Study of the resputtering effect during rf-sputter deposition of YBCO films

Jun-Hao Xu, B.M. Moon,[a] and K.V. Rao
Department of Condensed Matter Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

(Received 10 January 1994; accepted 9 December 1994)

We propose an angular redistribution model to understand the negative ions resputtering effect in sputter depositing $YBa_2Cu_3O_{7-x}$ (YBCO) films. On the basis of this model, the negative oxygen ions resputtering effect has been greatly minimized by introducing a Cu mask between the substrate and the target to block energetic oxygen particles from directly bombarding the growing film. Thus, YBCO films with almost exact stoichiometric composition and zero resistance critical temperatures as high as 90 K are obtained under oxygen partial pressure as low as 3 mTorr in a temperature regime well beyond that proposed by R.H. Hammond and R. Bormann. Preliminary results of a modified masking and shielding technique to eliminate the resputtering effect and fabricate large area (>1 in. × 1 in.) YBCO superconducting films with high uniformity are also presented.

I. INTRODUCTION

It is generally recognized that sputtering technique is one of the few effective ways to produce high T_c superconducting $YBa_2Cu_3O_{7-x}$ (YBCO) films. However, one serious drawback in this technique is the so-called negative oxygen ion resputtering effect which limits the capability of this technique to grow high quality large area (>1 sq. in.) YBCO films. A number of authors have reported methods to minimize or compensate the resputtering effect, including the use of very high sputtering pressure,[1] placing the substrate in an off-axis configuration,[2] changing the target composition in order to compensate for the resputtering effect,[3] using much stronger magnets than usual in the magnetron source,[4] or placing a grounded shield within the dark space above the target center to redefine the sputtering region.[5] However, there are not many systematic studies of the resputtering effect from the fundamentals of sputtering point of view.

In this paper, we present an angular redistribution model to understand the nature of the resputtering effect. In addition, we summarize results of our success in implementing this model to develop a simple but very effective method to eliminate the negative oxygen ion resputtering and deposit high quality YBCO films from a stoichiometric YBCO planar target at low sputtering pressures.

II. ANGULAR DISTRIBUTION MODEL AND EXPERIMENT

In our Leybold L560 Universal Deposition System, there is a 3 in. (radio frequency) rf-sputtering gun. Like most of the sputtering target surfaces, the ion sheath, typically 1 mm thick, between the plasma and the target is parallel to the target surface and sputtering ions impinge on the target at normal incidence. An average dc voltage at the target is about −1000 V. Generally, all the sputtered species ejected from the target surface with an average velocity of about 6×10^3 m/s show a cosine angular distribution along the normal at each sputtered spot on the target,[6] although the distribution function also depends on sputtering yields, masses of atoms, and binding energies of surface atoms; therefore, the substrate position will affect the composition and uniformity of sputtered films. The neutral sputtered species will cross the sheath freely without any change in their angular distribution. This is the case for Y, Ba, Cu, and neutral oxygen atoms. However, the negative sputtered oxygen ions gain an average kinetic energy as high as 1000 eV after crossing the sheath and are only partially neutralized in the plasma, as shown in Fig. 1. Obviously, these energetic oxygen particles have a much more preferred angular distribution along the normal to the target than the cosine distribution for the neutral sputtered atoms.

Suppose the initial average velocity of the negative oxygen ions V_0 is 6×10^3 m/s, the typical velocity of rf-sputtered species, and the velocity component normal to the target due to the acceleration in the dc electrical field across the sheath is V_N. For an average dc voltage 1000 V at the target, from kinetic energy consideration V_N, will be about 1.1×10^5 m/s. Assume initially that a negative oxygen ion travels with the average velocity V_0 along a direction with an angle α to the normal of the target. After gaining the kinetic energy, this oxygen ion becomes more energetic and thus changes its traveling direction with a reduced angle β to the normal of the target as shown in Fig. 1. The value β could be

---

[a] Present address: Department of Electrical Engineering, Korea University, Seoul, Korea.

