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〈 연구논문 〉

Preparation of $YBa_2Cu_3O_{7-y}$ Superconducting Thin Films by on-axis Sputtering

Jae Won Han, Jung Rae Park and Mu-yong Choi

Department of Physics, Sungkyunkwan University, Suwon 440-746, Korea
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on-axis 스퍼터링 방법에 의한 $YBa_2Cu_3O_{7-y}$ 초전도 박막 제조

한재원 · 박정래 · 최무용

성균관대학교 이과대학 물리학과
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Abstract — $YBa_2Cu_3O_{7-y}$ thin films have been prepared on MgO(100) substrates placed on-axis to the target by dc magnetron sputtering in a variety of oxygen/argon gas pressures with different substrate-target distances. We found that films with the *c*-axis perpendicular to the substrate deposited in an optimally high gas pressure with on-axis substrate-target configuration exhibit such good electrical and structural properties as those deposited with off-axis configuration do. Increasing the substrate-target distance was found to be effective in reducing the resputtering effect and enhancing superconductivity of films, but not so much as increasing the gas pressure was. We also found that high deposition rates may promote mixed *a*- and *c*-axis growth of YBCO films on MgO substrates. Dependences of the T_c, the ratio of resistances at 300 K and 100 K, and the X-ray diffraction pattern on the gas pressure and the substrate-target distance are described.

요 약 — 각기 다른 스퍼터링 기체 압력과 타겟-기판 사이 거리하에서 on-axis 스퍼터링 방법으로 MgO (100) 기판 위에 $YBa_2Cu_3O_{7-y}$ 초전도 박막을 제조하였다. 적정하게 높은 스퍼터링 기체 압력을 사용할 경우 on-axis 방법으로도 off-axis 방법으로 제조한 박막에 비해 전기적, 구조적으로 우수한 양질의 박막을 *c*축으로 성장시킬 수 있었다. 스퍼터링 기체 압력 증가에 의한 resputtering 감소 효과가 타겟과 기판 사이의 거리 증가에 의한 resputtering 감소 효과보다 성장되는 박막의 초전도성 향상에 더욱 효과적이었다. 박막의 성장 속도가 빠를 경우 MgO 위에 YBCO 박막이 *c*축보다는 *a*축으로 성장하려는 경향을 보였다. 스퍼터링 기체 압력과 타겟-기판 사이의 거리가 성장되는 박막에 미치는 영향에 대해 임계온도, 100 K와 300 K에서의 저항비, X선 회절분석 등을 통하여 고찰해 본다.

1. Introduction

Since the discovery of the copper-oxide-based high-T_c superconductors, much effort has been made for the thin-film synthesis of the materials by sputtering. Reactive magnetron sputtering using a single target has been widely used primarily because of its simplicity. The main disadvantage of this technique is large composition deviation from that of the target due to the substrate resputtering by the high-energy particles such as negative oxygen ions [1]. The off-axis substrate-to-target configuration has been adopted widely to minimize the substrate resputtering [2, 3]. Placing the substrate off-axis results in stoichiometric depositions of high-T_c superconductors, but nevertheless has some disadvantages of non-uniform deposition over the substrate and very low growth rate [4, 5]. The resputtering effect is also expected to be reduced by sputtering in a high gas pressure or with a large substrate-target distance where high-energy particles are thermalized. Li *et al.* have fabricated $YBa_2Cu_3O_{7-y}$ (YBCO) thin films with zero resistance at 83 K by on-axis sputtering in a high gas pressure [6].

We have prepared YBCO thin films on MgO (100) single crystal substrates placed on-axis to the target by dc magnetron sputtering in a variety of oxygen/argon gas pressures with different substrate-target distances. The film with the *c*-axis perpendicular to the substrate prepared in the optimal condition showed zero resistance at 89 K. We found that films prepared in the optimally high pressure with the on-axis configuration exhibit such good electrical and structural properties as those prepared with the off-axis configuration do. We also found that a large substrate-target distance is indeed effective in reducing the resputtering effect and enhancing superconductivity of the films, but not so much as a high gas pressure is.

