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Enhancement in superconducting properties of Y–Ba–Cu–O thin films by post-annealing in an inert atmosphere

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Y–Ba–Cu–O superconducting thin films were produced by *ex situ* r.f. magnetron sputtering. In the post-annealing procedure, several annealing conditions which were scheduled for heating rate and annealing atmosphere were tried systematically to determine major factors affecting the characteristics of post-annealed superconducting thin films. From the results of the study, it was found that the characteristics of the films are strongly dependent on the heating atmosphere rather than the heating cycle or heating time. Films with a high transition temperature were obtained by treatment in an argon atmosphere; this is considered to be attributable to the rapid atomic diffusion in tetragonal $YBa_2Cu_3O_{7-x}$ due to the high oxygen vacancy concentration and the expanded lattice in an inert atmosphere during heat treatment.

1. Introduction

R.f. sputtered [1, 2], thermal co-evaporated [3, 4], laser ablated [5, 6], or chemical-vapour deposited [7, 8] high-temperature superconducting thin films can be fabricated by *in situ* on a heated substrate or by *ex situ* post-annealing after deposition. Nowadays, the *in situ* method is commonly used to grow superconducting films because *in situ* grown films generally have good surface smoothness and epitaxial structure. However, the *ex situ* method is still widely used because of the easy process and the simplicity of the growth equipment. In the *ex situ* process, as-deposited amorphous films require post-annealing after deposition in order to be transformed into superconducting phases. Insulating tetragonal $YBa_2Cu_3O_{7-x}$(1–2–3) structure is generally known to be formed during heat treatment at about 900 °C and the tetragonal form is converted into superconducting orthorhombic structure during annealing at 500 °C in a flowing oxygen atmosphere.

In *ex situ* grown superconductor thin films, grain properties such as grain shape, grain size, grain structure, the amount of unreacted secondary phases, surface roughness, etc., which may also influence electrical properties, are mostly determined during the post-annealing process. Therefore several annealing conditions were scheduled for heating cycle and annealing atmosphere in order to determine these factors.

Two heating cycles (rapid heating–short holding time, and slow heating–long holding time) and two heat-treatment atmospheres (oxygen and argon) were employed in this study. In case of bulk superconductor, it has been reported [9, 10] that the inert atmosphere enhances the grain growth, resulting in an improvement of electrical properties. Introduction of argon gas during heat treatment of the thin films is also expected to be effective in promoting atomic diffusion, as reported in the bulk. The reason for employing rapid thermal annealing and a short heating time is that short annealing time is considered to be sufficient for crystallization of thin films and improved properties are expected due to the reduction of interdiffusion (interaction) between film and substrate. Several optimistic results on rapid heating effects have been reported [11–13]. In this paper, a comparison of heating rates, and the effects of annealing atmosphere on the characteristics of thin films are reported.

2. Experimental procedure

Amorphous Y–Ba–Cu–O thin films were deposited on polycrystalline yttria-stabilized zirconia (YSZ) substrates using a single-target planar-type r.f. magnetron sputtering. A stoichiometric $YBa_2Cu_3O_{7-x}$ target was prepared from 99.99% pure Y_2O_3, $BaCO_3$, and CuO powders by solid state sintering. The sintered target showed a sharp superconducting transition above 90 K. The substrates were placed outside the region of negative ion impact area to avoid resputtering [14] which may cause serious fluctuation in composition. To obtain uniform composition and thickness, we rotated the substrates at 20 r.p.m. during sputter deposition.

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R.f. power of 85 W was applied for the sputtering, and the chamber pressure was maintained to be 5 $\times 10^{-2}$ mbar by introducing argon gas. The deposition rate was about 8 nm min^{-1}. From the composition analysis results, films from a stoichiometric $YBa_2Cu_3O_{7-x}$ target were found to be deficient in copper therefore additional CuO pellets (8 mm diameter $\times$ 2 mm thick) were added, which were prepared by a separate process [15], to the $YBa_2Cu_3O_{7-x}$ target.