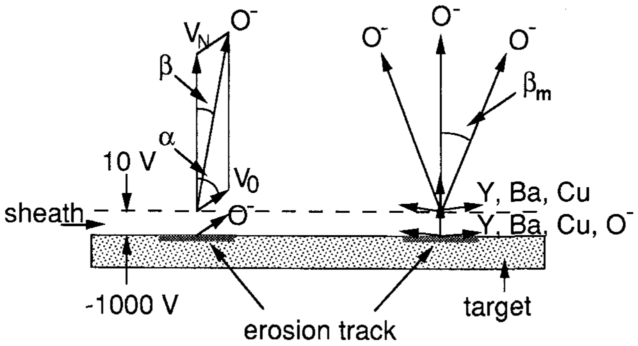

FIG. 1. The angular redistribution process for negative sputtered oxygen ions. β_m is defined as the maximum angle with respect to the normal of the target for energetic oxygen ions. Note that most of sputtered species are ejected from the erosion track of the target.

calculated as

$$\beta(\alpha) = \tan^{-1}[V_0 \sin \alpha/(V_0 \cos \alpha + V_N)]. \quad (1)$$

Substituting V_N and V_0 by 1.1×10^5 m/s and 6×10^3 m/s in Eq. (1), respectively, from the initial cosine angular distribution we could get the new angular distribution for the ionized energetic oxygen particles having the average kinetic energy. Figure 2 shows the initial cosine and the new angular distribution for the negative oxygen ions, where β_m is denoted as the maximum β value corresponding to $\alpha \sim 90°$, as can be seen in Fig. 1. Apparently, most of the energetic oxygen particles will travel nearly parallel to the normal of the target. Because the negative oxygen ions have high kinetic energy, the scattering rate at low sputtering pressure (2×10^{-2} mbar in our case) is small. We therefore neglect the scattering effect in our analyses.

In principle, if we could block the energetic oxygen particles from traveling directly onto the growing film, the resputtering effect should be greatly minimized. In order to estimate the critical β_m value of the energetic oxygen ions, which have the threshold energy to cause resputtering from the growing film, we take an Ar threshold energy of 17 eV for sputtering Cu (Ref. 7) as the oxygen threshold energy for sputtering Cu from the growing film. We find the corresponding critical V_N value is $V_{NC} = 1.43 \times 10^4$ m/s in this particular case. Take V_0 as the average velocity of 6×10^3 m/s, from Eq. (1) we obtain the critical β_m value

$$\beta_{mc} = 23°. \quad (2)$$

Therefore, if we could block all those energetic oxygen particles with incidence angles smaller than the critical angle β_{mc} and let only those sputtered species with minimum oblique incidence angle (MOIA) larger than β_{mc} travel toward and finally deposit onto the substrate, the resputtering from the growing film would not take place.

Based on the above discussion, we developed a masking technique in the conventional on-axis sputtering configuration for producing high quality YBCO films.[8] A Cu mask, electrically connected to the grounded substrate heater, was introduced between the substrate and the target to block the energetic particles in the plasma from directly bombarding the growing film. A schematic view of the substrate, mask, and the target geometry is depicted in Fig. 3. The diameter of the mask was systematically changed from 20 mm to 28 mm with a step of 2 mm, corresponding to the MOIA (see Fig. 3) of the deposited particles from 18.4° to 31.0°, respectively, to study the MOIA dependence of the degree of the elimination of the resputtering effect. Sputtering conditions are rf power, 100 W; substrate temperature, 780 °C; pressures of the sputtering gases, 10 mTorr Ar and 3 mTorr O_2; distance between substrate and target, 3 cm, and distance between mask and target, 1.5 cm.

III. RESULTS AND DISCUSSIONS

In our experiments, the YBCO films, typically 4200 Å thick, sputter deposited at a rate of 0.6 Å/s on 10 mm × 10 mm $SrTiO_3(100)$ substrates under identical sputtering conditions but with different sizes of the mask having slightly different zero critical temperature T_{c0}, transition width ΔT_c (90%–10%) and almost the same composition, as determined by resistive and Rutherford backscattering spectrometry (RBS) measurements, respectively. Table I lists T_{c0}'s, ΔT_c's, corresponding MOIA's, and the composition

