Epitaxial Y-Ba-Cu-O thin films on MgO deposited by high-pressure reactive magnetron sputtering

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Y-Ba-Cu-O thin films have been prepared on MgO(100) substrates by rf reactive magnetron sputtering from a single ceramic target. By adopting high total pressures, typically 280 mTorr, and relatively low substrate temperatures of approximately 650 °C, epitaxial films with the relations (001) $YBa_2Cu_3O_y \| (001)$MgO and $[100]YBa_2Cu_3O_y \| [100]$MgO can be reproducibly obtained. A high degree of epitaxy is confirmed by x-ray pole figure measurements and ion channeling. These films require a brief rapid thermal oxygen anneal at typically 850 °C, to exhibit sharp superconducting transitions with zero resistance around 75 K. Films deposited at higher temperatures above 700 °C show transitions as deposited with zero resistance near 80 K. The quality of the transition is correlated with expanded lattice constants with the best transitions occurring in films whose lattice constants approach that of the bulk. The films have high critical current densities of $1-5\times10^6$ A/cm^2 at 4.2 K. They also show good uniformity and excellent surface morphology with a roughness less than 10 nm and can be readily patterned to micrometer and submicrometer dimensions.

I. INTRODUCTION

Since the discovery of the layered copper-oxide-based compounds with high superconducting transition temperatures,[1,2] much attention has been focused on the thin-film synthesis of these materials for electronics applications. Almost all deposition techniques including sputtering,[3–5] evaporation,[6–9] laser deposition,[10,11] and chemical vapor deposition[12] have been applied with increasing success. Since these materials show weak link behaviors across the grain boundaries[13] as well as the inherent very strong anisotropic transport properties,[3,14] it is of great importance to make epitaxial thin films especially with the growth of c axis normal to substrates. Although epitaxially grown single-crystal $YBa_2Cu_3O_y$ thin films with possibly different domain size have been successfully formed on single-crystal $SrTiO_3$ substrates,[3,15] $SrTiO_3$ is not suitable for high-frequency applications because of its large dielectric loss.

Reactive magnetron sputtering using a single oxide target has been widely used primarily because of its instrumental simplicity. However, in the thin films deposited using this technique, large composition deviation from the composition of the targets and rugged surface morphology have been reported.[16,17] These are attributed to the substrate bombardment by the high-energy particles such as accelerated negative oxygen ions. Special substrate-to-target configurations[18,19] or very large magnetron cathodes[20] have been adopted to avoid the substrate bombardment. The bombardment effect is also expected to be substantially reduced by sputtering in a high gas pressure where high-energy particles are well thermalized. Recently, Li *et al.* have fabricated high-quality thin films on sapphire and $SrTiO_3$ substrates using such a technique.[21] The low degree of bombardment may also lead to the highly oriented growth of these damage-sensitive materials.

We have synthesized Y-Ba-Cu-O thin films by magnetron sputtering in a high-pressure oxygen/argon ambient and successfully obtained epitaxial $YBa_2Cu_3O_y$ films on MgO(100) single-crystal substrates having much better high-frequency properties than $SrTiO_3$. These films with c axis perpendicular to the substrate exhibit very smooth surfaces and good uniformity and can be readily patterned by conventional photolithography and ion milling techniques to micrometer and submicrometer dimensions. In this paper, the relationships between deposition parameters, film composition, and crystal orientation are described. Film properties determined from x-ray diffraction, Rutherford backscattering spectroscopy (RBS), and transport measurements of microstructures are then discussed.

II. EXPERIMENTS

Y-Ba-Cu-O thin films were deposited in a sputtering system with a single rf planar magnetron source (2 in. diameter). This system was evacuated to a typical background pressure of 2×10^{-6} Torr using a turbomolecular pump. A $YBa_2Cu_{4.2}O_y$ composition oxide target was made by sintering the pressed mixture of CuO and $YBa_2Cu_3O_y$ powders in a pure oxygen flow for 12 h at a temperature of 930 °C. Polished (both sides) MgO(100) single-crystal substrates (1 cm square, 0.6 mm thick) were heated to 600–750 °C using a quartz lamp placed in a stainless-steel block. The block temperature was monitored using a Chromel-Alumel thermocouple. The difference between substrate surface temperature and the block temperature was measured using another thermocouple embedded in a small gold ball which was attached to the substrates by annealing at a high temperature.

