Effect of Substrate Temperature on the Growth of Superconducting $YBa_2Cu_3O_{7-y}$ Thin Films Deposited by RF Magnetron Sputtering

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Abstract

Dependence of the c-axis lattice parameter, composition and surface morphology on substrate temperature was examined in superconducting $YBa_2Cu_3O_{7-y}$ thin films deposited by a single target 90° off-axis RF magnetron sputtering. The c-axis lattice parameter of the thin films decreases with elevating substrate temperature and attains the minimum at 700℃. The dependence of the composition of the deposited films on the substrate temperature is little. Films deposited at the substrate temperature of 660℃ have a rather smooth surface. Films deposited above the substrate temperature of 700℃ have outgrowths at the surface.

1. Introduction

Since the discovery of superconducting $YBa_2Cu_3O_{7-y}$ (YBCO, where y is the deficiency of oxygen)[1], many thin films have been prepared by several techniques, such as laser ablation[2], multi-source electron-beam thermal evaporation[3], single-target DC or RF magnetron sputtering[4], metal-organic chemical vapor deposition[5] and molecular beam epitaxy[6]. One of the most successful of these has been single-target sputtering. In the past few years there have been many papers describing the preparation and properties of YBCO films made by this technique. The most critical issues in preparation technology of high quality YBCO thin films are stoichiometry control of the metallic constituents, the correct oxygenation and the surface smoothness. In these papers, however, there are significant differences reported in the properties of the sputtered YBCO films. Also, there is no consensus regarding the optimum experimental procedures for depositing the high quality films. This should not be surprising since in sputtering there are very many experimental variables that influence film quality. These variables tend to be closely interdependent, which can make their identification and optimization a very difficult problem.

Especially, substrate temperature plays a key role in depositing *in situ* YBCO films. The substrate temperature must be high enough to allow sufficient atomic migration to form orthorhombic crystal structure. This minimum substrate temperature was reported to be 580℃[7]. The optimum substrate temperatures, however ranged from 600℃ to 750℃.

In this paper, superconducting YBCO thin films are deposited using the off-axis single-target RF magnetron sputtering. Properties of the deposited thin films are examined by X-

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ray diffraction and scanning electron microscopy. The effect of the substrate temperature on the c-axis lattice parameter, cation atomic percent and surface smoothness is investigated.

2. Experimental

Sputtering parameters used for film deposition in this work are listed in Table I. YBCO films were deposited using a 2 in. diameter RF magnetron sputter source (Lesker TRS-002C). In the case of YBCO and other multicomponent oxide systems, many problems arise from the formation of negatively charged oxygen ions at the target side. They are accelerated away from the target by the potential difference of the cathode dark space. This energetic particle flux is directed to the substrate in conventional on-axis sputtering geometries leading to selective resputtering of the growing film which modifies the film composition or gives rise -in extreme case- to etching of the substrate rather than deposition. Solutions to this problem were accomplished by increasing the sputtering gas pressure[8] and by changing the target-substrate orientation[9]. Both the techniques lower the energies of the particles bombarding the substrate and prevent the preferential backsputtering of Cu and Ba. In this work, the 90° off-axis target-substrate configuration was employed in the sputtering geometry. Substrates were positioned perpendicular to a target surface as shown in Fig. 1.

Stoichiometric YBCO targets were prepared by solid state reaction. The size of the sintered target was 50 mm in diameter and 4 mm in thickness. An RF power of 50 W was supplied to the magnetron sputter source.

A substrate holder used was a 5-cm-diameter stainless steel block. The block temperature was determined by a thermocouple located in a well in the back of the block, and was held constant during film growth. The actual substrate surface temperature was somewhat lower than that of the substrate holder.

MgO (100) single crystals were used for substrates. Their size was 10 mm × 10 mm × 1 mm. Substrates were mechanically polished to a optical finish with 1/4 μm diamond grit, and annealed in a flowing oxygen atmosphere at 1100℃. Thermal annealing of substrates was highly effective in producing epitaxial, c-axis normal films with good superconductive properties[10]. Three substrates were bonded by silver paste to the substrate holder.

