

X-ray Photoelectron Spectroscopy Study of $Ba_{1-x}Rb_xBiO_y$ Superconductors

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We prepared $BaRbBiO$ (BRBO) superconducting ceramics by a solid state reaction method, and measured the surfaces of as-prepared, polished and Ar^+ -etched BRBO specimens with the X-ray photoelectron spectroscopy (XPS). From the results, we found that carbon impurity on the surfaces of the BRBO specimens was removed by polishing them mechanically in air and by Ar^+ -etching them, and that the Ar^+ -etching caused selective sputtering. Therefore, the optimum method for cleaning the surface of BRBO ceramics is thought to be polishing them in air.

1. Introduction

$Ba_{0.6}Rb_{0.4}Bi_{1.0}O_y$ (BRBO) superconductors [1] have a long coherence length and approximately isotropic electrical property, although their critical transition temperature is about 30K and are lower than those of Bi-[2], Hg-[3], and Tl-based [4] superconductors. Therefore, BRBO superconductors take an advantage for superconducting devices. When BRBO specimens are left in air, a native oxide layer, namely, a deteriorated layer, is formed [5]. The layer is used as a native barrier for the fabrication of three-terminal devices [6]. In order to improve the performance of devices and to analyze the surfaces state exactly, it is necessary to obtain a clean surface of BRBO specimens.

So far, there were a few reports on the XPS studies of BRBO [7] and $BaBiO_3$ [8]. However, the effect of polishing in air and Ar^+ -etching on chemical bond natures of constituent elements in BRBO superconductors is not clarified satisfactorily. In this study, we prepared BRBO superconducting ceramics by a solid state reaction method, and carried out X-ray photoelectron spectroscopy (XPS) measurements for the as-prepared, polished and Ar^+ -etched surfaces of BRBO specimens in order to clarify surface chemical state and surface composition of them.

2. Experimental

BRBO superconducting ceramics prepared by a solid state reaction using the composition of $Ba : Rb : Bi = 0.5 : 0.75 : 1$ were used in our experiments. We measured XPS spectra from the as-prepared, polished and Ar^+ -etched surfaces of BRBO specimens. We carried out mechanically polishing using a diamond file in air. The shimadzu ESCA750 spectrometer

(base pressure : $< 3 \times 10^{-5}$ Pa, X-ray source : $MgK\alpha$, resolution : 1.15 eV) was used for XPS measurements. In addition, the position correction of XPS peaks was carried out using the C-1s peak at about 285 eV.

3. Results and Discussion

Figure 1 shows the XPS full spectra from (a) as-prepared, (b) polished and (c) Ar^+ -etched surfaces of a BRBO specimen. As shown in Fig. 1, the XPS peaks due to Ba-3d, Rb-3d, Bi-4f and O-1s, were observed at about 780 eV, 112 eV, 160 eV and 538 eV, respectively. Furthermore, the XPS peak of C-1s impurity was observed at about 285 eV, and the C-1s intensity decreased by polishing and Ar^+ -etching the BRBO specimen surfaces. At the same time the intensities of the XPS peaks due to Ba, Rb, Bi and O, which are the constituent

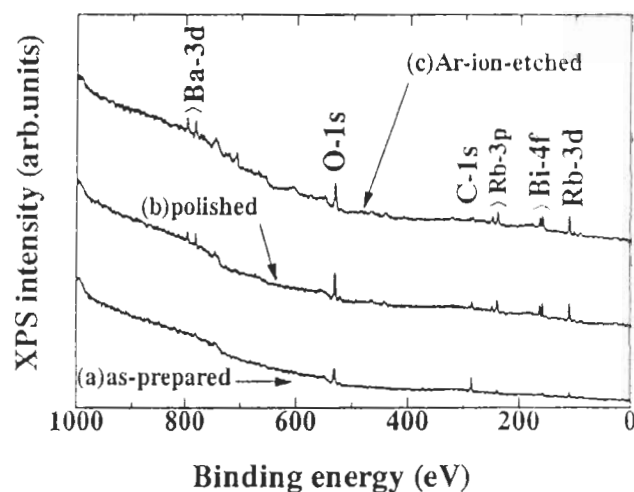


Figure 1. XPS full spectra from (a) as-prepared, (b) polished and (c) Ar^+ -etched surfaces of a BRBO specimen.

