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Diffusion Problems between Y-Ba-Cu-O Thin Films and MgO Substrates

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The interdiffusion properties between thin Y-Ba-Cu-O films of compositions near $YBa_2Cu_3O_{7-y}$ and MgO substrates are investigated by observing time evolution of both Rutherford backscattering spectra and SEM images during annealing. Actual diffusivities of Y, Ba and Cu elements in the MgO substrates have been found to be extremely smaller than those previously reported. The origins of the discrepancies are discussed in connection with the morphology variation during annealing of the thin Y-Ba-Cu-O films deposited on the MgO substrates.

Interdiffusion and/or interfacial reaction has been a serious probrem for both formation and application of superconducting $YBa_2Cu_3O_{7-y}$ thin films.[1,2] Therefore, diffusivities of Cu element of amorphous Y-Ba-Cu-O films into various substrates had actually been investigated by applying Rutherford backscattering spectrometry (RBS), and relatively large values of the diffusivities had been reported.[3]

However, morphology variation of thin films during heat treatments may seriously affect diffusion measurements by RBS.[4] The authors have found that the amounts of changes of the shapes of low energy portion of the RBS spectra from elements of Y-Ba-Cu-O films after annealing were remarkably small in the case of single-crystal films grown on MgO substrates, compared with the case of amorphous films grown on the same substrates substance.[5] This phenomena might be due to the dependence on crystallinities of either diffusivities or morphology variation during annealing. Thus, in order to elucidate the origin of this phenomena and to investigate in detail the diffusion properties, time evolution of both RBS spectra and SEM images during annealing were observed.

In this report, we describe the results of the investigation of both the diffusion properties between the thin Y-Ba-Cu-O films and MgO substrates, and morphology variation during annealing, which were studied by applying RBS combined with SEM observations. X-ray diffraction patterns, and reflection high energy electron diffraction (RHEED) patterns were also taken in order to characterize crystallinities of the films.

Single-crystal and amorphous films were prepared on MgO substrates by an RF magnetron sputtering deposition method with transverse magnetic field.[6] RF power applied was 80 W. Sputtering was carried out in Ar + 24 % O_2 at a pressure of $2x10^{-2}$ Torr. Single-crystal films were grown on the substrates heated to 680℃. Amorphous films were obtained simply by depositing on the substrates without heating. X-ray diffraction patterns of both the single-crystal and the amorphous films just deposited are shown in Fig. 1(a) and 1(b). Lattice constant along the C-axis calculated from the angular position of the peaks of (006) plane was about 11.88 Å, which is considerably larger than the value for the lattice constant of stoichiometric $YBa_2Cu_3O_{7-y}$ bulk crystal.[7] RHEED patterns showed that the films were single-crystal with smooth surface, though the patterns are not shown in the present paper. The films annealed for 2 days in the flow of pure oxygen gas of 1 atmospheric pressure at 950℃, keeping the Y-Ba-Cu-O film surface in face to face contact with the other Y-Ba-Cu-O film surface, consisted of single phase and were oriented with the C-axis perpendicular to the substrate surface (Figs. 1(c) and 1(d)). On the other hand, the films annealed by the usual method showed rather complex diffraction patterns and were seen to consist of mixed phases (Figs.1(e) and 1(f)). In addition, It was found from the RBS analyses that the close contact annealing method could dramatically reduce the sublimation of the film elements, compared with the usual annealing method. Thus, samples for the following study were subjected to the close contact annealing method.

In order to investigate the differences of the diffusion properties between the single-crystal and the amorphous films, detailed

