ACTA PHYSICA SINICA
Volume 1, Number 3 (Overseas Edition) November, 1992

SUPERCONDUCTING PROPERTIES AND STRUCTURAL PERFECTION OF EPITAXIAL $YBa_2Cu_3O_{7-x}$ THIN FILMS*

LI YI-JIE (李贻杰), XIONG GUANG-CHENG (熊光成), and GAN ZI-ZHAO (甘子钊)
Department of Physics, Peking University, Beijing 100871, China
REN CONG-XIN (任琮欣), CHEN GUO-LIANG (陈国梁), and ZOU SHI-CHANG (邹世昌)
Ion Beam Laboratory, Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 200050, China

(Received 5 December 1991)

High quality epitaxial $YBa_2Cu_3O_{7-x}$ thin films have been successfully prepared by dc magnetron sputtering deposition, on (100) and (110) aligned $SrTiO_3$, $LaAlO_3$ and yttria-stabilized zirconia (YSZ) substrates. The films showed zero resistance around 90 K and had a J_c (at 77 K, $H=0$) over 10^6 A/cm^2. It was found that superconducting properties and structures of the films were strongly dependent on oxygen pressure and substrate temperature. The epitaxial structure of the films have been studied by X-ray diffraction, Rutherford backscattering and channeling spectroscopy, X-ray double-crystal diffraction and transmission electron microscopy. The experimental results demonstrated that the epitaxial $YBa_2Cu_3O_{7-x}$ films had excellent superconducting properties and quite perfect structure.

PACC: 7470; 7470J

I. INTRODUCTION

Since Bednorz and Müller discovered high-T_c oxide superconductivity in Ba-La-Cu-O system in 1986[1], $YBa_2Cu_3O_{7-x}$ superconducting thin films have been extensively studied. This is because high-T_c superconducting films not only have important potential applications in micro-electronics field, but also can contribute to better understanding of the superconducting mechanism. A number of deposition techniques have been used to prepare $YBa_2Cu_3O_{7-x}$ superconducting films and achieved excellent results. These deposition methods include sputtering [2], laser ablation[3-5], molecular beam epitaxy[6], metalorganic chemical vapor deposition (MOCVD)[7], and electron beam evaporation[8, 9]. Up to now, $YBa_2Cu_3O_{7-x}$ superconducting films with rather high upper critical field, B_{c2}, and the capability of carrying very high critical current density, J_c, offer the possibility of making passive microwave devices, Josephson junctions and electrical circuitry. This is because most applications of electronic devices will depend, to a large degree, on their capability to carry high current densities.

For the deposition of polybasic oxide compound superconducting thin films, such as $YBa_2Cu_3O_{7-x}$, there exists a major difficulty related to the controlling of chemical stoichiometry. However, it has been known that the superconductivity in $YBa_2Cu_3O_{7-x}$

* Project supported by the National Center for Research and Development on Superconductivity of China.

system is very sensitive to its composition. Thus the essential problem in fabricating $YBa_2Cu_3O_{7-x}$ films is the production of epitaxial films containing pure (123) phase. From the many year's experience in semiconductor film synthesis, it is well known that reactive sputtering is suitable for the deposition of oxide thin film. Therefore, this technique is now being extensively used to fabricate high-T_c superconducting thin films. Especially by reducing anode voltage and increasing the pressure of the sputtering gas, the effect of negative oxygen ion resputtering can be avoided[10]. In fact, by using simple dc (or rf) magnetron sputtering, it is possible to obtain films having almost the same composition as the target. This makes the fabrication of $YBa_2Cu_3O_{7-x}$ thin films quite easy. In this paper, we present the investigations on superconducting properties and epitaxial growth of $YBa_2Cu_3O_{7-x}$ thin films, deposited on (100) and (110) $SrTiO_3$, $LaAlO_3$ and YSZ substrates. On the basis of successful preparation of high quality epitaxial $YBa_2Cu_3O_{7-x}$ thin films by dc magnetron sputtering, we have measured the microwave surface resistance of the films, and studied their epitaxial structure using X-ray diffraction (XRD), Rutherford backscattering (RBS) and channeling spectroscopy, X-ray double-crystal diffraction and transmission electron microscopy (TEM) techniques.