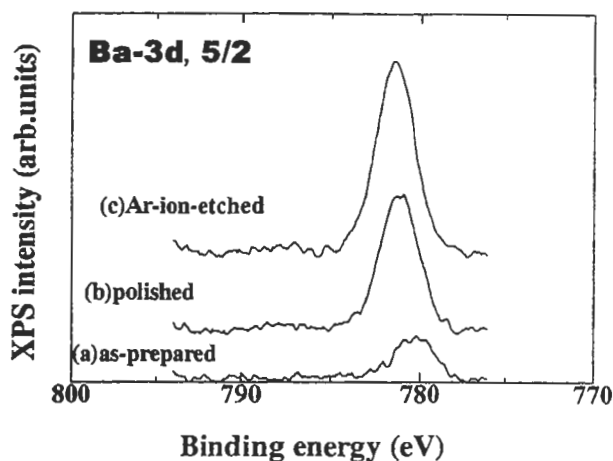


Figure 2. XPS spectra of Ba-3d core levels from (a)as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen.

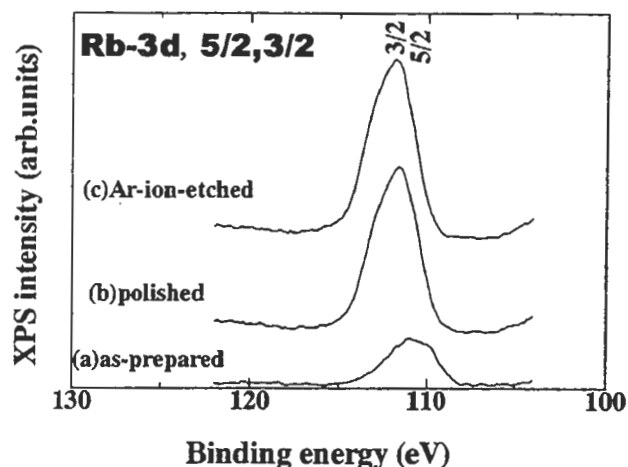


Figure 3. XPS spectra of Rb-3d core levels from (a)as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen.

elements of a BRBO superconductor, increased. From the results, we found that the prepared specimens included all the constituent elements of BRBO superconductors, that is Ba, Rb, Bi and O, and that the carbon impurity on the surface of the BRBO specimen was removed by polishing and Ar⁺-etching it.

Figure 2 shows the XPS spectra of Ba-3d core levels from (a) as-prepared, (b)polished and (c) Ar⁺-etched surfaces of a BRBO specimen. As shown in Fig.2, the XPS peak from the surface of (a) was observed at about 780eV. On the other hand, the XPS peaks from the surfaces of (b) and (c) were observed at about 781eV. The half-width of the Ba-3d, 5/2 XPS peak from the surface of (b) was approximately equal to that from the surface of (c)and were narrower than that from the surface of (a). Since the carbon impurity was removed by polishing and Ar⁺-etching the BRBO specimen, the Ba peak at about 781eV from the surfaces of (b) and (c) may be related to Ba from BRBO superconductors, whereas the Ba peak at about 780eV from the surface of (a) may be related to an impurity Ba compound. The Ba impurity on the as-prepared surface may be the flux and the sludge produced during and after preparation. Figure 3 shows the XPS spectra of Rb-3d core levels from (a) as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen. Since the XPS peaks due to Rb-3d, 5/2 and 3/2 are close each other, we can not distinguish Rb-3d, 5/2 from 3/2 peaks in the spectra. Since the carbon impurity was removed by polishing

