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Surface Analysis of $YBa_2Cu_3O_{7-x}$ Thin Films by QMS, XPS and LEED: Effects of IN-VACUUM Annealing

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The effects of in-vacuum annealing on the crystal structure and the superconductivity near the surface region of $YBa_2Cu_3O_{7-X}$ thin films were investigated by QMS, XPS and LEED. There exists non-superconductive layer near the surface after being exposed to the air. By annealing at around 350°C in a vacuum chamber whose pressure was greater than $1X10^{-9}$Torr, clean surface with both crystal structure and superconductivity could be obtained.

1. INTRODUCTION

One of the most important properties for electric applications of high Tc superconductors is surface structure. Many workers have studied these surface structures and reported that there exist non-superconducting layers on these films.[1] Taking the short coherent length into consideration, it may be essential to develop a surface cleaning process for device constructions.

We will report the effects of in-vacuum annealing on surfaces of c-axis oriented YBCO thin films by low energy electron diffraction(LEED), quadro-pole mass spectroscopy (QMS) and X-ray photoelectron spectroscopy (XPS). These results confirm that in-vacuum annealing is effective to obtain film surfaces with both crystal structure and superconductivity.

2. EXPERIMENTAL

The YBCO thin films were prepared on MgO(100) heated at 700 °C using a single-target pulse laser deposition technique[2] or sputtering. As-deposited films exhibited superconducting transition at 88K. Sample films were transported into an angle resolved XPS analysis chamber or a LEED analysis chamber, after being exposed to the air. These films were annealed in ultra-high vacuum greater than 1X10-9 Torr for 3 minutes at each annealing temperature up to 700°C. The heating rate was 26 °C/min. During the annealing process, desorption spectra of gases from YBCO films were examined by QMS attached to each analysis chamber. After the annealing process, XPS or LEED measurements were performed below 100°C. The oxygen-deficiency of films was estimated by Raman scattering and the compositional changes in depth were examined by Auger electron spectroscopy(AES) after these analyses.

3. RESULT AND DISCUSSION

Angle-resolved XPS spectra of the as-deposited film indicated there existed surface layers, which were not representative of the bulk. The surface layers were mainly composed of hydrocarbon and carbonate. No image could be observed by LEED. These results suggest the surface layer can be regarded as a disordered layer.

Figure 1 shows temperature programmed desorption spectra from YBCO films and MgO substrates. CO_2 desorption started at 100 °C and decreased at 300 °C. At this stage, the XPS intensity which came from the surface layer decreased as the sample temperature increased. This suggests carbonates decomposed at this temperature range. O_2 desorption started at 350°C and decreased at 400°C. At the early stage of oxygen desorption, it was noted that the XPS spectra attributed to the surface layer almost disappeared. After the decrease of the surface layer, an orthogonal YBCO(001)1x1 pattern began to appear by LEED but background intensity was still high as shown in Fig.2(a). Such an image can be considered to show the coexistence of poorly ordered small domains. Spot intensity of LEED patterns gradually became higher with increasing sample temperature as shown in Fig 2(b). In some cases, the ordering of surface atoms was much improved and a 2x1 superstructure appeared at about 700°C as shown in Fig.3(c). Many electron-diffraction studies have been published showing different kinds of superstructure reflections depending on oxygen concentration and several oxygen ordering models have been proposed.[3] D. de Fontaine reported that ortho(II) phase gave a doubling of a axis with every second CuO chain occupied along the b direction.[4] YBCO(001) 2X1 superstructure observed by LEED almost agrees with this model. The oxygen content of ortho(II) phase is 6.28-6.61. The oxygen content of YBCO thin film annealed at 700°C was about 6.1.(the oxygen content of the film annealed at 600°C was 6.3 estimated by Raman scattering.) This discrepancy can be accounted for if oxygen atom were segregated near the surface, because in this case, oxygen atoms were removed from the film by in vacuum annealing. However more careful observations and analyses will be required to confirm the oxygen ordering by LEED. Anyway, these results suggest that in-vacuum annealing at above 350°C is effective to obtain film surfaces with crystal structure. It is noted that the samples after oxygen desorption show no superconductivity.

Furthermore, we investigated changes of Cu2p spectra to evaluate superconductivity at film surfaces because the intensity of Cu2p satellite peak reflect the Cu state.

