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Superconducting characteristics and epitaxial-growth analyses of $YBa_2Cu_3O_{7-x}$ thin films by direct-current magnetron sputtering

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Using direct-current magnetron sputtering deposition, we have successfully prepared high-quality epitaxial $YBa_2Cu_3O_{7-x}$ thin films, on (1 0 0) and (1 1 0) ZrO_2, $SrTiO_3$ and $LaAlO_3$ substrates. The films reached zero resistance at about 90 K and had a critical current density, J_c (at 77 K, H = 0), above 10^6 A cm^{-2}. Electrical measurements showed that the films had a small microwave surface resistance. The epitaxial structure of the films was studied by X-ray diffraction (XRD), Rutherford backscattering (RBS) and channeling spectroscopy, X-ray double-crystalline diffraction and transmission electron microscopy (TEM). It was found that the *c-axis* of the film grown on the (1 0 0) substrates under optimum deposition conditions was perpendicular to the substrate surface. But on the (1 1 0) substrates, epitaxial growth was along the (1 1 0) or (1 0 3) direction. The experimental results indicate that the films had excellent superconducting properties and complete epitaxial structure.

1. Introduction

Since the discovery of high-T_c (zero-resistance transition temperature) oxide superconductivity, $YBa_2Cu_3O_{7-x}$ superconducting thin films have been extensively studied. Some of the earliest practical applications of high-T_c superconductors are likely to be in the form of thin films [1]. A number of deposition techniques have been used to make $YBa_2Cu_3O_{7-x}$ superconducting thin films and they have achieved excellent results. These deposition methods include sputtering [2], laser ablation [3–5], molecular-beam epitaxy [6], metallorganic chemical vapour deposition (MOCVD) [7], and electron-beam evaporation [8, 9]. Up to now, $YBa_2Cu_3O_{7-x}$ superconducting thin films with a rather high upper critical field, B_{c2}, and the capability of carrying a very high critical current density, J_c, offers the possibility of making passive microwave devices, Josephson junctions and electrical circuitry. This is because most applications in electronic devices will depend, to a large degree, on their capability to carry high current densities.

For oxide-compound superconductors, the critical current density is closely related to grain boundaries and the textured microstructure. Moreover, it has been known that the superconductivity in $YBa_2Cu_3O_{7-x}$ system is strongly confined to its *a–b* planes. Thus the focus of fabricating $YBa_2Cu_3O_{7-x}$ thin films is the production of *c*-axis-oriented thin films. In general, $YBa_2Cu_3O_{7-x}$ thin films are polycrystalline, which will affect their critical current density, J_c. In this paper, we present investigations on the superconducting characteristics and epitaxial-growth analyses of $YBa_2Cu_3O_{7-x}$ thin films, which were deposited on (100) and (110) $SrTiO_3$, ZrO_2, and $LaAlO_3$ substrates.

2. Experimental procedure

In the present study, $YBa_2Cu_3O_{7-x}$ superconducting thin films were grown on (100) and (110) aligned $SrTiO_3$, ZrO_2, and $LaAlO_3$ substrates by direct-current (d.c.) magnetron sputtering. During the deposition of the films, the superconducting (123) phase could be directly achieved. A detailed description of the deposition conditions has been reported elsewhere [10]. The composition of Y, Ba and Cu was determined from inductively coupled plasma (ICP) atomic-emission spectroscopy. The microwave surface resistance was measured at a frequency of 50.9 GHz. The epitaxial structure of the films was analysed by X-ray diffraction (XRD), Rutherford backscattering (RBS) and channeling spectroscopy, and transmission electron microscopy (TEM). TEM cross-sectional samples were prepared by epoxying, mechanical thinning, dimpling and argon-ion milling with liquid-nitrogen cooling. TEM observations were carried out in a JEOL JEM-200CX at 200 keV at a point-to-point resolution of 0.25–0.26 nm.

