

Water-Immersion-Induced Surface Reactions in $\text{EuBa}_2\text{Cu}_3\text{O}_y$ Thin Films

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Synchrotron-radiation photoelectron spectroscopy and x-ray photoelectron spectroscopy were performed on epitaxial quality $\text{EuBa}_2\text{Cu}_3\text{O}_y$ thin films before and after a short (five minutes) immersion into de-ionized pure water to clarify the effect of rinsing on copper oxide superconductors during device fabrication. The surface Ba compounds were found to drastically decrease, while the bulk $\text{EuBa}_2\text{Cu}_3\text{O}_y$ was barely affected.

1. Introduction

The $\text{YBa}_2\text{Cu}_3\text{O}_y$ (YBCO) family is one of the most widely investigated group of materials for device applications. Their applicability has been confirmed by the growth of axis-oriented thin films with epitaxial quality. However, the YBCO family is degraded by water or humidity and water immersion is inevitable during photoresist processing in the fabrication of semiconductor devices. For future application of high- T_c superconducting devices, it is important to investigate the effect of water on high T_c superconducting materials with epitaxial quality. In previous experiments, the samples were immersed in water for a long time¹; therefore, short-time effects could not be clarified even though short-time water immersion is used in device processing. To study the effect of brief water immersion on the surface of superconductor thin films, we examined the chemical bonds in $\text{EuBa}_2\text{Cu}_3\text{O}_y$ (EBCO) thin film surfaces by using photoelectron spectroscopy, comparing water-immersed samples with as-received samples.

2. EXPERIMENTAL

Our samples were c-axis-oriented $\text{EuBa}_2\text{Cu}_3\text{O}_y$ thin films grown on MgO (001) substrates and a-axis-oriented thin films grown on SrTiO_3 (001) substrates by using dc magnetron sputtering. The thickness of these thin films was about 300 nm. After growth, some samples were kept for seven days in ambient air and the others were retained for four months in ambient air. The samples were then cut into two pieces. One piece was placed in an analysis chamber without any treatment. The other piece was immersed in de-ionized water for five minutes at room temperature; the water was then blown from the surface with nitrogen gas. The electrical resistivity of the de-ionized water was $18 \text{ M}\Omega\cdot\text{cm}$ at 20°C .

X-ray photoelectron spectroscopy (XPS) and synchrotron-radiation photoelectron spectroscopy (SRPES) measurements were performed using Beamline BL-1A² in the Photon Factory at the National Laboratory for High-Energy Physics. The x-ray source was $\text{Mg K}\alpha$ (1253.6 eV). To ensure the surface sensitivity of the Ba 4d photoelectron spectra, the photon energy was set at 140 eV to minimize the photoelectron escape depth. The monochromatized photon energy was calibrated by measuring the Fermi edge of the Au. The total resolution was set at 0.4 eV for the SRPES measurements.

3. Results and Discussion

The Ba 3d_{5/2} spectra of the c-axis-oriented thin film are shown in Fig. 1(i). The as-received sample spectra can be resolved into two components. The higher binding energy (BE) peak, which corresponds to a non-superconducting compound (NSC), is located at around 779.5 eV³. The shoulder peak at around 777.5 eV can be assigned to a superconducting phase component (SC).³ After water immersion, the lower BE peak intensity increases, while the higher BE peak intensity drastically decreases. This indicates that NSC Ba impurities are soluble in water.

We also measured the Ba 3d_{5/2} peak for two other samples: a c-axis-oriented thin film retained for four months in ambient air and an a-axis oriented thin film retained for seven days in ambient air. Figures 1(ii) and (iii) show the XPS spectra of these samples. The NSC contaminant component intensities are drastically lower compared to the spectra in Fig. 1(i). We can therefore conclude that Ba compounds on the surface are removed by water immersion and that this is not limited to new c-axis-oriented samples.

The SRPES Ba 4d peak spectra of the c-axis-oriented thin film are shown in Fig. 2. The higher and

