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COMPOSITION OF SUPERCONDUCTING YBCO THIN FILMS WITH RF REACTIVE SPUTTERING CONDITIONS

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ABSTRACT

Superconducting YBaCuO thin films were deposited on MgO (100) single crystal substrate by rf reactive sputtering method. Sputtering target was prepared by mixing the original powders of Y_2O_3, $BaCO_3$, and CuO at 830℃, and its composition was $YBa_2Cu_{3.3}O_X$ adding the excess CuO to compensate for the loss of Cu in the deposition process. The sputtering conditions for a high quality of YBCO thin film were: substrate temperature of 130 ℃; gas pressure of 10 mTorr; gas mixture (O_2:Ar=10:90); distance of 2.5 inch; and rf power density of 4.87 W/㎠. The deposition rate was 2.4~2.6 nm/min. From the RBS results, it was found that Cu and Ba contents in thin films decreased with the increase of substrate temperature. The increase of gas pressure resulted in significant deficiency of Ba elements.

INTRODUCTION

After the discovery of high-T_c superconductor above 90℃[1], thin film (d<2㎛) of this material has been important from the stand-point of its application to superconducting electronics such as Josepson junction, interconnections and other devices. Most researchers have studied about superconducting thin film using the various deposition techniques[2]. Among many deposition methods, it is well known that the sputtering deposition system is most commonly used and can easily achieve the stoichiometric composition for the complex compounds. Furthermore, the advantages of the sputtering technique from a single target are a well defined deposition rate and reproducible composition over a relatively large deposition area. The thin films were prepared by rf diode reactive sputtering from a YBaCuO single target on a MgO substrate. Deposition conditions affect significantly the physical and electrical properties of superconducting thin films as well as the controlling manner of deposition parameters is also important for these properties. In order to transfer from non-superconducting phase of as-deposited film to superconducting phase, the films deal with the heat treatment at high temperature. But the high temperature annealing leads to the formation of cracks in the films and a deterioration of the YBaCuO film-substrate interface[3]. Therefore, the annealing method for the films should be treated carefully, and the heat treatment as a function of substrate temperature and post-deposition annealing method was estimated. The primary goal of this paper is to develop the optimum preparation condition for obtaining high quality with stoichiometric composition of YBaCuO film. The variation of film composition and thickness was measured by the sputtering conditions: radial position of substrate, gas pressure, target-substrate distance, and substrate temperature. The composition of YBaCuO thin film was investigated by RBS.

EXPERIMENTAL PROCEDURE

YBaCuO thin films were grown on MgO (100) single crystal substrate using the rf diode sputtering method. A disk-type sputtering target was prepared by mixing the stoichiometric amount of powders Y_2O_3, $BaCO_3$ and CuO at 930℃ for 12 hours. It was recrushed and fired again for 24 hours. After air quenching and regrinding the powder was pressed into a pellet with 2.25 inch in diameter and 0.25 inch in thickness by mechanical press at the pressure of 80000 pounds. The pellet was sintered again at 930℃ for 18 hours and cooled slowly in the furnace. The single target composition obtained by furnace cooling was close to $Y1Ba_2Cu_{3.3}O_X$ orthorhombic phase. After YBaCuO deposition on MgO substrate, the pure O_2 gas was subsequently introduced into the chamber and finally the thin films were cooled slowly in the chamber for 3 hours. The substrate temperature of 130℃ was measured as the temperature of the copper substrate holder. The post-annealing treatment under oxygen pressure over 100 Torr was applied to the films at 500~650℃. The deposited YBaCuO thin films were black and had a smooth mirror-like surface. Typical sputtering conditions were listed in Table 1.

Table 1. Sputtering Conditions

Base Pressure	1×10^{-6}Torr
Gas pressure	10~30 mTorr
Mixing gas(O_2 : Ar)	10 : 99
rf power density	4.87 W㎠
Target-sub distance	1.8~3.6inch
Substrate temp.	130℃

RESULT AND DISCUSSION

Radial angle effect

The compositions of YBaCuO thin films was estimated with the changes of radial angle, that is, the distance from the substrate holder center as shown in Figure 1. The sputtering gas was a 9:1 mixture of Ar and O_2 at the pressure of 10 mTorr. The forward power was 125 W, and the distance of target -substrate holder was 2.5 inch. The composition and thickness of the deposited film as a function of radial angle is shown in Figure 2. Hence, the film which was located directly under the target was completely resputtered as well as the substrate holder also eroded. As the resputtering effect decreases gradually beyond the edge of the target, film composition approaches that of the bulk target.

