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Effects of Activated Oxygen Plasma on the Crystallinity and Superconductivity of $YBa_2Cu_3O_{7-x}$ Thin Films Prepared by Reactive Co-evaporation Method

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Abstract As-grown $YBa_2Cu_3O_{7-x}$ films on MgO(100) substrates were prepared by a reactive co-evaporation method, and effects of activated oxygen plasma on the crystallinity and superconductivity at substrate temperature ranging from 450℃ to 590℃ were investigated. The film deposited under the activated oxygen plasma at the substrate temperature of 590℃ had a single crystal phase. Whereas, when films were deposited under only oxygen gas, they were not in perfect single crystal phase but with slight polycrystalline nature. When the substrate temperature was 590℃, Tc_{zero}'s were 83K and 80K for films with and without activated oxygen plasma, respectively. The critical temperature, the crystal structure and the surface morphology of as-grown films were found to be insensitive to the activated oxygen plasma which is introduced during deposition instead of oxygen gas, but the crystalline quality was improved somewhat by the introduction of activated oxygen plasma.

1. Introduction

High-Tc superconducting thin films with good properties can be produced successfully by various techniques[1~4]. However, for the practical application, it is desirable to fabricate films on the suitable substrate at the lower growth temperature and lower oxygen partial pressure, because they can minimize problems of the thermal stress of films and the inter-reaction between film and substrate. Recently, there have been several reports[5~6] on the studies of the crystalline quality and morphology of high-Tc superconducting films. Generally, it is well recognized that crystalline qualities and surface morphologies of films are affected by the growth temperature and oxygen partial pressure at the substrate. However, there are few detalied reports on the effects of activated oxygen plasma during deposition on the superconductivity and crystallinity of as-grown superconducting thin films. In our previous papers[7~8], we reported on the detailed fabrication procedure and experimental results on superconducting properties of as-grown films as a function of substrate temperature and oxygen partial pressure.

In this paper, we describe the effect of the activated oxygen plasma at substrate temperature ranging from 450℃ to 590℃ on the crystallinity and superconductivity of as-grown $YBa_2Cu_3O_{7-x}$ (YBCO) thin films prepared by a reactive co-evaporation method.

2. Experimental procedure

As-grown thin films were prepared by a reactive co-evaporation method on MgO(100) single crystal substrate. Source materials of Y_2O_3 and Cu were evaporated from electron beam guns and Ba was evaporated from a Knudsen cell.

The ultimate pressure before introduction of oxygen into the main chamber was about 1×10^{-6} Torr. The chamber pressure after introduction of oxygen was maintained about 9.5×10^{-5}Torr. In order to increase the oxygen partial pressure at the substrate, oxygen gas was introduced through the oxygen injection nozzle located near the substrate. The evaporation rate of each source was controlled individually by the three separated quartz crystal sensors located near the substrate to yield the stoichiometry of films. The evaporation rate was about 40 Å/min. The film thickness was 2500 to 3000 Å. After deposition, the film was cooled down with the same oxygen pressure as in the deposition. In order to investigate the effects of activated oxygen plasma on crystalline properties and the superconductivity, films were prepared under different oxidization conditions. That is, one group of samples was deposited and cooled down under the activated oxygen plasma (herein-after referred to as AOP) and another group was deposited and cooled down only in the pure oxygen gas (without AOP treatment). For the activated oxygen plasma, the bias coil with RF input power of 100W was introduced into the vacuum chamber. Atomic compositions in as-grown films were analyzed by the inductively coupled plasma spectroscopy (ICP) and the energy dispersive X-ray (EDX). The crystal orientation and the phase were analyzed by X-ray diffraction (XRD). The reflection high energy electron diffraction (RHEED) was used to study the crystalline properties. Surface morphologies of films were also studied by scanning electron microscopy (SEM). The critical temperature was determined using a standard four probe method.

