Journal of the Korean Vacuum Society
Vol. 3, No. 1, March 1994, pp. 117-121

〈연구논문〉

The Effect of Substrate Surface Treatment by Ion Bombardment on Y-Ba-Cu-O Thin Film Growth

Kyung Joong Kim, Keunseup Park, Yong Ki Park and Dae Won Moon

Korea Research Institute of Standards and Science
P.O. Box 102, Yuseong, Taejon 305-606, Republic of Korea

(Received February 14, 1994)

이온충돌에 의한 기판 표면처리가 Y-Ba-Cu-O 박막의 성장에 미치는 영향

김경중 · 박근섭 · 박용기 · 문대원

한국표준과학연구원

(1994년 2월 14일 접수)

Abstract – When the surface of $SrTiO_3$ (100) single crystal was etched by 3 keV Ar^+ ion milling, it was observed through XPS and SEM measurements that the oxidation states of elements on the surface were reduced and the surface was roughened. The surface of $SrTiO_3$ etched by 3 keV O_2^+ ion milling, however, remained smooth and the chemical states were not changed. $YBa_2Cu_3O_x$ thin film deposited by off-axis rf sputtering on $SrTiO_3$ cleaned by O_2^+ ion bombardment has higher $T_{c,zero}$ and J_c at 77 K than that on the substrate sputtered by Ar^+ ions. This report suggests that the ion milling condition must be carelfully selected for substrate cleaning and lithographic processings for YBCO superconductor thin film growth and microelectronic applications.

요 약 – $SrTiO_3$(100) 단결정을 3 keV 아르곤 이온으로 에칭하면 표면 원소의 산화 상태가 환원되고 표면의 거칠기가 증가하는 것이 XPS와 SEM으로 측정되었다. 그러나 3 keV의 산소이온으로 에칭하면 표면 원소의 화학적 상태도 변하지 않고 표면도 평탄한 상태로 계속 유지된다. 산소 이온에 의하여 에칭된 $SrTiO_3$ 기판상에 off-axis rf 스퍼트링 방법으로성장된 $YBa_2Cu_3O_x$ 박막이 아르곤 이온에 의하여 에칭된 $SrTiO_3$ 기판상에 성장된 $YBa_2Cu_3O_x$ 박막보다 높은 $T_{c,zero}$ and J_c를 보여주었다. 이 논문은 YBCO 초전도 박막의 성장과 전자공학적 활용을 위한 리토그라피 공정에서 이온밀링 공정의 조건은 매우 주의하여 선택되어야 함을 보여준다.

1. Introduction

The quality of thin films grown on substrates is generally affected by how the substrate surface is treated. One of the widely used techniques for substrate treatment is ion beam bombardment. It has been reported that the properties of high T_c superconductor thin films deposited on substrates are changed by etching the surfaces of substrates by ion milling before deposition [1-4]. However, it has been generally recognized that ion beam bombardment changes the surface chemical composition [5, 6].

Especially for oxide surfaces, the oxygen atoms were sputtered more rapidly than heavy metals so that even the oxidation states of metallic elements changes with Ar^+ ion bombardment [7].

In addition to this preferential sputtering problem, the surface topography generally changes with ion milling. The surface topographic development due to ion bombardment has been studied extensively to understand the basic mechanism of topographic development and its dependence on various ion beam parameters such as ion energy, ion species, ion incidence angle, ion current density, and etc. [8-10] The control of atomic-scale surface roughness becomes more and more important in microelectronics, as the thickness of thin films approaches several atomic layers.

In this report, it was carefully studied how the surface of a $SrTiO_3$(100) single crystal substrate which is widely used as substrates for YBCO thin film growth is affected by ion beam bombardment under various conditions. The change of chemical states of the constituent elements on the substrate surface and surface topographic development were studied by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM), respectively. The effect of different ion milling conditions on $T_{c,zero}$ and J_c of Y-Ba-Cu-O (YBCO) thin films which were deposited on $SrTiO_3$ (100) single crystal substrates were investigated.