Typically, 300–500-nm thick films were sputter-deposited in a mixture of O_2 and Ar gases. Their flow rates were regulated to 1–4 and 10 sccm, respectively, using mass flow controllers. The target-to-substrate distance and rf power applied to the target were fixed at 45–50 mm and 100 W. The deposition rate under the conditions to achieve correct stoichiometry (substrate temperature $T_s = 625$–645 °C, total

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pressure $P = 200$–300 mTorr) was approximately 9 nm/min. After the deposition was finished, the heater power was immediately turned off and an additional 10 Torr of O_2 gas was introduced. The substrate stage cooled to 200 °C in 1 h. This slow postdeposition cooldown in oxygen has been found to be important in producing *in situ* superconducting films, although it has not yet been optimized. A rapid thermal annealing typically at 850 °C for 2 min in pure oxygen flow was required to get good transitions for films deposited at substrate temperatures lower than 700 °C.

The composition of the thin films was determined by x-ray microprobe analysis using $YBa_2Cu_3O_y$ single crystals as a standard. Rutherford backscattering measurements gave composition values which agreed very well with the microprobe results. The superconducting transition temperature (T_c) was determined by resistance measurements with four-probe configuration.

III. RESULTS AND DISCUSSION

The film composition was found to be sensitive to the sputtering parameters, in particular, total gas pressure and substrate temperature. Figure 1 shows the dependence of the Ba/Y and Cu/Y atomic ratios on the total pressure. With a decrease in the pressure below 280 mTorr, both ratios rapidly decrease and more Ba- and Cu-deficient films are formed. The deficiencies of these elements at lower pressures are attributable to the resputtering by high-energy particles. At higher pressures where all particles are expected to be well thermalized, nearly stoichiometric films, though slightly Ba rich, are reproducibly obtained. This threshold pressure is very similar to those observed in the sputter depositions of damage-sensitive metastable A 15 compounds.[22,23] The Cu/Y ratio also showed a slight increase with the O_2/Ar flow ratio from 0.1 to 0.25. However, more O_2 flow resulted in substantial decreases in the deposition rate and Cu content.

Figure 2 shows the substrate temperature (T_s) dependence of the Cu/Y ratio for films deposited at higher pressures. The Cu content rapidly decreases with an increase in T_s above 600 °C, while the Ba/Y ratio was almost unchanged. A stoichiometric ratio is achieved at approximately 640 °C with this target. In the sputtering configuration where the substrate is located outside the plasma region, much smaller decrease in the Cu content has been reported even at T_s as high as 800 °C.[18,19] This difference suggests that high-energy particles, possibly secondary electrons,[18] still bombard the substrate to some degree in the present configuration and cause the decrease in the sticking coefficient of the more volatile Cu.

X-ray diffraction patterns of typical films deposited at different substrate temperatures are shown in Fig. 3. Diffraction peaks from the 1:2:3 structure were observed even for films deposited at $T_s \sim 500$ °C, although their intensities were relatively small. Films deposited at $T_s \sim 620$ °C show patterns with dominant (l00) peaks of the 1:2:3 structure [Fig. 3(a)]. Patterns showing (00n) and (l00) peaks with comparable intensities [Fig. 3(b)] are observed for films deposited at $620 < T_s < 640$ °C. For nearly stoichiometric films deposited at $T_s > 640$ °C, only very strong (00n) peaks are observed [Fig. 3(c)], showing highly oriented growth of the c axis perpendicular to the substrate. Similar tendency of the crystal orientation has been observed in the films prepared by high-pressure reactive evaporation.[24] However, the peak intensities of (00n) diffractions were higher by approximately an order of magnitude in the present films. They also showed a halfwidth of the rocking curve as small as 0.6° for the (005) peak.

Figure 4 illustrates the x-ray pole figure for these films. Comparatively sharp spots indicate a high degree of crystal orientation even in the directions parallel to the substrate surface. This figure also shows that the a or b axis of the 1:2:3

