Electrode Formation and Surface Analysis of Bi-based Superconducting Ceramics

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Au metals were deposited on the surface of Bi-Sr-Ca-Cu-O (Bi-based) superconducting ceramics to form electrodes. The contact resistance of the specimen decreased by heating at 400℃ for 5h in air. The X-ray photoelectron spectroscopy spectra from the surface of the ceramics and electrodes showed that the chemical bond nature of constituent elements from the specimen surface did not change by heating it. From the XPS depth profile of the heated specimen, we found that there was the diffusion layer on the surface, where Au diffused into the bulk of the ceramics. The diffusion layer is thought to cause the decrease of the contact resistance between the specimen and electrodes.

1. Introduction

In order to apply the high-Tc superconducting oxides into the field of power electronics, it is necessary to form ohmic electrodes with low contact resistivity on superconductor surfaces. Au metal is thought to be a good electrode materials, because of their low resistivity and chemical stability. We formed the Au electrodes on 2212-phase Bi-based superconducting single crystal[1-2] and obtained the low contact resistance[3]. However, superconducting devices with a high current density generally are made from polycrystals.

In this study, we deposited the Au metals on the various surfaces of Bi-based superconducting ceramics and heated the specimen in order to decrease the contact resistance. We investigated the surface composition and surface state of the specimens by X-ray photoelectron spectroscopy (XPS) to clarify the mechanism and to decrease the contact resistivity.

2. Experimental

The Bi-Sr-Ca-Cu-O (Bi-based) superconducting ceramics used in this study [4] were prepared by a solid-state reaction method. The typical critical temperature of the ceramics was about 100K. The surfaces of the ceramics were polished by several kinds of sandpaper (polished). Next, Au metal (~20nm) were evaporated on the polished surfaces by a vacuum deposition method in a base pressure of 10^{-3}Pa (Au deposited). After Au depositing, the specimens were heated at 400℃ for 5h in air (heat treated). The electrodes were formed on the surfaces. Cu wires were fixed on the surfaces of the specimens using Ag-paste and the contact resistances were measured.

The chemical bond natures of the constituent elements on the Bi-based superconducting ceramics surfaces and Au electrodes were investigated by X-ray photoelectron spectroscopy (XPS). The XPS measurements were carried out using an ESCA-750 spectrometer (source: MgKα_2, resolution: 1.15eV, base pressure: $1\text{-}3\times10^{-6}$ Pa). In the case of the specimens used for XPS measurements, Au metal (~5nm) were evaporated on the surfaces polished by #240 sandpaper and heated at 400℃ for 5h in air. The depth profiles of the specimens (Ar^+-sputter etching conditions; Ar^+ beam energy: 2keV, ion beam current: 5μA, Ar gas pressure: 5×10^{-4}Pa) were also investigated by XPS.

3. Results and Discussion

Figure 1 shows the contact resistance between Bi-based ceramics and electrodes, which were prepared using (a) the surfaces of the ceramics polished by several kinds of sandpaper, (b) the surfaces obtained by depositing Au metal on the surfaces of (a) and (c) the surfaces by heating the surfaces of (b) at 400℃ for 5h in air. The number of

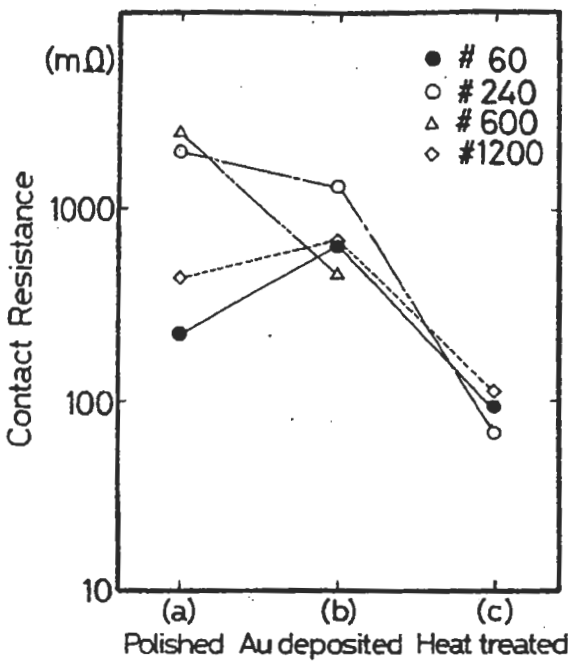

Fig.1 The contact resistance between Bi-based ceramics and electrodes, which were prepared using (a) the surface polished by sandpaper, (b) depositing Au metal on the surfaces of (a) and (c) the surface heating the surfaces of (b) at 400 ℃ for 5h in air.

