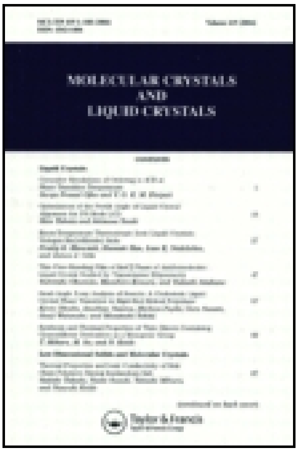

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Grain Boundaries of the Y-Ba-Cu-O System Studied by X-ray Photoelectron Spectroscopy (XPS)

Y. Fukuda [a] , T. Suzuki [b] , M. Nagoshi [b] , Y. Syono [c] & M. Tachiki [c]

[a] Research Institute of Electronics, Shizuoka University, Hamamatsu, 432, Japan

[b] Steel Research Center, NKK, Kawasaki, 210, Japan

[c] Institute for Materials Research, Tohoku University, Sendai, 980, Japan

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GRAIN BOUNDARIES OF THE Y-Ba-Cu-O SYSTEM STUDIED BY X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Y.FUKUDA
Research Institute of Electronics, Shizuoka University, Hamamatsu 432, Japan
T.SUZUKI AND M.NAGOSHI
Steel Research Center, NKK, Kawasaki 210, Japan
Y.SYONO AND M.TACHIKI
Institute for Materials Research, Tohoku University, Sendai 980, Japan

Abstract We have studied the grain boundaries of the $YBa_2Cu_3O_7$ superconductor using micro-focused X-ray photoelectron spectroscopy. It is found that barium carbonate, barium hydroxide, and barium species with a low binding energy (777.8 eV) are more predominant on the grain boundary surfaces than on scraped surfaces. The Ba $3d_{5/2}$ line at 777.8 eV is more intense for the orthorhombic superconducting oxide than for the tetragonal insulator. The origin of this line is discussed.

Introduction

It is expected that high-Tc superconductors will be applied in superconducting magnets. However, the critical current density (Jc) is presently too low for that practical application. One possible reason for the low Jc may be the weak link at grain boundaries in polycrystal samples, since the transport Jc is about two orders of magnitude lower than that calculated from magnetization data[1] and since 2-3 orders of magnitude higer Jc values were obtained with highly oriented thin films grown on single crystal $SrTiO_3$ substrates.[2]

Although the grain boundaries have been studied by scanning Auger electron spectroscopy (SAM),[3,4] trasmission electron spectroscopy (TEM),[5] and X-ray photoelectron spectroscopy (XPS),[6,7] the results are still controvertial. The segregation of carbon,[3] yttrium,[5] barium,[5] Ba-Cu oxides,[7] and barium carbonate[6] at the grain boundaries has been reported. While it was found that no impurities exist, boundary layers of 15-50 Å thickness were deficient in oxygen and are rich in copper compared to the bulk.[4]

In this paper, we present the results of studies of the grain boundaries of YBa2Cu3O7 using micro-focused X-ray photoelectron spectroscopy (XPS) in order to elucidate the chemical states of elements at the boundaries.

Experimental

Polycrystal ortho-YBa2Cu3O7 samples were prepared from the mixture of barium, yttrium and copper oxalates obtained by the co-precipitation of the corresponding nitrates with NH4OH and oxalic acid solution at pH=4.6. The details are described elsewhere.[8] X-ray diffraction data showed only an orthorhombic phase. The Tc for zero resistivity was 90 K.

The sintered samples were fractured in an ultra-high vacuum chamber in order to obtain the grain boundary surfaces.[9] The morphology of the intergranular cleavage is observed for the surface using electron microscopy. Samples were also scraped using a grinder in the chamber in order to obtain clean surfaces.

XPS measurements were carried out using a SSX-100 (Surface Science Instruments) equipped with a monochromatized AlK_α X-ray source with 300μm diameter.

