JOURNAL OF SOLID STATE CHEMISTRY 100, 388–392 (1992)

Chemical Studies of (001)-Oriented $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ High-Temperature Superconductor Thin Films by Photoemission Spectroscopy

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Communicated by J. M. Honig, July 24, 1992

Clean surfaces of (001)-oriented $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ high-temperature superconductor thin films were studied by photoemission spectroscopy using high-energy ultraviolet photons ($h\nu$ in the 50 to 200 eV range). The surfaces were cleaned by heating in an ultrahigh-vacuum electron spectrometer at 400°C (or 350°C) in 1×10^{-3} Torr oxygen. Valence bands and outer core levels were studied. Ba 4*d* and Ba 5*p* doublet photopeaks showed spin–orbit splitting of 2.6 and 2.2 eV, respectively, as expected. Er, Ba, Cu, and O features in the valence band were identified.

Chemistry of $R_1Ba_2Cu_3O_{7-\delta}$ (R = Y, Nd, Sm, Eu, Gd, Dy, or Er) high-temperature superconductors is an active area of solid-state research (*1, 2*). These cuprate superconductors have an interesting crystal structure and their critical transition temperature (T_c) is just above 90 K. Recently, several $Er_{1+x}Ba_{2-x}Cu_3O_y$ (x between 0 and 0.5) thin films were prepared in our laboratory for studies of compositional modulation in the $R_1Ba_2Cu_3O_{7-\delta}$-type crystal structure (*3*). The films were prepared by molecular beam deposition and postannealing. In $Eu_{1+x}Ba_{2-x}Cu_3O_y$ (Refs. (*4, 5*)), $Nd_{1+x}Ba_{2-x}Cu_3O_y$ (Ref. (*4*)), and $Dy_{1+x}Ba_{2-x}Cu_3O_y$ (Ref. (*6*)) oxides for x between 0 and 0.5, it is understood that the excess R atoms substitute for Ba sites, which results in a decrease in the lattice constant c_0 and a lowering of T_c. Surprisingly, two compositions in $Er_{1+x}Ba_{2-x}Cu_3O_y$ thin films were discovered which displayed zero resistivity transition temperatures of 95 and 93 K, respectively (Ref. (*3*)). Chemically, these two materials were identified as $Er_5Ba_7Cu_{12}O_y$ and $Er_4Ba_5Cu_9O_y$. The lattice constant c_0 for the (001)-oriented $Er_5Ba_7Cu_{12}O_y$ and $Er_4Ba_5Cu_9O_y$ thin films was determined to be 11.65 Å by X-ray diffraction (XRD). The films were found as single phase materials by X-ray diffraction and scanning electron microscopy (SEM). It is still not clear if the excess Er atoms substitute for Ba sites in these materials or whether there are superstructures in their unit cell along the *a*- or *b*-axis. Further experiments to understand the chemistry and structure of these materials are in progress. $Er_{1+x}Ba_{2-x}Cu_3O_y$ films of other composition did not have a $T_{c,0}$ of 90 K.

In this letter we report on the chemical studies of (001)-oriented $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ thin films by photoemission spectroscopy using high-

0022-4596/92 $5.00

energy ultraviolet light. Core-level spectroscopy was used to compare the binding energies of outer core levels in $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$, whereas valence band spectroscopy was applied to obtain information on the chemical bonding of the atoms in these materials. In the following text, the $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ materials are also referred to as EBCO.

The experiments were performed at the Synchrotron Radiation Center (SRC), University of Wisconsin–Madison, on the MARK II beamline, which has a "Grasshopper"-type monochromator. Synchrotron radiation at 1 GeV and 800 MeV injections in the electron storage ring was used. An ultrahigh-vacuum (UHV) electron spectrometer equipped with a double-pass cylindrical mirror analyzer (CMA), sample heater, sample transfer system, and an oxygen manifold was used for the photoemission measurements. The UHV system was pumped down to a base pressure of 2×10^{-10} Torr. Epitaxial $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ thin films on $LaAlO_3(100)$ substrates were prepared by molecular beam deposition (MBD) and postannealing in separate experiments. The basic deposition parameters for coevaporation of $Er_1Ba_2Cu_3O_{7-\delta}$ thin films were determined during preparation of high-temperature thin films in the Dy–Ba–Cu–O system (*6*). In our experience, in MBD, if any constituent of the vapors deviates more than 3% during coevaporation, then the sample after postannealing will not be a 90-K superconductor. The film thickness was 2050 Å in each case, which was measured with a stylus profilometer.