The desired Y:Ba:Cu ratio of 1:2:3 was obtained at the radial distance between 2.5

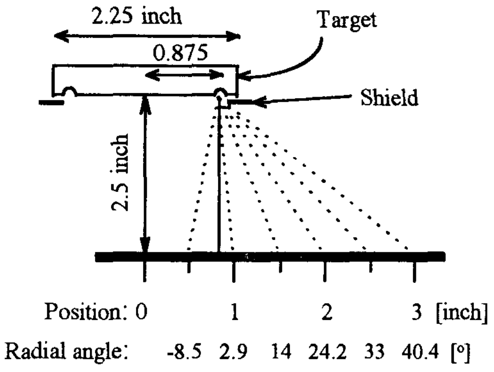

Fig. 1. Radial angle and substrate position from holder center under target.

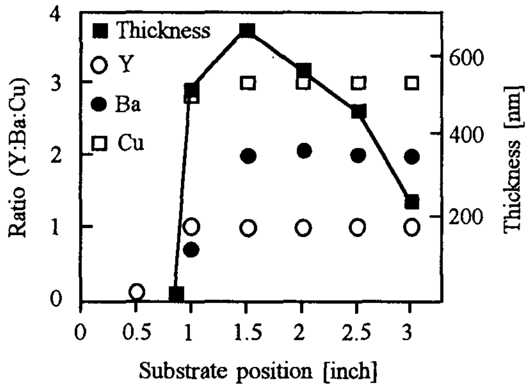

Fig. 2. Film composition and thickness as a function of radial postion

and 3.0 inch. Film loss during sputtering from a Y_2O_3 target has been reported by Hanak[4], while Shintani[5] observed the intense substrate heat and film loss in the case of $BaTiO_3$ due to a high yield of energetic sputtered neutrals. The same phenomenon may also be applicable to YBaCuO resputtering. Oxygen anion can also cause resputtering. O^- and O^{-2} anions have been known to form during sputtering and then accelerated to the substrate across the applied electric field. Thus, the resputtering effect may be caused by the energetic neutral particle bombardment and negative ion bombardment. The erosion phenomenon occurred in a sharply defined region which closely matched the size and shape of the ground shield on target. The substrate temperature was about 130℃. The substrate heating can be caused by the following sources of energy: (1) radiation from the plasma, (2) kinetic energy of argon ions, electrons and gaseous neutrals, (3) release of latent heat by atoms deposited on the substrate, and (4) kinetic energy of atoms deposited on the substrate. It was also observed that the deposition rate depended strongly on the radial angle. The film thickness was decreased generally with the increase of radial angle, as the angle distance exceeded 1.5 inch.

GAS PRESSURE EFFECT

Figure 3 shows the variation of composition and thickness on the deposited YBaCuO films as a function of gas pressure. The film deposition conditions were: radial distance of 2.0 inch; target-substrate distance of 2.5 inch; forward power of 125 W; and substrate temperature of 130℃. The increase of the total gas pressure resulted in significant deficiency of Ba elements. As shown in figure, Ba/Y ratio was 1.2 at the gas pressure above 20 mTorr. The deposition rate of deposited film at 20 mTorr of several gas pressures was the highest.

Target-substrate distance effect

The film composition and thickness as a function of distance between target and substrate are shown in Figure 4 under the following deposition condition: radial position of 2.0 inch; gas pressure of 10mTorr; forward

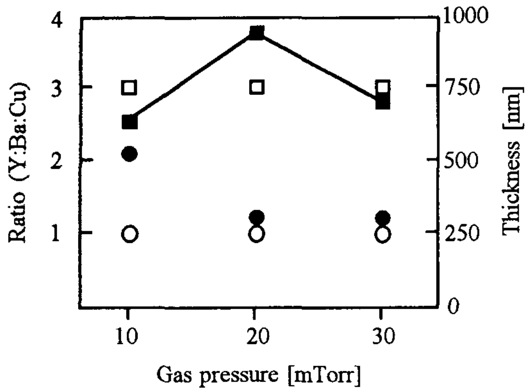

Fig. 3. Film compostion and thickness as a function of gas pressure

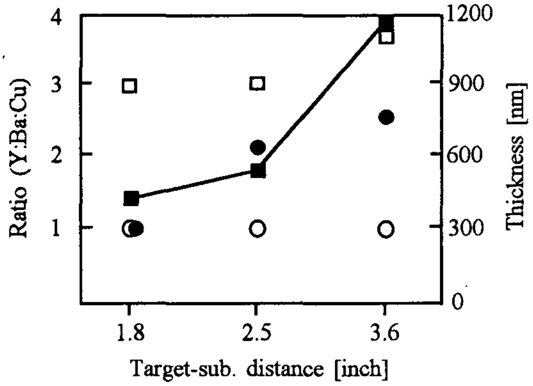

Fig. 4. Film composition and thickness as a function of target-sub. distance

power of 125W; and substrate temperature of 130℃. It was observed that the ratio of Ba/Y was 1 for the distance of 1.8 inch, and that of Ba/Y increased to 2.5 with a increasing target distance to 3.6 inches. Ba deficiency in the films was reported by Gilbert et al[6]. They mentioned that it was generated by the preferential resputtering of Ba from the film or by the substoichiometric sputtering due to formation of Ba^+ ions. These ions were believed to be recaptured by the cathode causing the film to be Ba deficient. In addition, an evaporation of the Ba atoms is also probable at the substrate temperature of 130℃.