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3. Results and discussion

3.1. Superconducting characteristics

The epitaxial $YBa_2Cu_3O_{7-x}$ superconducting thin films, prepared under the optimum growth temperature and oxygen pressures, generally had a zero-resistance transition temperature, T_c, of about 90 K. Fig. 1 gives the results of four-probe d.c. transport measurements of the resistance, R, of films as a function of temperature, T. It can be seen that the residual resistance ratio, R_{300K}/R_{100K}, of the films was near 3.

It was found that transition temperatures and other transport properties, like the residual resistance and especially the critical current density, were closely related to the growth quality of the films. The polycrystalline fraction in the films resulted in superconducting degradation. Fig. 2 demonstrates critical-current-density measurements as a function of temperature for a film grown on a (100) $SrTiO_3$ substrate. The maximum value was about 2.5×10^6 A cm^{-2}. The high-T_c superconducting thin films generated are potential candidates for passive microwave devices. So the microwave surface resistance is an important parameter in the description of the quality of a superconducting thin film. The microwave surface resistance, R_s, of the films was measured at 50.9 GHz. Fig. 3 gives the R_s-curve of a sample grown on a (100) $SrTiO_3$ substrate. For the sake of contrast, the results of copper (dotted curve) are also given in Fig. 3. It can be seen from Fig. 3 that the curve of the film oscillated in the normal state. This is because the dielectric constant of $SrTiO_3$ is rather large, and changes with temperature. When millimetre-wave transmitted $SrTiO_3$ and reflected at the bottom surface, constructive interference caused R_s to decrease, but destructive interference made R_s increase. The transition temperature of the sample was about 89 K, and R_s at 77 K was 37 mΩ. Films on the other substrates had similar results. Since the application of high-T_c superconducting thin films in microwave fields is mainly focused below a frequency of 10 GHz, R_s is often used at 10 GHz as a criterion to judge the microwave properties of a superconducting thin film. According to the relation $R_s \propto f^2$, at a frequency of 10 GHz, the microwave surface resistance of the film grown on (1 0 0) $SrTiO_3$ at 77 K was 1.4 mΩ, and the value for copper was 18 mΩ. Thus, the microwave surface resistance of a $YBa_2Cu_3O_{7-x}$ film was about one thirteenth of the value of copper at 10 GHz, $T = 77$ K. The R_s values of our films were bigger than the best reported [11]. The main reason is that outgrowth regions existed on the film surface, which was confirmed by scanning electron microscopy (SEM) images.

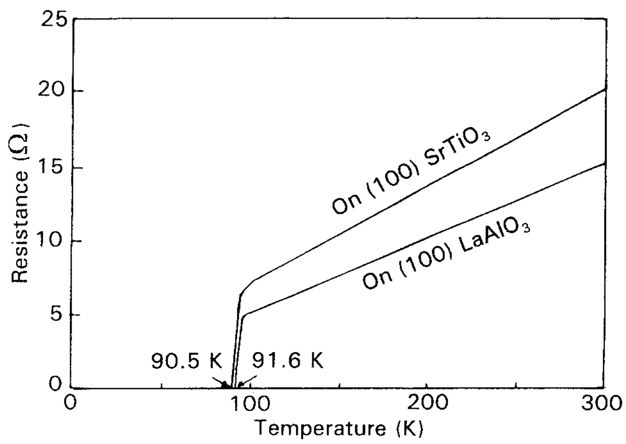

Figure 1 Resistance versus temperature curves of $YBa_2Cu_3O_{7-x}$ superconducting thin films deposited on (1 0 0) $SrTiO_3$ and $LaAlO_3$ substrates.

3.2. Epitaxial-growth analyses

XRD patterns showed that the films grown on (1 0 0) substrates had an epitaxial structure with the c-axis perpendicular to the surface of the substrates at an optimum growth temperature of 750°C. But at lower temperatures, both c-axis and a-axis orientation were observed. Fig. 4 gives three sample spectra representing the different growth temperatures on (1 0 0)