Results and discussion

Figures 1 and 2 show C 1s and O 1s core-level lines, respectively, for the surfaces as received (a), fractured (b), and scraped (c). The C 1s lines at 285.0 and 289.4 eV are ascribed to hydrocarbons and carbonates, respectively, in which the former is due to typical contamimation from

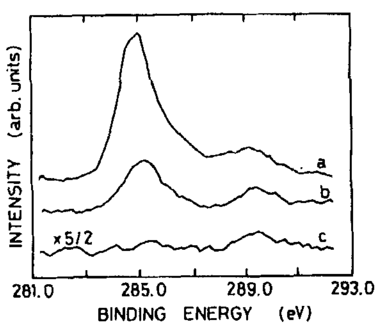

FIG.1 C 1s core-level line for YBa2Cu3O7 surfaces as received (a), fractured (b), and scraped (c).

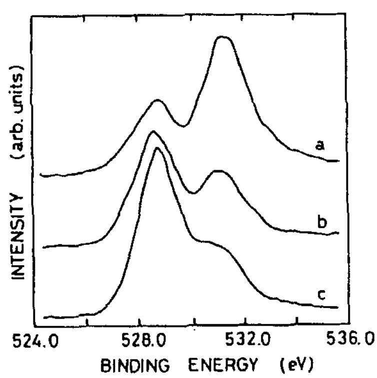

FIG.2 O 1s core-level line for YBa2Cu3O7 surfaces as received (a), fractured (b), and scraped (c).

the atmosphere. The fractured surface consists of not only the grain boundary but also the surfaces within pours. The ratios of the peak area of the C 1s line at 289.4 eV to that at 285.0 eV are 0.15 and 0.36 for the surface as received and fractured, respectively. By assuming that the hydrocarbon on the fractured surface comes from the pours where the ratio is the same as for the surface as received, we can estimate the amount of the carbonate at the grain boundary : (0.36-0.15)/0.36x100=58.3%. The carbonate is still present on the scraped surface, which implies that not only the transgranular surfaces but also the boundary and the pour surfaces are exposed by scraping.

The O 1s lines at 528.8 and 531.3 eV are due to oxygen in the superconducting oxide and carbonate and/or hydroxide.[10] The surface as received is almost covered by carbonate and/or hydroxide which are reduced on the fractured surface. They still remain upon scraping due to the same reasons as described for the C 1s lines.

Ba 3d5/2 core-lines for the surfaces as received (a), fractured (b), and scraped (c) are displayed in Fig 3, in which each of the lines can be divided into three with 1.6-eV width at 777.8, 779.0, and 780.2 eV. The intensities of each of thse lines are quite different at each surfaces; the 777.8-, 779.0- and 780.2-eV lines are most intense in (b), (c) and (a), respectively.

The 779.0- and 780.2-eV lines have been ascribed to barium in the superconducting oxide and barium carbonate and/or hydroxide,[10] respectively. The 777.8-eV line have been previously observed but the origin is not clear.[11] A low-binding-energy line was also observed for Ba 4d on the cleaved single crystal surface using synchrotron radiation. This peak was identified as a surface component since it is most intense at E=50 eV in the constant final state measurements.[12]

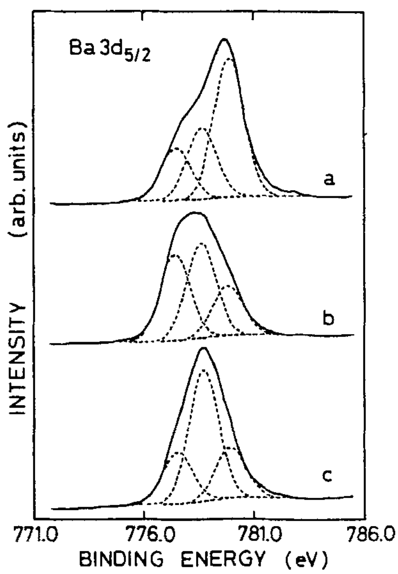

FIG.3 Ba 3d5/2 core-level lines for YBa2-Cu3O7 surfaces as received (a), fractured (b)and scraped (c).