For photoemission experiments, the samples were introduced in the UHV system after reaching the base pressure. The clean surfaces were prepared by heating the samples in a pressure of 1×10^{-3} Torr of oxygen at 400°C (or 350°C) for 30 min, followed by cooling in oxygen (1 hr). Then the oxygen gas was pumped out. The UHV pressure during measurements was in the 1×10^{-8} to 5×10^{-9} Torr range, at which the residual gas should be mainly oxygen. The samples stayed clean for a few hours, after which the degradation of the samples could be observed, as described later. The CMA was operated in the fixed retarding ratio (FRR) mode [CMA pass energy (E_p)/electron kinetic energy (E_k) = 1] (*7*). For $E_k > 40$ eV in the FRR mode, the resolution became poor but the counts were high. It was necessary to run in the FRR mode to acquire several energy distribution curves (EDC) for a sample in a few hours. The Fermi level position was checked by taking EDCs for a gold foil which was cleaned by heating in vacuum. The CMA factor, which is the ratio of actual kinetic energy to applied voltage on the outer cylinder of the CMA, was found to be 1.74, assuming that the photon energy calibration of the monochromator is correct.

Figure 1 shows several energy distribution curves for a fairly clean $Er_1Ba_2Cu_3O_{7-\delta}(001)$ surface for photon energy values in the 53–180 eV range. For $h\nu = 53$ eV, the resolution is better because the kinetic energies of the photoelectrons are lower. In the EDC at photon energy of 53 eV, there is a small bump at the Fermi level (BE = 0 eV) which is due to photoemission caused by second-order light. In this EDC, the observable features have been marked as A–H. In the 0 to 10 eV binding energy range, which displays an integrated density of states in the valence band, features of Er, Ba, Cu, and O photoemission from orbitals involved in chemical bonding are present. Peak A should be due to photoemission from Cu 3*d* or Cu 3*p*–O 2*p* hybrid orbitals (*8–11*). Peak B, in our understanding, may have Er 4*f* and Cu 3*d* photoemission in the background, but the shoulder (peak) is mainly due to oxygen bonded to Ba on the surface, as reported for BaO and for chemisorbed oxygen on Ba (*12–14*). Peak C is strong at the photon energy of 90-eV, just above the

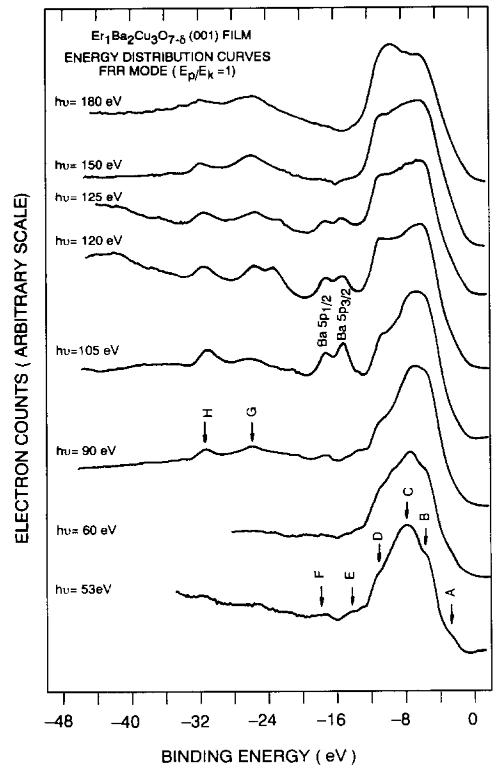

FIG. 1. Valence band and outer core-level spectra for (001)-oriented clean surface of $Er_1Ba_2Cu_3O_{7-\delta}$ thin films in the 53–180 eV photon energy range. The resolution is better at lower photon energy values. The sample was cleaned in the UHV measurement system by heating at 400°C in 1×10^{-3} Torr oxygen for 30 min.