3. Results and discussion

Figure 1 shows the XRD patterns of as-grown films with and without AOP treatment at various substrate temperatures of 450℃, 510℃, 550℃ and 590℃. As-grown superconducting films with AOP treatment show preferentially c-axis normal orientation with small peaks of secondary phases near the (004) peak. In order to investigate whether these secondary phases are related to the discrepancy from 1:2:3 composition of the film or not, film compositions were analyzed for above both samples.

Figure 2 shows the changes of the film composition, which is indicated by molar ratios of Cu/Y+Ba and Y/Ba for films with and without AOP treatment at various substrate temperatures. The molar ratio of Cu/Y+Ba was ranged from 1.0 to 1.1 for films deposited under the activated oxygen plasma. Whereas,

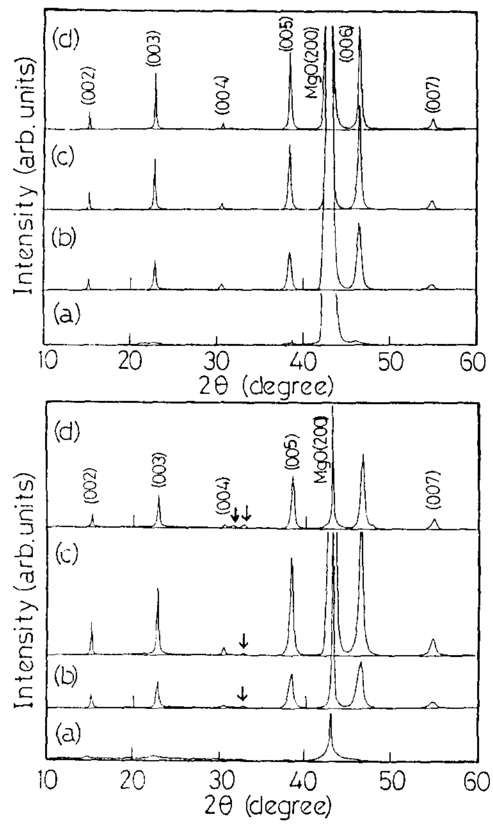

Fig. 1. X-ray diffraction patterns of as-grown YBCO films with (top figure) and without activated oxygen plasma treatment (bottom figure) at various substrate temperatures of (a) 450℃ (b) 510℃ (c) 550℃ (d) 590℃. The peaks of secondary phases are indicate with an arrow.

when the film was deposited only in oxygen, Cu concentration was increased by about 24%, having the Cu/Y+Ba molar ratio of about 1.3 as shown in Fig 2. There was no remarkable difference in the molar ratio of Y/Ba for both samples. The increase of Cu content may bear a direct relation to the origin of secondary phase corresponding to the Cu rich compound. In order to clarify whether the off-stoichiometry causes the secondary phase or not, we prepared the as-grown film with the composition close to the stoichiometry under the deposition condition without AOP treatment by adjusting the evaporation speed of the Cu source material. For these samples, XRD pattern and film composition were investigated.

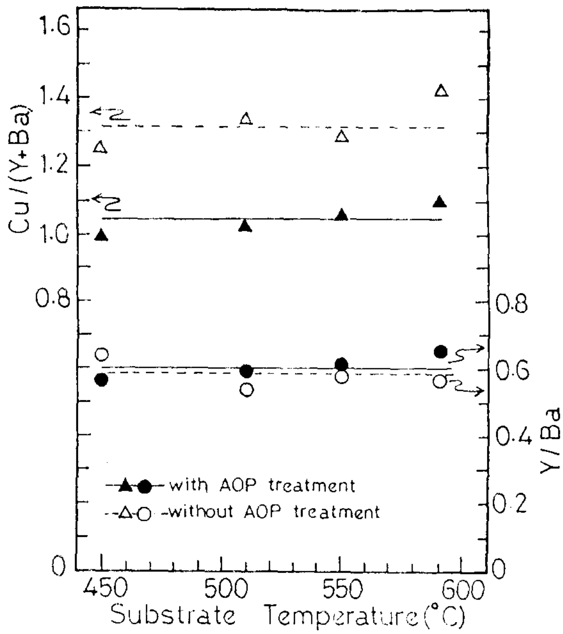

Fig. 2. Dependence of composition ratios of Cu/Y+Ba and Y/Ba for YBCO films with and without activated oxygen plasma (AOP) treatment at various substrate temperatures.