2. Experimentals

$SrTiO_3$ single crystal substrates with mechanically polished (100) surfaces were etched by 3 keV Ar^+ and O_2^+ ion milling using a cold cathode ion gun (VG Microtech, Model AG-10). The chemical states of elements on the surface of $SrTiO_3$ after ion bombardment were observed in the same chamber by an XPS system (Vacuum Science Workshop, HAC 5000).

Al K_α radiation (1486.6 eV) was used as the X-ray source. The base pressure of the system was lower than 3×10^{-10} torr, but the pressure during ion milling was around 4×10^{-6} torr. The milling conditions of the substrates are shown in Table 1. XPS and SEM were taken after the substrates were bombarded with 3 keV Ar^+ and O_2^+ ion beams upto 5-9 hours until saturation. The ion beam current density was about 25 $\mu A/cm^2$.

YBCO superconductor was deposited on ion milled substrates by *in-situ* off-axis rf sputtering [11, 12]. A 2 inch diameter target with the composition of $Y_1Ba_1Cu_{2.5}O_x$ was used. The deposition was carried out with rf power of 50 W and at the substrate temperature of 760℃. The total pressure of Ar (50 %) and O_2 (50%) gas mixture was 1×10^{-2} torr during deposition. The deposition rate was about 1.6 nm/min. After deposition, samples were cooled in the sputtering chamber to 480℃ and maintained at about 1 atmosphere of O_2 for 1-2 hours after deposition. The resistivity of samples was measured by the standard 4-probe method and J_c was determined from the I-V curve measured with patterned thin film of which the line width was about 100 μm.

3. Results and Discussions

Fig. 1 shows the XPS spectrum of Ti 2p of the $SrTiO_3$ after bombardment by Ar^+ and O_2^+ ion beam upto saturation. Ti was reduced by bombardment of Ar^+ ion beams. The degree of reduction of Ti by normal incident Ar^+ ion beam was higher than that by 600 glancing incident Ar^+ ion beam. The change of chemical states due to Ar^+ ion bombardment could be explained by former results that the oxygen atoms in metal oxide are preferentially sputtered than metal atoms [7, 13]. The incidence angle dependence of Ti reduction by Ar^+ ion bombardment shows that the oxygen atoms preferentially sputtered more efficiently by the normal incident Ar^+ ion beams than by the 60° glancing incident Ar^+ beam.

With O_2^+ ion beams, Ti was not reduced by O_2^+ ion beams irrespective of the incidence angle. In O_2^+ ion bombardment, preferentially sputtered oxygen atoms might be compensated by trapped primary oxygen ions. It can be expected that the balance between the preferentially sputtered oxygen atoms and the trapped primary oxygen ions is dependent on the incidence angle from the well understood angle dependence of sputtering yields and trapping probability of primary oxygen ions [14]. It has been generally observed that the sputtering yield increases as the ion incidence angle increases from the surface normal. Calculations for 1.5 keV O^+ ion bombardment onto SrTiO3 with the TRIM code [15] showed that the trapping probability of primary O^+ ions decreased as the ion incidence angle increased from the surface normal, as expec-