Cu 3*p* threshold. Therefore, this peak should contain photoemission signals from Cu 3*d*, because there should be intensity enhancement in Cu 3*d* photoemission due to a *p*–*d* resonance (*11*). Peak D is an erbium 4*f* satellite peak. Its intensity increases just above the Er 4*d* threshold, due to a giant resonance, as reported for rare earth metals in Ref. (*15*). For Er metal, strong Er 4*f* satellite photoemission in the 9–11 eV binding energy range has been reported in the literature (*16*). Peaks E and F are due to some degradation of the surface, since their intensities go up in the PES data for degraded surfaces (EDCs not shown). The strong Ba $5p_{1/2}$ and $5p_{3/2}$ photopeaks are observed just above the Ba 4*d* threshold, where their intensities are dramatically enhanced by resonance effects (*17, 18*). G and H are Er 5*p* photopeaks with a large spin–orbit splitting, but Ba 5*s* photoemission also occurs at the position of peak H (*19*).

In Fig. 2, the energy distribution curves for the clean $Er_5Ba_7Cu_{12}O_y(001)$ surface are shown. This sample was cleaned at a lower temperature (350°C). The Ba $5p_{1/2}$ and $5p_{3/2}$ photoemission peaks with a spin–orbit splitting of 2.2 eV are observable even at lower photon energy values. Peaks A, B, C, and D are present at positions similar to those found in Fig. 1 for $Er_1Ba_2Cu_3O_{7-\delta}$. Peak B is very pronounced in Fig. 2. This peak represents photoemission from O on the surface (BaO layer), as discussed earlier. This peak was found to vanish in the EDCs of degraded samples (not shown). On degraded

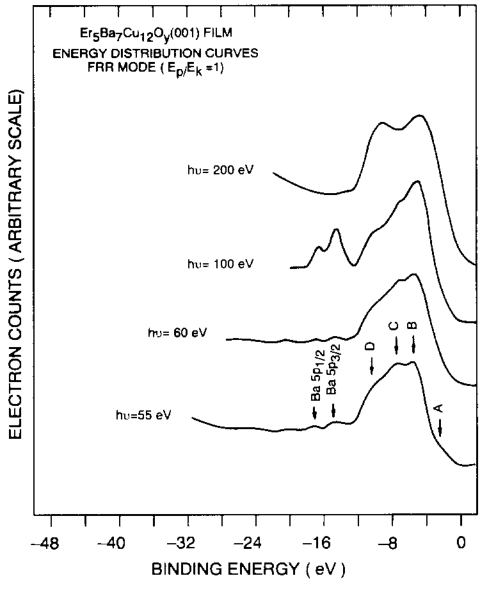

FIG. 2. Valence band and outer core-level spectra for (001)-oriented clean surface of $Er_5Ba_7Cu_{12}O_y$ thin films in the 55–200 eV photon energy range. The sample was cleaned by heating at 350°C in 1×10^{-3} Torr oxygen for 30 min.

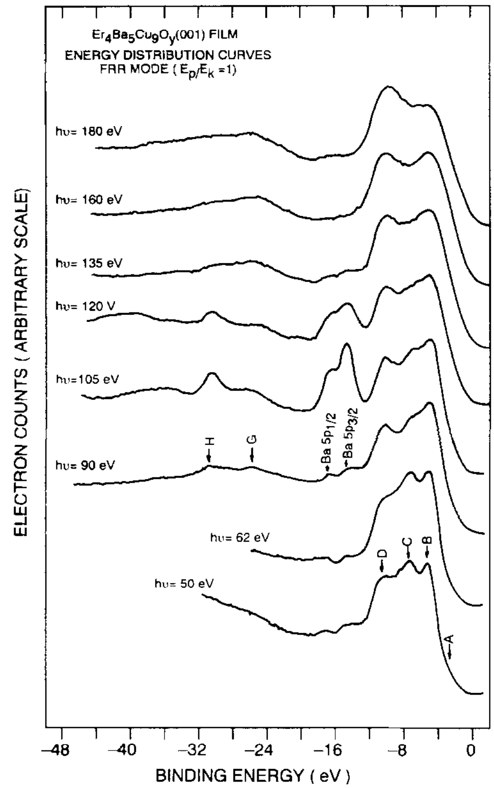

FIG. 3. Valence band and outer core-level spectra for (001)-oriented clean surface of $Er_4Ba_5Cu_9O_y$ thin films in the 50–180 eV photon energy range. The sample was cleaned by heating at 400°C in 1×10^{-3} Torr oxygen for 30 min.

surfaces, the Ba–O layer on the surface is believed to react with gaseous contaminants.

