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Optimum sputtering conditions on the in-situ growth of superconducting $\text{YBa}_2\text{Cu}_3\text{O}_y$ films with an off-axis RF sputtering configuration

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Abstract

The effects of sputtering conditions on the transport properties of $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) thin films were investigated in this work using an off-axis RF sputtering configuration. These conditions included the substrate temperature, the distance from the substrate to the target, the total pressure of the sputtering gas and the gas composition. The substrates were MgO (001) and SrTiO_3 (001) and the sputtering gas was a mixture of Ar and O_2 . The YBCO films were characterized by resistivity measurements, X-ray diffraction and scanning force microscopy (SFM). Additionally, the optimum conditions of growing high-quality YBCO films were obtained. Those conditions were found to be: (1) the substrate is 3.5 cm horizontal and 3.0 cm vertical away from center of target, (2) the substrate temperature is 680°C for MgO and it is 720°C for SrTiO_3 , and (3) the pressure of the sputtering gas of Ar: O_2 is (3:7) at 300 mTorr. The high-quality YBCO films revealed a transition temperature $T_c(R=0)$ at 87~90 K, a normal-state resistance ratio $R_{300\text{K}}/R_{100\text{K}} \sim 3$ and a normal-state resistivity at 300 K smaller than 200 $\mu\Omega$ cm.

1. Introduction

Since $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) films have potential applications for superconducting electronics, a variety of techniques, such as electron-beam evaporation [1,2], molecular beam epitaxy [3], laser ablation [4,5] and sputtering [6–10], have been developed to prepare YBCO thin films. Among these techniques, the off-axis RF sputtering method has found extensive application because it offers the advantage of producing uniform, high-quality and large area YBCO

thin films. However, various groups have pointed out that reproducing YBCO films with a T_c higher than 87 K is relatively difficult except for films grown by the pulsed-laser deposition technique. The quality of YBCO films is affected by several factors, e.g., the sputtering power, the pressure, the composition of the gas, the position of the substrate with respect to the target and the substrate temperature. Nevertheless, these factors sometimes depend on each other. Therefore, finding the optimum sputtering conditions is deemed necessary. In this work, we report the optimum sputtering conditions on the growth of YBCO films which were characterized by measurements of resistivity. Furthermore, a simple method

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Fig. 1. Schematic diagram of the RF sputtering system.

for achieving a controllable deposition process is derived for reproducing high-quality YBCO thin films.

2. Experiments

An RF sputtering system with a rotational quartz substrate holder was constructed in this study. Fig. 1 shows the configuration of the off-axis RF magnetron sputtering system used in this work. Two sputter guns were mounted face to face in a stainless-steel vacuum chamber pumped by a mechanical and a turbo pump. The magnetic structures in two magnetrons are identical. One target was a stoichiometric superconducting $\text{YBa}_2\text{Cu}_3\text{O}_y$ compound; the other was YBCO-heterostructure compounds, e.g., $\text{MBa}_2\text{Cu}_3\text{O}_y$ ($\text{M} = \text{Dy}, \text{Pr}$), for the growth of a superconducting superlattice. Both $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{PrBa}_2\text{Cu}_3\text{O}_y$ (PBCO) targets were 2 inches in diameter. The sputtering atmosphere varied between 50 to 210 mTorr for O_2 and 100 to 210 mTorr for Ar. A RF plasma generated by a RF power supply (13.56 MHz, 100 W) gave rise to a cathode self-bias of -50 to -5 V, producing a deposition rate around $12 \sim 14 \text{ \AA}/\text{min}$ depending on the total pressure and Ar/ O_2 ratio for this off-axis geometry. Two quartz lamps (1000 W each) were mounted in the heater to provide radiation heating of the sample. The heater has a water-cooled stainless-steel shielding which can reduce the contamination caused by the heater in the sample preparation at higher temperatures. The sample seated on the quartz holder was rotated when the YBCO films were grown and radiation heated.

The rotation speed of the sample was 3 turns per minute. The size of the substrate was $5 \text{ mm} \times 5 \text{ mm} \times 0.5 \text{ mm}$. The temperature of the sample was measured by a thermocouple. The temperature of the sample was determined as follows: First, we measured the temperature of the substrate and the output power of the heater simultaneously with the thermocouple attached to the substrate when the sample was not rotated. Secondly, the sample was then prepared at a fixed output power of the heater with the sample rotating. The fixed output power of the heater gives a sample-preparation temperature. All of the films were grown at $630 \sim 720^\circ\text{C}$ with a total thickness of $150 \sim 200 \text{ nm}$. After the deposition, oxygen gas at one atmospheric pressure was introduced into the chamber. The cooling rate was $5^\circ\text{C}/\text{min}$ and the films were maintained at the growth temperature for an hour before the cooling process. The resistance of the as-grown YBCO films was measured by a conventional four-probe method and the temperature was monitored by a silicon diode. The X-ray diffraction pattern of YBCO films measured with a diffractometer (Siemens Model D500) showed preferred orientation with the crystal c -axis perpendicular to the plane of the substrate.