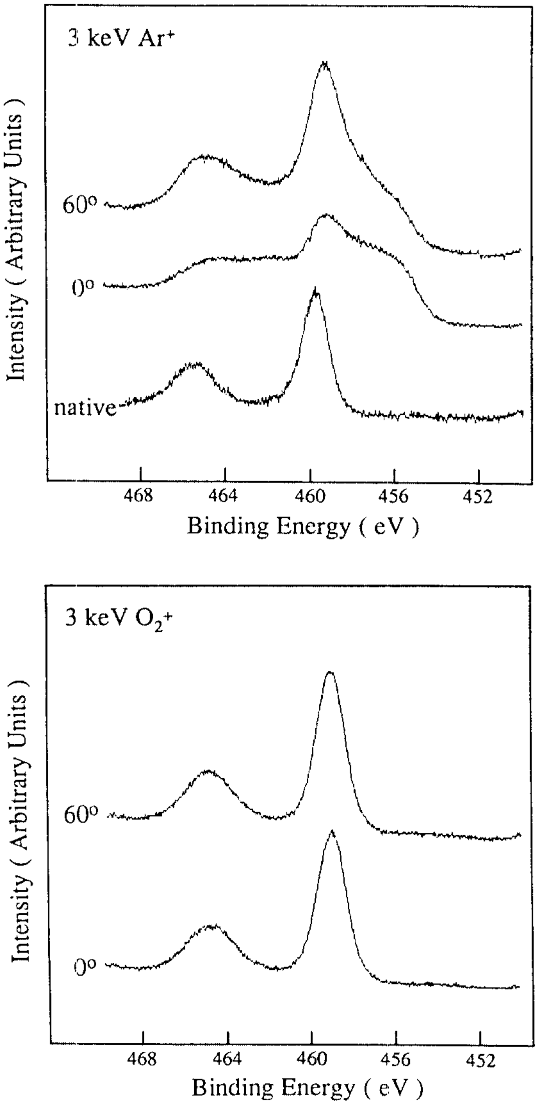

Fig. 1. XPS Ti 2p peaks of $SrTiO_3$ after. (a) native: no ion milling, 0°: milling by normal incident Ar^+ ion beams, 60°: milling by glancing incident (60°) Ar^+ ion beams, (b) 0°: milling by normal incident O_2^+ ion beams, 60°: milling by glancing incident (60°) Ar^+ ion beams.

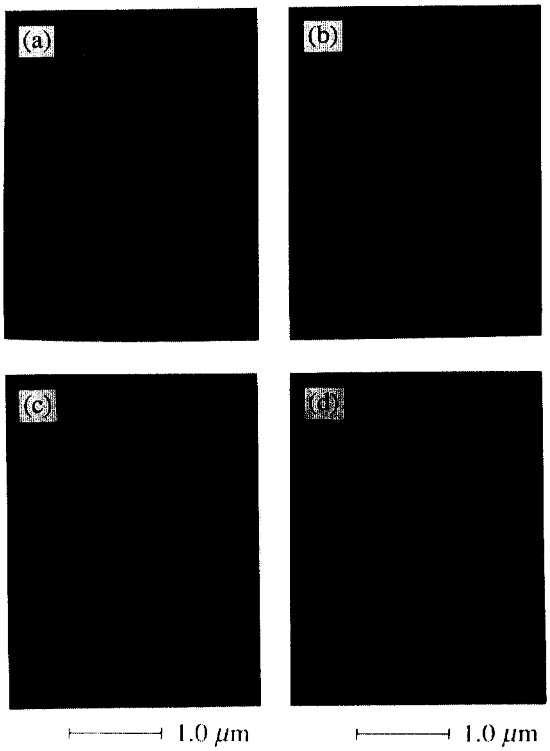

Fig. 2. The surface topographies of $SrTiO_3$ observed by SEM after milling by (a) normal incident Ar^+ ion beam, (b) glancing incident (60°) Ar^+ ion beam, (c) normal incident O_2^+ ion beam, and (d) glancing incident (60°) O_2^+ ion beam.

ted. As shown in Fig. 1(b), $SrTiO_3$ was not reduced by 3 keV O_2^+ ion bombardment both for the incidence angles of the surface normal and 60°. This indicates that the oxygen primary ion incidence angle for balancing oxygen stoichiometry is higher than 60° from the surface normal. For Ta_2O_5, it was recently reported that the angle is 30° from the surface normal [16].

To study the effect of the reduction by bombardment of Ar^+ ion beams on the development of surface topography, SEM images were taken after ion milling. As shown in Fig. 2(a) and (b), in the case of ion milling by Ar^+ ion beams, the surface topography developed significantly. There were fine wrinkles on the surface after normal incident Ar^+ ion bombardment, while the surface became rough with larger wrinkles after 60° glancing incident Ar^+ ion bombardment. However, surface topographic development was hardly observed after the bombardment of O_2^+ ion beams, as shown in Fig. 2(c) and (d).

Even though much work has been done to understand the topographic development of surfaces due to energetic ion beam bombardment [8, 17, 18], it is still difficult to fully understand all the complicated features. However, recent works suggested that surface topographic development of Si and metal surfaces due to energetic oxygen ion beam bombardment could be caused by local inhomogeneity from incomplete oxidation [9, 19]. According to the report, the surface topography was not developed at fully oxidized metal surface by bombardment of normal incident O_2^+ ion beams, but the surface was roughened significantly with increasing the incidence angle of ion beams because of partial oxidation [19].