The energy distribution curves for the $Er_4Ba_5Cu_9O_y$(001) surface are depicted in Fig. 3. Features in the spectra are the same as those observed for $Er_1Ba_2Cu_3O_{7-\delta}$ and $Er_5Ba_7Cu_{12}O_y$ in Figs. 1 and 2.

Comparison of the valence band spectra for (001)-oriented $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ surfaces clearly shows that atoms in these EBCO films have similar binding characteristics. No new peaks corresponding to atomic binding in any second phase are seen.

The Ba 4*d* core level was investigated at several photon energy values. Figure 4 shows the Ba $4d_{3/2}$ and Ba $4d_{5/2}$ photopeaks at 120 eV photon energy. The Ba 4*d* doublets show a spin–orbit splitting of 2.6 eV, as found in BaO (*20*). Note the appearance of a Ba 4*d* satellite peak at 104 eV binding energy. The existence of this satellite photoemission peak was confirmed by separate ESCA (electron spectroscopy for chemical analysis) experiments using an MgK_α ($h\nu$ = 1254 eV) X-ray source (*21*). This Ba 4*d* photoemission at 104 eV binding energy has not been reported for metallic Ba or for any Ba compound in the solid state. Its binding energy is similar to the Ba 4*d* binding energy in Ba vapor (*22*). The large shift of Ba 4*d* photopeaks in solid Ba and BaO to lower binding energy values has been attributed to extra atomic relaxation effects (*17*, *18*). The intensity of the Ba 4*d* satellite peak at 104 eV binding energy can be taken as a measure of degradation of EBCO surfaces.

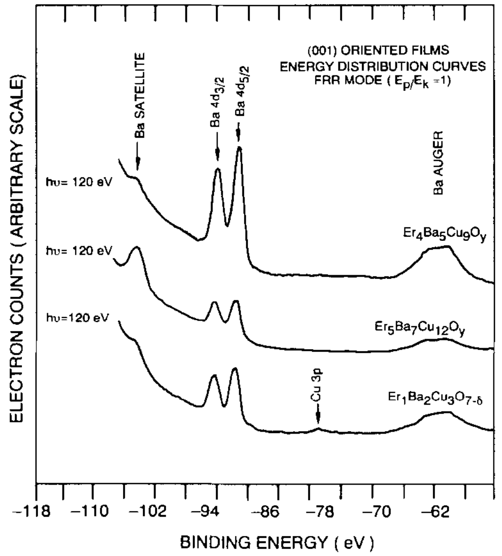

FIG. 4. Ba 4*d* core-level spectra for (001)-oriented clean surfaces of $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ high-temperature superconductor thin films.

Ba is known to be an attractant for hydrocarbons in vacuum (*23*). Again, the Ba core-level spectra for (001)- oriented clean $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ surfaces do not show additional photopeaks with chemical shifts corresponding to any second phase. There is a difference of about 0.3 eV in the Ba 4*d* peak positions, which may be due to a shift of the Fermi level.

In conclusion, clean surfaces of (001)-oriented $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_5Ba_7Cu_{12}O_y$, and $Er_4Ba_5Cu_9O_y$ high-temperature superconductor thin films were studied by photoemission spectroscopy using synchrotron radiation. The surfaces were cleaned by heating in an ultrahigh-vacuum electron spectrometer at 400°C (or 350°C) in 1×10^{-3} Torr oxygen. Valence bands and outer core levels were studied using photons in the 50–200 eV range. Ba 4*d* and Ba 5*p* doublet photopeaks showed spin–orbit splitting of 2.6 and 2.2 eV, respectively, as expected. Er, Ba, Cu, and O features in the valence band were identified.

Acknowledgments

This research was supported by the Midwest Superconductivity Consortium (MISCON), Purdue University, under Department of Energy Grant DE-FG02-90ER45427. We are grateful to Professor Marshall Onellion (University of Wisconsin, Madison) and Professor David Lynch (Iowa State University) for some fruitful discussions. We thank Professor Giorgio Margaritondo, Institut de Physique Appliquée, Ecole Polytechnique Fédérale, Lausanne, Switzerland, for providing us with experimental help. We are also thankful to the staff of the Synchrotron Radiation Center, University of Wisconsin–Madison, for their support.

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