Resputtering-induced chemical inhomogeneity during the growth of high T_c superconductor thin film

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Abstract. High T_c films belonging to Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O and Tl–Ba–Ca–Cu–O systems have been fabricated by reactive sputtering of single targets in a planar magnetron and Ar + O₂ sputtering atmosphere. Although it was possible to deposit films of correct composition, resputtering related composition variation was a problem. The key to obtaining correct chemistry was a proper control of the deposition parameters. The pressure and oxygen content of the sputtering gas were found to be the most critical parameters. Results of the variation of these parameters on the cation chemistry are presented in this paper. Results from Monte-Carlo simulation of the sputtering process are also presented showing that low pressure and oxygen content of the sputtering gas result in a higher yield of energetic reflected neutrals which can cause compositional variation in the film mainly due to preferential sputtering of the growing film. The effect was particularly noticeable directly underneath the target. The energetic particle bombardment can be controlled by using moderately high pressures and low oxygen concentration in the gas.

Keywords. High T_c superconductors; thin films; sputtering; Monte-Carlo simulation.

1. Introduction

Several thin film deposition techniques have been used to grow high T_c thin films including sputtering (Shah and Carcia 1987), electron beam evaporation (Ginley *et al* 1988), metallorganic chemical vapour deposition (MOCVD) (Yamane *et al* 1988), molecular beam epitaxy (MBE) (Kwo *et al* 1987), laser ablation (Johs *et al* 1989), etc. Perhaps the most extensively utilized technique is magnetron sputtering because a high deposition rate and large area coverage is possible with this method. The main disadvantage of magnetron sputtering is the difficulty in composition control especially if a single target is used. This could be due to resputtering of the film by energetic particle bombardment, preferential sputtering at the target surface and at the film surface, atmospheric reaction of the target upon exposure to air, etc. In this paper we present a detailed study of the effects of different sputtering parameters, target power, sputtering atmosphere, sputtering gas pressure, etc. on the composition uniformity of the films.

We also present results obtained from Monte-Carlo simulation of the sputtering process of high T_c ceramic oxides using TRIMSPUT program (Ziegler *et al* 1985). This enables us to understand the nature of impinging flux onto the substrate during sputtering and makes it possible to predict the end composition of the deposited film. Results of the simulation also allow us to vary the process parameters in order to obtain correct stoichiometry.

2. Experimental

Three different high T_c materials were studied which included Y–Ba–Cu–O (123), Bi–Sr–Ca–Cu–O (2212), and Ba–Ca–Cu–O (212). 212 is the precursor for Tl–Ba–Ca–

Cu–O films obtained by the thallination of these films. Targets were fabricated by pressing pre-reacted stoichiometric powders to obtain 7.6 cm diameter and 0.635 cm thick disks. The 212 target was fabricated from 1:1 mixture of $\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ and $\text{Ba}_2\text{CaCu}_2\text{O}_x$ powders. All sputtering experiments were carried out in a rf planar magnetron system. Typical base pressure in the system was 2×10^{-7} torr. A sputtering atmosphere of Ar + O₂ was used. Oxygen fraction in the sputtering gas was varied between 0 and 0.5. Sputtering pressure ranged between 3 and 25 mtorr. A low target power density of 5 W/cm² was used. The targets were sputter-etched for at least 6 h before the first film was deposited and after that they were sputter-cleaned for 30 min prior to the commencement of each deposition experiment. Target substrate separation ranged between 4 and 10 cm. Films, typically 1 μm thick, were deposited onto (100) MgO substrates placed on a water-cooled substrate platen. Some thinner, 200–300 Å thick, films were also deposited on graphite and Si substrates for Rutherford backscattering spectroscopy (RBS).

Film composition was determined by a JOEL electron beam microprobe and by RBS. To study the radial composition variations, substrates were placed in radial direction under the target. Energy-dispersive X-ray analysis was used in the microprobe. RBS was used for complementary composition confirmation. A 2.5 MeV Van de Graaf accelerator was employed. RBS spectra were obtained using 2.0 MeV He⁺ ions from film deposited on the graphite and Si substrates. Structural analyses were carried out in a Rigaku thin film diffractometer and a Rigaku conventional θ - 2θ diffractometer. CuK α radiations at 40 keV and 15 mA were used.