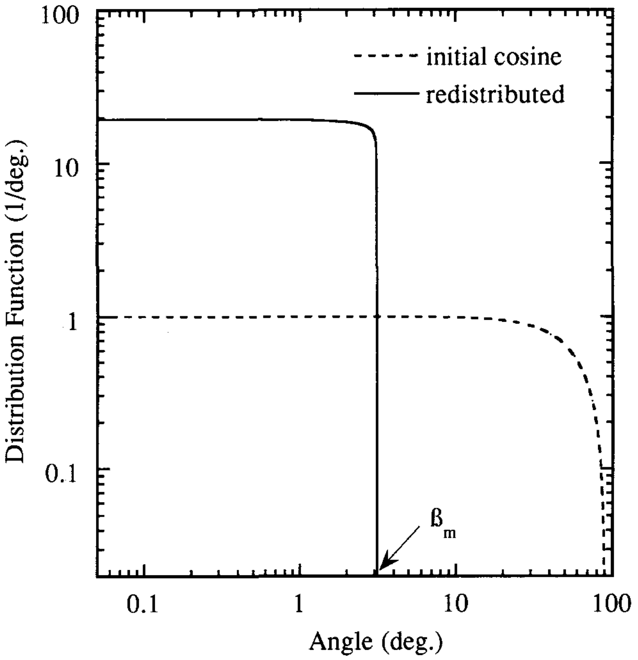

FIG. 2. The initial cosine angular distribution and the redistributed one after being accelerated through the sheath for negative sputtered oxygen ions at each sputtered spot on the erosion track of the target.

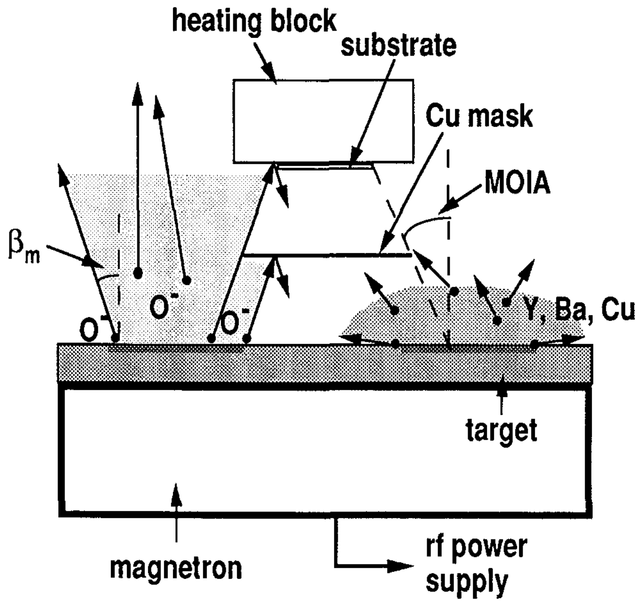

FIG. 3. The schematic view of the substrate, mask, and target geometry and the illustration of the elimination of the energetic oxygen ions resputtering effect in an on-axis configuration with a Cu mask. MOIA is defined as the minimum oblique incidence angle for those deposited species onto the substrate.

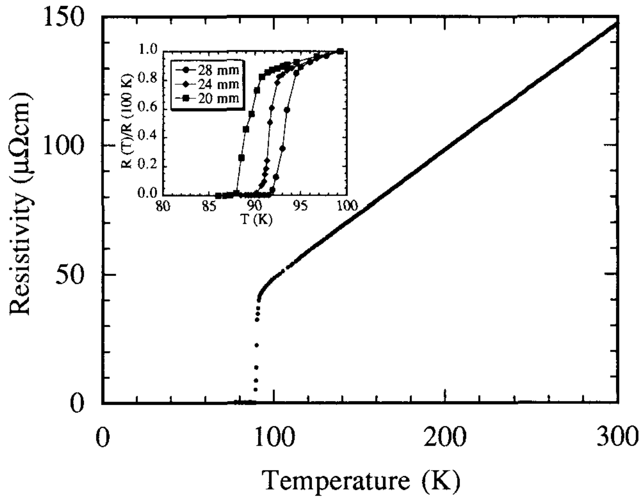

FIG. 4. Resistive transition YBCO film grown on $LaAlO_3(100)$ with a 26 mm Cu mask. Inset: resistive transitions for three YBCO films grown on $SrTiO_3(100)$ substrates with Cu mask sizes of 20, 24, and 28 mm, respectively.

of these $YBCO/SrTiO_3(100)$ films. In spite of small differences in T_{c0} for these films made with different mask sizes, they have quite similar normal-state resistivity, resistance ratio, and transition onset. Figure 4 shows a typical resistive transition for a YBCO film on $LaAlO_3(100)$ grown with a 26 mm Cu mask, and in the inset of Fig. 4 are shown the plots of resistive transitions for three YBCO films grown on $SrTiO_3(100)$ substrates with different sizes of Cu mask. Low normal-state resistivities, $\rho(300\ K) \sim 150\ \mu\Omega$ cm, and good resistance ratios $\rho(300\ K)/\rho(100\ K) \sim 3.0$, suggest reasonable good quality of the YBCO films. RBS measurements on different parts of the films indicate that the composition and thickness of the on-axis sputtered films are the same within the measurement accuracy over 10 mm × 10 mm substrates. Clearly, the conventional on-axis sputtering resulted in an insulating YBCO film with a serious Cu poor composition of $YBa_{2.1(7)}Cu_{1.6(5)}O_y$, as determined in RBS analyses. Notice that the film is not Ba poor, rather it is the Cu concentration which is low. This could be due to the preferential sputtering of Cu from the growing film (the sputtering yields for Cu, Au, and Ag are about twice as much as those of other metallic elements). On the other hand, as long as we shielded the substrate during sputter deposition, superconducting films with T_{c0} higher than 85 K and almost exact stoichiometric composition were achieved.