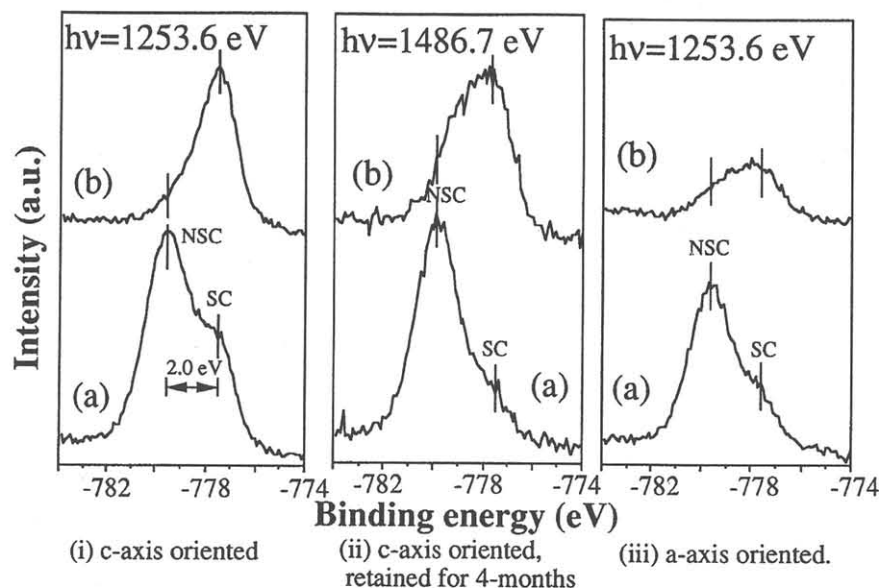


Fig.1 Ba $3d_{5/2}$ XPS spectra of EBCO thin films: (a) as-received and (b) water-immersed.

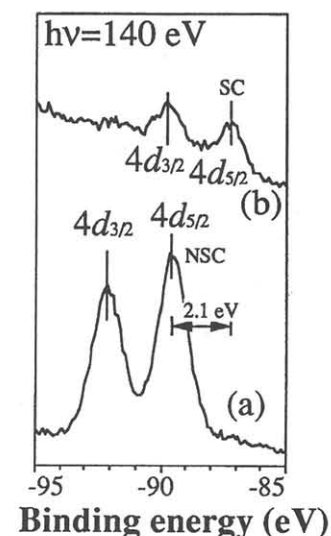


Fig. 2 Ba $4d$ SRPES spectra of EBCO thin films: (a) as-received and (b) water-immersed.

lower BE peaks can be assigned as Ba $4d_{3/2}$ and Ba $4d_{5/2}$ peaks of a single chemical component, because the energy separation is almost the same as previously reported⁴. These peaks disappeared and new ones appeared at a 2.1-eV-lower BE after water treatment. This energy difference in Ba $4d_{5/2}$ is consistent with the energy shift of the Ba $3d_{5/2}$ main peak. Since the Ba $4d_{5/2}$ BE position is almost the same as the bulk EBCO component,⁵ the new peaks can be assigned to the bulk EBCO component.

The in-depth profile of the Ba impurities can be determined by using the difference in surface sensitivities between XPS (~ 2 nm) and SRPES (~ 0.5 nm). In the Ba $3d_{5/2}$ XPS spectra (Fig. 1), the superconducting bulk peak increased and the non-superconducting peak decreased after water immersion. We would like to emphasize that the non-superconducting peak still remains, although the component intensity drastically decreased. In contrast, in the Ba $4d_{5/2}$ SRPES spectra (Fig. 2), the non-superconducting peak disappeared and an EBCO bulk peak appeared after water immersion. These variations can be explained by the differences in surface sensitivity between XPS and SRPES. While the topmost surface Ba compounds are removed by water immersion, the Ba compounds distributed inside remain unchanged. This phenomenon is common to all three kinds of samples. For the a-axis sample and the four-month-retained c-axis sample, the Ba $4d_{5/2}$ peaks completely disappeared. In both, the Ba compounds are thicker, so only the compounds near the Ba surface are removed.

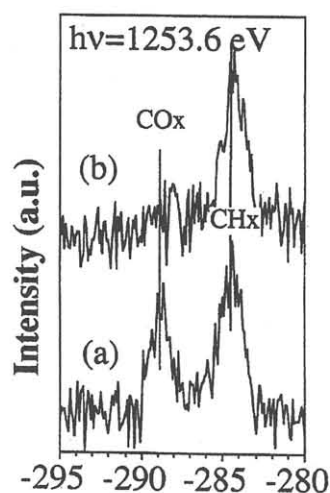
Figure 3 shows the C $1s$ spectra of c-axis-oriented EBCO before and after water immersion. The spectrum of the as-received sample has two peaks: one at 289 eV and the other at 285 eV. The lower BE peak near 285 eV corresponds to hydrocarbon and the higher

BE peak near 289 eV represents carbon oxide.⁶ After water immersion, the higher BE peak almost disappears, whereas the lower BE peak remains unchanged. This indicates that the carbon oxide impurities are completely removed by the water immersion, while the hydrocarbon impurities remain. Even if the hydrocarbon was removed by water immersion, the surface would be covered again with hydrocarbon due to air exposure. Therefore, it is difficult to discuss the water immersion effect on carbon impurities. A similar spectral change in the C $1s$ was obtained for the a-axis-oriented EBCO.