II. SAMPLE PREPARATION AND EXPERIMENTS

$YBa_2Cu_3O_{7-x}$ superconducting thin films were grown on (100) and (110) aligned $SrTiO_3$, $LaAlO_3$ and YSZ substrates by dc magnetron sputtering. The planar magnetron sputtering device is shown in Fig. 1. The target was a reacted and sintered (123) phase superconducting pellet with a 50 mm diameter. The sputtering gas used was a mixture of

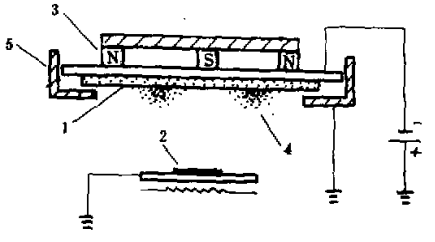

Fig. 1. Schematic diagram of dc magnetron sputtering device.
1—$YBa_2Cu_3O_{7-x}$ target; 2—substrate; 3—magnet; 4—plasma-ring; 5—shield.

Ar and O_2 with pressures of 51.6 and 25.8 Pa, respectively. Substrate temperature was in the range of 700—800 ℃ . The target-to-substrate distance was 35 mm. The discharge was run with a cathode potential of −110 V and a current 450 mA. The deposition rate was about 2.5 nm/min. The YBCO films we used were typically of a thickness of 200 nm. After the deposition, the substrates were allowed to cool down to 450 ℃ , and the vacumm chamber was flooded with pure O_2 to pressures in the range of 0.5 to 1 atmosphere. The films were held at this temperature for 20 min and then cooled down to room temperature

During the deposition, the superconducting (123) phase could be directly produced.

The contents of Y, Ba and Cu were determined from the inductively coupled plasma (ICP) atomic emission spectroscopy. Superconducting transition temperature T_c and critical current J_c of the film were measured by the standard four probe technique. The microwave surface resistance was measured at a frequency of 50.9 GHz. And according to the relationship of $R_s \propto f^2$, the R_s value at other frequencies could be calculated. The epitaxial structure of the films was analyzed by XRD, RBS and channeling spectroscopy, and TEM. XRD measurements were performed using a Rigaku diffractometer with Cu$K\alpha$ radiation. RBS-channeling spectra were measured along [100] and also randomly ($\varphi = 165°$) with 2.0 MeV He^+ ions. 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.

III. RESULTS AND DISCUSSION

A. Relationship between superconducting properties and deposition parameters

During the deposition of YBCO films, it was found that oxygen partial pressure and substrate temperature were two most important factors affecting their superconducting properties. Since high-T_c superconductors were oxide compounds, if oxygen partial pressure was too low, the film would be oxygen-defficient, and this made the epitaxial growth impossible. Only with a relatively high oxygen partial pressure could the crystalline (123) phase be *in situ* deposited. In our sputtering equipment, oxygen pressure of 25.8Pa was most favourable to the growth of films. On the other hand, substrate temperature T_s controlled the diffusion or mobility of deposited atoms along the film surface. Thus T_s had an important influence on whether atoms of each species could get into correct lattice sites. Figure 2 shows the influence of the substrate temperature T_s on the superconducting transition temperature T_c. It can be seen from the figure that the T_s ranging from 700 to 800 ℃ provides an excellent superconducting properties for an oxygen partial pressure of 25.8 Pa in our deposition system, and the optimum T_s is about 750 ℃. We know that

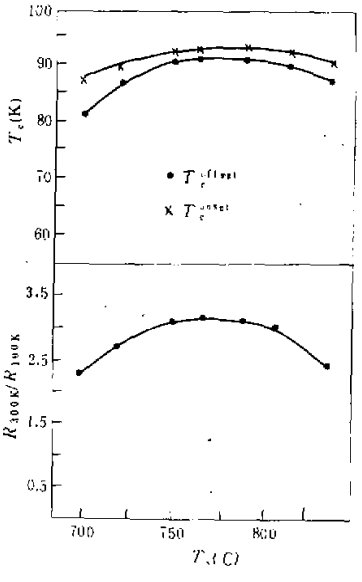

Fig. 2. Transition temperature and residual resistivity ratio R_{300K}/R_{100K} versus temperature curves.

a too low T_s(< 650 ℃) is unfavourable for phase formation, while a too high T_s(> 820 ℃) will result in severe interface reaction between the film and the substrate[11], and the composition of the film will easily deviate from the original stoichiometry. Of course, this will degrade the superconducting properties of the film. The epitaxial $YBa_2Cu_3O_{7-x}$ superconducting thin films, prepared under the optimum growth temperature and oxygen pressures, generally have a zero resistance transition temperature T_c above 90 K. Figure 3 gives the results of four probe dc transport measurements of the resistance R of the films as a function of temperature T. It can be seen that the residual resistance ratio, R_{300K}/R_{100K}, of the films is close to 3. The critical current density J_c in a zero field at 77 K was determined to be over 10^6 A/cm^2, and the maximum value was about 2.5×10^6 A/cm^2.

