film thickness of our ultrathin films by means of cross-sectional high-resolution transmission electron microscopy (XHRTEM).

Figure 5 shows a typical XHRTEM micrograph taken from the 40-Å-thick ultrathin film ($T_{c,0}=88$ K) under the imaging condition where the atomic structure of the (001) MgO crystal is best resolved. Although overall images of the superconducting phase layers are somewhat smeared out, we observe a set of layered structures of the half-unit-cell (18.6 Å thick) layer of the high-T_c (2223) phase and the half-unit-cell (15.3 Å thick) layer of the low-T_c (2212) phase. It is

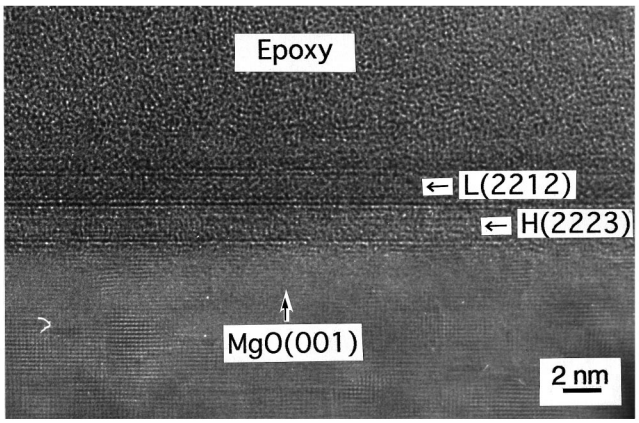

FIG. 5. Cross-sectional high-resolution TEM images of a 40-Å-thick ultrathin film with $T_{c,0}$ of 88 K.

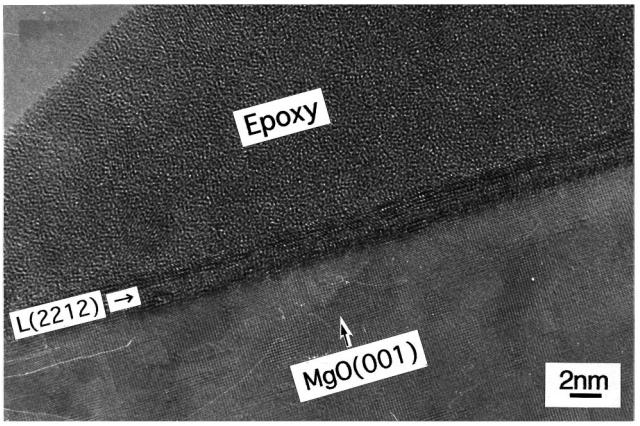

FIG. 6. Cross-sectional high-resolution TEM images of a 20-Å-thick ultrathin film with $T_{c,0}$ of 58 K.

interesting to note that a half-unit-cell thick (2223) layer grows just on the MgO substrate surface.

Figure 6 is an XHRTEM micrograph for a 20-Å-thick ultrathin film ($T_{c,0}=58$ K), showing nearly a half-unit-cell thick layer of the (2212) phase. Although the film appeared to be heavily damaged, we recognize discontinuous images of the BiO double layers probably due to the incommensurate modulation of the Bi atom and/or the oxygen content.[12] The damages in the film and the substrate may be caused by Ar ions used for ion milling during the preparation of the HREM sample. These cross-sectional observations proved that the film thicknesses have been determined within an accuracy of the order of half-unit-cell thickness. It was confirmed that the minimum unit for the occurrence of superconductivity is a half-unit-cell thick layer of the Bi system. Figure 7 shows a feature of the interface between the film and the substrate. Close examination of the micrograph revealed that two misfit dislocations are regularly inserted into every seven (100) planes of the BSCCO crystal against nine (100) planes of the MgO crystal. With this semicoherent configuration, the large misfit ($\sim 29\%$) can be relaxed to be totally zero according to the relation

$$9\times d_{\mathrm{MgO}}\ (2.1\ \text{Å})=7\times d_{\mathrm{BSCCO}}\ (2.7\ \text{Å})=18.9\ \text{Å},$$