The O $1s$ XPS spectra of c-axis-oriented EBCO are shown in Fig. 4. In these spectra, two peaks can be clearly seen, indicating the existence of a bulk superconducting phase (lower BE component) and a non-superconducting impurity (higher BE component).⁷ In this spectra, the higher BE peak intensity also decreased.

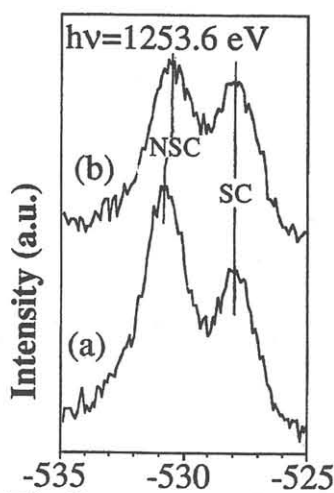
The Cu $2p_{3/2}$ XPS spectra are shown in Fig. 5. They consist of a main peak and a satellite one. This satellite peak is typical for copper oxide superconductors.^{8,9} The main peak intensities of the water-immersed samples are almost the same as those of the as-received samples. These results suggest that the water immersion time was too short to affect the surface Cu compounds in the XPS-detection range. The surface Cu compounds are not chemically active in water compared with the Ba compounds judging from the XPS spectra.

In the O $1s$, Ba $3d$, and Ba $4d$ spectra, the non-superconducting components decreased after water immersion. In the Ba $3d$ and $4d$ spectra, the change was especially drastic. In the Cu $2p_{3/2}$ spectra, the Cu $2p$ satellite peak barely changed after water immersion. This indicates that bulk Cu atoms are not affected by water immersion. As described above, the surface is



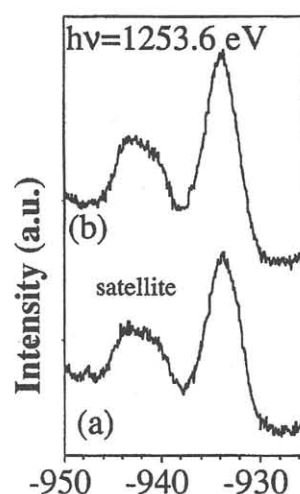
Binding energy (eV)

Fig. 3 C 1s XPS spectra of c-axis oriented 7-day retained samples (a) before and (b) after water immersion.



Binding energy (eV)

Fig. 4 O 1s XPS spectra of c-axis-oriented 7-day-retained samples: (a) before and (b) after water immersion



Binding energy (eV)

Fig. 5 Cu 2p_{3/2} XPS spectra of c-axis-oriented 7-day-retained samples (a) before and (b) after water immersion.

covered with compounds decomposed from bulk EBCO. The candidates for the surface compound are the related EBCO compounds, such as $\text{Eu}_2\text{BaCuO}_5$ and BaCuO_2 , and the reaction products of the decomposition, such as $\text{Ba}(\text{OH})_2$, BaO , CuO , and Cu_2O . $\text{Ba}(\text{OH})_2$ is a water soluble material, while CuO , Y_2BaCuO_5 , and BaCO_3 are water insoluble materials. Therefore, the surface Ba compound soluted in water may be $\text{Ba}(\text{OH})_2$. Furthermore, we believe that the carbon oxide peak in the C 1s XPS spectrum is due to BaCO_3 , because the peak disappeared after water immersion and the non-superconducting Ba peak disappeared during the same process. However, solid BaCO_3 is not soluble in water. Therefore, we cannot presently explain why the carbon oxide peak diminished after water immersion.

While several experiments have been performed on the effect of water on YBCO, none have indicated that the surface Ba is removed or that bulk is little affected by a short water immersion. Previous experiments indicated that water corrodes the surface, whereas our results show that only the surface compounds are removed by water without causing any damage to the bulk. We think that there are three reasons for this. First, we used thin films with epitaxial quality. Second, the samples were immersed for only a short time. Third, the samples were immersed in pure de-ionized water.

In conclusion, x-ray photoelectron spectroscopy and synchrotron radiation photoelectron spectroscopy of $\text{EuBa}_2\text{Cu}_3\text{O}_y$ thin films before and after water immersion showed that almost all carbon oxides and non-superconducting Ba compounds on the surface can be removed by water treatment. Bulk Cu atoms, however, are not affected by water immersion, as evidenced by almost no peak shift in the Cu 2p and no increase in the Cu 2p satellite. We also found that the

Ba compound reaction on the surface depends on surface conditions, such as axis orientation and surface quality.

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