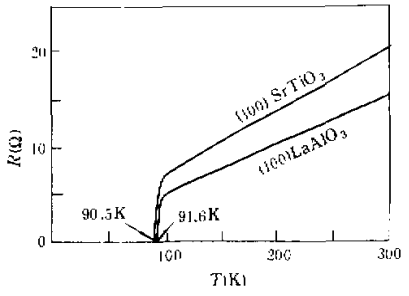

Fig. 3. *R-T* curves for $YBa_2Cu_3O_{7-x}$ superconducting thin films deposited on (100) $SrTiO_3$ and $LaAlO_3$ substrates.

B. Microwave surface resistance

The high-T_c superconducting thin films are potential candidates for passive microwave devices. So the microwave surface resistance is an important parameter to describe the quality of a superconducting film. The microwave surface resistance R_s of the films was measured at a frequency of 50.9 GHz. Figure 4 shows the R_s curve of a sample grown on (100) $SrTiO_3$ substrate. The results of copper (dotted curve) is also given in the figure for comparison. It can be seen from the figure that the curve of the film is oscillatory in normal state. This is because the dielectric constant of $SrTiO_3$ is rather large and changes with temperature. When a millimeter wave traveled into $SrTiO_3$ and was reflected from its 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 other substrates showed similar results. Since the application of high-T_c superconducting thin films in microwave field is mainly at frequencies below 10 GHz, R_s at 10 GHz is often used as a criterion to judge the microwave property of a superconducting film. According to the relation of $R_s \propto f^2$, at the frequency of 10 GHz, the microwave surface resistance (MSR) of the film grown on (100) $SrTiO_3$ at 77 K was 1.4 mΩ. And the MSR of copper was 40 mΩ at 50.9 GHz. Since the surface resistance of

a conductor is proportional to the square root of frequency, that is, $R_s \propto f^{1/2}$, the MSR of copper at 10 GHz is about 18 mΩ. Thus the MSR of the $YBa_2Cu_3O_{7-x}$ film was about one thirteenth of that of copper at 10 GHz and $T=77$ K. The R_s values of our films were larger than the best reported[12]. The main reason is that there existed out-growth regions on the film surface, which was confirmed by scanning electron micrographs.

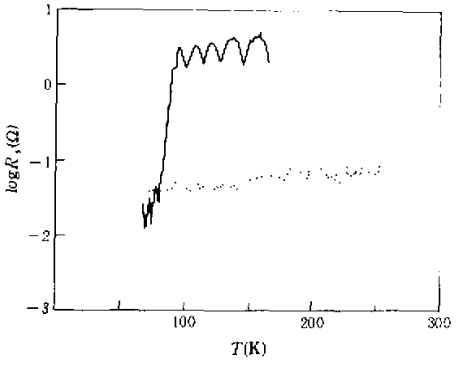

Fig. 4. Microwave surface resistance as a function of temperature for an $YBa_2Cu_3O_{7-x}$ thin film deposited on (100) $SrTiO_3$ substrate, measured at a frequency of 50.9 GHz.

C. Structure and orientation of the films

XRD patterns showed that the films grown on (100) aligned substrates had textured structure in the whole temperature range of 700 – 800℃. At higher temperatures, the *c*-axis of the films was perpendicular to the surface of the substrates. But at lower temperatures, both *c*-axis and *a*-axis orientations were observed. Figure 5 shows X-ray patterns of $YBa_2Cu_3O_{7-x}$ films for three growth temperatures on (100) $SrTiO_3$ substrates. Perfect growth was indicated by the profiles of a film deposited at the optimum growth temperature of 750℃, revealing only(001) peaks. TEM observations showed that the film had a structure of perfect epitaxial growth, as shown in Fig. 6. It can be seen from the photograph that the *c*-axis of the film is perpendicular to the surface of the substrate. During the observation we found that the film had the same epitaxial structure along the whole cross-section of the sample.