As-deposited Y–Ba–Cu–O films were post-annealed in order to transform them to superconducting phases. Heat treatment by several methods was tried, as shown in Fig. 1, and the effects of each process were compared. These conditions can be largely classified into two kinds of process: one is normal thermal annealing (NTA) which is based on the bulk superconductor process consisting of slow heating and slow cooling, and the other is rapid thermal annealing (RTA) which is commonly used in semiconductor processes [16, 17] to form thin oxide or nitride layers on semiconductor thin films with good control of dopant concentration by depressing the diffusion of dopants. As shown in Fig. 1, for the NTA process, as-deposited amorphous films were heated to 900 °C over 1.5 h (heating rate 10 °C min^{-1}), held at 900 °C for 1 h, cooled to 500 °C over 8 h ($\sim$ 1 °C min^{-1}), held at 500 °C for 5 h, followed by furnace cooling to room temperature. For the RTA process, the films were heated to 900 °C in as short as 1 min, held at 900 °C for 20 min, followed by the same cycle as NTA.

Annealing atmosphere as well as heating rate is known to be important in the heat treatment of superconducting thin films. Argon and oxygen atmospheres were used for both NTA and RTA during heating to and holding at 900 °C. On cooling to and holding at 500 °C, only an oxygen atmosphere was used to supply sufficient oxygen to the films. As shown in Fig. 1, four post-annealing conditions were employed: (1) normal thermal annealing in oxygen (denoted NTA/O_2), (2) normal thermal annealing in argon (NTA/Ar), (3) rapid thermal annealing in oxygen (RTA/O_2) and (4) rapid thermal annealing in argon (RTA/Ar).

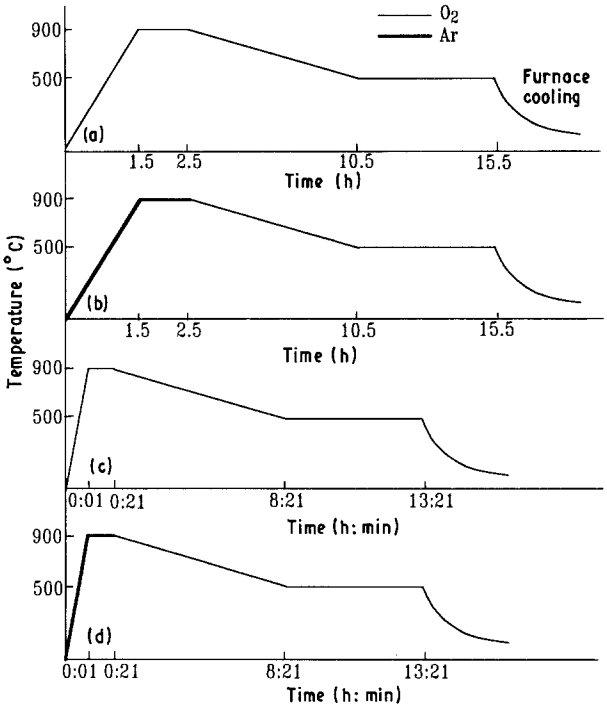

Figure 1 Heat-treatment schedules of as-deposited films for (a) NTA/O_2, (b) NTA/Ar, (c) RTA/O_2 and (d) RTA/Ar.

The electrical properties of the post-annealed films were measured by a d.c. four-probe method, and the microstructures were observed using scanning electron microscopy (SEM). For the four-probe resistivity measurement, silver electrodes were vacuum evaporated and annealed at 500 °C for 1 h to reduce the contact resistance.

3. Results and discussion

Fig. 2 shows the microstructures of films which were post-annealed under four different conditions. In NTA/O_2, the grains are small (< 1 μm) and not uniform in size. However, in NTA/Ar, the grains grew to a size as large as a few micrometres. In the case of RTA, grains grown in an argon atmosphere (RTA/Ar) are also larger than those grown in an oxygen atmosphere (RTA/O_2).

According to the report of Ra *et al.* [9], grain growth of Y–Ba–Cu–O bulk superconductors is enhanced in an inert (nitrogen) atmosphere. Mingard *et al.* [10] reported that they could reduce the sintering temperature of Y–Ba–Cu–O by 40 °C in an argon atmosphere, even when the superconducting properties are better than those of a sample annealed in air. Ra *et al.* [9] insist that the role of an inert atmosphere is as follows. In a low oxygen partial pressure, defect structures are formed from the generation of oxygen vacancies, and the 1–2–3 tetragonal lattice expands because of the increase in ionic radius of copper resulting from the decrease in its atomic valence. Therefore, it becomes easy for atoms to diffuse through the 1–2–3 lattices, which results in enhancement of the superconducting phase formation and grain growth. The growth of large grains, which were found in our films annealed in an argon atmosphere (Fig. 2b and d) may be explained by such an easy atomic diffusion.