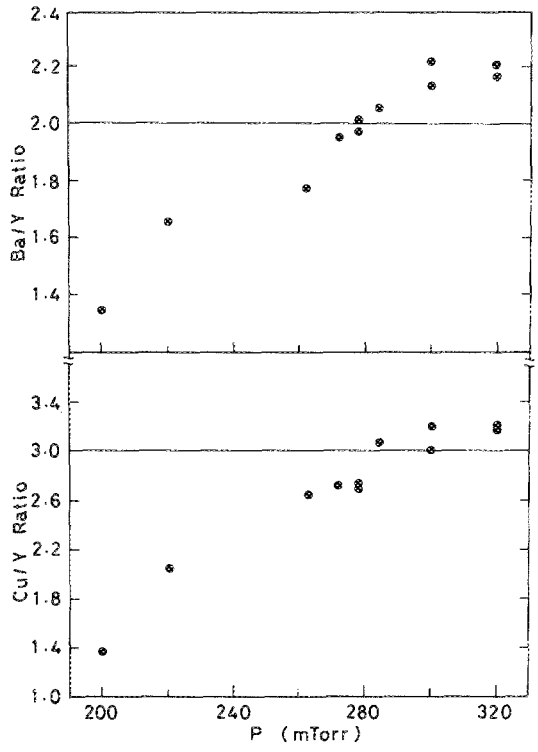


FIG. 1. Dependence of Ba/Y and Cu/Y atomic ratios on total gas pressure for Y-Ba-Cu-O thin films deposited at a substrate temperature of 640 °C. The flow ratio of O_2 to Ar was fixed at approximately 0.25.

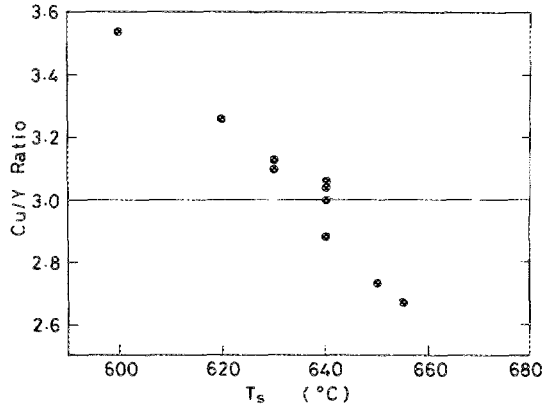


FIG. 2. Dependence of Cu/Y ratio on substrate temperature for films deposited at total pressures higher than 280 mTorr. The flow ratio of O_2 to Ar was fixed at approximately 0.1.

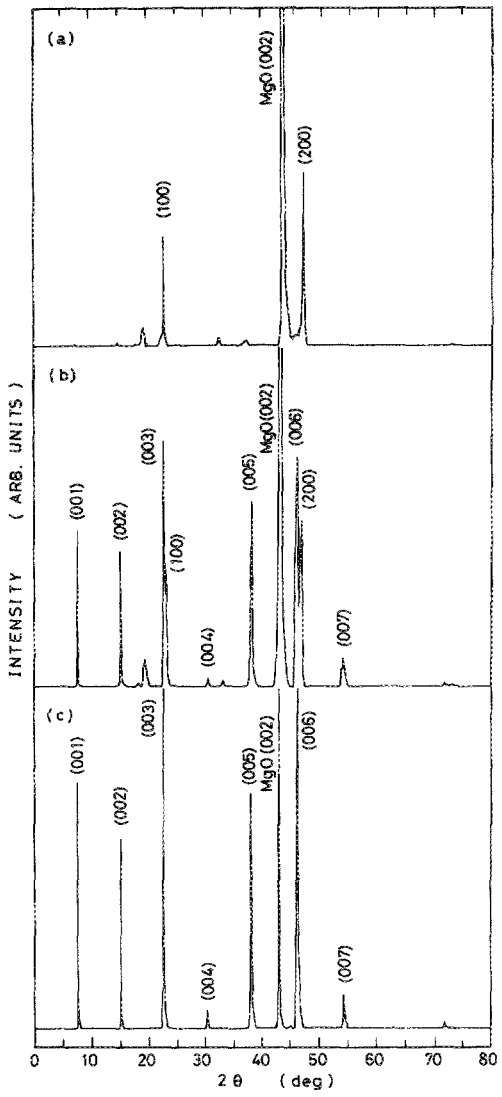


FIG. 3. X-ray diffraction patterns for films deposited at different substrate temperatures: (a) film deposited at $T_s \sim 620$ °C (3S-8), (b) film deposited at $620\,°C < T_s < 640\,°C$ (3S-5), (c) nearly stoichiometric film deposited at $T_s > 640$ °C (3S-6). The total pressure during sputtering was 280–300 mTorr.