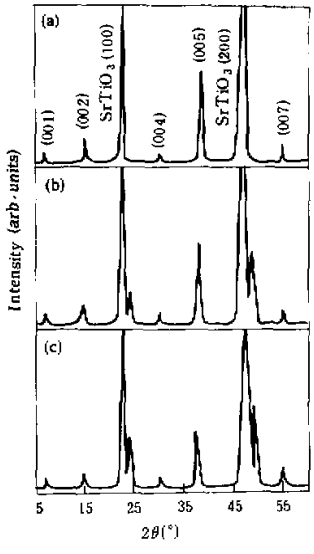

Fig. 5. X-ray diffraction patterns of $YBa_2Cu_3O_{7-x}$ thin films grown on (100) $SrTiO_3$ substrates. Substrate temperature is (a) 750℃; (b) 720℃; (c) 680℃.

When gradually changing the selected point, we did not detect other than *c*-axis orientations nor clear grain boundaries. This indicated that the atomic epitaxial growth was realized not in some small regions but over the whole surface of the substrate. In the film grown at 720 ℃, both *a* and *c* orientations existed, and the *c*-orientation predominated. The sample had a typical textured structure, as shown in Fig. 7. When T_s further decreased to 680℃, in XRD pattern, (*h*00) peaks became stronger and only very weak (001) peaks appeared. The film was basically *a*-orientated. With the decrease of deposition temperature, *c*-axis growth gradually changed into *a*-axis growth by accommodating the fractions of both orientations in the mixture. During the deposition of films, a substrate temperature T_s too high or too low would all result in the appearance of a faint phase which could not be assigned to the (123) phase. On (110) aligned substrates, $YBa_2Cu_3O_{7-x}$ thin films also had the feature of epitaxial growth, however, the orientation was [110] or [103] aligned.

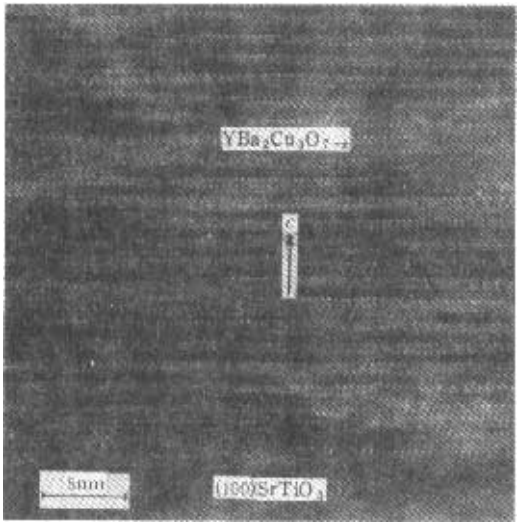

Fig. 6. TEM micrograph of a $YBa_2Cu_3O_{7-x}$ thin film grown on (100) SrTiO substrat at 750 ℃ The *c*-axis of the film is perpendicular to the surface of the substrate.

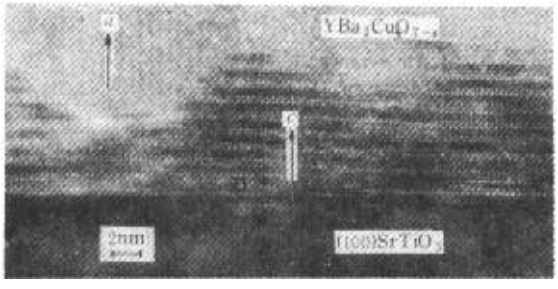

Fig. 7. TEM micrograph of the $YBa_2Cu_3O_{7-x}$ thin film grown on (100) $SrTiO_3$ substrate at 720 ℃ The film had a mixture of *a* and *c* orientations.

D. Analyses of the structural perfection

In order to determine the epitaxial quality of the films on the whole, we have measured Rutherford backscattering and channeling spectroscopy for films and substrates. Figure 8 shows the results on (100) $SrTiO_3$ substrate and the $YBa_2Cu_3O_{7-x}$ superconducting films deposited on it. Although the substrate surfaces were polished and etched, they still exibited quite high surface peaks. The minimum yield value was about 25%. Ordinarily, a defect-free substrate surface is necessary for high quality epitaxial growth. We used annealing and ion beam etching processes to improve substrate surfaces. After annealing in oxygen atmosphere at 1000 ℃ for 10 hours, and then etched off a thickness of 500 nm along the surface by an argon ion beam with 1 keV energy at an incident angle of 45°, the minimum yield value was decreased to about 3%, as shown in Fig. 8 (a). In Fig. 8 (b), RBS random and aligned spectra are shown for an $YBa_2Cu_3O_{7-x}$ film deposited on (100) $SrTiO_3$ substrate. The minimum yield was about 13% for Ba near the film surface. This is higher than the value of 3% for $YBa_2Cu_3O_{7-x}$ single crystals[13]. The difference can be attributed to the film surface, on which there are out-growth regions.