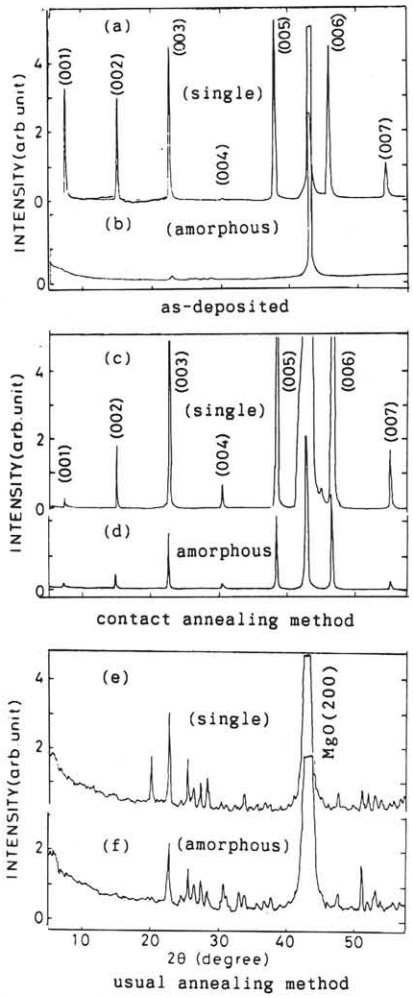


Fig. 1 X-ray diffraction patterns of thin Y-Ba-Cu-O films.

analyses by RBS using 3.2 MeV He ions were applied. The time evolutions of the RBS spectra during annealing for single and amorphous films are shown in Fig. 2. The RBS spectra were appreciably different between single-crystal and amorphous films. Because of overlapping of the spectra, high accuracy of quantitative analyses of RBS spectra from Ba and Y element could not be expected. Thus, only diffusivities of Cu element of Y-Ba-Cu-O were quantitatively evaluated in the following. In case of amorphous films, low energy tail of the spectra from Cu element grew rather rapidly and the slope of the high energy edge of Mg spectra, which corresponds to the interface, became less steep with increasing annealing times during the early stages within about one day. The time evolution of the RBS spectra became very slow afterwards. It should be noted that there is not so much differences between the spectra from samples annealed for one day and those annealed for 30 days at 950℃. In case of single-crystal films, on the other hand, both the shape of the low energy tail of the Cu spectra and the slope of the high energy edge of Mg spectra changed only very slightly with the increase of annealing times.

Considering the model of one-dimensional diffusion, the distance of penetration of Cu element into MgO substrates should be proportional to the square root of time.[8] Then, the above-mentioned results of the RBS analyses in the case of amorphous sample were difficult to ascribe only to diffusion. The authors interpreted that the rather rapid initial evolution of low energy tail of the RBS spectra from Cu element was due largely to

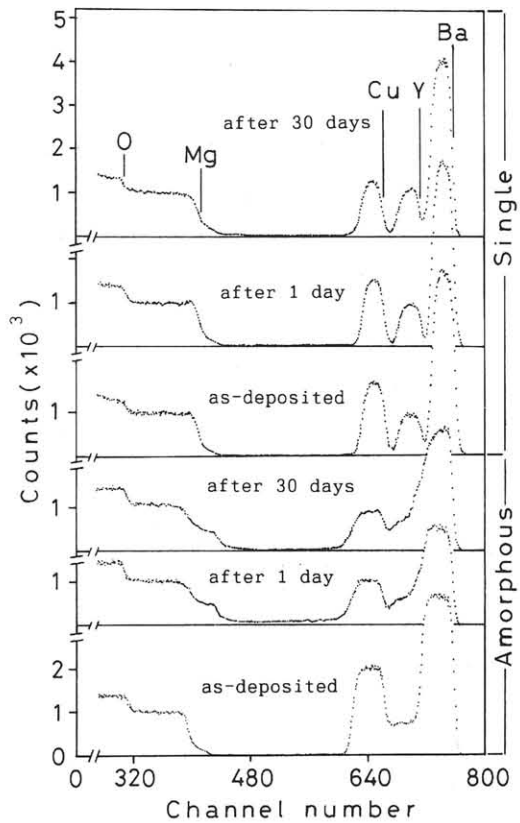
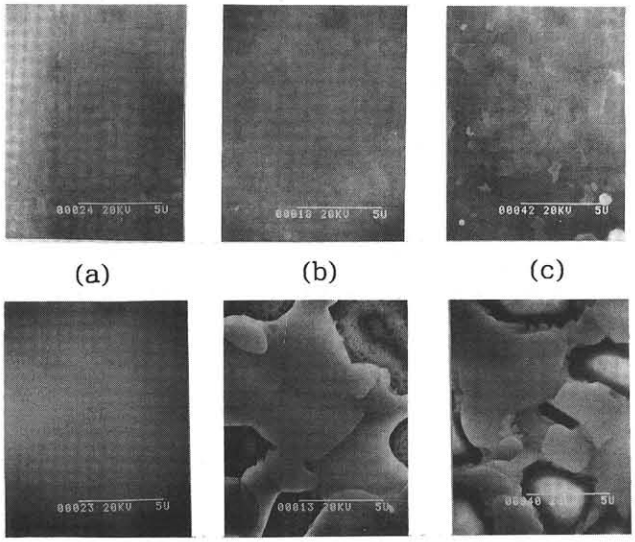