In this context, the development of surface topography of oxide material by milling with Ar^+ ion beams can be understood. For inhomogeneous oxide surfaces of $SrTiO_3$ due to partial reduction by Ar^+ ion bombardment, the difference in the sputtering yields of small islands of $SrTiO_3$ oxide phase and reduced suboxide phase could be a part of reasons for the initiation of the surface topographic development. However, the details of the incidence angle dependence of the developed surface roughness and the shape of surface topography due to Ar^+ ion beams could not be explained clearly. The surface of $SrTiO_3$ after 60° glancing incident Ar^+ ion beam bombardment was slightly reduced while the surface was severely reduced after normal incident Ar^+ ion beam bombardment as can be seen in Fig. 1(a). But the surface of $SrTiO_3$ after 60° glancing incident Ar^+ ion beam bombardment was rougher than that after normal incident Ar^+ ion beam bombardment. Details of surface roughening processes due to ion bombardment must be studied further. With O_2^+ ion bombardment, the oxide surface can keep its homogeneity as fully oxidized as can be seen from Fig. 1(b) and therefore no surface topographic development was observed at least in this SEM resolution, which is consistent with the former reports [9, 19].

The effects of $SrTiO_3$ substrate ion milling on YBCO thin film growth were studied. The ion milling conditions of the substrates and $T_{c,zero}$ and J_c at 77 K of YBCO thin films deposited on ion milled surfaces are shown in Table 1. Samples A and B were milled by Ar^+ ion and samples C and D were milled by O_2^+ ions with the energy of 3 keV for 5-9 hours. The incidence angle of ion beam was normal to the substrate surface for samples A and C and it was 60° from the surface normal for samples B and D. Fig. 3 shows the resistivity curve of thin films deposited on etched substrates on milling conditions shown in Table 1. Thin films which were deposited on substrates etched by Ar^+ ion beams have higher resistivity than those deposited on the substrates etched by O_2^+ ion beams. Also, as shown in Fig. 3 and Table 1, the latters have relatively higher $T_{c,zero}$ and J_c at 77 K than the formers. Regarding to the incidence angle of ion beams, the normal

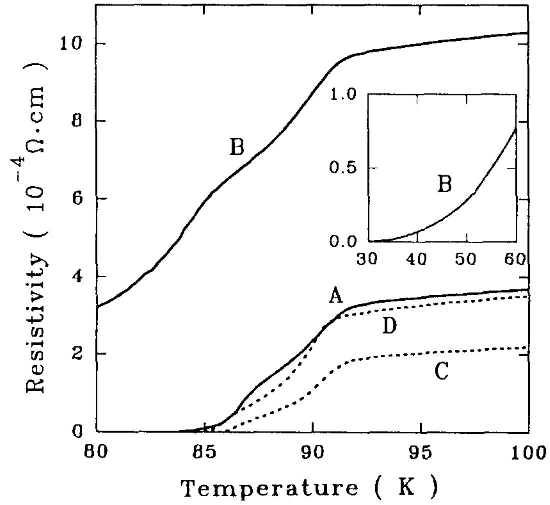

Fig. 3. The resistivity curve of thin films deposited on etched substrates on milling conditions shown in Table 1.

Table 1. $T_{c,zero}$ and J_c at 77 K of YBCO thin films deposited by *in-situ* off-axis rf sputtering on $SrTiO_3$ (100) etched by 3 keV Ar^+ or O_2^+ ion beam

Sample	Milling condition	$T_{c,zero}$ (K)	J_c at 77 K (A/cm^2)
A	Ar^+ ion beam, norml incident	83	8.8×10^3
B	Ar^+ ion beam, 60° incident	29.5	–
C	O_2^+ ion beam, norml incident	85.5	4.5×10^5
D	O_2^+ ion beam, 60° incident	84.5	1.67×10^5

incident beams gave better properties of deposited films than the glancing incident beams. The above all observations of XPS, SEM, and the eletrical properties show that the homogeneous and fully oxidized $SrTiO_3$ surface with smooth topograpgy improves the electrical properties of YBCO superconcuctor thin films.