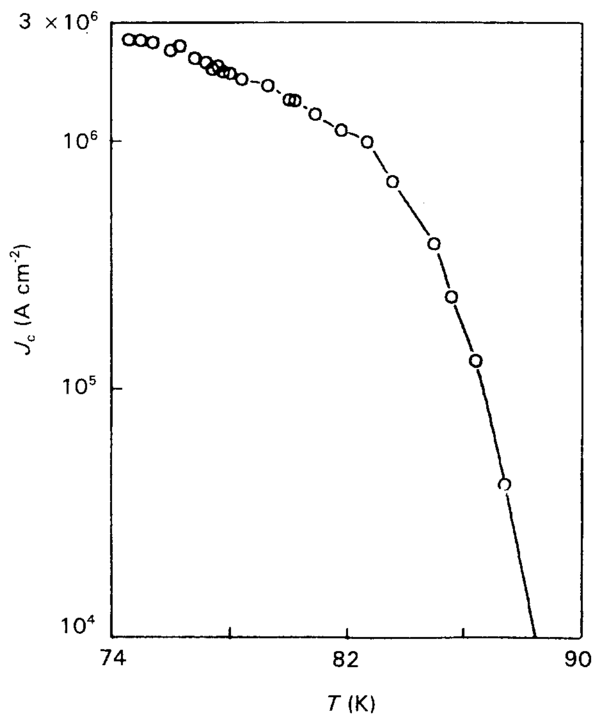

Figure 2 Critical current density versus temperature for the $YBa_2Cu_3O_{7-x}$ thin film grown on a (1 0 0) $SrTiO_3$ substrate, measured in a zero magnetic field.

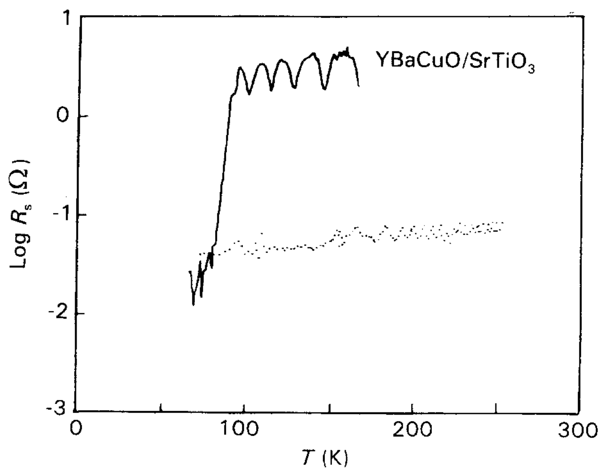

Figure 3 Microwave surface resistance versus temperature curve of an $YBa_2Cu_3O_{7-x}$ thin film deposited on a (1 0 0) $SrTiO_3$ substrate, measured at a frequency of 50.9 GHz.