3. Results and discussion

3.1. Effect of the target–substrate geometry

Two configurations, on-axis and off-axis, have been reported in the development of sputtering for preparing YBCO films [9], and the off-axis configuration is suggested to be a preferred technique [9,10] because it can reduce the effect of the negative ion resputtering. However, the relative position of the substrate with respect to the target is an important parameter in growing high-quality YBCO thin films in an off-axis sputtering system. The substrate position away from the target can be described by two parameters: D_H and D_V as indicated in Fig. 1 where D_H is the horizontal distance from the center of the target to the substrate and D_V is the vertical distance from the substrate to the line drawn between the centers of the targets. The effects of the parameter D_H have been discussed elsewhere [7,9]; in addition, an optimum value at $D_H \geq 4.5 \text{ cm}$ for an on-axis RF

sputtering system was reported in Ref. [7]. However, a detailed description of the influence of the substrate–target geometry when using an off-axis RF sputtering system has not yet been provided.

Figs. 2 and 3 show the resistive transition of YBCO films deposited on MgO (001) at various positions. Notably, the sputtering conditions shown in the inset are not yet the optimum conditions. As shown in Fig. 2, as D_V decreased from 5.5 cm to 3.0 cm at a constant D_H value of 4.0 cm, T_c is increased from 82 to 86 K and the ratio of $R_{100\text{ K}}/R_{300\text{ K}}$ was lowered at $D_V = 3.0$ cm than that at higher D_V values. If D_V is larger than 3.5 cm, the composition of the films was varied because the density and energy of the sputtering atoms or ions arriving at the substrates are not optimized. The superconducting properties are also affected by the other parameter D_H as shown in Fig. 3. The optimum horizontal distance D_H is about 3.5 cm with a constant D_V of 4.0 cm. When D_H is larger than 4.0 cm or smaller than 3.0 cm, the deviation of the composition of YBCO films from the optimum conditions is probably due to high energy particle bombardment or the difference in the distribution of the atomic species. Especially for $D_H \leq 3.0$ cm, an intense plasma was observed close to the substrate. Therefore, ion bombardments can cause a serious deviation from the

Fig. 2. Resistive characteristics of YBCO films grown on MgO (001) for various substrate position of the vertical D_V 's. The inset shows the sputtering conditions for the preparation of these films.

Fig. 3. Resistive characteristics of YBCO films grown on MgO (001) at various substrate–target configurations for different D_H 's. The inset shows the sputtering conditions used in the preparation of these films.

stoichiometric YBCO films. The variation of the film composition at different substrate positions has been analyzed in Ref. [9].

3.2. Sputtering gas

The film composition, especially the oxygen content, is known to be affected by the total pressure and the Ar/O₂ ratio. As shown in Fig. 4, the total pressure of 300 mTorr exhibits a higher $T_c \sim 86$ K and a lower $R_{100\text{ K}}/R_{300\text{ K}} \approx 0.3$, however, T_c was suppressed seriously and the value of the $R_{100\text{ K}}/R_{300\text{ K}}$ ratio became larger when the deposition pressure was increased up to 400 mTorr. Many authors [9,10] have reported that a high-quality film can be achieved in YBCO films grown with an on-axis configuration by increasing the pressure of sputtering gas over 400 mTorr to prevent the resputtering effect on YBCO films. In this off-axis RF configuration, similar solutions to this problem of the resputtering effects can be accomplished by increasing the pressure of the sputtering gas or by adjusting the target–substrate position. However, the optimum deposition pressure cannot be over 300 mTorr because of the low energies of the particles reaching the substrate. The T_c , which depends on the energies

Fig. 4. Temperature dependence of the resistance for YBCO films deposited at various gas pressures with the sputtering conditions shown in the inset.

of the incident particles, is also expected to depend on the sputtering pressure as well as the target–substrate position. In an off-axis sputtering, the sputtering pressure is as important a parameter as the substrate–target position is.

Fig. 5 shows the temperature dependence of

Fig. 5. Temperature dependence of the resistance for YBCO films deposited at various partial pressures of O_2 . The sputtering conditions are shown in the inset.