Figure 3 shows XRD patterns of the as-grown films without AOP treatment having the molar ratios of Cu/Y+Ba and Y/Ba ranged in 0.97-0.99 and 0.56-0.61, respectively. These films have the preferentially c-axis normal oriention with the absence of secondary phase. The XRD patterns for these samples are exactly the same as those with AOP treatment as shown Fig. 1(top figure). This result reflects the fact that there is clear correlation between the secondary phase and the off-stoichiometry of films.

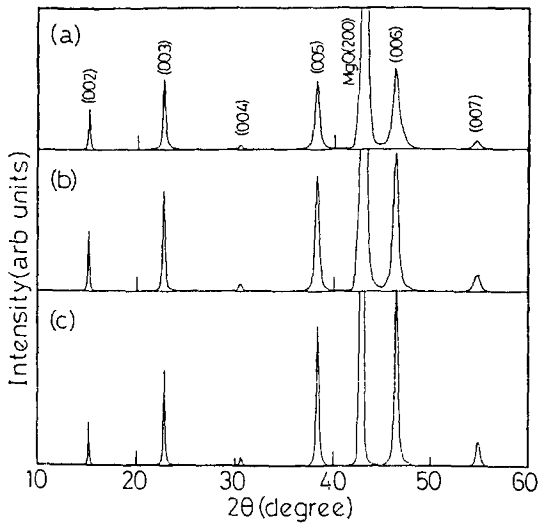

Fig. 3. X-ray diffraction patterns of as-grown YBCO films without activated oxygen plasma treatment at the substrate temperature of (a) 510℃ (b) 550℃ and (c) 590℃. Molar ratios of Cu/Y+Ba and Y/Ba are ranged in 0.97-0.99 and 0.56-0.61, respectively.

Figure 4 shows SEM micrographs of film surfaces deposited with and without AOP treatment. There was no distinct difference in surface morphology between two sample groups, indicating that the outgrowth nuclei occurred at the substrate temperature of 510℃ and these outgrowths enlarged with increasing the substrate temperature from 510℃ to 590℃.

Furthermore, when the films were deposited under the AOP, the full width at half maximum (FWHM) of rocking curve decreased from 1.8° to 0.7° with increasing the substrate temperature from 510℃ to 590℃. It was lowered one as compared to those of films deposited without AOP treatment. These results suggest that the crystalline quality can be improved by increasing the substrate temperature and the introduction of activated oxygen plasma during deposition and cooling process. Changes of FWHM of rocking curves for films