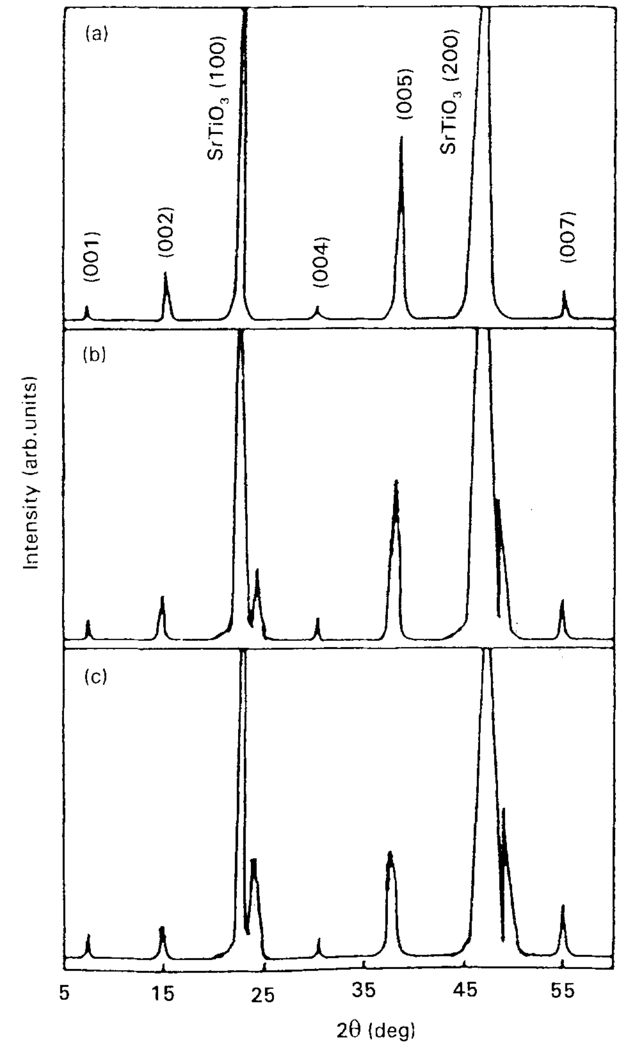

Figure 4 XRD patterns of a $YBa_2Cu_3O_{7-x}$ thin film grown on a (1 0 0) $SrTiO_3$ substrate, at substrate temperatures: (a) 750 °C, (b) 720 °C, and (c) 680 °C.

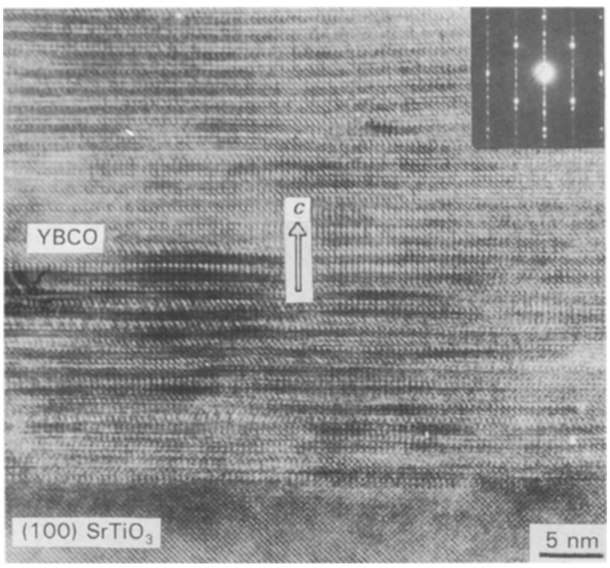

Figure 5 TEM image of the $YBa_2Cu_3O_{7-x}$ thin film grown on a (1 0 0) $SrTiO_3$ substrate at 750 °C. The *c*-axis of the film is perpendicular to the surface of the substrate.

$SrTiO_3$ substrates. Perfect growth was indicated by the spectrum of a film deposited at 750°C, revealing only (0 0 *l*) peaks. TEM observations showed that the film had perfect epitaxial growth, as shown in Fig. 5.

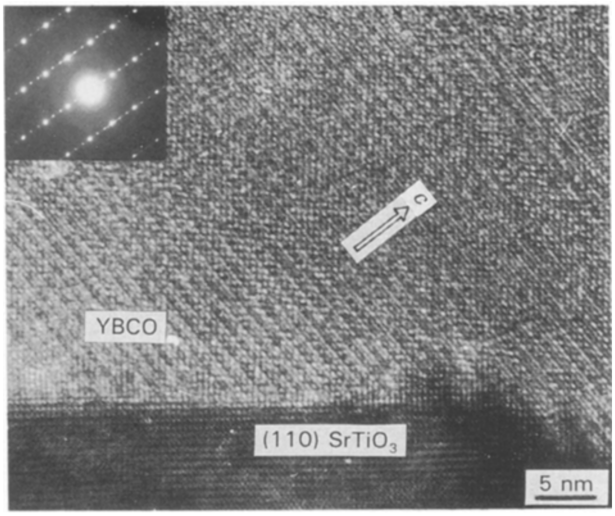

Figure 6 TEM image of the $YBa_2Cu_3O_{7-x}$ thin film grown on a (1 1 0) $SrTiO_3$ substrate. The *c*-axis of the film is along a (103) alignment.

With decreasing deposition temperature, the *c*-axis growth gradually changed to *a*-axis growth by accommodating a mixture of both orientations. During the deposition of films, a substrate temperature, T_s, which was too high or too low resulted in the appearance of a faint phase, which could not be assigned to the (123) phase. On (1 1 0) aligned substrates, $YBa_2Cu_3O_{7-x}$ thin films also featured epitaxial growth. However, the orientation was a (1 1 0) or a (103) alignment, as shown in Fig. 6.