grain size of the sandpaper was shown in the figure. The wide range difference of the contact resistance among (a) polished surfaces was obtained by a grain size of the sandpaper. This may indicate that polished surfaces are different from specimen to specimen. The contact resistances of (b) Au deposited surfaces were about 1Ω. The contact resistances of the (c) heat treated surface decreased, and were about 100mΩ. Here, the contact resistance is independent of the grain size of the sandpaper. From the results, we found that the contact resistance decreased by heating Au deposited surface in air. In order to clarify the reason, the XPS measurements from the (b) Au deposited and (c) heat treated surfaces were carried out.

Figure 2 shows the XPS spectra of Bi-4f core levels from (a) the surface obtained by depositing Au on the Bi-based ceramics (Au deposited) and (b) the surface by heating Au deposited specimen at 400℃ for 5h in air (heat treated). The two peaks due to Bi-4f 7/2 and 5/2 were observed in the XPS spectra of (a) and (b). The peak energy of Bi-4f 7/2 and 5/2 from the surface of (a) were nearly as same as that from the surface of (b).

Figure 3 shows the XPS spectra of Sr-3d and Pb-4f from the surfaces of (a) Au

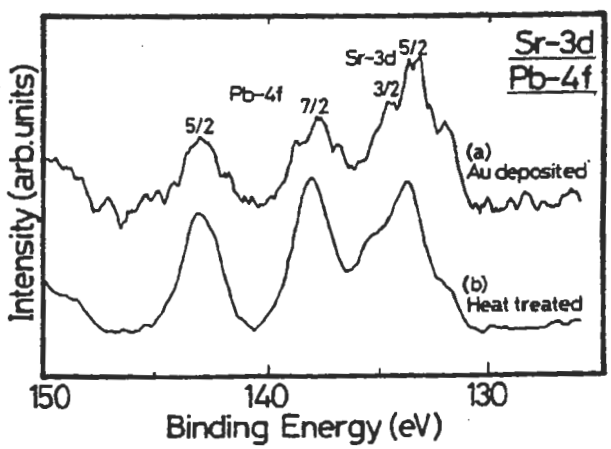

Fig.3 The XPS spectra of Sr-3d and Pb-4f core levels from the surfaces of (a) Au deposited and (b) heat treated specimens.

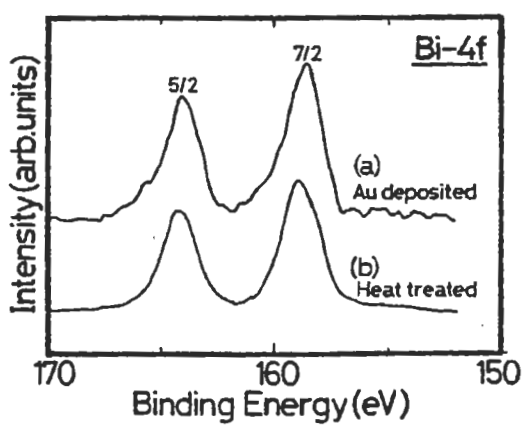

Fig.2 The XPS spectra of Bi-4f core levels from the surfaces of (a) Au deposited and (b) heat treated specimens.