Microstructures were also found to have different appearances depending on the heating rate and annealing time at 900 °C. In an oxygen atmosphere, the film annealed by the RTA (RTA/O_2) has a larger grain size and denser grain structure than that annealed by the NTA process (NTA/O_2). On heating up by NTA, the film passes the nucleation temperature range slowly due to the slow heating rate, resulting in the nucleation of a large number of nuclei. In the RTA process, the film passes the nucleation temperature range rapidly (in about 1 min) and the film has insufficient time for full nucleation. Thus only a small number of nuclei can be formed.

The nuclei which are created in small numbers throughout the matrix can grow to large sizes during heat treatment. However, when a large number of nuclei are formed, it is difficult for the grains to grow

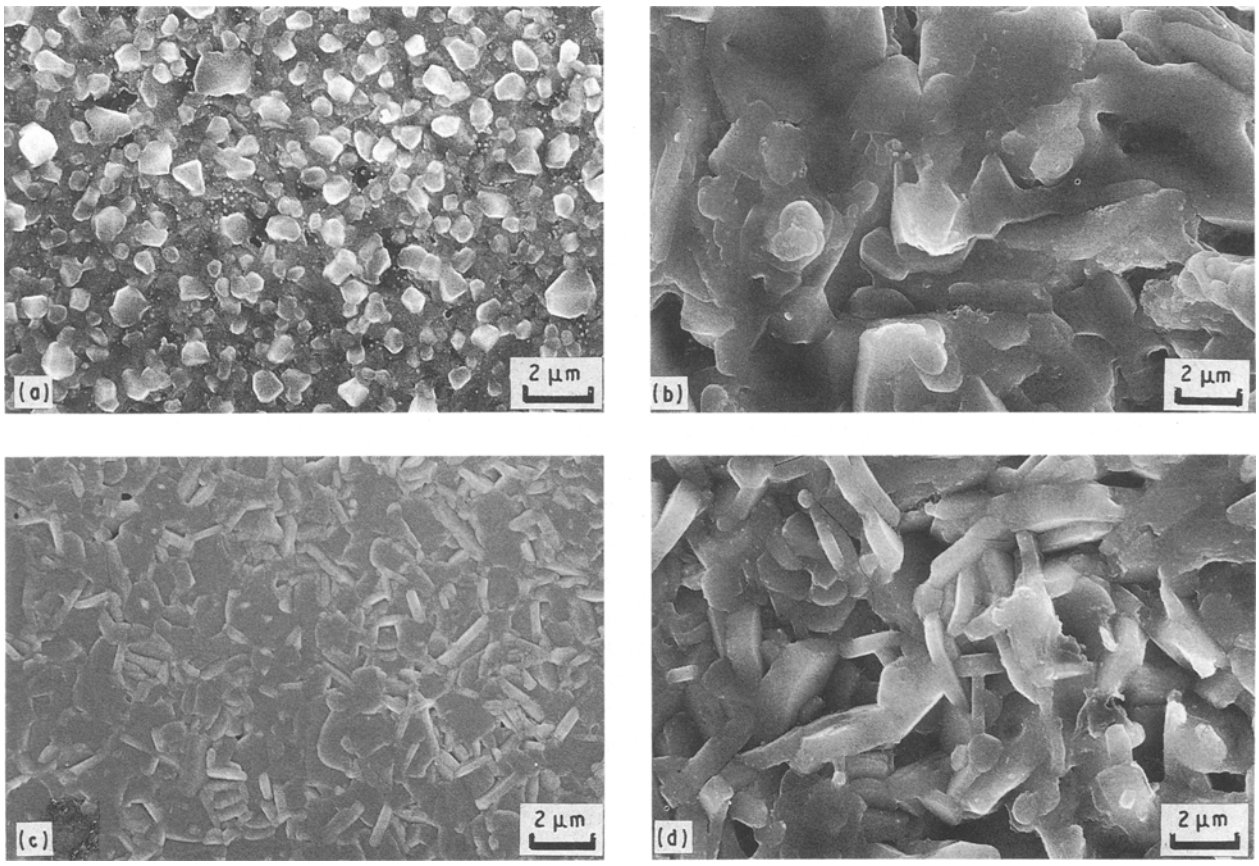

Figure 2 Microstructures of thin films prepared by (a) NTA/O_2, (b) NTA/Ar, (c) RTA/O_2 and (d) RTA/Ar.

to large sizes because of the numerous grain boundaries. Therefore, it is considered that the grain size of films annealed by the NTA or RTA processes in an oxygen atmosphere (Fig. 2a and c) is dependent on the number of nuclei created during heating to 900 °C; the nucleation mechanism is dominant in NTA and the crystal growth mechanism is dominant in the RTA process.