Fig. 6. Resistive transitions for YBCO films grown at various substrate temperatures. The dashed line is the resistance as a function of temperature for a YBCO film grown at 700°C and reveals a worse $T_{c,onset}$ and a $R_{100K}/R_{300K} = 5$. However, the transition for film grown at 630°C reveals a $T_{c,onset}$ slightly higher than that in dashed line (e) and an even worse R_{100K}/R_{300K} ratio ~ 0.9 . The inset shows the sputtering conditions used in the preparation of these films.

$R(T)/R_{300K}$ for YBCO films deposited at different partial pressures of oxygen with the sputtering conditions shown in the inset. At the oxygen pressure of about 210 mTorr (300 mTorr $\times$ 70%), the YBCO film has $T_c \sim 86$ K which is higher than that of the YBCO films deposited at a lower partial pressure of oxygen. In several reports, the dependence of the oxygen pressure on the in-situ growth of $YBa_2Cu_3O_y$ films as employed in various deposition techniques (sputtering, laser ablation) was studied [4,10,11]. Investigations also included the effects of bombardment and compositional deviation caused by the lack of oxygen in the sputtering gas. The optimum oxygen pressure of about 210 mTorr is nearly comparable to that of films produced by the in-situ laser ablation [12].

3.3. Substrate temperature

T_c depends on the energies of the sputtering atoms or ions, and it is also expected to depend on the substrate temperature. Fig. 6 shows the resistance as a function of temperature for YBCO films grown on

MgO (001) at different temperatures. When the substrate (MgO) temperature is increased to 680°C, T_c of YBCO films is improved and the ratio of $R_{100\text{K}}/R_{300\text{K}}$ becomes lower. This YBCO film is grown under optimum conditions and reveals good transport properties. If the substrate (MgO) temperature is increased above 700°C, however, T_c is suppressed seriously as shown in curve e. The substrate temperature must be appropriate during deposition so that the mobility of the sputtering atoms or ions can be optimized to allow them to grow on their own lattice sites. If the temperature is too high, there are the possibilities of reaction with the substrate, re-evaporation or even decomposition driven by entropy. If the temperature is too low, there is not enough energy for the atoms to form the YBCO compound. Those effects are revealed in the temperature dependence of the resistivity. As one increased the temperature of the sample from 630 to 680°C, T_c is increased, the $R_{100\text{K}}/R_{300\text{K}}$ ratio is reduced, and the value of dR/dT (for T above 100 K) is increased. If the deposition temperature is over the optimum substrate temperature, however, the $T_{c,\text{onset}}$ will be obviously down to near 80 K. From the characteristics of the $R_{100\text{K}}/R_{300\text{K}}$ ratio, the slope of dR/dT and $T_{c,\text{onset}}$, the substrate temperature can be easily regulated to provide good growth of YBCO films.

3.4. Substrate materials

Among the substrates studied by others, YSZ, MgO, SrTiO₃ and LaAlO₃ are commonly used and T_c obtained was close to optimum values. Because of the benefit of economics and lattice match, MgO (001) and SrTiO₃ (001) have found extensive application and YBCO films with an optimum $T_c \sim 90$ K were obtained. In this article, we report the high-quality YBCO films grown on MgO (001) and SrTiO₃ (001) under the optimum growth conditions shown in the upper inset. Interestingly, the optimum growth temperature (720°C) for a YBCO film on SrTiO₃ (001) is higher than that of a YBCO film on MgO (001) which is about 680°C. The resistive curves show a metallic behavior in the normal state and a sharp superconducting transition as shown in the lower inset. $T_c(R$

Fig. 7. The resistive transition of YBCO films deposited on MgO (001) and SrTiO₃ (001) with optimum sputtering conditions shown in the inset.

= 0) for a YBCO film deposited on MgO (001) is around 87 K which is slightly lower than that of a YBCO film deposited on SrTiO₃ (001) ($T_c \sim 90$ K). Furthermore, the resistivity is extrapolated to about zero at zero temperature.