In order to determine the epitaxial quality of films as a whole, RBS and channeling spectroscopy were measured both for films and substrates. Fig. 7 shows the results for the film and substrate of $YBa_2Cu_3O_{7-x}$ superconducting thin films deposited on a (1 0 0) $SrTiO_3$ substrate. Although the substrate surfaces were polished and etched, they still revealed quite high surface peaks. The minimum yield value was about 25%. On the other hand, a defect-free substrate surface is a necessary precondition for epitaxial growth. We used annealing and an ion-beam etching process to improve the substrate surfaces. After annealing in an oxygen atmosphere at 1000°C for 10 h, and then etching off a 500 nm thickness along the surface using an argon-ion beam with 1 keV energy at an incident angle of 45°, the minimum yield value decreased to about 3%. In Fig. 7b, RBS random and aligned spectra are shown for a $YBa_2Cu_3O_{7-x}$ film deposited on (1 0 0) $SrTiO_3$. The minimum yield was about 13% for Ba near the film surface. This is higher than the value of 3% for single crystalline $YBa_2Cu_3O_{7-x}$ [12]. The difference was attributed to the film surface, on which out-growth regions existed.

Finally, we measured the rocking curve of the films by X-ray double-crystalline diffraction. The first crystalline was a (0 0 6) peak of $LiNbO_3$ single crystalline. And the second crystalline was a (0 0 5) peak of a $YBa_2Cu_3O_{7-x}$ sample. Fig. 8 gives the rocking curve of the (0 0 5) peak for the $YBa_2Cu_3O_{7-x}$ film deposited on a (1 0 0) $SrTiO_3$ substrate. The full width at half maximum (FWHM) was 0.22°. This result indicates

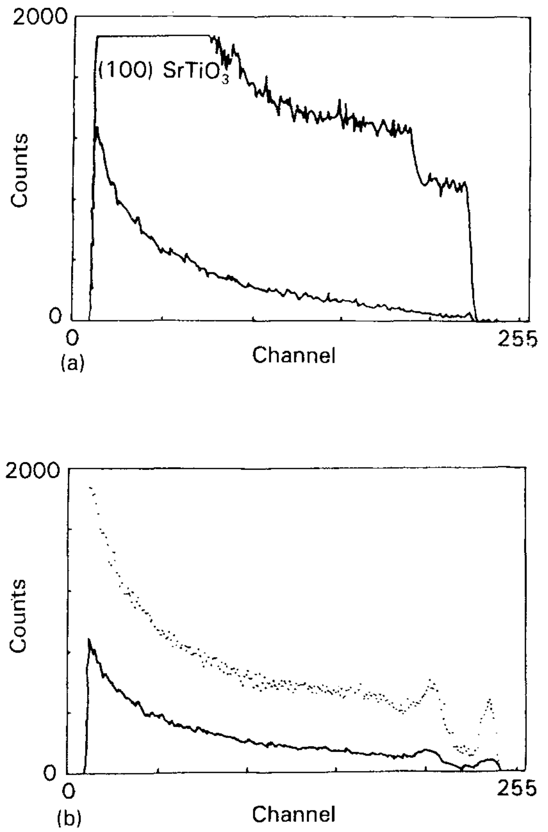

Figure 7 RBS and channeling spectroscopy: (a) (1 0 0) $SrTiO_3$ substrate (2MeV, He^+ beam, at $\theta = 165°$ and $\phi = 0°$.), and (b) $YBa_2Cu_3O_{7-x}$ thin film grown on a (1 0 0) $SrTiO_3$ substrate.

that the film had excellent epitaxial growth on the whole.

4. Conclusion

In conclusion, we have successfully prepared high-quality epitaxial $YBa_2Cu_3O_{7-x}$ superconducting thin films on (100) and (110) $SrTiO_3$, ZrO_2 and $LaAlO_3$ substrates using d.c. magnetron sputtering deposition. The films had a zero-resistance temperature and a critical current density in a zero field of about 90 K and exceeding $10^6 A\,cm^{-2}$ at 77 K, respectively. In addition, we studied the epitaxial growth by XRD, RBS and channeling spectroscopy, X-ray double-crystalline diffraction,and TEM. The experimental results demonstrate that $YBa_2Cu_3O_{7-x}$ superconducting thin films had quite perfect epitaxial growth.