2. Experiments

YBCO thin films were prepared by dc planar-magnetron sputtering using a stoichiometric target. The YBCO target of 50 mm diameter was fabricated by sintering the adequate mixture of Y_2O_3, $BaCO_3$, and CuO powders. MgO(100) single-crystal substrates were placed on-axis to the target. The substrate-target distances were 35, 50 and 70 mm. During deposition the substrates were heated to 670℃ and the partial-pressure ratio of O_2 and Ar was kept to be 1 : 5. The total pressure of O_2/Ar gas ranged between 200 mtorr and 800 mtorr. The films were deposited for 3 h with the bias voltage on the target of 100 V (500 mA). The film thickness was 2000~2700Å. After deposition the films were cooled to 450℃ and held at this temperature for about 30 min in 20 torr of O_2. We used the same deposition parameters except the total pressure and the substrate-target distance that we found to be optimal for off-axis depositions in the same sputtering system.

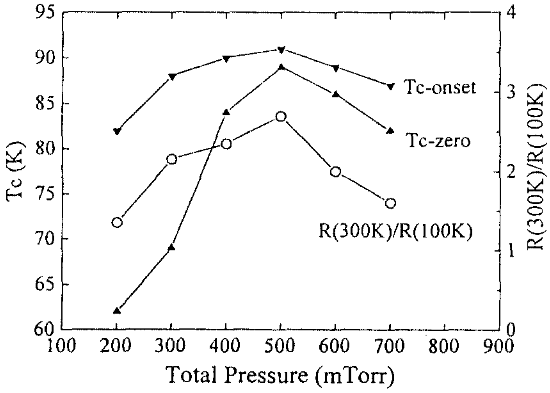

Fig. 1. Total pressure dependences of $T_{c\text{-}onset}$, $T_{c\text{-}zero}$ and R(300 K)/R(100 K) of $YBa_2Cu_3O_{7-y}$ films grown with the substrate-target distance of 50 mm.

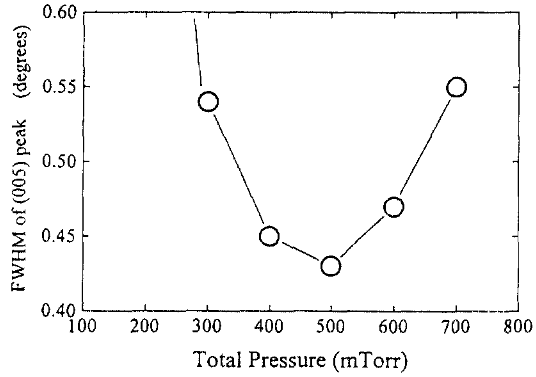

Fig. 2. FWHM of (005) peak as a function of the total pressure for YBCO films grown with the substrate-target distance of 50 mm.

The film growth direction and quality was characterized by X-ray diffraction (XRD) measurements. The superconducting transition temperatures were determined by resistance measurements with four probe configuration.

3. Results and Discussion

Fig. 1 shows the total-pressure dependences of the superconducting transition onset temperature ($T_{c\text{-}onset}$), the zero-resistance temperature ($T_{c\text{-}zero}$), and

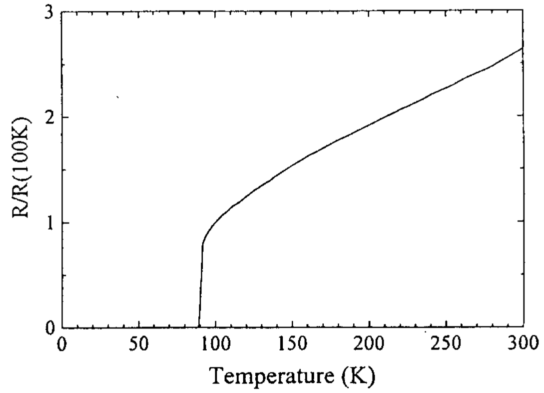

Fig. 3. Normalized resistance versus temperature of the YBCO film deposited under the pressure of 500 mtorr with the substrate-target distance of 50 mm.

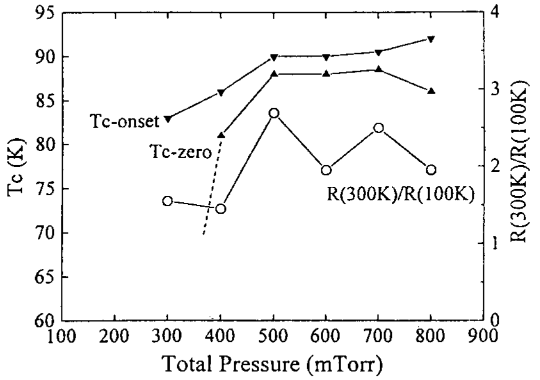

Fig. 5. Total pressure dependences of $T_{c\text{-}onset}$, $T_{c\text{-}zero}$ and R(300 K)/R(100 K) of YBCO films deposited with the substrate-target distance of 35 mm.