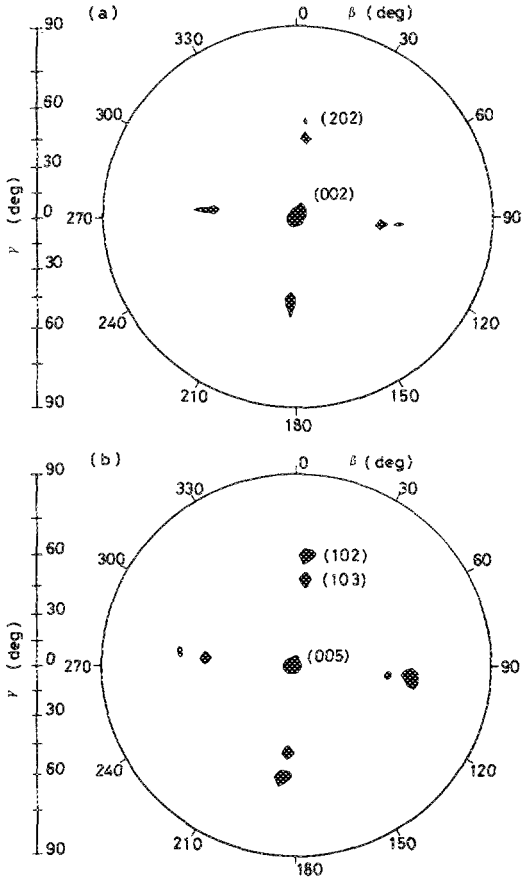


FIG. 4. X-ray pole figures for a thin film with a strong c-axis orientation perpendicular to the substrate surface as well as a MgO(100) substrate: (a) MgO and (b) Y-Ba-Cu-O (3S-13). Diffractions from a few crystal planes are superimposed on the same figures.

structure is aligned parallel to the [100] axis of MgO, and thus suggests the epitaxial growth of 1:2:3 structure. The epitaxial growth was also confirmed by selective-area diffraction (SAD) and high-resolution cross-sectional transmission electron microscope (TEM) observations.[25] The TEM images clearly showed that there was no interfacial amorphous or diffused layer between the film and MgO. Figure 5(a) shows a random RBS spectrum for a typical highly oriented thin film. The spectrum is well fitted by the simulated curve calculated using a nearly stoichiometric atomic ratio, again indicating the absence of substantial mutual diffusion at the film-substrate interface. Figure 5(b) shows channeled and random RBS spectra for the same film after a rapid thermal annealing. Approximately 60% decrease in the yield with respect to the random spectrum is observed. This supports a considerable degree of epitaxy. Even larger values have been reported for films deposited on $SrTiO_3$ by dc reactive magnetron sputtering under total pressures as high as 600 mTorr.[26] Moreover, Höhler *et al.* have recently reported fully textured growth of $YBa_2Cu_3O_{7-y}$ on $LiNbO_3$ achieved under a total pressure of 500 mTorr.[27] These results support the fact that a low degree of substrate bombardment realized in high-pressure environments favors a high degree of epitaxy as well as excellent surface morphology, although the lowest pressure to achieve good results may depend on preparation methods and configurations of the deposition systems.[28]

Since the lattice misfit between $YBa_2Cu_3O_{7-y}$ and MgO is as large as 8%, the crystal of the present films may be stabilized by the formation of dislocation networks or fine grains (or domains). Further detailed TEM studies are required to clarify the mechanism of the epitaxial growth, and these results will be reported elsewhere.

The films deposited at 640 °C with nearly stoichiometric compositions were not superconducting even with a cool-down anneal. They exhibited room-temperature resistivity of typically 2–3 mΩ cm and a slight increase in the resistance at lower temperatures. X-ray results showed that their lattice parameters were unusually large ($a \sim 3.91$ Å, $c \sim 12.0$ Å), suggesting an oxygen-deficient tetragonal structure. However, these large lattice parameters could be readily reduced by applying brief rapid thermal oxygen anneal (RTOA) steps. Figure 6 illustrates a typical pronounced change in the x-ray peak positions of the 1:2:3 structure.