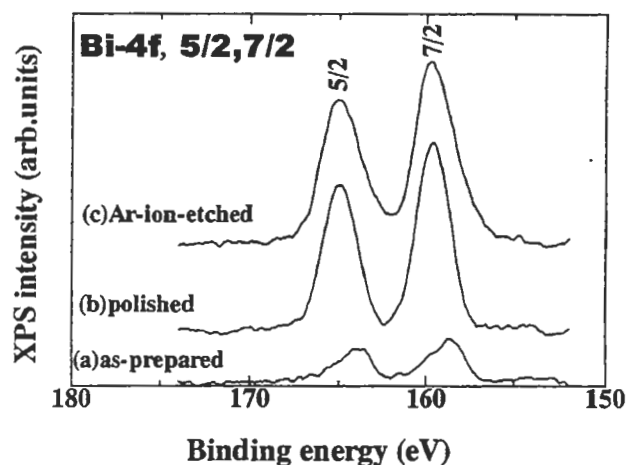


Figure 4. XPS spectra of Bi-4f core levels from (a)as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen.

BRBO specimens in air, the results may indicate that the Rb-3d, 5/2 peaks at about 110eV and 112eV are related to impurity Rb compound and Rb from BRBO superconductors, respectively. The impurity peak at about 110eV may be related to RbOH or Rb₂CO₃. As shown in Fig.3, the half-widths of the XPS peaks from the surfaces of (b) and (c) were narrower than that from the surface of (a). This may indicate that the polished and Ar⁺-etched surfaces are cleaned by polishing mechanically and Ar⁺-etching the BRBO specimens.

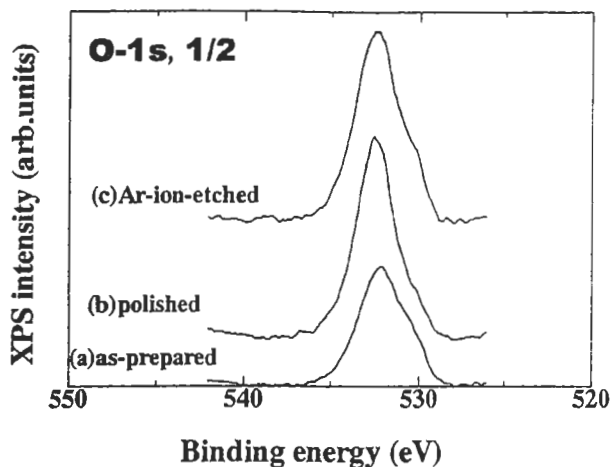


Figure 5. XPS spectra of O-1s core levels from (a)as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen.

Figure 4 shows the XPS spectra of Bi-4f core levels from (a) as-prepared, (b)polished and (c) Ar⁺-etched surfaces of a BRBO specimen. As shown in Fig.4, the Bi-4f_{7/2} and 5/2 XPS peaks from the surface of (a) were observed at about 160eV and 165eV, respectively. On the other hand, the XPS peaks from the surfaces of (b) and (c) shifted toward high energy side. The half-width of the XPS peak from the surface of (b) was narrower than those from the surfaces of (a) and (c). Therefore, the XPS peak from the polished surface is related to Bi from BRBO superconductor. On the as-prepared surface, there are impurity compounds produced during and after the preparation of ceramics. As a result, the half-width of the peak from the as-prepared surface is thought to become broad, since the peak includes two or more Bi peaks with different chemical bond natures. In general, the cleaning method of oxide surfaces by Ar⁺-etching is unsuitable since selective sputtering occurred by Ar⁺. Therefore, Bi oxide and metal may be produced by Ar⁺-etching BRBO specimens. As a result, the half-width of the XPS peak from the Ar⁺-etched surface may become broad. From the results, we found that the chemical bond nature of Bi changed by Ar⁺-etching BRBO specimens, and was different from that of BRBO superconductors although the impurity carbon was removed by Ar⁺-etching them.