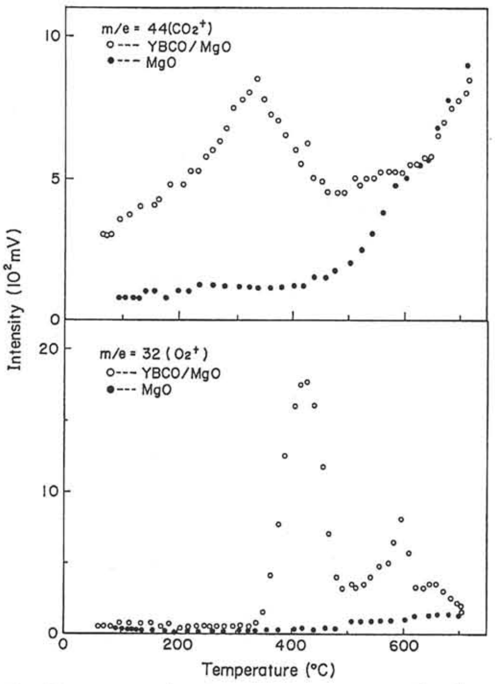

Fig.1 Temperature programmed desorption spectra from YBCO thin films.

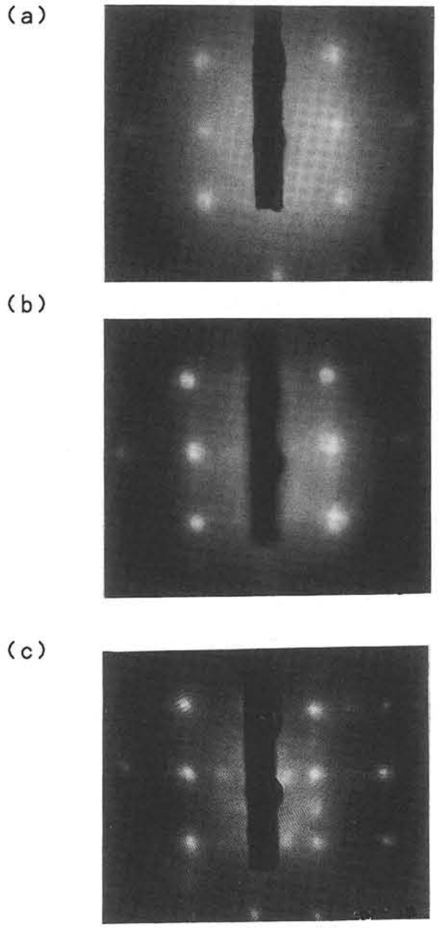

Fig.2 LEED patterns of YBCO(1x1) thin film after in-vacuum annealing at (a)400°C and (b)700°C, and of (c)YBCO(2x1). (Ep=71eV)

Figure 3(a) shows Cu2p spectra from different escape depths of as-deposited film and Fig.3(b) shows that of in-vacuum annealed film at 350°C. Intensities of Cu2p satellites are characteristic of Cu^{2+}/Cu^{3+} compounds.[5] These spectra indicated the as-deposited film have a surface layer and the film after in-vacuum annealing at 350°C have a negligible surface layer thinner than the Cu escape depth of this analysis condition(0.3nm). The intensity ratios of the satellite peaks to the main peaks of bulk scraped samples were reported to be 35%. The intensity ratio of this film were 33% in good agreement with the bulk scraped samples. These results suggested in-vacuum annealing at about 350°C is also effective to obtain film surfaces with superconductivity.

In order to investigate the effect of in vacuum annealing on the inside of the film, AES measurements were also performed. Figure 4 shows the change of the intensity ratios in depth of the YBCO thin film after annealing at around 350°C. Any changes and the segregation of oxygen atoms could not be detected compared with the as deposited film. This results confirmed that in-vacuum annealing changed only the surface region and superconductivity maintain from the film surface region to the near-substrate region.

4. CONCLUSIONS

1)Surface cleanness and crystallinity of YBCO thin films were improved as the temperature of in-vacuum annealing increased.

2)In-vacuum annealing at about 350°C is critical to obtain film surfaces with both crystal structure and superconductivity.