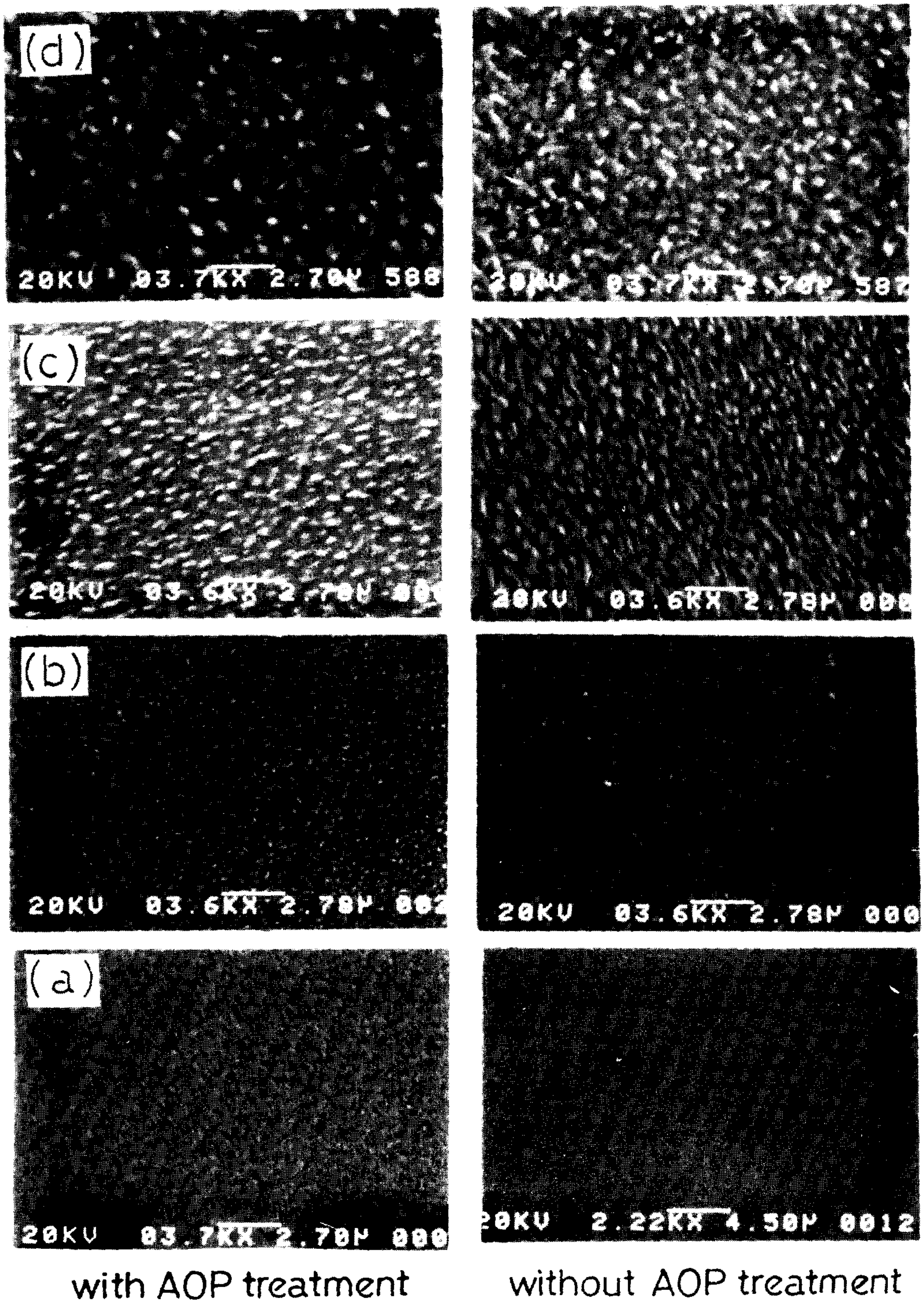

Fig. 4. SEM micrographs of the surfaces of as-grown YBCO films with and without activated oxygen plasma (AOP) treatment at various substrate temperatures of (a) 450℃ (b) 510℃ (c) 550℃ (d) 590℃.

with and without AOP treatment as a function of substrate temperature are shown in Figure 5.

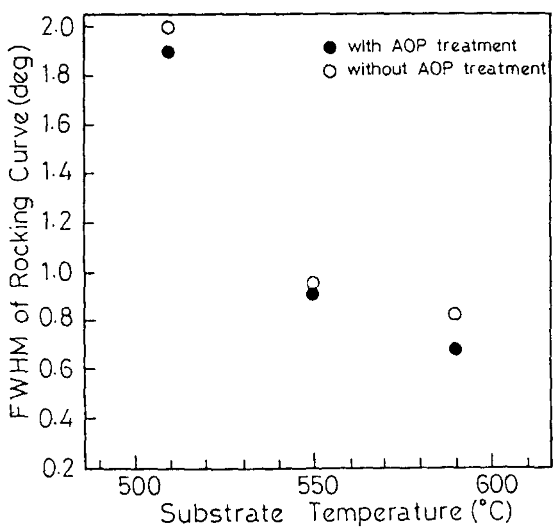

Fig. 5. Changes of FWHM of rocking curves for as-grown films with and without activated oxygen plasma (AOP) treatment as a function of substrate temperature.