Figure 5 shows the XPS spectra of O-1s core levels from (a) as-prepared, (b)polished and (c) Ar⁺-etched surfaces of a BRBO specimen. As shown in Fig.5, the XPS peaks from the

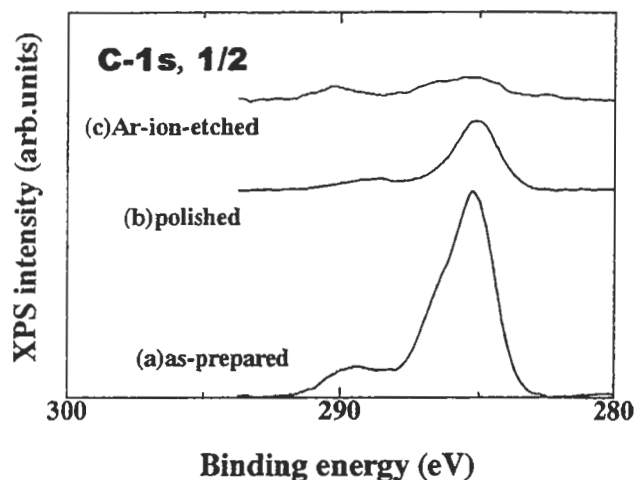


Figure 6. XPS spectra of C-1s core levels from (a)as-prepared, (b)polished and (c)Ar⁺-etched surfaces of a BRBO specimen.

surfaces of (a), (b) and (c) were observed at about 532eV. On the other hand, the half-widths of the O-1s XPS peaks from the surfaces of (b) and (c) was narrower than that from the surface of (a) and a shoulder was observed at about 529eV. The O-1s XPS spectrum from the surface of (b) was approximately a single XPS peak. The O-1s peak related to oxygen impurities in $Bi_2Sr_2CaCu_2O_y$ single crystals were observed at about 532eV[9]. The 532eV XPS peak in BRBO superconductors may also be related to oxygen impurity such as (OH), since BRBO superconductors get a water included in air and easily react with it. The O-1s XPS spectra from the surfaces of (a) and (c) consisted of the peaks related to the oxygen of impurity and BRBO superconductors. As shown in Fig.5, it is difficult to remove the impurity oxygen on the surface of the BRBO specimen by polishing it mechanically. This reason may be that BRBO superconductors easily react with a water included in air. As a result, the cleaning effect by polishing the BRBO superconductors in air is not clearer than that of $Bi_2Sr_2CaCu_2O_y$ superconductors [10].

Figure 6 shows the XPS spectra of C-1s core levels from (a) as-prepared, (b)polished and (c) Ar⁺-etched surfaces of a BRBO specimen. As shown in Fig.6, two XPS peaks from the surfaces of (a), (b) and (c) were observed at about 285eV and 290eV. The XPS peaks at about 290eV may be related to carbonate. Since the half-width of the C-1s peak from the surface of (a) was broader than that of the XPS date[11], the C-1s XPS spectrum is

thought to consist of two or more XPS peaks.

4. Conclusions

We measured XPS spectra from as-prepared, polished and Ar^+ -etched surfaces of BRBO superconducting ceramics prepared by a solid state reaction method. From the results, we found that carbon impurity was removed by polishing mechanically and Ar^+ -etching the BRBO specimens, and that the Ar^+ -etching caused selective sputtering. Therefore, the optimum method for cleaning the surface of BRBO ceramics is thought to be polishing in air.

5. References

- [1] J. Cava: Nature, **332**, 814 (1988).
- [2] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano: Jpn. J. Appl. Phys., **27**, L209 (1988).
- [3] A. Schilling et al.: *ibid*, **363**, 56 (1988).
- [4] Z. Z. Sheng and A.M. Hermann: Nature, **332**, 138 (1988).
- [5] S. Suzuki, H. Suzuki, M. Iyori, K. Takahashi, T. Usuki and Y. Yoshisato: Jpn. J. Appl. Phys., **31**, 3834 (1992).
- [6] Y. Yoshisato, T. Usuki : OYO BUTURI, **62**, 475 (1993).
- [7] R. Itti et al. : Phys. Rev. B, **43**, 435(1991)
- [8] Z. Shen et al. Phys. Rev. B, **40**, 6912(1989)
- [9] A. Shibasaki, S. Kishida, H. Tokutaka, K. Fujimura and H. Naoe: Proc. 9th ISS'96, 1997, p. 403.
- [10] A. Fujimori et al.: Phys. Rev. B, **39**, 2255 (1989).
- [11] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder : HANDBOOK OF X-RAY PHOTOELECTRON SPECTROSCOPY (1979)