The sputtering gas was 80% Ar + 20% O_2, and sputtering pressure was measured by Schultz gauge, and was held constant at 10 Pa using two gas flow controllers (MKS Instru-

Table I. Set of sputtering conditions for preparing YBCO thin films

Target-substrate configuration	90° off-axis
Power	RF 50W
Sputtering target	2 in. diameter stoichiometric YBCO
Gas pressure	8 Pa argon, 2 Pa oxygen
Substrate temperature	from 660℃ to 740℃
Substrate material	single crystal MgO (100)

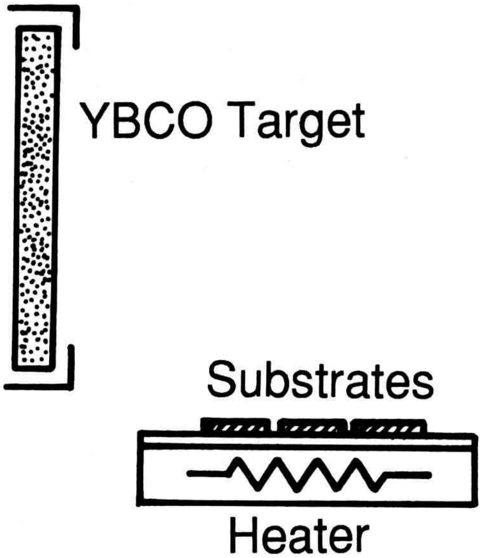

Fig. 1. A 90° off-axis single target sputtering configuration.

ments). Following the deposition, the films were annealed *in situ* in 1/2 atm. of pure oxygen for 30 min. at 450℃ and then allowed to cool to room temperature before being removed from the sputtering system.

An X-ray diffraction analysis was performed with RIGAKU RAD-C diffractmeter using CuKα radiation. Surface morphology was analyzed by scanning electron microscopy (SEM). The compositions of thin films were determined by energy dispersive x-ray analysis (EDX) with JEOL JXA 840A scanning electron microscope. Polished YBCO bulk ceramics were used as standards for EDX.

3. Results and Discussion

In order to understand the effect of the substrate temperature (T_s) on the properties of deposited films, we have prepared films at various substrate temperatures: (a) T_s=660℃, (b) 680℃, (c) 700℃, (d) 720℃ and (e) 740℃.

Figure 2 shows the X-ray diffraction spectra of the deposited films. A diffraction peak at 38.6° is due to MgO (200) CuKβ, and a peak at 42.8° is due to MgO (200) CuKα. The other sharp peaks can be indexed as from YBCO (001) to YBCO (009) as labeled in Fig. 2. As the substrate temperature elevates, diffraction peaks of YBCO (110) and (103) appear. This result reveals that deposited films are grown mainly with the c-axis perpendicular to the film plane at the low substrate temperature. As the substrate temperature elevates, grains with the c-axis parallel to the substrate surface appear in the deposited films. In addition to the sharp peaks, there are also broad peaks which suggest the existence of amorphous phase in the films. The amorphous phase decreases with elevating substrate temperature.

The c-axis lattice parameter as a function of the substrate temperature is shown in Fig. 3. In all cases, the lattice parameter was calculated by the (007) peak. This standard was chosen because the width of the (007) peak is narrower than that of the (009) peak. The c-axis lattice parameter decreases with elevating substrate temperature and attains the minimum around 700℃. Increase of lattice parameter at low substrate temperatures is the result of increased atomic disorder due to lower atomic mobility. The crystal structure of bulk YBCO ceramics is orthorhombic for $y<0.5$, and tetragonal for $y>0.5$. In the orthorhombic phase, YBCO is superconductive and lattice parameters are $a=0.388$ nm, $b=0.382$ nm and $c=1.169$ nm[11]. In the tetragonal phase, YBCO is semiconductive and lattice parameters are $a=0.386$ nm and $c=1.178$ nm[11]. The observed minimum value of the c-axis lattice parameter of the film is still larger than that of the orthorhombic phase in bulk YBCO ceramics. The c-axis lattice parameter of *in situ* films deposited by sputtering increased