However, a different phenomenon is observed in case of an argon atmosphere. As shown in Fig. 2b and d, the grains grown in the NTA process are larger than those grown in the RTA process. Although a large number of nuclei is formed in NTA, it is considered that fast atomic diffusion in an argon atmosphere makes the grains grow to a large size. Thus in an argon atmosphere, the grain size may be simply dependent on the annealing time at 900 °C and not on the annealing method (NTA or RTA).

Fig. 3 shows the resistance–temperature (R–T) characteristics of the films. The films annealed in an argon atmosphere (by both RTA and NTA) shows strikingly better characteristics than those annealed in oxygen. In both oxygen and argon atmospheres, the film grown by NTA (Fig. 2a) shows a higher T_c than those grown by RTA. As a whole, films annealed in an argon atmosphere show metallic behaviour with sharp superconducting transition, while those annealed in an oxygen atmosphere show semiconducting behaviour with long tails.

In general, it is known that 1–2–3 tetragonal structure is formed at 750–800 °C by solid state reaction [9]. In an oxygen atmosphere, oxygen sites of the 1–2–3 tetragonal lattice are fully occupied during calcination and the diffusion rate of atoms through the lattice is very low; however, in an argon atmosphere, a defect structure of the 1–2–3 tetragonal phase with oxygen deficiencies is formed and the atomic diffusion rate is large. Owing to the difference in the atomic diffusion rate depending on atmosphere, it is considered that the amount of unreacted residual non-superconducting intermediate products such as 2–1–1 phase, $BaCuO_2$, or CuO present in the film, is different. Therefore, a large amount of residual secondary phase may be included in the film which is heat treated in an oxygen atmosphere, while a small amount of non-superconducting phases are included in the film annealed in argon. For these reasons, films annealed in an argon atmosphere seem to show better R–T characteristics than those annealed in an oxygen atmosphere.

There is little difference in R–T characteristics between the NTA and RTA processes in the same atmosphere. Films annealed by the NTA process have a slightly higher value of $T_{c,\,zero}$ than those annealed by RTA. These results seem to be responsible for the difference in the coupling energy which is dependent on the coupling shape of the superconducting grains. In granular superconductors, Josephson coupling between superconducting grains is formed when the coupling energy, E_J, exceeds the thermal energy, $\sim k_B T$. As temperature decreases, the coupling energy increases while thermal energy decreases. $T_{c,zero}$ is defined as the temperature at which coupling probability reaches the same value as the percolation