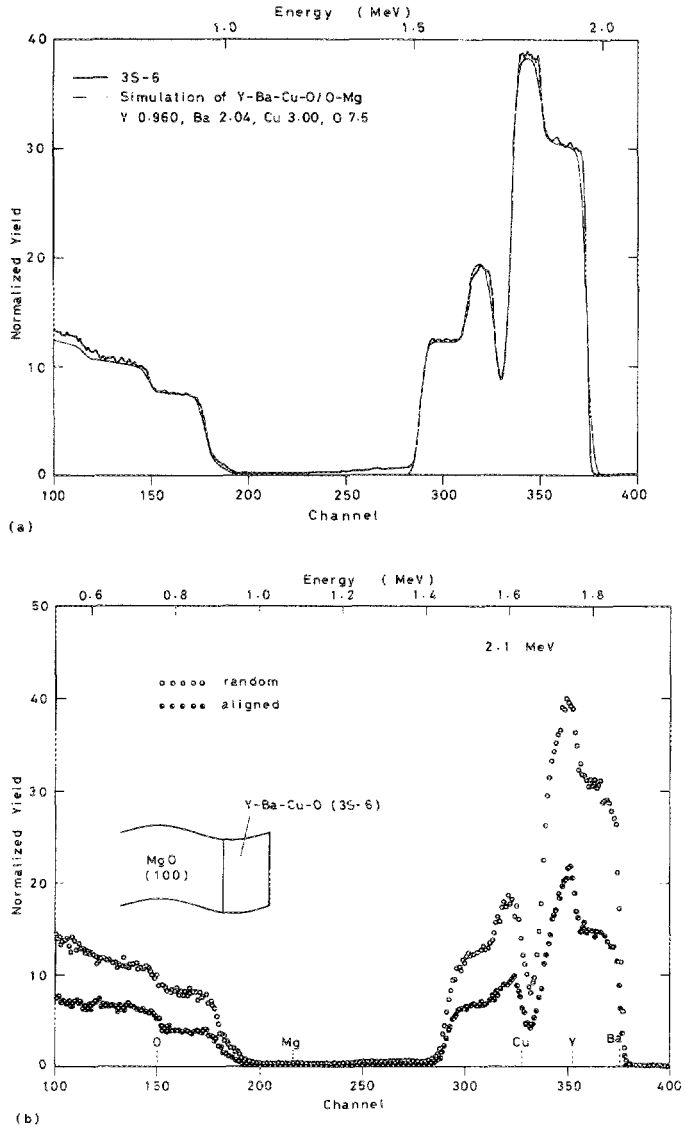


FIG. 5. Rutherford backscattering spectra (2.1 MeV He^+) for a highly oriented thin film; (a) random spectrum for 3S-6 (180 nm thick) and the result of a computer simulation, and (b) random and channeled spectra for the same film after a 2-min RTOA at 850 °C. The χ_{min} is 42%.

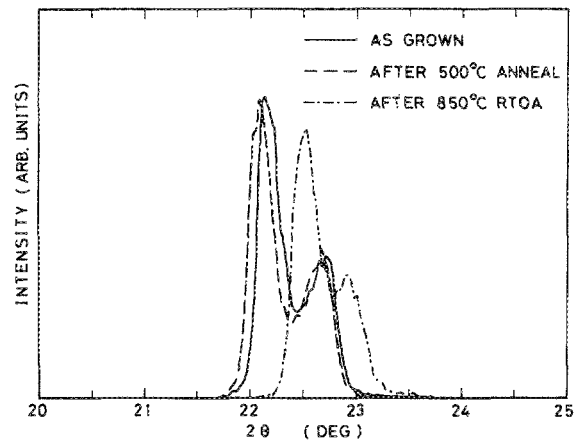


FIG. 6. Variations of (003) and (100) diffraction peaks after a 2-min RTOA step for a mixed orientation film (3S-5). The effect of a longer anneal at 500 °C in pure oxygen is also shown.

After annealing for 2 min at 850 °C, the lattice parameters decreased to $a = 3.86$ Å and $c = 11.80$ Å, respectively. The room-temperature resistivity was also reduced typically by a factor of 2–5 by the same annealing procedure. However, observed c values of 11.78–11.83 Å are still larger than the values reported in the reactively evaporated thin films (11.72 Å)[8,24] and in bulk materials (11.68 Å),[29] showing that the lattice is substantially strained. The strain could not be relaxed by annealing at temperatures lower than 800 °C. For example, the annealing for 1 h at 500 °C in oxygen increases the lattice constant further as shown in Fig. 6, and increases the film resistance. An annealing temperature as high as 920 °C to achieve good superconducting transitions has also been reported for single-crystal thin films on $SrTiO_3$ showing semiconductorlike resistance behavior.[3] These results suggest that the lattice strain observed in the present thin films is not simply due to oxygen deficiency but attributable to another mechanism such as stabilization caused by the large lattice misfit or the difference in the symmetry.