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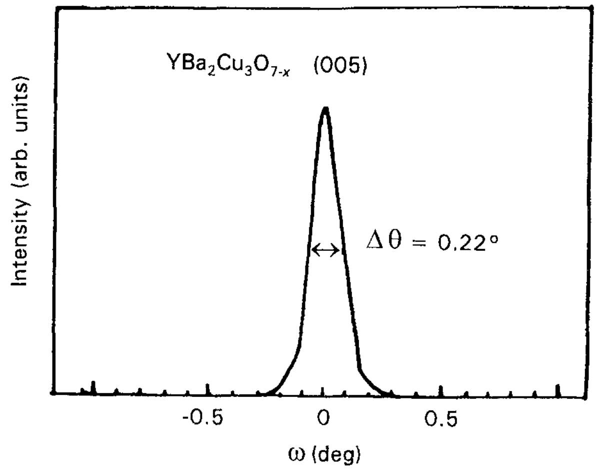

Figure 8 Rocking curve of the $YBa_2Cu_3O_{7-x}$ thin film deposited on a (1 0 0) $SrTiO_3$ substrate. The half-width of the distribution is a measure of the growth quality of the film; the result of 0.22° is excellent.

References

1. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG and C. W. CHU, *Phys. Rev. Lett.* **58** (1987) 908.
2. K. TANABE, D. K. LATHROP, S. E. RUSSEK and R. A. BUHRMAN, *J. Appl. Phys.* **66** (1989) 3148.
3. T. VENCATESAN, X. D. WU, B. DUTTA, A. INAM, M. S. HEDGE, D. M. HWANG, C. C. CHANG, L. NAZAR and B. WILKENS, *Appl. Phys. Lett.* **54** (1989) 581.
4. G. KOREN, A. GUPTA, E. A. GIESS, A. SEGMULLER and R. B. LABOWITZ, *Appl. Phys. Lett.* **54** (1989) 1054.
5. R. K. SINGH, J. NARAYAN, A. K. SINGH and J. KRISHNASWAMY, *Appl. Phys. Lett.* **54** (1989) 2271.
6. C. WEBB, S. L. WENG, J. N. ECKSTEIN, N. MISSERT, K. CHAR, D. G. SCHLOM, E. S. HELLMAN, M. R. BEASLEY, A. KAPITULNIK and J. S. HARRIS Jr, *Appl. Phys. Lett.* **51** (1987) 1191.
7. H. YAMANE, H. MASUMOTO, T. HIRAI, J. IWASAKI, K. WATANABE, N. KOBAYASHI and Y. MUTO, *Appl. Phys. Lett.* **53** (1988) 1548.
8. L. A. TIETZ, C. B. CARTER, D. K. LATHROP, S. E. RUSEK, R. A. BUHRMAN and J. R. MICHAEL, *J. Mater. Res.* **4** (1989) 1072.
9. M. NAITO, R. H. HAMMOND, B. OH, M. R. HAHN, J. W. P. HSU, P. ROSENTHAL, A. F. MARSHALL, M. R. BAESLY, T. H. GEBALLE and A. KAPITULNICK, *J. Mater. Res.* **2** (1987) 713.
10. YIJIE LI, CONGXIN REN, GUOLIANG CHEN, JIANMIN CHEN and SHICHANG ZOU, *J. Appl. Phys.* **69** (1991) 7915.
11. K. CHAR, N. NEWMAN, S. M. GARRISON, R. W. BARTON, R. C. TABER, S. S. LADERMAN and R. D. JACOWITZ, *Appl. Phys. Lett.* **57** (1990) 409.
12. M. G. STOFFEL, P. A. MORRIS, W. A. BONNER and B. J. WILKENS, *Phys. Rev. B* **37** (1988) 2297.

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