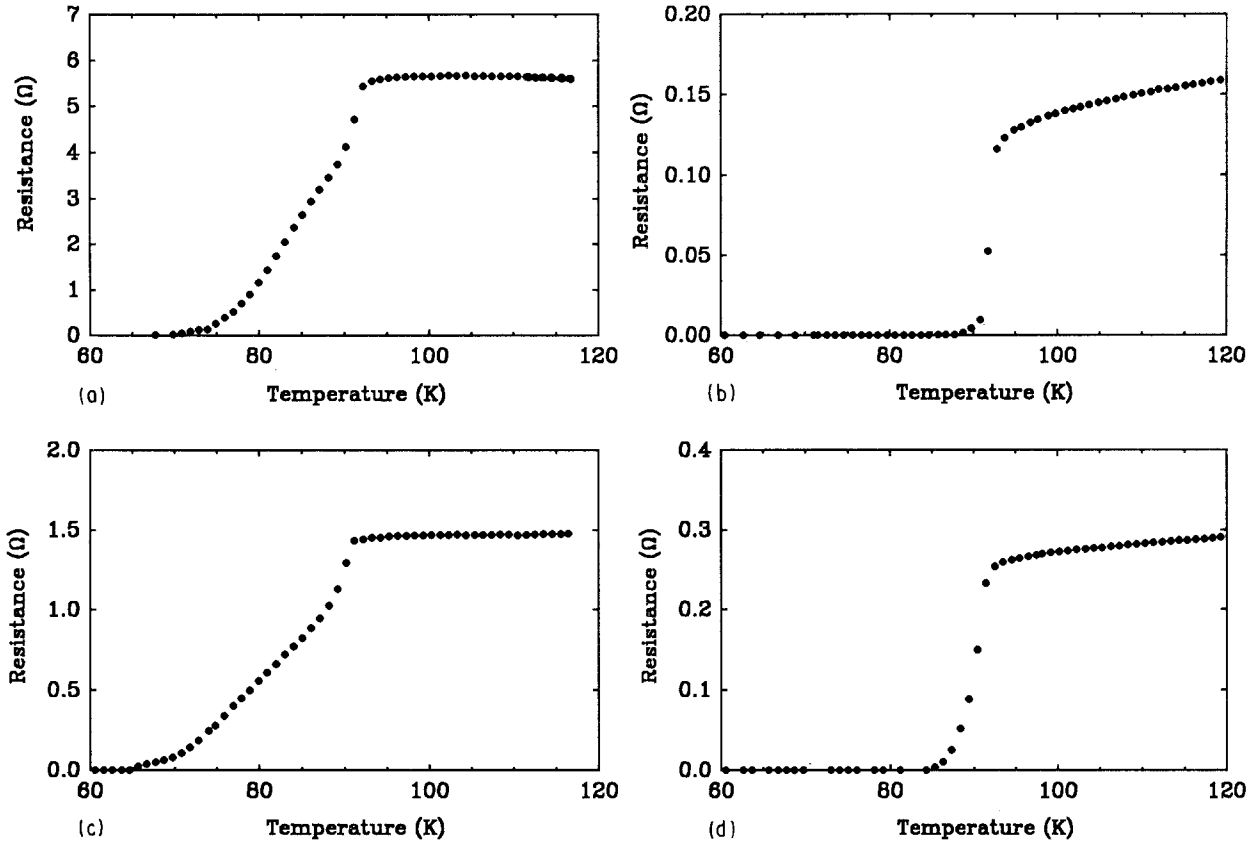

Figure 3 Resistance–temperature curves of Y–Ba–Cu–O films post-annealed by (a) NTA/O_2, (b) NTA/Ar, (c) RTA/O_2 and (d) RTA/Ar.

threshold, so that an infinite cluster of superconducting grains forms [18]. Accordingly, $T_{c,\,zero}$ is determined by the coupling energy, which depends on the coupling shape of superconducting grains such as grain boundaries, pores, and secondary phases. In an argon atmosphere, the film annealed by the NTA process has larger grains and a denser structure than that by RTA, from which we can imagine that the film by NTA has higher coupling energy. So the film annealed by NTA process has a little higher value of $T_{c,\,zero}$ than that by RTA.

From the results of our study, we can show that post-annealing in an inert atmosphere contributes to the good quality of superconducting thin films, which was also found by Ma *et al.* [12] and Ra *et al.* [9]. Davidson *et al.* [11] reported that they obtained superconducting film with $T_{c,\,zero}$ = 30 K through slow heating and slow cooling in an oxygen atmosphere; however, they could obtain 80 K as a $T_{c,\,zero}$ from the same sample by rapid heating and slow cooling in a helium atmosphere. They insist that the T_c enhancement is due to the effect of rapid heating. However, from the results of our study, the T_c increment in their sample seems to be due to the effect of the inert (helium) atmosphere rather than the effect of rapid heating.

4. Conclusion

Several annealing conditions were investigated to determine the major factors affecting the characteristics of post-annealed superconducting thin films made by *ex situ* r.f. magnetron sputtering. From the results of our study, we found that the characteristics of films are strongly dependent on the annealing atmosphere (gas) rather than annealing methods (heating cycle). Films with a high transition temperature were obtained by post-annealing in an argon atmosphere, which is considered to be attributed to the rapid atomic diffusion in tetragonal $YBa_2Cu_3O_{7-x}$ due to a high oxygen vacancy concentration and an expanded lattice in an inert atmosphere during heat treatment as reported in the bulk [9]. Thus the promising effects of an inert (argon) atmosphere on the properties of post-annealed thin film superconductors can be confirmed.

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