Figure 6 shows typical RHEED patterns of as-grown films with and without AOP treatment at various substrate temperatures, 450℃, 510℃ and 590℃, respectively. For the as-grown film with AOP treatment at T_{sub}= 590℃, the RHEED shows spotty patterns indicating that this film is a single crystal with a rough film surface.[6,9] In contrast, the film deposited without AOP treatment shows mixed phases with spotty pattern, containing a small amount of ring pattern in RHEED photograph. This result suggests that the film depsoited without AOP treatment at T_{sub}=590℃ is not a perfect single crystal. However, for films of T_{sub}=450℃ and T_{sub}=510℃, it was found that there was no remarkable difference in RHEED patterns, and those films both with and without AOP treatment, show ring patterns for T_{sub}=510℃ and halo-like patterns for T_{sub}=450℃, respectively. On basis of above results, the crystallinity of films which were deposited at the high temperature, 590℃ was improved more or less by introduction of AOP instead of oxygen gas during deposition. Therefore, it is likely that the improvement of crystallinity may originate from the enhanced mobility of the excited ions of the source elements(Y, Ba and Cu) on film surface by means of activated plasma during deposition. Additional experiments with various RF input power, are now in progress to study effects of the degree of ionization on the film compositions and superconducting properties.

Figure 7 shows the transition temperature of as-grown films with and without AOP treatment as a function of substrate temperature ranging from 450℃ to 590℃. For T_{sub}= 590℃, the Tc_{zero}'s were 83K and 80K with Tc_{onset} of 88K for films with and without AOP treatment, respectively. When films were deposited under the activated oxygen plasma at the substrate temperature of above 510℃, the Tc_{zero} slightly increased as compared to films deposited only in the oxygen gas. This result is different from that reported by M. Matsumoto, et al[10], where the Tc_{zero} was greatly improved by exposing as-grown films in the RF oxygen plasma during the cooling process.

4. Conclusion

We investigated effects of the activated oxygen plasma on the crystallinity and superconductivity of YBCO thin films prepared by a reactive co-evaporation method at various substrate temperatures from 450℃ to 590℃. The as-grown film deposited at T_{sub}=590℃ under the activated oxygen plasma has a single crystalline nature with a rough film surface. Whereas, the film deposited in the pure oxygen gas shows the mixed phases with spotty pattern containing a small amount of ring pattern in RHEED photograph. This suggests that this film is not a perfect single crystal. At T_{sub}=590℃, Tc_{zero}'s were 83K and 80K with Tc_{onset} of 88K for films with and without activated oxygen plasma treatment, respectively. The introduction of activated oxygen