Fig. 2 Time evolution of RBS spectra of thin Y-Ba-Cu-O films.

the variation of the morphology of the Y-Ba-Cu-O films on the MgO substrates during annealing. The above interpretation were additionally supported by SEM observations. The SEM images of both as-deposited single-crystal and amorphous films are shown in Figs. 3(a) and 3(d), respectively. The SEM images of both as-deposited single-crystal and amorphous films indicate rather smooth surfaces. In the case of amorphous films, the SEM images changed distinctly and showed the morphology of "lake-like" structure after no more than one-day of annealing at 950 ℃ as shown in Figs. 3(d),3(e) and 3(f). The "lake-like" structure of the film was almost the same even after 30 days of annealing, although the coverage of the film seemed to be little bit reduced. On the other hand, in the case of single-crystal films, the SEM images did



(a) (b) (c)

(d) (e) (f)

Fig. 3 Time evolution of SEM micrographs of thin Y-Ba-Cu-O films annealed at 950℃.
(a), (b) and (c): single crystal.
(d), (e) and (f): amorphous.
(a) and (d): as-deposited.
(b) and (e): after one day.
(c) and (f): after 30 days.

not changed so much with the annealing time, as shown in Figs. 3(a), 3(b) and 3(c), though "lakes" began to appear sporadically after about 30 days of annealing.

The diffusivities of Cu element into MgO substrates was evaluated from the RBS spactra obtained for samples annealed for 30 days. As stated above, the measured RBS spectra were, however, broadened not only by diffusion effect but also by both the finite resolution of the detection system and the effect of morphology variation (uneveness). Thus, taking into account the fact that morphology variation mostly occured within about one day of annealing and did not changed so much afterwards, the effects of finite resolution and the morphology variation were subtracted in the present analyses, by using the data from the RBS spectra obtained for samples annealed for one day. Here, Gaussian type functions were assumed both for the effects of finite resolution of the detection system and for the effect of morphology variations.

Diffusivities at 950 thus obtained were $7.1\times10^{-23}m^2/s$ for single-crystal films and $1.9\times10^{-23}m^2/s$ for amorphous films. The larger value of diffusivity for single-crystal films than that for amorphous films may come from the morphology variation occuring after one day of annealing in case of singe-crystal films. This reasoning is supported by comparing the SEM images from samples annealed for one day (Fig. 3(b)) and for 30 days (Fig. 3(C)). In addition, it is difficult by nature to accurately assess the effect of morphology variation on the RBS spectra. So, some uncertainty still remains inevitably in the measured diffusivities. Thus, no definite conclusion can be drawn on the effects of crystallinity on interdiffusion between thin Y-Ba-Cu-O films and MgO substrates. It is safe at present to say that the diffusivity of Cu element of Y-Ba-Cu-O films into MgO substrates at 950 ℃ is, if any, not larger than the value of the order of $10^{-23}m^2/s$. This value is smaller than that previously reported by about four orders of magnitude.

Moreover, by simply comparing the shapes of the RBS spectra of the present study with those of previously reported, it is likely that actual diffusivities of Ba and Y elements into MgO substrates are also very small, though the quantitative analyses are difficult.

The above-mensioned results are highly favourable from the view points of both formation and application of superconducting $YBa_2Cu_3O_{7-y}$ thin films.

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