Resistance transitions for typical highly oriented thin films after RTOA are shown in Fig. 7. Curve (a) with a c value of 11.78 Å shows a desired strong metal-like resistance variation with the temperature and a fairly sharp superconducting transition. However, the zero-resistance T_c value is substantially suppressed. Some films with larger c values showed two distinct sharp transitions around 90 and 60 K, as illustrated by curve (b). Zero-resistance T_c values of almost all films deposited at $T_s \sim 640$ °C were distributed in the temperature range from 60 to 77 K. Since Auger electron spectroscopy (AES) depth profiles as well as RBS spectra for annealed films showed no evidence of interdiffusion between the films and MgO, the suppressed T_c values in the

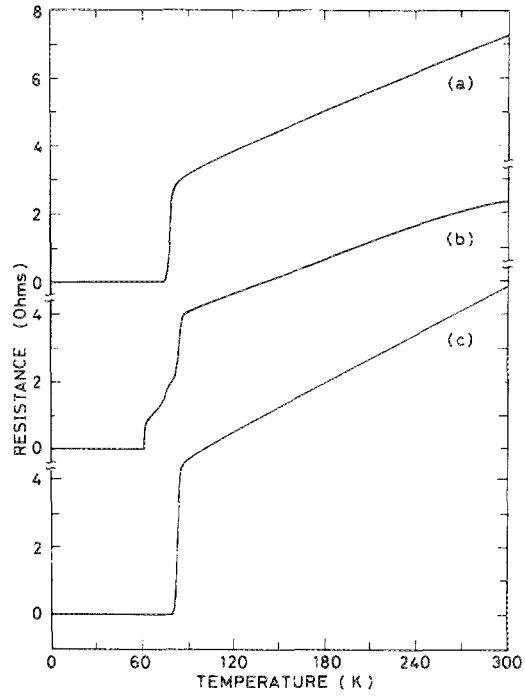
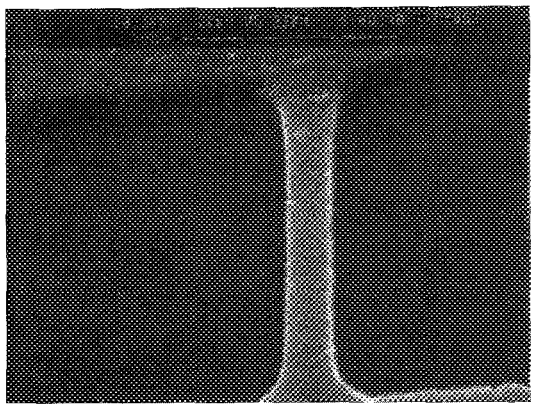


FIG. 7. Typical temperature dependence of resistance observed in highly oriented thin films after RTOA steps: (a) 3S-81 and (b) 3S-7. Resistance variation for an *in situ* grown film deposited at $T_s \sim 700$ °C (3S-86) is also shown [curve (c)].

present films are primarily attributed to the lattice expansion which leads to a decreased hole concentration in the Cu-O planes.[30] On the other hand, as-deposited films produced at $T_s > 700$ °C showed sharp transitions as shown by curve (c) with a zero resistance T_c of 80 K. The films have c values of 11.73–11.75 Å, supporting the correlation between the quality of the transition and c values.

In order to investigate critical current density, film uniformity, and weak-link properties, 0.5–100-μm-wide lines and constrictions were fabricated by standard photolithography and ion milling. Low-resistance ($< 10^{-8}\ \Omega\ \text{cm}^2$) electrical contacts to the films were formed by evaporating Ag on ion-mill cleaned surfaces and applying a brief RTOA. Details of these procedures have been already described elsewhere.[31] Figure 8 shows scanning electron microscopy (SEM) photographs of such patterns. The surface of the films with a strong c-axis orientation is very smooth. Their surface roughness determined by a surface profiler is less than 10 nm, while the roughness for the films with mixed orientations is typically 20 nm. Thus clear patterns with submicrometer dimensions can be formed on the former films. These films also showed good uniformity. The deviations of the resistance and the critical current density among the constrictions with the same dimensions distributed on a 5×5 mm area were less than 5% and 20%, respectively.