In order to further confirm the validity of the masking technique, we placed the substrate directly above the plasma ring of the sputtering gas with a Cu mask. The schematic illustration of the elimination of the energetic oxygen ions resputtering effect in such an *asymmetric* on-axis configuration is shown in Fig. 5. Under identical sputtering conditions, we again obtained YBCO films with T_{c0}'s around 90 K. In addition, we deposited films with off-axis configuration (see Fig. 5) under the same sputtering conditions. We find that at such a low oxygen partial pressure (3 mTorr), only when the substrates are located very close to the plasma region, superconducting YBCO films with T_{c0}'s around 90 K could be obtained. Otherwise, films were not superconducting when substrates are located well outside the plasma region. This indicates that stoichiometric deposition is necessary but

TABLE I. MOIA dependence of the critical temperature T_{c0}, transition width ΔT_c, and composition for YBCO films on $SrTiO_3(100)$ substrates.

Mask dia. (mm)	MOIA (deg)	T_{c0} (K)	ΔT_c (K)	Film composition
...	...	...	...	$Y_1Ba_{2.17}Cu_{1.65}O_y$
20	18.4	87	2	...
22	21.8	87.5	1.5	...
24	25	89	1.2	...
26	28	91.5	1	$Y_{1.09}Ba_{2.08}Cu_3O_y$
28	31	91.5	1	$Y_{1.05}Ba_{2.1}Cu_3O_y$

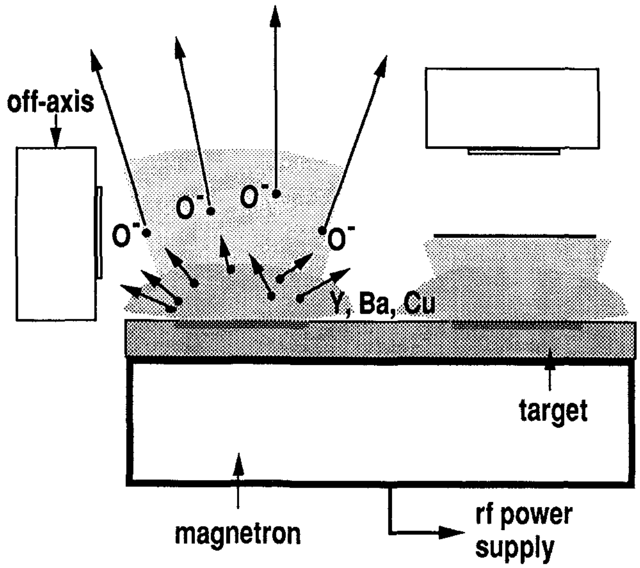

FIG. 5. The schematic illustration of the elimination of the energetic oxygen ions resputtering effect in an asymmetric on-axis and off-axis configurations.

not sufficient to produce superconducting YBCO films at low molecular oxygen partial pressure. However, placing substrates in the plasma region allows us to grow high quality YBCO films even at oxygen partial pressure as low as 2 mTorr with both masked on-axis and off-axis configurations because of the high reactivity of the atomic oxygen or ions. We note that this pressure-temperature regime in which we obtained good films is well outside the ones empirically clarified by Hammond and Bormann.[9]

The agreement of our experimental results with the prediction of the angular redistribution model indicates that the model we propose here could at least serve as a good starting point for further studies of the negative oxygen resputtering effect. In addition, from the angular redistribution model, it is not difficult to understand why placing the substrate in a commonly used off-axis configuration, the stoichiometric deposition of YBCO films, can be achieved. This is because in that particular geometry only those sputtered species travel at incidence angles larger than at least 45° could deposit onto the substrate, as can be seen in Fig. 5. These incidence angles are well beyond the critical angle β_{mc} derived from the model. Thus, there would not be sufficiently energetic oxygen particles traveling toward the substrate during sputter deposition in this off-axis configuration, and consequently the resputtering from the growing film would not occur.

