Chemical State Analysis of $Bi_2Sr_2CaCu_2O_y$ Single Crystals heated in Air

Y.Yamauchi, S.Kishida and H.Tokutaka

Department of Electrical and Electronic Engineering, Tottori University, 4-101 Minami, Koyama-cho, Tottori 680-8552, Japan

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In order to clean the surfaces of $Bi_2Sr_2CaCu_2O_y$(BSCCO) single crystals, we heated them in air and in the atmospheres of Ar and O_2 gases, and then investigated the surface compositions and the chemical bond natures of constituent elements by X-ray photoelectron spectroscopy(XPS). From the results, we found that carbon and impurity oxygen on the surfaces of BSCCO single crystals were effectively removed by heat-treatments in air and in O_2 gas, and that the chemical bond natures of Cu and O did not change. Therefore, the heat-treatments are thought to be useful to obtain a clean surface of BSCCO single crystals.

1. Introduction

In order to fabricate superconducting devices and to analyze the superconductor surfaces exactly, it is necessary to obtain a clean surface of superconductors. The clean surfaces of $Bi_2Sr_2CaCu_2O_y$(BSCCO) single crystals were obtained by cleaving them in vacuum[1,2], by heating them in vacuum after cleaving in air[3,4] and so on. It is necessary to find easier method for obtaining a clean surface of single crystals ex-situ.

In this study, we heat-treated BSCCO single crystals at various temperatures in air, and in the atmospheres of Ar and O_2 gases, and then investigated their surfaces with X-ray photoelectron spectroscopy(XPS).

2. Experimental

BSCCO single crystals were prepared by a self flux method[5]. The samples were easily cleaved in air using an adhesive tape, and the cleaved surface is known to be (001) face and a Bi-O layer. They were heated at the temperatures from room temperature to 800℃ for 1h in air and in Ar and O_2 gases. Then, the samples were quickly transferred into an XPS chamber. The XPS measurements were carried out with Shimadzu ESCA 750 spectrometer in the base pressure less than 3×10^{-5} Pa using X-ray source of MgKα. The XPS peak positions of all the constituent elements were corrected by that of C-1s at near 285eV.

3. Results and Discussion

Figure 1 shows the XPS spectra of C-1s core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air. As shown in Fig.1, the C-1s XPS peak due

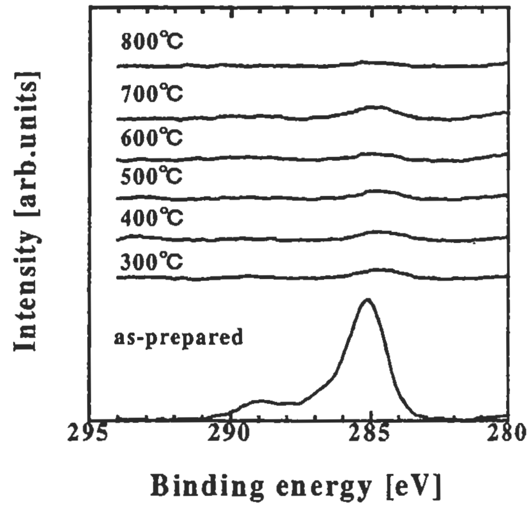

Figure 1. The XPS spectra of C-1s core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air.

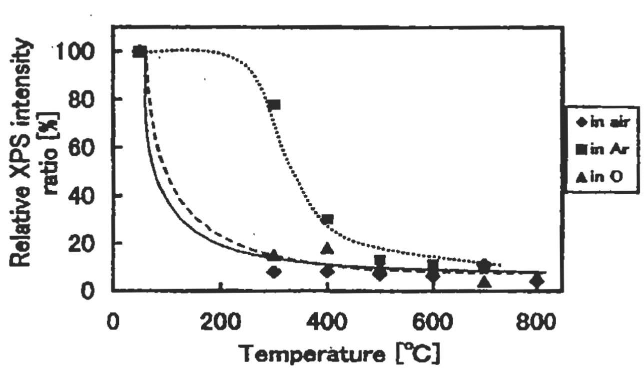

Figure 2. The relative C-1s XPS intensity ratio of after to before the treatments in various atmospheres as a function of heat-treatment temperatures.

to impurity was observed at near 285eV. With increasing the temperature of heat-treatments, the intensities of C-1s peak decreased. This indicated that the carbon impurity on the surfaces of BSCCO single crystals was removed by the heat-treatment in air.