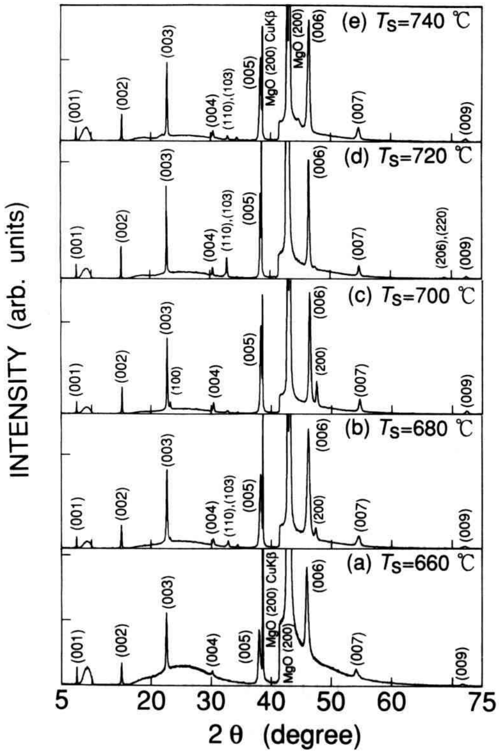

Fig. 2. X-ray diffraction patterns of the thin films using CuKα source. The peak labeled "MgO (200)" is due to MgO substrate. Films were prepared at various substrate temperature: (a) T_s=660℃, (b) 680℃, (c) 700℃, (d) 720℃ and (e) 740℃.

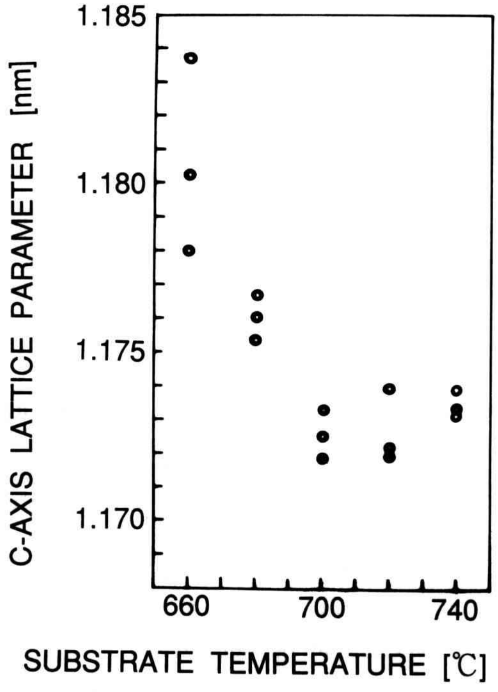

Fig. 3. The c-axis lattice parameter as a function of the substrate temperature.

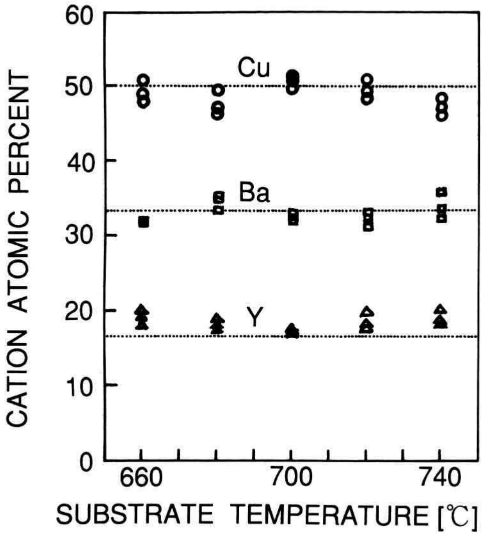

Fig. 4. The cation atomic percent as a function of the substrate temperature. The correct composition is indicated by the dotted lines.

with decreasing substrate temperature and with decreasing oxygen pressure, and varied from 1.167 to 1.182 nm due to atomic disorder[12].

The composition of the film is measured by EDX. The cation atomic percent as a function of the substrate temperature is shown in Fig. 4. In normalized atomic units, stoichiometric $YBa_2Cu_3O_{7-y}$ would have elemental concentrations of Y=17%, Ba=33% and Cu=50% as shown by dotted lines in Fig. 4. The dependence of the cation atomic percent on the substrate temperature is little. We see that the film is enriched in Y, and deficient in Cu.