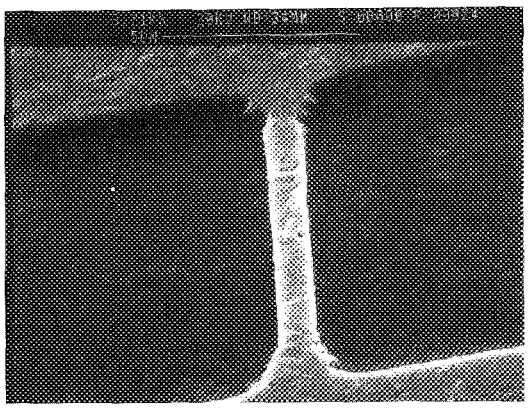


FIG. 8. Scanning electron micrographs of 1-μm-wide constrictions patterned on (a) a film with a strong c-axis orientation, and (b) a mixed orientation thin film.

I-V characteristics for constrictions of different sizes were measured with varying temperature. Variations of the critical current density (J_c) for a typical film are shown in Fig. 9. The current density rapidly increases at lower temperatures and exceeds 10^6 A/cm^2 below 10–20 K. A maximum J_c value at 4.2 K of 5×10^6 A/cm^2 was observed in better films. No constrictions with the dimension down to 1 μm showed microwave-induced steps in their I-V curves. However, the observed rather slow rise in J_c near the zero-resistance T_c suggests that J_c is still limited by weak links between grains which are possibly caused by slightly Ba-rich compositions.

IV. SUMMARY

$YBa_2Cu_3O_y$ thin films were sputter deposited on MgO(100) substrates from a $YBa_2Cu_{4.2}O_y$ ceramic target. The film composition was found to strongly depend on the total pressure as well as the substrate temperature. Nearly stoichiometric thin films were reproducibly obtained by sputtering under a total pressure higher than 280 mTorr. In particular, films with very strong c-axis orientation normal to the substrate surface were formed at substrate temperatures higher than 640 °C. X-ray pole figures for such films clearly indicated epitaxial relations: (001)$YBa_2Cu_3O_y$ ‖ (001)MgO and [100]$YBa_2Cu_3O_y$ ‖ [100]MgO. Ion channeling, SAD, and high-resolution cross-sectional TEM measurements supported a high degree of epitaxy. It is probably due to the low degree of substrate bombardment realized in the high-pressure environment.

Although as-deposited films formed at temperatures lower than 650 °C were nonsuperconducting, sharp transitions with zero resistance around 75 K could be readily achieved by applying a brief RTOA at temperatures higher than 800 °C. Annealed thin films with a strong c-axis orientation had very smooth surfaces showing roughness smaller than 10 nm, and could be readily patterned to micrometer and submicrometer dimensions. They also exhibited critical current densities of $1\text{–}5 \times 10^6$ A/cm^2 at 4.2 K. As-grown thin films with zero-resistance T_c's near 80 K were also ob-

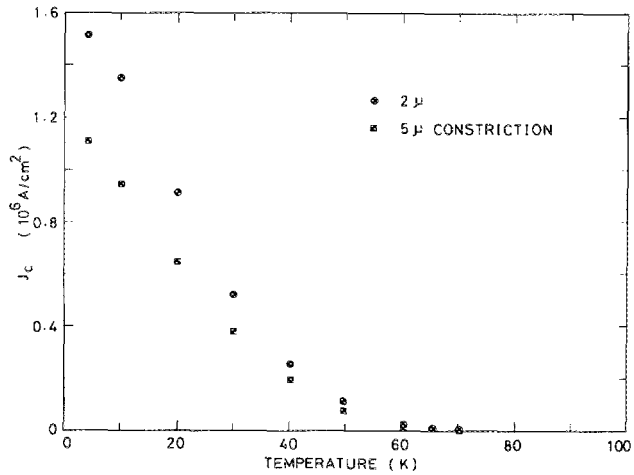


FIG. 9. Critical current density vs temperature for microbridges with differnet widths fabricated on a highly oriented thin film (3S-30).

tained at substrate temperatures above 700 °C. The quality of the transition was correlated with expanded lattice constants in conjunction with oxygen deficiency. The best transitions occurred in films whose lattice constants approached that of the bulk. To improve the transition, further approaches to *in situ* grown films such as optimization of the substrate position[32] and the activated atomic oxygen density[33] may be efficacious.

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