We find that this line is more intense for the fractured surface than for the scraped, which suggests that the species with the low binding energy is preferentially formed at the grain boundaries. Therefore, we have to take impurities at the boundaries into account. We have measured the binding energy for BaCuO2 and Y2BaCuO7 which are regarded as possible impurities for the YBa2Cu3O7 superconductor because of their low melting point. The binging energy of Ba 3d5/2 is found to be 778.9 and 778.7 eV for BaCuO2 and Y2BaCuO7, respectively. These are close to the value for Ba (779.0 eV) in the superconducting oxide. We also find that the line is more intense for the orthorhombic structure than for the tetragonal, which suggests that the origin of the line would be due to the reduced oxygen coordination. The origin is still under investigation.

Changes in intensity of the C 1s line at 289.2 eV (carbonate) and the Ba 3d5/2 line at 780.2 eV (carbonate and/or hydroxide) as functions of the O 1s line at 531.4 eV (carbonate and/or hydroxide) are shown in Fig 4 and 5, respectively, where the intensities were measured for the surfaces as received (●), fractured (O), and scraped (⊙). The intensities are each normalized to the O 1s line at 528.4 eV. A linear relation ship between them is obtained. It is found that the straight line in Fig 4 does not intercept the vertical axis, which implies that the O 1s

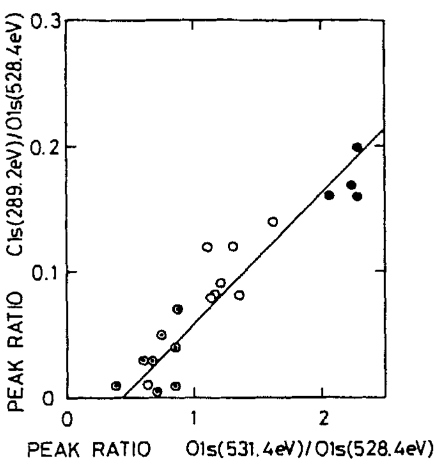

FIG.4 Changes in intensity of the C 1s line at 289.2 eV as a function of the O 1s line at 531.4 eV. ●, O, and ⊙ correspond to the surfaces as received, fractured, and scraped, respectively.

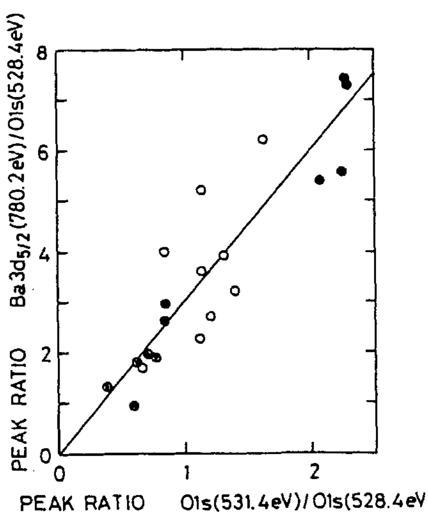

FIG.5 Changes in intensity of the Ba 3d5/2 line at 780.2 eV as a function of the O 1s line at 531.4 eV. The symbols are the same as in FIG.4.

line at 531.4 eV consists of carbonate and hydroxide. Fig 5 suggests that the Ba 3d5/2 line at 780.2 eV consists of carbonate and hydroxide since the straight line is through the origin. These results along with the discussion of Fig 1 suggest that there exists not only barium carbonate but also hydroxide at the grain boundary. The hydroxide could originate from the atmosphere during slow cooling. However, it is hard to judge whether the carbonate comes from the atmosphere or from segregation of unreacted carbonate.

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