Figure 2 shows the relative C-1s XPS intensity ratio of after to before the treatments in various atmospheres as a function of heat-treatment temperatures. In Fig.2, relative XPS intensity ratio decreased with increasing the temperature of heat-treatments. The intensity ratio in air and in O_2 gas abruptly decreased at about 300℃, whereas the intensity ratio at the temperatures from 300℃ to 400℃ in Ar gas was larger than those in air and in O_2 gas, and the intensity ratio at the temperatures more than 500℃ in Ar gas was nearly equal to those in air and in O_2 gas. This indicates that in order to remove efficiently carbon on the surfaces of BSCCO single crystals, it is necessary to use the atmosphere including oxygen.

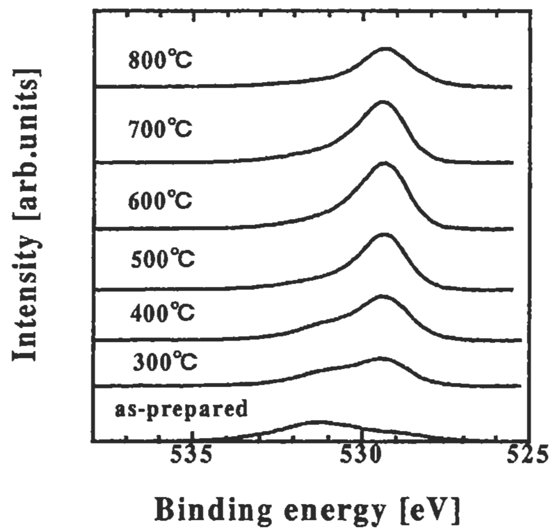

Figure 3. The XPS spectra of O-1s core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air.

Figure 3 shows the XPS spectra of O-1s core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air. In Fig.3, the O-1s XPS peaks at near 529 eV and 532 eV which were related to a BSCCO single crystal and an impurity oxygen were observed, respectively. In Fig.3, with increasing the temperature of heat-treatments, the intensity of O-1s XPS peak at about 532 eV decreased, whereas the intensity of O-1s XPS peak at about 529 eV increased and became dominant in the O-1s spectra. In addition, the XPS intensities at about 529 and 532eV are approximately proportional to the concentrations of BSCCO and impurity oxygen on the surfaces, respectively. Therefore, we can estimate the cleaning degree of the surfaces from the intensity ratio of 532 to 529eV in O-1s spectra.

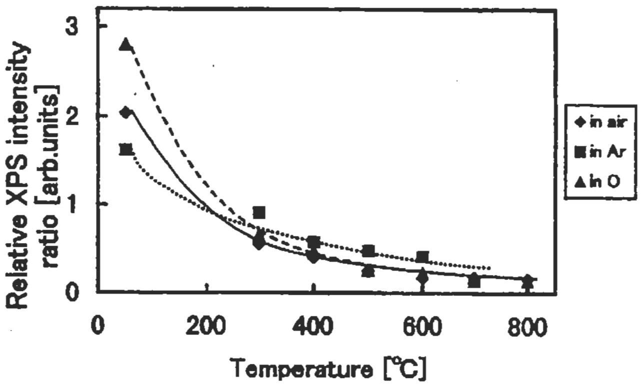

Figure 4. The relative O-1s XPS intensity ratio of 532 eV to 529 eV peak from the surfaces of BSCCO single crystals heated in various atmospheres as a function of heat-treatment temperatures.