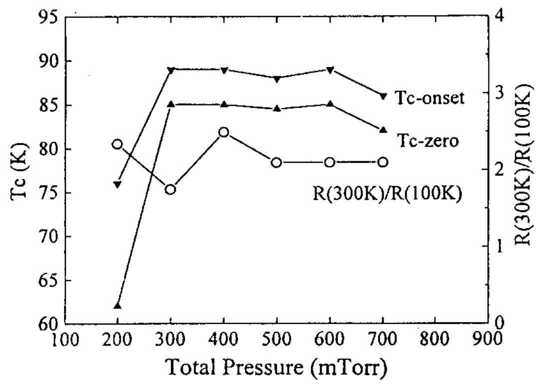

Fig. 4. Total pressure dependences of $T_{c\text{-}onset}$, $T_{c\text{-}zero}$ and R(300 K)/R(100 K) of YBCO films deposited with the substrate-target distance of 70 mm.

the ratio of resistances (RR) at 300 K and 100 K of YBCO films prepared with the substrate-target distance of 50 mm. The films were observed to have XRD patterns with only very strong (00*l*) peaks showing highly oriented growth of the *c*-axis perpendicular to the substrate. With an increase in the pressure to 500 mtorr, T_c and RR of the films increase and the superconducting transition width decreases. This is believed to be accounted for by progressive reduction of the resputtering effect in increased gas pressures. However, when the pressure increases above 500 mtorr, the pressure dependences of T_c, ΔT_c and RR change to the opposite. This implies that raising the pressure above the optimal value degrades superconductivity of the film. Similar behavior was observed for the structural properties. Fig. 2 shows the full width at half maximum (FWHM) of (005) peak as a function of the pressure obtained from XRD patterns of the films. The FWHM has the smallest value for 500 mtorr, implying that the film grown at 500 mtorr, which shows the highest T_c has the largest crystalline coherence in the growth direction. The *c*-axis lattice parameter of the film grown at 500 mtorr is as small as 11.72Å.

In Fig. 3 is shown the temperature dependence of the resistance normalized at 100 K for the film grown at 500 mtorr. The film has $T_{c\text{-}zero}=89$ K, ΔT_c (defined as 10% and 90% of the normal state resistance above the transition) ≤ 1 K, and RR$=$2.65. The best film deposited with the off-axis configuration in the same sputtering system was obtained in the total pressure of 300 mtorr and has $T_{c\text{-}zero}=88$ K, $\Delta T_c=1$ K, and RR$=$2.55 [7]. This implies that the on-axis sputtering can avoid effectively the substrate resputtering by negative ions in a high pressure and may produce such a good superconducting film as the off-axis technique does.

The observed degradation of the superconducting properties for pressures above 500 mtorr

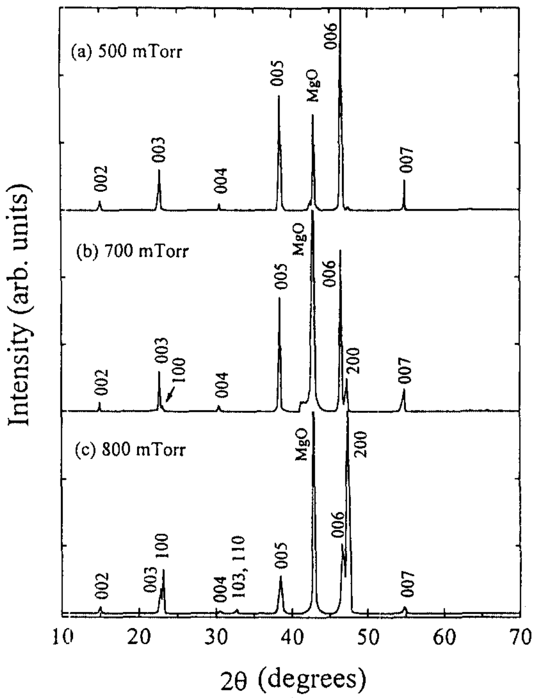

Fig. 6. X-ray diffraction patterns of YBCO films grown with the substrate-target distance of 35 mm under different pressures: (a) 500 mtorr, (b) 700 mtorr, (c) 800 mtorr. The current applied to the target during deposition was 500 mA. Film growth rates were (a) 0.21Å/s, (b) 0.23Å/s and (c) 0.25Å/s.