Finally, we would like to point out a possible way to produce large area (>1 in. × 1 in.) YBCO films with a combined masking[8] and shielding[5] technique. A grounded washer-shaped Cu mask is placed between the substrate and target, and a grounded Cu shield with diameter slightly larger than the inner diameter of the Cu mask is placed within the dark space above the target center. Because the Cu shield prevents the shielded middle part of the target from the bombardments of the sputtering ions, there is nearly no sputtering taking place in the shielded region of the target. The process of the elimination of the resputtering effect in this technique is shown in Fig. 6. Our preliminary results indicate that YBCO films grown by this technique have T_{c0}'s larger than 80 K everywhere over the entire 1 in. × 1 in. $LaAlO_3(100)$ substrates.

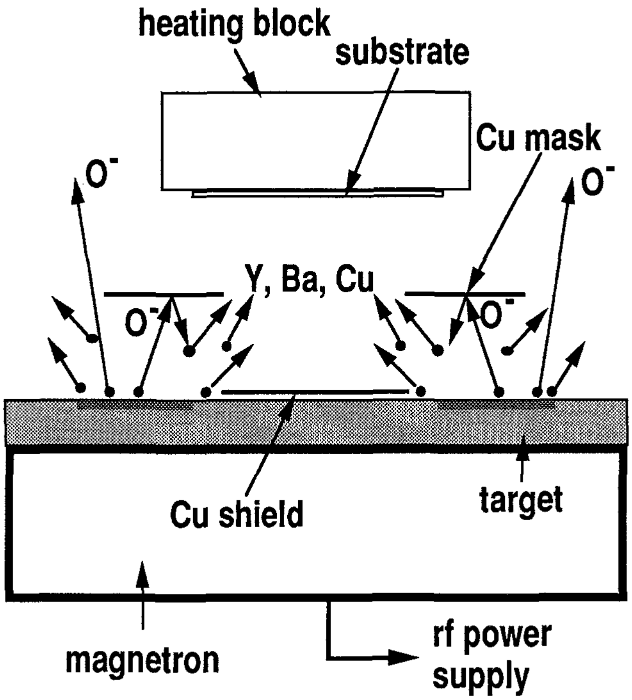

FIG. 6. The process of the elimination of the oxygen ions resputtering effect in the combined masking and shielding technique for growing large area YBCO films.

IV. SUMMARY

In summary, we present an angular redistribution model which enables us to understand the nature of the negative oxygen ions resputtering effect. Based on this model, we developed a masked on-axis sputtering configuration to eliminate the resputtering effect and fabricated high quality *in situ* YBCO films with much higher growth rate than that of the off-axis technique. In addition, a combined masking and shielding technique is proposed to fabricate large area (>1 in. × 1 in.) YBCO films.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge many valuable discussions with A. M. Grishin. This work was supported by the Swedish funding agencies NUTEK and NFR.

REFERENCES

1. W.Y. Lee, J. Salem, V. Lee, C.T. Rettner, G. Lim, R. Savoy, and V. Deline, in *Thin Film Processing and Characterization at High-Temperature Superconductors*, edited by J.M. Harper, R.J. Colton, and L.C. Feldman, AIP Conf. Proc. No. 165 (AIP, New York, 1987).
2. C.B. Eom, J.Z. Sun, K. Yamamoto, A.F. Marshall, K.E. Luther, T.H. Geballe, and S.S. Laderman, Appl. Phys. Lett. **55**, 595 (1989).
3. M. Migliuolo, A.K. Stamper, D.W. Greve, and T.E. Schlesinger, Appl. Lett. **54**, 859 (1989).
4. M. Migliuolo, R.M. Belan, and J.A. Brewer, Appl. Phys. Lett. **56**, 2572 (1990).
5. P.H. Ballentine, A.M. Kadin, and D.S. Mallory, IEEE Trans. Magn. **27**, 997 (1991).
6. R.V. Stuart, *Vacuum Technology, Thin Film, and Sputtering: An Introduction* (Academic Press, New York, 1983).
7. M. Ohring, *The Material Science of Thin Films* (Academic Press Inc., London, 1992).
8. J.-H. Xu, G.-G. Zheng, A.M. Grishin, B.M. Moon, K.V. Rao, and J. Morland, Appl. Phys. Lett. **64**, 1874 (1994).
9. R.H. Hammond and R. Bormann, Physica C **162–164**, 703 (1989).