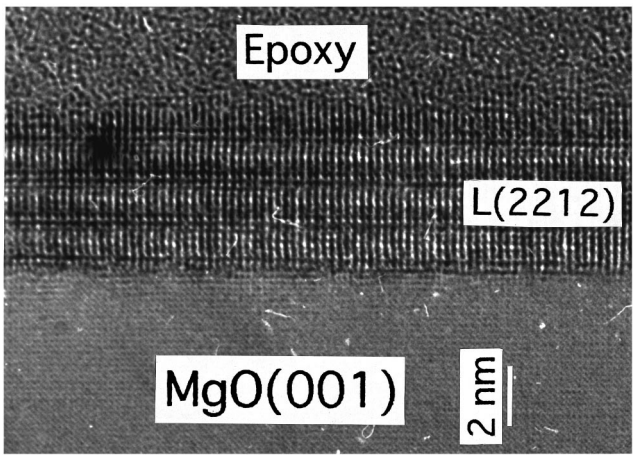

FIG. 7. TEM images of the film-substrate interface, showing the semicoherent feature.

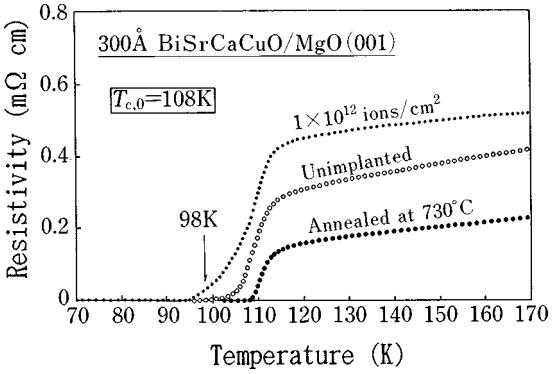

FIG. 8. Resistivity-temperature curves for a 300-Å-thick thin film, (a) unirradiated, (b) irradiated with 100-keV Ar ions to 1×10^{12} ions/cm^2 at 15 K, and (c) postannealed for 0.5 h at 730 °C.

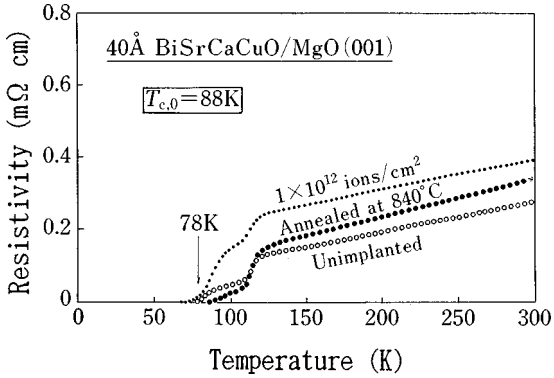

FIG. 9. Resistivity-temperature curves for a 40-Å-thick ultrathin thin film, (a) unirradiated, (b) irradiated with 100-keV Ar ions to 1×10^{12} ions/cm^2 at 20 K, and (c) postannealed for 0.1 h at 840 °C.

where d_{MgO} and d_{BSCCO} are the lattice constants of MgO and BSCCO crystals, respectively. This means that the large mismatch between the film and the substrate may not provide a serious obstacle for the epitaxial growth of ultrathin films. The polished (001) MgO substrate surface may contain steps due to unavoidable tilt from the ideal crystallographic orientation. Chaiken *et al.*[13] have made HRTEM observations of the Bi system films grown on a lattice matched $SrTiO_3$ (001) substrate and have shown that structural disorder resulting from the roughness of the substrate is healed within a single unit-cell thickness. Similar short-distance healing of structural disorder may also occur in our case, though the film-MgO substrate interface is semicoherent. Bulk $T_{c,0}$ of our ultrathin films indicates the inherent, two-dimensional nature of superconductivity in the (2223) and (2212) compounds and suggests that structural (and/or compositional) disorders occur only locally and allow the superconducting phase layers to connect in a coherent manner. The critical current density J_c was measured to be about 10^2 A/cm^2 at 77 K. This is several orders of magnitude smaller than the thicker films[14] suggesting that our ultrathin film may contain some amount of weak links.