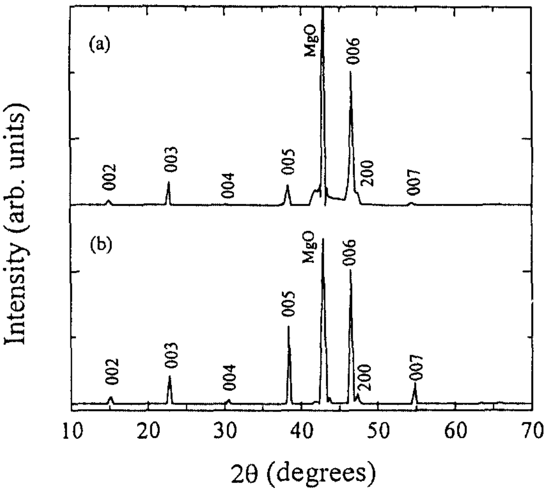

Fig. 7. X-ray diffraction patterns of YBCO films deposited with a reduced sputtering current (I) or an elevated substrate temperature (T_s): (a) film deposited with I=300 mA at T_s=670 ℃, (b) film deposited with I=500 mA at T_s=750 ℃. The substrate-target distance was 35 mm and the total pressure during deposition was 800 mtorr.

may come from unnecessary thermalization of Y, Ba and Cu metal atoms arriving at the substrate from the target. According to detailed studies of the reaction kinetics between metal atoms and oxidizing gases by Tang *et al.* [8] the reaction cross sections for oxide formation are enhanced by the high kinetic energy of neutral metallic atoms. A high gas pressure which is introduced to thermalize the negative oxygen ions lowers the kinetic energy of the metallic atoms as well as of the negative oxygen ions.

The resputtering effects by negative ions can also be reduced by increasing the substrate-target distance instead of increasing the gas pressure. Fig. 4 shows the T_c and RR versus the total pressure for films prepared with an enhanced substrate-target distance of 70 mm. Note that the film deposited in the relatively low pressure of 300 mtorr has the $T_{c\text{-}zero}$ as high as 85 K. Note also that the highest T_c and RR for the distance of 70 mm are 85 K and 2.45, respectively, lower than those for 50 mm. This implies that increasing the substrate-target distance does reduce the resputtering of negative ions, but is not so effective in enhancing film quality as increasing the pressure is. We do not have any explanation for the difference at the moment. Further investigations are necessary to give an answer to this difference.

On Fig. 5 are displayed the T_c and RR as functions of the total pressure for films deposited with a reduced substrate-target distance to 35 mm. XRD patterns of the films are shown in Fig. 6. Films deposited under pressures between 500 mtorr and 700 mtorr show high $T_{c\text{-}zero}$'s (88~88.5 K). However XRD patterns of the films show (n00) peaks as well as (00*l*) peaks indicating mixed growth of the *a*- and the *c*-axis perpendicular to the substrate. As can be seen in Fig. 6, the intensity of the (200) peak increases with an increase in the pressure above 500 mtorr. With an increase in the pressure from 500 mtorr to 800 mtorr, the film growth rate was found to increase from 0.21Å/s to 0.25Å/s. In order to find that the mixed growth comes from the enhanced growth rate, we have fabricated YBCO films with a reduced growth rate of 0.19Å/s by decreasing the current applied to the target to 300 mA instead of decreasing the gas pressure. The total gas pressure was 800 mtorr. Fig. 7(a) shows the XRD pattern of the film. The peak intensities of (n00) diffractions in Fig. 7(a) are lower by approximately an order of magnitude than those in Fig. 6(c). As can be seen in Fig. 7(b), the *a*-axis growth can be suppressed also by elevating the substrate temperature.

4. Conclusion

We found that the YBCO film grown by sputtering in a high gas pressure with the on-axis configuration exhibits such good electrical and structural properties as those grown with the off-axis configuration. Increasing the substrate-target distance was found to suppress the substrate resputtering and enhance the superconductivity of films, but not so effectively as increasing the gas pressure was. We also found that high deposition rates may result in partial *a*-axis growth of YBCO films on MgO substrates.

Acknowledgements

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