3. Results and discussion

Figure 1 shows deposition rates at different radial positions underneath the 212 target for Ar + 10% O₂ and pure Ar sputtering at 3 and 10 mtorr. There are two very distinct regions in the low pressure Ar + 10% O₂ deposition rate curve shown in figure 1a. Region 1 extends from directly underneath the centre of the target up to the edge of the target. Region 2 is beyond the edge of the target. In region 1, the deposition rate is half the deposition rate in region 2. This is the resputtered region. The severity of resputtering decreases as the pressure is increased (figure 1b). Deposition done at 20 mtorr pressures shows no sign of resputtering, however, films had a strong columnar structure, low density and did not exhibit good superconducting properties upon annealing. Best T_c results were obtained when films were deposited at pressures higher than 5 mtorr. Resputtering also decreased by reducing the oxygen content of the sputtering gas. Figures 1c and 1d show a very small decrease in the deposition rate in region 1 of a film deposited with pure argon at 10 mtorr. Decreasing the pressure, however, again enhanced the resputtering.

Resputtering has been known to occur during high T_c thin film deposition by sputtering because of energetic particle bombardment (Shah 1989; Rosnagel and Cuomo 1988). Increasing the pressure increases the number of collisions the reflected neutrals and the energetic sputtered atoms experience during the transit from the target to the substrate. This thermalization of the energetic particles decreases the total resputtering rate thereby increasing the net deposition rate. Table 1 lists the yields of the reflected neutrals for 123, 2212 and 212 sputtering calculated by using TRIMSPUT program for pure Ar and Ar + 10% O₂ sputtering gases. Figure 2 is a

Figure 1. Deposition rates at different radial positions underneath the target for Ar + 10% O₂ and pure Ar sputtering at 3 and 10 mtorr. 'O' on the x-axis is the centre of the target.

Table 1. Yield and energy of the reflected neutrals from Monte-Carlo simulation based on 10^4 incident ions.

	Fraction of reflected neutrals, total reflected neutrals/ 10^4		Average energy of reflected neutrals (eV)	
	Ar	Ar + 10% O ₂	Ar	Ar + 10% O ₂
Bi ₂ Sr ₂ CaCu ₂ O _x	0.087	0.0947	97.36	110.23
YBa ₂ Ca ₃ O _x	0.0795	0.0892	76.35	87.21
Ba ₂ CaCu ₂ O _x	0.0657	0.0702	83.28	94.42

Figure 2. Histogram of the calculated energies of sputtered atoms and reflected neutrals for pure Ar sputtering of a Ba–Ca–Cu–O target. 10^4 incident Ar ions at 0.5 keV energy were used for the calculations.

plot of the distribution of the energies of reflected neutrals and sputtered atoms for 0.5 keV applied target voltage and 10,000 incident Ar ions on 212 target. Similar plots were also obtained for 123 and 2212 targets. The average energy calculated from this distribution was 114 eV. With this initial energy, and if the sputtering pressure is low, the reflected neutrals could reach the growing film with sufficient energy to cause resputtering at the surface of the film. Energetic sputtered atoms, on the other hand, have average initial energy too low to do any damage to the film, however, they could still have enough momentum to cause increased diffusivities (Averbach 1982) and/or induce compressive stresses (Hoffman and Thornton 1982) in the film. As the pressure increases, the remnant energy of the particles arriving at the substrate decreases as a result of increased collisions with the gas atoms and, therefore, the net resputtering also decreases.

Increasing the oxygen content of the sputtering gas also increases the yield and the energy of the reflected neutrals as indicated in table 1. Figure 3 is a histogram of the energy distribution of the reflected neutrals coming off of a 212 target incident with 0.5 keV Ar + 10% O₂ sputtering gas. The average energy of the reflected neutrals is 128 eV which is higher than the pure Ar sputtering case. Hence, the film growth experiences higher energetic particle impingement with O₂ containing plasma. The presence of some oxygen is, however, necessary. Severe target aging was noticed when sputtering was carried out continuously with pure Ar. The optimum sputtering gas composition was found to be Ar + 10% O₂.

Figure 3. Histogram of the calculated energies of reflected neutrals for Ar + 10% O₂ sputtering of Ba-Ca-Cu-O target.