C. Ion beam modification of ultrathin films

For film thicknesses below 50 Å, it has become experimentally difficult to reproduce high-T_c films, since ultrathin films may transform in a subtly different manner even under experimentally identical heat treatments. In order to modify further these ultrathin films, the films must be annealed again at somewhat higher temperatures, but the repeated treatment at high temperatures is unfavorable to ultrathin films owing to inevitable evaporation of constituent atoms and chemical reaction with the substrate. Instead, we used irradiation of Ar ions in the medium energy range of 100 keV that induce atomic displacements, atomic mixing, and radiation-induced or radiation-enhanced diffusion without any thermodynamical restrictions.

Figure 8 demonstrates the modification of a mainly high-T_c phase film of 300 Å thickness.[15] Before Ar ion irradiation, the film exhibited a single transition step due to the high-T_c phase with $T_{c,0}$ as high as 90 K. However, the transition width was still as large as 10–15 K, leaving incompleteness in the superconducting phase crystal. After a dose of 1×10^{12} ions/cm^2, $T_{c,0}$ decreased by 5–8 K. On subsequent annealing at 730 °C for 30 min, the $T_{c,0}$ was increased to 108 K, which is equivalent to the maximum value observed so far for the bulk Bi system.

Figure 9 shows a typical example for a 40-Å-thick ultrathin film. Before irradiation, the film exhibits two transition steps due to the high-T_c and low-T_c phases, having $T_{c,\mathrm{onset}}$ around 110 K and $T_{c,0}$ at 78 K. After a dose of 1×10^{12} ions/cm^2 at 20 K and postannealing at 840 °C for 1 min, $T_{c,0}$ was increased to 88 K. Although a resistive tail on the low-temperature side remains still, it should be noted that the $T_{c,0}$ of 88 K approaches $T_{c,0}$ of the high-T_c phase and is equivalent to the highest value obtained by optimizing the heat treatment for a 40-Å-thick ultrathin film. The critical current density was also improved from 10^2 to 10^3 A/cm^2 at 77 K.

Now we discuss the effect of an Ar ion irradiation in terms of nuclear elastic collision events.[16] The mean ion range of 100-keV Ar ions in the Bi system is calculated to be about 600 Å, much larger than the thickness of our ultrathin films. Therefore, almost all the Ar ions penetrate the films, and primary knock-on atoms (PKA's) produced by the incident Ar ions, should play the most important role in the thin-film modification processes. Table I lists calculated values of several important collision parameters for each PKA. It is shown that mean-transferred energy for each PKA is as low as 1 keV. In the low-energy collision regime, each PKA displaces self atoms most frequently and forms an individual cascade with specific volume $V_c \sim R_p x(\Delta R_p)^2$ and with the mean distance $\lambda_m = 1/N\ \sigma_d$, where N is the atomic density. As shown in Table I, the values of V_c are of the order of the

TABLE I. Calculated values of collision parameters for each PKA; displacement cross section σ_d, mean transferred energy T, mean ion range R_p, mean ion range straggling ΔR_p, cascade volume V_c, and mean collision distance λ_m, respectively.

PKA's	σ_d (Å^2)	T (keV)	R_p (Å)	ΔR_p (Å)	V_c (Å^3)	λ_m (Å)
Bi	1.002	1.512	15.0	4.6	317	14.2
Sr	0.850	1.655	18.4	7.2	954	16.8
Ca	0.748	1.574	20.5	11.3	2618	19.1
Cu	0.805	1.643	18.5	8.7	1400	17.7
O	0.541	1.210	26.2	20.8	11335	26.4

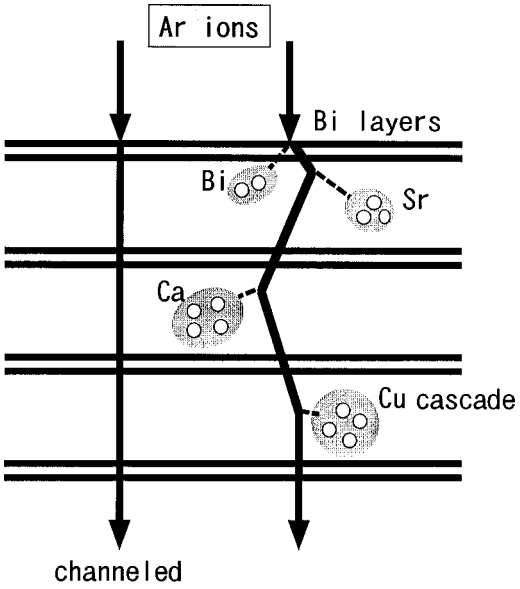

FIG. 10. Schematic illustration of ion channeling and creation of a collision cascade of each PKA in passing through the Bi system layered structure.

unit cell volume, about 10^3 Å^3, except for PKA's of oxygen O, and those of λm are close to the subunit cell length.