4. Conclusions

It was observed by XPS and SEM that the surface of $SrTiO_3$ (100) single crystal substrate which is widely used as substrates for YBCO thin film growth is reduced and roughened by Ar^+ ion beam bombardment beam. But it stayed oxidized and smooth after O_2^+ ion beam bombardment. The effect of different ion milling conditions on $T_{c,zero}$ and J_c of Y-Ba-Cu-O (YBCO) thin films which were deposited on $SrTiO_3$ (100) single crystal substrates were investigated. The smooth and oxidized $SrTiO_3$ substrates gave better electrical properties. These results suggest that the ion milling conditions such as ion beam species, ion incidence anlges must be carefully selected for substrate cleaning and lithographic processings for YBCO superconductor thin film growth and microelectronic applications. For $SrTiO_3$ substrates, normal incident oxygen ion beams are recommended rather than argon ion beams in ion beam milling processes for oxidized and homogeneous surface stoichiometry and smooth surface topography.

Acknowledgements

This work was financially supported by the Ministry of Science and Technology, Republic of Korea. One of authors (D.W. Moon) appreciates the financial support from Center for Molecular Science, Korea.

References

1. B. H. Moeckly, S. E. Russek, D. K. Lathrop, R. A. Buhrman, J. Li and J. W. Mayer, *Appl. Phys. Lett.* **57**, 1687 (1990).
2. M. S. Dilorio, S. Yoshizumi, M. Maung, K.-Y. Yang, J. Zhang and N. Q. Fan, *Nature* **354**, 513 (1991).
3. J. Gao, W. A. M. Aarnink, G. J. Gerritsma and H. Rogalla, *Physica* **C171**, 126 (1990).
4. R. H. Ono, J. A. Beall, M. W. Cromar, T. E. Harvey, M. E. Johansson, C. D. Reintsema and D. A. Rudman, *Appl. Phys. Lett.* **59**, 1126 (1991).
5. K. Wittmaack, *Vacuum* **34**, 119 (1984).
6. S. Hofmann, Practical Surface Analysis 2nd ed., Ed. D.Briggs and M. P. Seah (John Wiley & Sons, New York, 1990) Ch. 4.
7. J. B. Malherbe, S. Hofmann and J. M. Sanz, *Appl. Surf. Sci.* **27**, 355 (1986).
8. G. Carter, B. Navinsek and J. L. Whitton, Sputtering by Particle Bombardment II, Ed. R. Behrish (Springer, Berlin, 1984) Ch. 6.
9. K. Wittmaak, *J. Vac. Sci. Technol.* **A8**, 2246 (1990).
10. J. Fine, P. A. Lindfors, M. E. Gorman, R. L. Gerlach, D. F. Mitchell and G. P. Chambers, *J. Vac. Sci. Technol.* **A3**, 1413(1985).
11. E. J. Cukauskas, L. H. Allen, R. T. Holm and G. K. Sherrill, *Appl. Phys. Lett.* **60**, 389 (1992).
12. C. B. Eom, J. Z. Sun, K. Yamamoto, A. F. Marshall, K. E. Luther and T. H. Geballe, *Appl. Phys. Lett.* **55**, 595 (1989).
13. S. Hofmann and J. M. Sanz, *J. Trace and Microprobe Techniques* **1**, 213 (1982-1983).
14. H. H. Andersen and H. L. Bay, Sputtering by Particle Bombardment I, Ed. R. Behrisch (Springer, Berlin, 1981) Ch. 4.
15. J. P. Biersack and L. G. Haggmark, *Nucl. Instrum. Methods* **174**, 257 (1980).
16. D. W. Moon and K. J. Kim, *Appl. Phys. Lett.* **62**, 3094 (1993).
17. G. W. Lewis, M. J. Nobes, G. Carter and J. L. Witton, *Nucl. Instrum. Methods* **170**, 363 (1980).
18. R. M. Bradley and J. M. E. Harper, *J. Vac. Sci. Technol.* **A6**, 76 (1988).
19. K. J. Kim and D. W. Moon, *Appl. Phys. Lett.* **60**, 1178 (1992).