Figure 5 shows scanning electron micrograhs of the surface of the thin films deposited at various substrate temperatures: (a) 660℃, (c) 700℃, (d) 720℃ and (e) 740℃. The film in Fig. 5(a) has a relatively smooth surface, apart from a number of holes. In Fig. 5(a), "canals" are due to scratches at the substrate surface. The film in Fig. 5(c) has a small amount of outgrowths at the surface. The film in Fig. 5(d) has many outgrowths. The film in Fig. 5(e) consists of large and small grains and has an extremely rough surface. As the substrate temperature elevates, grain size increases and the surface becomes rough. As the crystallographic planes of the c-axis oriented film are wavy due to frequent faults in the stacking sequence, c-axis oriented films commonly have many outgrowths[13].

This result suggests that the substrate temperature must be as low as possible to produce thin films having smooth surface. But c-axis lattice parameter of the films deposited at low substrate temperatures is elongated and the superconducting properties are degraded. As deviations from the stoichiometry lead to outgrowths, a correct stoichiometry should be obtained in films. An oxygen pressure also play a key role. The role of oxygen is two-fold: there must be sufficient oxygen incorporation during film growth to form the orthorhombic crystal structure and sufficient oxygen over-pressure to prevent the existing film from decomposing at required deposition temperatures. In YBCO, its optimum oxygen content is

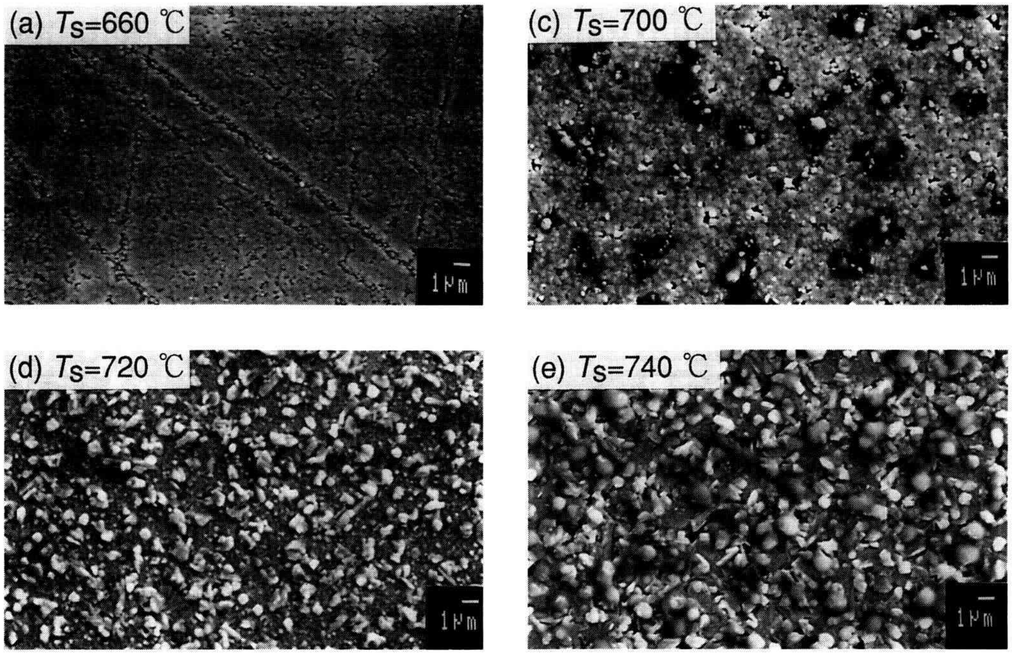

Fig. 5. Scanning electron micrographs of the thin films prepared at various substrate temperatures: (a) T_s=660℃, (c) 700℃, (d) 720℃ and (e)740℃.

critical and its phase transformations can introduce undesired defects. It has been pointed that the generation of atomic oxygen is important in the oxidation of YBCO films[14]. It may be necessary to introduce active oxygen such as ozone for easier oxidation at low substrate temperatures. The influence of oxygen in depositing YBCO thin films is currently being inventigated.

4. Conclusions

Thin films, with approximate $YBa_2Cu_3O_{7-y}$ composition, were deposited on single crystal MgO(100) substrates by a single target 90° off-axis RF magnetron sputtering. We investigated the dependence of structural property and surface morphology on the substrate temperature. As the substrate temperature increases, the c-axis lattice parameter of the thin films decreases and attains the minimum at the substrate temperature of 700℃. The dependence of the composition of the deposited films on the substrate temperature is little. The films deposited at the substrate temperature of 660℃ have a rather smooth surface. The films deposited above the substrate temperature of 700℃ have many outgrowths at the surface.

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