In addition to the erosion of the film, the cation composition is also affected by the energetic particle bombardment. Figure 4 is a plot of the variation of cation composition with the radial distance underneath the target for a film grown at 3 mtorr of Ar + 10% O₂. Cu is the most abundant element with concentration about two times the target Cu concentration. Cu concentration decreases very rapidly away from the target, approaching the target composition at about 3 cm away from the centre of the target. The other two cations, Ca and Ba are in sub-stoichiometric proportions underneath the target and their concentrations also reach target concentrations beyond the edge of the target. This result is markedly different from the 2212 sputtering results (Shah 1989) where an abundance of Ca was observed in the films deposited directly under the target. Heavy Bi may have contributed to the composition variation in 2212. Ca is the lightest of the cations in Ba-Ca-Cu-O target and a preferential resputtering of Ca in the irradiated area is as expected. Ba is heavier than Cu but it has the lowest melting point of the three. Ba is, therefore, preferentially sputtered from the film as a result of the energetic particle bombardment. Away from the target edge the flux of the impinging energetic particles decreases and, therefore, the composition approaches the target composition.

Off-stoichiometric film deposition can, however, be controlled by either increasing the sputtering pressure or by changing the target-substrate separation. Figure 5 is a plot of the Ca/Cu ratio as a function of the pressure and oxygen concentration in the sputtering gas. The effect of oxygen on the composition will be discussed later. At low sputtering pressures, the ratio is very small and far away from the stoichiometric value of 0.5 due to the Cu enrichment. As the pressure increases, the Ca/Cu ratio increases and approaches the stoichiometric value at around 5 mtorr. An increase in the pressure causes an increase in the collision frequency of the energetic particles with the sputtering gas atoms thereby thermalizing them. This reduces the resputtering effects on the film. Preferential sputtering decreases as the sputtering pressure increases. It is therefore possible to obtain a stoichiometric film directly underneath the target at

Figure 4. Cation composition as a function of the radial distance underneath the target. Film was grown at 3 mtorr pressure of Ar + 10% O₂.

Figure 5. Ca/Cu ratio as a function of (a) the sputtering pressure and (b) the oxygen content of the sputtering gas.

moderately high sputtering pressures. Deposition experiments for films for transport measurements were carried out at sputtering pressures of 5 mtorr or above.

The partial pressure of oxygen is also very critical in obtaining correct composition of the film. Figure 5b shows a decrease in the Ca/Cu ratio with the increase in the fraction of O₂ in the sputtering gas. Stoichiometric compositions could only be obtained if the O₂ fraction is less than 0.1. As presented in table 1, both the number and the energy of the reflected neutrals increase as the O₂ is added to the sputtering gas.

This again translates to more energetic particle bombardment of the film leading to compositional non-uniformity. It should, however, be noted that this change in the Ca/Cu ratio as a result of O₂ partial pressure change does not have a significant effect on the d.c. transport properties of the film. The variation in Ca/Cu ratio only changes the proportion of 2212 phase. A high T_c is still obtainable even if the ratio is 0.5 ± 0.15 . This composition variation, however, very severely affects the a.c. or microwave properties of the film.

Through the control of the sputtering parameters it is possible to deposit films of correct stoichiometry without resorting to design changes in the sputtering system. RBS analyses of thin as-grown 300 Å films on (100)Si substrates indicated that the composition was Ba_{1.9}Ca_{0.95}Cu_{2.1}O_x. As-grown films were subsequently annealed by sealing with measured-amount of Tl₂Ba₂Ca₂Cu₃O_x powder in gold tube. The annealing sequence included heating to 850°C and soaking at this temperature for 10 min followed by another soak at 720°C for 12 h. Samples were then furnace-cooled. Figure 6 is a typical XRD pattern from these films. The pattern mainly consists of (001) type reflections indicating that the films are preferentially oriented with *c*-axis perpendicular to the film surface. The reflections belong mainly to 2212 phase. Lattice constant calculated from this diffraction pattern was $c = 29.2 \pm 0.05$ Å which is very close to the reported value for the bulk 2212 (Ginley *et al* 1989). Figure 7 is a plot of the resistivity as a function of the measurement temperature for these films. The superconductivity onset temperature was 120 K and T_c at zero resistance was 104 K.

4. Conclusion

Although the exact mechanism of resputtering is not very well understood, through our experiments and theoretical simulation of sputtering process we are able to specify critical sputtering parameters, namely target-substrate separation, sputtering pressure, and sputtering gas composition. Through proper control of these parameters, it is

Figure 6. XRD pattern from a Tl-Ba-Ca-Cu-O film.

Figure 7. Resistivity as a function of the measurement temperature for a Tl-Ba-Ca-Cu-O film.

possible to deposit films of right composition and good superconducting properties without making changes in the system design or resorting to off-axis deposition.

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