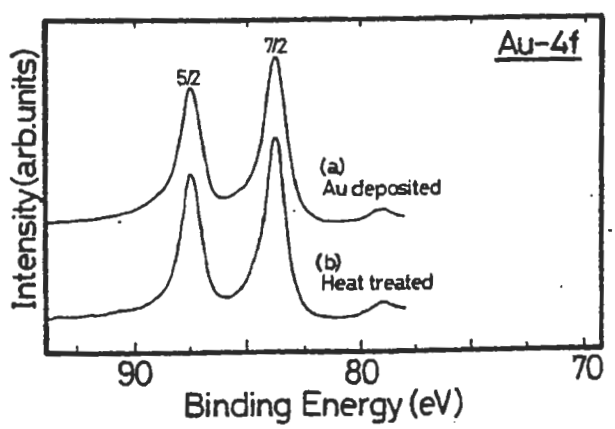

Fig.4 The XPS spectra of Au-4f core levels from the surfaces of (a) Au deposited and (b) heat treated specimens.

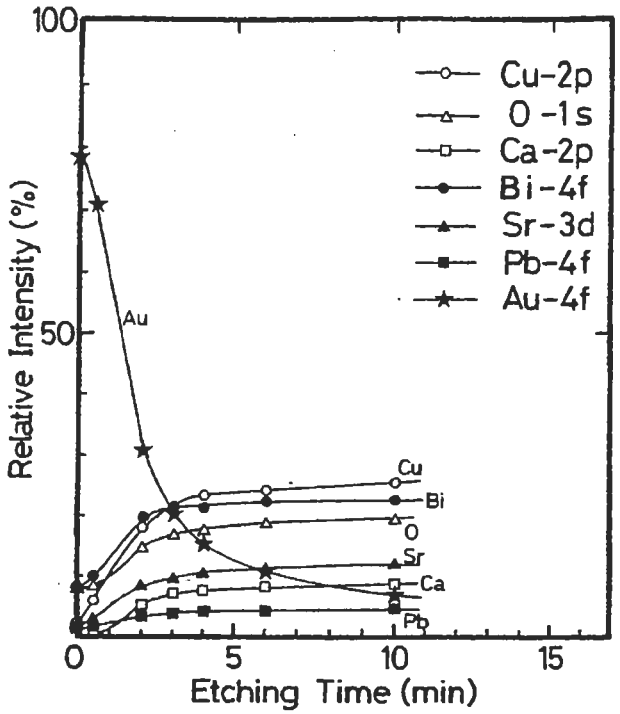

Fig.5 The XPS depth profiles of Bi-based ceramics obtained by depositing Au on the surface polished using #240 sandpaper.

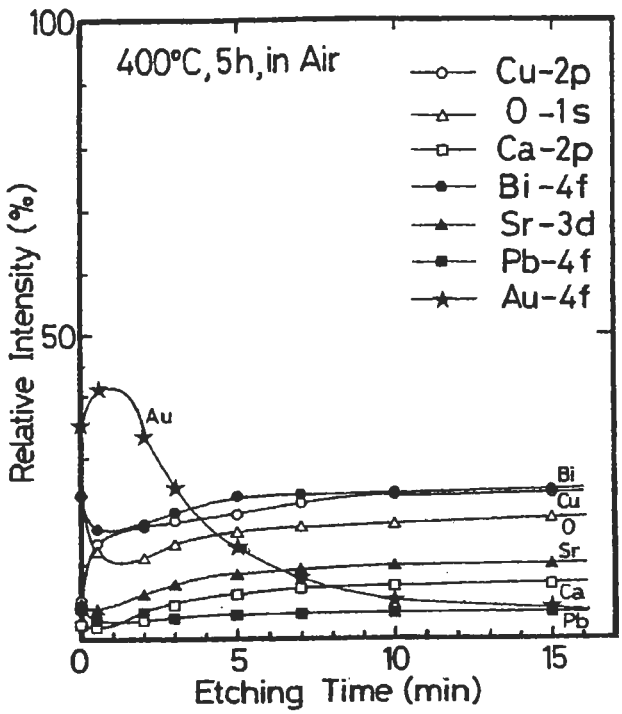

Fig.6 The XPS depth profiles of Bi-based ceramics obtained by heating the Au-deposited surface at 400℃ for 5h in air

deposited specimen and (b) heat treated specimen. The peak energy of Sr-3d 5/2, 3/2 and Pb-4f 7/2, 5/2 from the surface of (a) were also as same as that from the surface of (b). Figs. 2 and 3 indicate that chemical bond nature of the constituent elements did not change by heating the specimen at 400℃ for 5h in air.