Growth mechanisms have been investigated by scanning tunneling microscopy (STM) [14–16] or scanning force microscopy (SFM) [4,13]. Figs. 8(a) and (b) show the surface morphology of YBCO films observed by SFM on MgO (001) and SrTiO₃ (001), respectively. A distinct screw dislocation was identified in SFM images for films deposited on MgO (001) and SrTiO₃ (001). An additional feature is the layer-cake-like morphology neighboring the screw dislocation image in YBCO films deposited on SrTiO₃ as shown in Fig. 8(b). On both substrates, the size of the grains is 100 nm ~ 500 nm in diameters and have a circular cross-section. Recent reports [13] on sputtered YBCO films show the feature of the screw growth patterns both in the films deposited on MgO and SrTiO₃. However, the layer-by-layer growth was only observed in the early stages of the epitaxial growth of laser-ablated YBCO thin film deposited on SrTiO₃ [14] or that deposited on the substrate which was slightly off the ideal (001) plane [15]. Our observations for a YBCO film with ~ 150

Fig. 8. AFM images of a YBCO film grown on (a) MgO (001) (b) SrTiO₃ (001). The terraced surface and the spiral growth pattern are clearly visible. The vertical height difference between terraces is one unit cell (~ 12 Å). The size of the image is (a) $1 \times 1 \mu\text{m}^2$, (b) $1.2 \times 1.2 \mu\text{m}^2$.

units of YBCO cells thick on the SrTiO₃ (001) substrate were distinct from the observations reported in Refs. [14] and [15] in which the surface morphology showed only the screw dislocation.

4. Conclusions

YBCO films were in-situ deposited on MgO (001) and SrTiO₃ (001) substrates by an off-axis RF mag-

neutron sputtering technique. Optimum conditions for reproducing high-quality YBCO films including the substrate position, the substrate temperature, the total pressure of the sputtering gas and the gas compositions were also found. The necessary conditions are:

(1) the substrate is 3.5 cm horizontal and the 3.0 cm vertical away from the target center,

(2) the pressure of the sputtering gas is 300 mTorr with Ar/O_2 ratio = $\frac{3}{7}$ and

(3) the substrate temperature is at 680–720°C. The optimum temperature for YBCO films on MgO (001) was lower than that of YBCO films on SrTiO_3 (001). Additionally, a SFM was successfully used to characterize the spiral and pancake topography of sputtered YBCO films.

References

- [1] D.K. Lathrop, S.E. Russek and R.A. Buhrman, *Appl. Phys. Lett.* 51 (1987) 1554.
- [2] T. Terashima, K. Iijima, K. Yamamoto, J. Takada, K. Hirata, H. Mazaki and Y. Bando, *J. Cryst. Growth* 95 (1989) 617.
- [3] B.R. Johnson, K.M. Beaucham, P.T. Wang, J.X. Liu, K.M. McGree, J.C. Wan, M. Tuminen, Y.J. Zhang, M.L. McCartney and A.M. Goldman, *Appl. Phys. Lett.* 56 (1990) 1911.
- [4] M. Kawaswki, J.-P. Gong, M. Nantoh and T. Hasegawa, *Jpn. J. Appl. Phys.* 32 (1993) 1612.
- [5] D.K. Fork, D.B. Fenner, G.B. Fenner, G.A.N. Connell, J.M. Phillips and T.H. Geballe, *Appl. Phys. Lett.* 57 (1990) 1137.
- [6] A.C. Westerheim, A.C. Anderson and D.E. Oates, *J. Appl. Phys.* 75 (1994) 393.
- [7] T. Kobayashi, S. Eto, Y. Kato, K. Usumi and T. Goto, *Jpn. J. Appl. Phys.* 32 (1993) 3150.
- [8] L.M. Wang, H.H. Sung, J.H. Chern, H.C. Yang and H.E. Horng, *J. Appl. Phys.* 73 (1993) 8419.
- [9] C.B. Eom, J.Z. Sun, B.M. Lairson, S.K. Streiffer, A.F. Marshall, K. Yamamoto, S.M. Anlage, J.C. Bravman and T.H. Geballe, *Physica C* 171 (1990) 354.
- [10] J.R. Gavaler, J. Talvacchio, T.T. Braggins, M.G. Forrester and J. Gregg, *J. Appl. Phys.* 70 (1991) 4383.
- [11] H. Enami, T. Shinohara, N. Kawahara, S. Kawabata, H. Hoshizaki and T. Imura, *Jpn. J. Appl. Phys.* 29 (1990) L782.
- [12] S. Pramanick and J. Narayan, *J. Appl. Phys.* 73 (1993) 316.
- [13] M. Hawley, I.D. Raistrick, J.G. Beery and R.J. Houlton, *Science* 251 (1991) 1587.
- [14] M.A. Harmer, C.R. Fincher and B.A. Parkinson, *J. Appl. Phys.* 70 (1991) 2760.
- [15] X.Y. Zheng, D.H. Lowndes, S. Zhu, J.D. Budai and R.J. Warmack, *Phys. Rev. B* 45 (1992) 7584.
- [16] X. Zhu, G.C. Xiong, R. Liu, Y.J. Li, G.J. Lian, J. Li and Z.Z. Gan, *Physica C* 216 (1993) 153.