Consequently, as a result of postannealing at appropriate temperatures these ''unit-cell'' scales of collision cascades will rearrange themselves and regrow epitaxially into more perfect crystals on the surrounding good crystals. Here, it is important to note the effect of ion channeling in crystalline films, as shown schematically in Fig. 10. Since in our case Ar ions are irradiated along the *c*-axis direction of the films, energetic ions pass through oriented good crystals by channeling, while if they come across defective lattices or irregular interfaces, they cause atomic displacements and collision cascades there in a selective manner. In this way, ion irradiation techniques combined with radiation-induced or radiation-enhanced diffusion at relatively low temperatures is a unique method for modifying defective parts of thin crystals in a selective manner without disturbing good crystalline regions.

The superconducting characteristics of the Bi system thin films so far obtained in our experiment are summarized in Table II as a function of film thickness. Observed values of $T_{c,0}$ are grouped into the higher- and lower-temperature regions.

In view of these arguments, such high T_c of our ultrathin films suggests the two-dimensional nature of superconductivity in the Bi system layered structure. In the case of ultrathin films the deposited Bi-Sr-Ca-Cu-O material grows epitaxially into highly two-dimensional superconducting layered crystals under a strong interaction with the (001) surface atoms of the MgO substrate. Impurity atoms, if any, do not deteriorate superconducting properties of ultrathin films, because they can easily migrate to the external surface in sufficiently short time and form the surface oxides upon annealing.

TABLE II. The values of $T_{c,0}$, $T_{c,\text{onset}}$, and J_c as a function of film thickness, which were obtained by thermal treatments or by additional ion beam treatments. Observed values of $T_{c,0}$ are grouped into two temperature regions and are given in upper and lower lines. Numbers marked with asterisks denote highest value observed for each of the film thicknesses examined. J_c were measured for these highest $T_{c,0}$ specimens.

Thickness (Å)	$T_{c,0}$ (K)	$T_{c,\text{onset}}$ (K)	J_c (A/cm^2)
70	87–106*	110	$\sim 10^4$ (at 77 K)
	62–76	110	
40	76–88*	110	$\sim 10^3$ (at 77 K)
	55–66	110	
20	76–84*	110	$\sim 10^3$ (at 25 K)
	54–60	110	
10			

Furthermore, ion irradiation combined with annealing at relatively low temperatures is a unique technique for modifying structural disorders or defects in ultrathin films and improving their superconducting properties significantly.

IV. CONCLUSION

High $T_{c,0}$ well above 80 K was obtained in half-unit-cell and one-unit-cell thick Bi-Sr-Ca-Cu-O ultrathin films grown just on the (001)MgO substrate, neither buffered nor covered with other materials. This provides strong evidence for the inherent two-dimensional nature of superconductivity in the Bi system superconductor. Cross-sectional high-resolution electron microscopy revealed that a 20-Å-thick ultrathin film consisted of a half-unit-cell thick layer of the low-T_c (2212) phase and that a 40-Å-thick ultrathin film with $T_{c,0}$ of 88 K consisted of a set of the half-unit cell layers of the low-T_c (2212) and the high-T_c (2223) phases. We confirmed that the half-unit-cell thickness is the minimum unit for the occurrence of superconductivity in the Bi system. In spite of the large misfit between the film and the MgO substrate, the film-substrate interface was found to be semicoherent, containing regularly two misfit dislocations in every seven (100) planes of the BSCCO crystal. Ion irradiation techniques combined with annealing at low temperatures was useful to modify the crystal quality and related superconducting properties of our ultrathin films. The role of Ar ions was interpreted in terms of a selective creation of ''unit-cell'' scales of collision cascades and atomic reordering within the cascades under the action of radiation-enhanced or radiation-induced diffusion upon annealing at relatively low temperatures.

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