Figure 4 shows the XPS spectra of Au-4f from the surfaces of (a) Au deposited specimen and (b) heat treated specimen. The peak energies of Au-4f 7/2 and 5/2 from the surface of (a) were as same as those from the surface of (b). The result indicates that Au does not react with constituent elements by heating the specimen at 400℃ for 5h in air. Therefore, Au is thought to be the good materials as the electrode.

Figure 5 shows the XPS depth profile of Bi-based ceramics obtained by depositing Au on the surface without any heat treatments. As shown in Fig. 5, the relative intensity of Au decreased with increasing the Ar^+-etching time, while the relative XPS intensities of Bi, Pb, Sr, Ca, Cu and O increased and finally, were saturated at the etching time of 4min. From the depth profile of Au deposited specimen, we found that the Au existed on the surface of ceramics, which did not diffuse into the ceramics.

Figure 6 shows the XPS depth profile of Bi-based ceramics obtained by heating the Au deposited specimen at 400℃ for 5h in air. The relative XPS intensity of Au showed the maximum value at the Ar^+-etching time of 30sec and then, decreased. In contrast with the Au, the relative XPS intensity of Bi, Pb and O showed the minimum at the etching time of 30sec and then, increased with increasing the Ar^+-etching time. The relative XPS intensities of Sr, Ca and Cu increased with the Ar^+ etching time. From the results, we found that there was the diffusion layer (Ar^+-etching time: 0-30sec) on the surface of heat treated specimen, where Bi, Pb and O moved toward the surface and Au diffused into the ceramics.

In the diffusion layer between Au and ceramics, Bi, Pb and O moved toward the surface. In general, the surface of the Bi-based superconducting ceramics tends to be (001)-oriented and their top most layer may

be a Bi-O layer since the cleavage surface of Bi-based superconducting single crystals is a Bi-O layer [5-6]. The contact resistance between Au and Bi-based superconducting ceramics decreased by forming the diffusion layer. This may due to the increase of the contact area by Au diffusion at 400℃ and the removement of the deteriorated layer between Au and the ceramics, which is produced when the ceramics were prepared.

The decrease of the contact resistance between Bi-based superconductor and Au electrode after the heat treatment at 400℃ caused by that the Au diffuses into the specimen and Bi moves toward the specimen surface. These behavior were also obtained in the 2212-phase Bi-based superconducting single crystals[3]. Therefore, the Au diffusion by the heat treatment is thought to be the original properties of the Bi-based superconductor, not only the ceramics.

4. Conclusion

We prepared the Au electrodes onto the Bi-based superconducting ceramics. Contact resistance of the specimen did not decrease by depositing Au on the surface of the ceramics. They decreased by heating the specimen at 400℃ for 5h in air. The XPS spectra of constituent elements from the surfaces of ceramics and electrodes showed that the chemical bond nature did not change by heating. However, XPS depth profile of the specimen indicated that Au diffused into the ceramics and Bi moved toward the surface by heating. This may caused the decrease of the contact resistance.

Acknowledgement

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References

1) M. Katayama, H. Tokutaka, S. Nakanishi, H. Fujimoto, K. Nishimori, N. Ishihara and T. Yumoto: Y.Bando H.Yamauchi Eds. Adv. Superconductivity V, Springer-Verlag, Tokyo, (1993) 635.

2) S. Kishida, T. Yumoto, S. Nakashima, H. Tokutaka and K. Fujimura: J. Crystal Growth, **153** (1995) 146.

3) S. Kishida, H. Tokutaka, S. Nakanishi, H. Fujimoto, K. Nishimori, N. Ishihara, Y. Watanabe and W. Futo: J. Cryst. Growth, **99** (1990) 937.

4) H. Imao, S. Kishida and H. Tokutaka: phys. stat. sol. (a), **148** (1995) 537.

5) S. Kishida, H. Tokutaka, S. Nakanishi, K. Nishimori, N. Ishihara and H. Fujimoto: Jpn. J. Appl. Phys., **28** (1989) L406.

6) S. Kishida, H. Tokutaka, H. Toda, H. Fujimoto, W. Futo, K. Nishimori and N. Ishihara: Jpn. J. Appl. Phys., **29** (1990) L438.