Figure 4 shows the relative O-1s XPS intensity ratio of 532 eV to 529 eV peak from the surfaces of BSCCO single crystals heated in various atmospheres as a function of heat-treatment temperatures. In Fig.4, the intensity ratio in all atmospheres was decreased with increasing the temperature of heat-treatments. This indicated that the impurity oxygen on surfaces of BSCCO single crystals was effectively removed regardless of heat-treatment atmospheres.

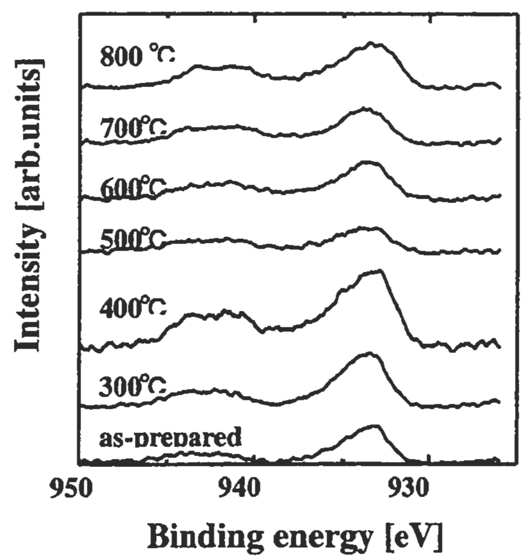

Figure 5. The XPS spectra of Cu-2p 3/2 core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air.

Figure 5 shows the XPS spectra of Cu-2p 3/2 core levels from the surfaces of BSCCO single crystal heat-treated at various temperatures in air. In Fig.5, the Cu-2p 3/2 main and satellite peaks were observed at about 934 eV and 943 eV, respectively. The satellite peak showed the existence of Cu with the valence of 2+. There is Cu^{2+} on the clean surface of BSCCO single crystals, where the intensity ratio of Cu-2p 3/2 satellite to main peaks is about 50%.

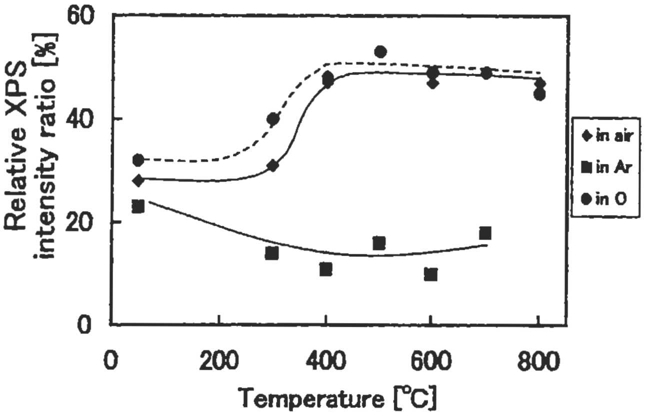

Figure 6. The relative XPS intensity ratio of Cu-2p 3/2 satellite to main peaks in various atmospheres as a function of heat-treatment temperatures.

Figure 6 shows the relative XPS intensity ratio of Cu-2p 3/2 satellite to main peaks in various atmospheres as a function of heat-treatment temperatures. In Fig.6, in the case of heat-treatments in air and in O_2 gas, the intensity ratio of the satellite to main peaks increased with increasing the temperature of heat-treatments and then, tends to saturate at about 400℃. This indicated that the chemical bond natures of Cu on the surfaces heat-treated at the temperatures more than 400℃ did not change. In Ar gas, the intensity ratio decreased with increasing the temperature of heat-treatments. This indicated that Cu was oxygen-reduced by the heat-treatment under the condition in the absence of O_2 gas. From the results, we found that the optimum atmospheres for obtaining a clean surface of BSCCO single crystals were in air and in O_2 gas, and that the optimum temperature of heat-treatment was about 400℃.

4. Conclusions

We carried out the cleaning of BSCCO single crystal surfaces by the heat-treatments at various temperatures in various atmospheres, and investigated their surfaces with XPS. From the results, we found the carbon and impurity oxygen on the surfaces of BSCCO single crystals were effectively removed by heat-treatments at about 400℃ in air and in O_2 gas, and that the chemical bond natures of Cu and O did not change.

5. References

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