5. REFERENCES

1)C.C.Chang et al.:J. Appl. Phys. 67(1990)7483.

2)N.Yoshida et al.:Proc. ISS'89 853, Tukuba.

3)R.Beyers et al.:Nature 340(1989)619.

4)D. de Fontaine et al.:Nature 343(1990)544.

5)F.Werfel et al.:Z.Phys. B-Condensed Matter 70(1988)317.

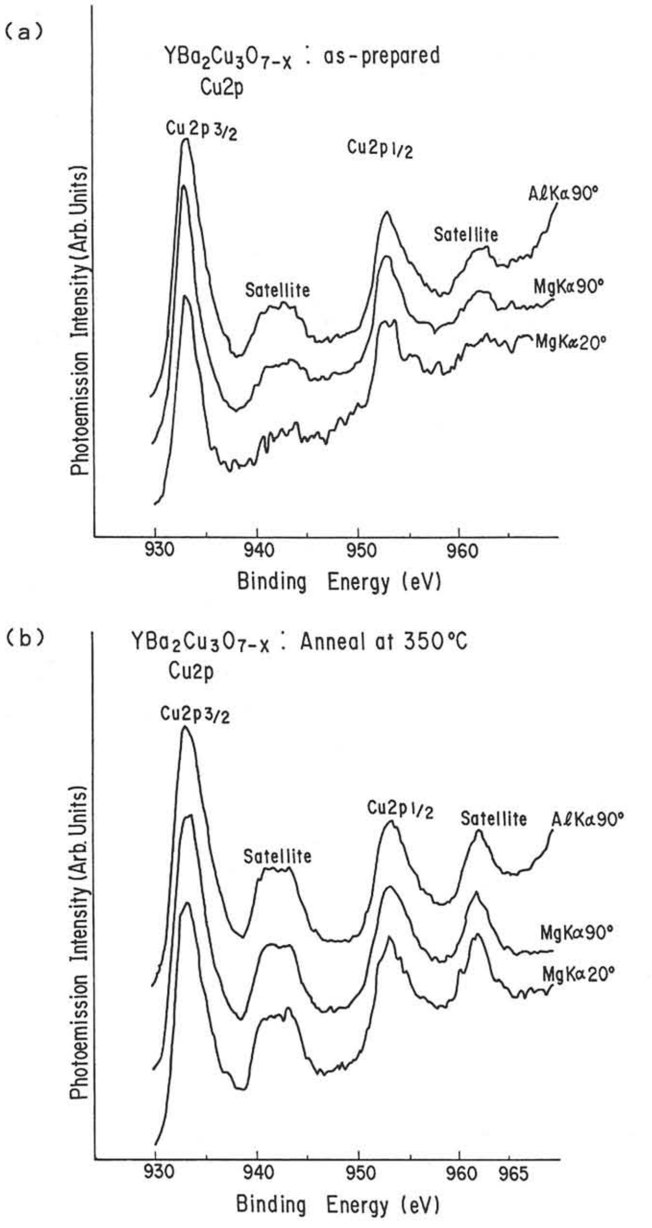

Fig.3 Cu2p spectra from different escape depths of YBCO thin film.
(a)as-deposited film.
(b)in-vacuum annealed film at 350°C.

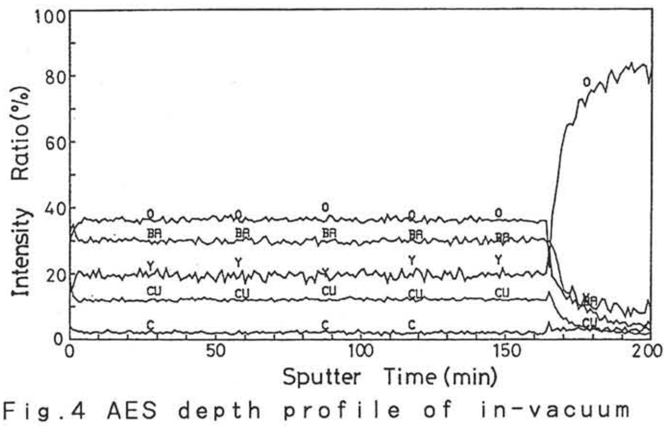

Fig.4 AES depth profile of in-vacuum annealed YBCO thin film.