Substrate temperature effect

Figure 5 shows the film composition and thickness with the increase of substrate temperature from 500 to 650℃. The sputtering conditions were: radial distance of 2 inch; gas pressure of 35 mTorr; forward power of 100 W; and target-substrate distance of 2.5 inch. The resistances of as-deposited films were measured in the order of few ohms. It was found that Cu and Ba contents in the superconducting films decreased with the increase of substrate temperature. The deposi-

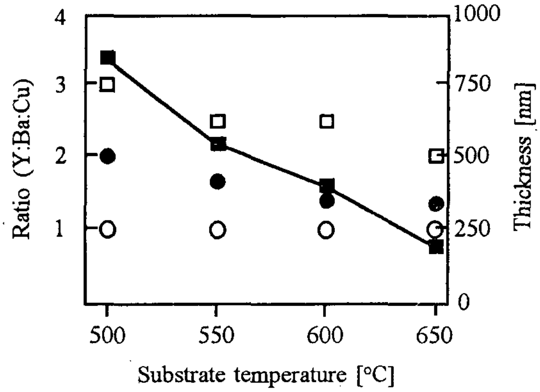

Fig. .5 Film compostion and thickness as a function of substrate temp.

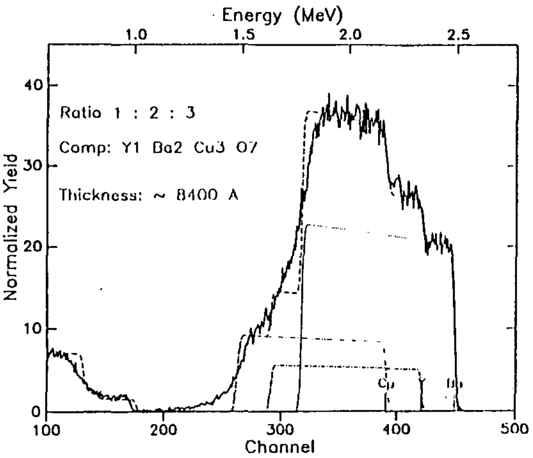

Fig. 6. Typical RBS spectrum of stoichiometric film (Y : Ba : Cu=1 : 2 : 3)

tion rate decreased with a rise of substrate temperature from 500 to 650 ℃. It seemed that the sticking coefficient of deposited particles on substrate surface was inversely proportional to the substrate temperature. As shown in Figure 5, the film prepared at the substrate temperature of 500 ℃ showed stoichiometric composition, while the films deposited from 550 to 650 ℃ were non-stoichiometric phase. Typical RBS data of the stoichiometric film shows in Figure 6.

CONCLUSIONS

The stoichiometric $Y_1Ba_2Cu_3O_7$-X thin film was successfully deposited on MgO substrate from a $Y_1Ba_2Cu_{3.3}$OX target by rf sputtering method under the following conditions: substrate temperature of 130℃, gas pressure of 10 mTorr, radial position of 2.5 inch, target power density of 4.87 W/㎠, and deposition time of 4 hrs.

The deposition rate depended strongly on the radial angle. The film thickness was decreased generally with the increase of radial angle at the angle distance above 1.5 inch. The desired Y:Ba:Cu ratio of 1:2:3 was obtained at the radial distance between 2.5 and 3.0 inch. In gas pressure effect, the increase of the total gas pressure resulted in significant deficiency of Ba elements. In target-substrate distance effect, the ratio of Ba/Y was 1 for the distance of 1.8 inch, but Ba deficiency in the films with the increasing distance was observed. The film prepared at the substrate temperature of 500℃ showed stoichiometric composition.

REFERENCES

1. C. W. Chu et al., Phys. Rev. Lett. 58 (1987) 908
2. T. Aida et al., Jpn. J. Appl. Phys. 26 (1987) L1489
3. T. Venkatesan et al., J. Appl. Phys. 63 (1988) 4591
4. J. J. Hanak et al., J. Vac. Sci. Tech. 13 (1976) 406
5. Y. Shintani et al., Jpn. J. Appl. Phys. 14 (1975) 1875
6. L. R. Gilbert et al., J. Vac. Sci. Tech. 17 (1980) 389