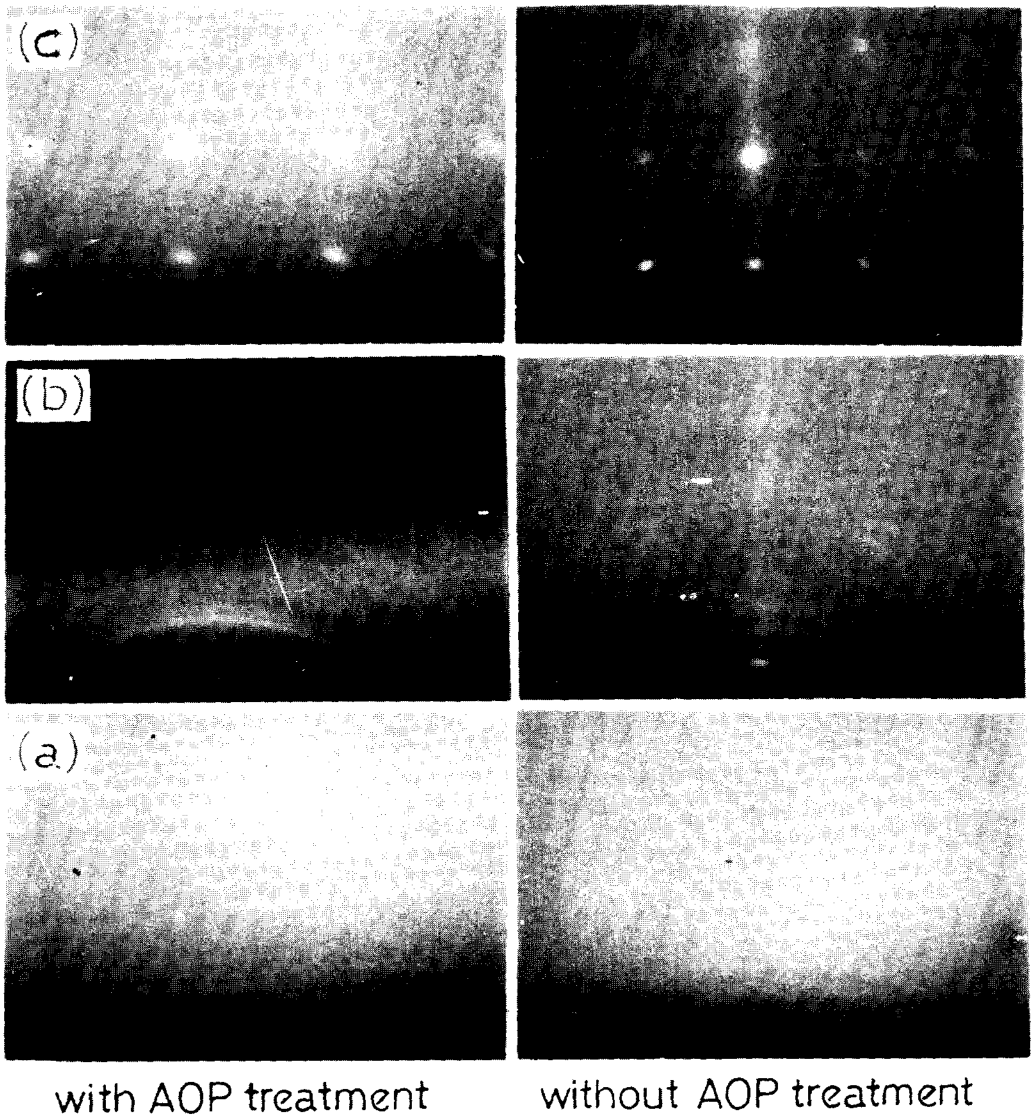

Fig. 6. RHEED patterns of as-grown films with and without activated oxygen plasma (AOP) treatment at various substrate temperatures of (a) 450℃ (b) 510℃ (c) 590℃.

plasma instead of pure oxygen gas during deposition did not make a large change in properties of Tc and surface morphology of as-grown films. However, the crystalline quality was improved somewhat by the introduction of activated oxygen plasma. This improved crystalline quality may be ascribed to the enhanced mobility of excited ions of source materials (Y, Ba and Cu) by the activated plasma.

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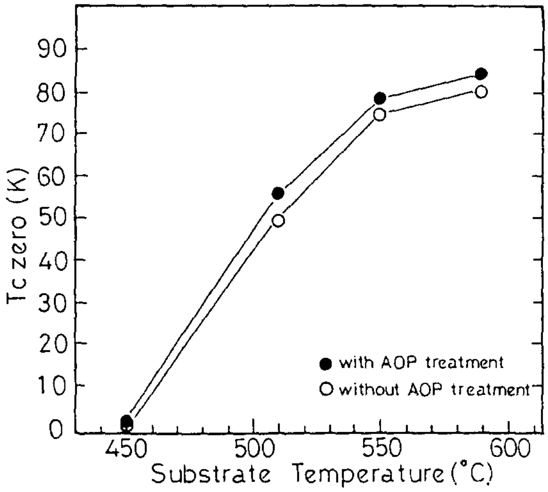

Fig. 7. Transition temperature of as-grown films with (solid circles) and without activated oxygen plasma (AOP) treatment (open circles) as a function of substrate temperature.

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