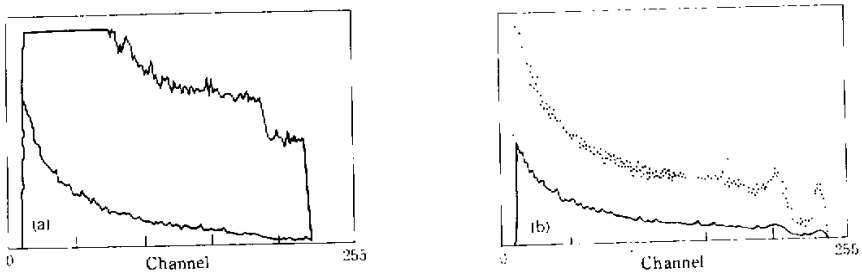

Fig. 8. Rutherford backscattering and channeling spectroscopy for (a) (100) $SrTiO_3$ substrate and (b) $YBa_2Cu_3O_{7-x}$ films grown on (100) $SrTiO_3$ substrate.

Finally, we have measured the rocking curve of the films by X-ray double-crystal diffractometry. The first crystal was $LiNbO_3$ with (006) reflection, and the second crystal

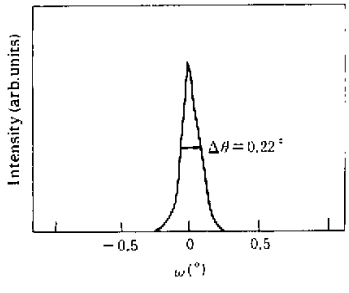

Fig. 9. Rocking curve for (005) peak of the $YBa_2Cu_3O_{7-x}$ film deposited on (100) $SrTiO_3$ substrate.

was the $YBa_2Cu_3O_{7-x}$ sample with (005) reflection. Figure 9 shows the rocking curve of (005) peak for the $YBa_2Cu_3O_{7-x}$ film deposited on (100) $SrTiO_3$ substrate. The full width at half maximum (FWHM) was measured as 0.22 °. This result indicates that the film had excellent epitaxial growth on the whole.

IV. SUMMARY

In conclusion, we have successfully prepared high quality epitaxial $YBa_2Cu_3O_{7-x}$ superconducting films on (100) and (110) $SrTiO_3$, YSZ and $LaAlO_3$ substrates using dc magnetron sputtering deposition. The films had a zero resistance temperature around 90 K and critical current density in a zero field over 10^6 A/cm^2 at 77 K, as well as a small microwave surface resistance. It was found that the superconducting properties and structure of the films were strongly related to oxygen partial pressures and substrate temperatures. In addition, we have studied the epitaxial growth characteristics by XRD, RBS and channeling spectroscopy, X-ray double-crystal diffraction, as well as TEM. Experimental results demonstrated that $YBa_2Cu_3O_{7-x}$ superconducting films had quite perfect epitaxial growth.

ACKNOWLEDGEMENTS

We would like to thank Zhou Zu-yao for RBS analysis.

REFERENCES

[1] J. G. Bednorz and K. A. Müller, *Z. Phys. B*, **64** (1986), 189.
[2] K. Tanabe, D. K. Lathrop, S. E. Russek and R. A. Buhrman, *J. Appl. Phys.*, **66** (1989), 3148.
[3] T. Venkatesan, 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. Laibowitz, *Appl. Phys. Lett.*, **54** (1989), 1054.
[5] R. K. Singh, J. Narayan, A. K. Singh and J. Kishnaswamy, *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] H. Li, G. Linker, F. Ratzel, R. Smithey and J. Geerk, *Appl. Phys. Lett.*, **52** (1988), 1098.
[12] 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.
[13] M. G. Stoffel, P. A. Morris, W. A. Bonner and B. J. Wilkens, *Phys. Rev.*, **B37** (1988), 2297.