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COMPOSITION AND THICKNESS OF THE SURFACE LAYER ON HIGH T_c SUPERCONDUCTING $YBa_2Cu_3O_{7-d}$ THIN FILMS, STUDIED BY ARXPS *

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With ARXPS, we investigated the surface layer on c-axis oriented high T_c superconducting $YBa_2Cu_3O_{7-d}$ thin films. In the Y 3d feature, no chemical shift has been observed, indicating that Y is present in one chemical state only. In the Ba 3d and Ba 4d features, contributions of Ba components in two different chemical states have been found. We assign these two Ba lines to Ba in the superconducting $YBa_2Cu_3O_{7-d}$ material and to Ba in a non superconducting top layer. Also in the O 1s feature, two O lines have been discovered, one belonging to O in the $YBa_2Cu_3O_{7-d}$, and one belonging to O in the top layer. From the ARXPS measurements, indications have been found that in the surface layer 30 at. % O is missing. The ARXPS experiments show that the stable surface of c-axis oriented high T_c superconducting $YBa_2Cu_3O_{7-d}$ thin films is the Ba-O plain, above the Y and that the superconducting film is covered with a non superconducting top layer with a typical thickness of 1.1 nm, containing Ba- and Cu-oxides and, due to transport through ambient, graphite, some carbonates and hydroxides.

1. INTRODUCTION

Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) is a widely used non destructive method to study the chemical composition and thickness of the outermost top layer of solid materials (thickness $\leq$ 6 nm) and therefore very attractive for the investigation of very thin layers. The depth range of the method is limited by the effective escape depth of the photoelectrons in the top layer of the material and within this range ($\leq$ 6 nm) the layer thickness can be obtained from the ratio of the measured angular peak intensities between the layer and substrate. In this report, an alternative method for determining film thicknesses using ARXPS will be pointed out. This method will be used to study the composition and thickness of the surface layer on high T_c superconducting $YBa_2Cu_3O_{7-\delta}$ thin films.

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2. QUANTITATIVE ANALYSIS OF ARXPS SPECTRA

The photoelectron energy distribution $dI_{i,k}(E)$ from orbital k in an atom of element i, detected at photoelectron take-off angle φ may be written as[1]:

$$dI_{i,k} = \eta \; \gamma_{i,k} \int_x \int_y T_{tot}F \; dx \; dy \; 2\pi(1-\cos\vartheta_m) \int_z n_i \; \exp\left(- \frac{z}{\lambda_i \cos\varphi}\right) dz \; dE. \quad (1)$$

where ϑ_m denotes the photoelectron analyser acceptance angle (aperture); the electron detector has an efficiency $\eta(E_d)$ with E_d the kinetic energy of the photoelectrons after being transmitted through the lense and just before entering the electron detector. $T_{tot}(\vartheta,\phi,E,E_d)$ is the total transmission of the analyser. The X-ray flux inside the sample is given by $F(x,y,\varphi)$ and $n_i(x,y,z)$ is the atomic concentration of element i. The probability of an electron, absorbing an X-ray dose and being ejected from orbital k in an atom of element i with an energy (E,dE) is given by $\gamma_{i,k}(\vartheta_k,E)$, the angular differential photoionization cross-section, where ϑ_k is the angle between photon and photoelectron path. z denotes the depth below the sample surface at which the electron was being ejected and $\lambda_i(E)$ is the inelastic mean free path of the photoelectrons inside the material.

By means of eq. (1), quantitative information, for example the thickness of a surface layer, can be obtained by comparing the peak intensities of the atoms present in the substrate and surface layer, taken at varying photoelectron take off angle φ. In ref. 1, we showed that these ARXPS ratio measurements (or: relative ARXPS measurements) may induce large errors in determining film thicknesses. This commonly used method contains two parameters: the film thickness and a constant, containing the ratios of atomic concentrations and inelastic mean free paths of the photoelectrons in the substrate and the film. Due to a strong correlation between these two parameters, large errors in the calculated film thickness may be expected.

Therefore, we propose an alternative way of obtaining quantitative information, by looking at the same XPS peak at varying photoelectron take off angle and normalizing its intensity to the normal take off angle. This method we called absolute ARXPS measurements[1] and with this method, we are able to eliminate one parameter and, because now only one parameter, the film thickness, is used to describe these absolute ARXPS measurements, it can be calculated with much higher accuracy.

If we look at the same XPS peak of element i at different electron take off angles φ and normalize its intensity to the intensity at normal take off angle we obtain, using eq. (1):

$$N = \frac{I_{i,k}(\varphi)}{I_{i,k}(0)} = \frac{\underset{x \ y}{\int \int} T_{tot} \cdot F(x,y,\varphi)dxdy}{\underset{x \ y}{\int \int} T_{tot} \cdot F(x,y,0)dxdy} \cdot \frac{\int_0^\infty n_i \exp\left(-\frac{z}{\lambda_i \cos\varphi}\right) dz}{\int_0^\infty n_i \exp\left(-\frac{z}{\lambda_i}\right) dz} \; . \qquad (2)$$

If the 2p peak on a clean sputtered silicon sample is measured, eq. (2) results in:

$$N = \frac{I_{Si,2p}(\varphi)}{I_{Si,2p}(0)} = \frac{\underset{x \ y}{\int \int} T_{tot} \cdot F(x,y,\varphi) \ dxdy}{\underset{x \ y}{\int \int} T_{tot} \cdot F(x,y,0) \ dxdy} \cos \varphi = G(\varphi) \qquad (3)$$

So this function $G(\varphi)$, depending on geometry of the experimental setup, sample and sample holder, can be measured directly and this value can be used in eq. (2).

For the intensity of the XPS peak of barium in the superconducting material below the non superconducting surface layer, measured at different electron take off angles and normalized to its intensity at normal take off angle, we may write using eq. (2) and (3):

$$N = \frac{I_{Ba,4d}(\varphi)}{I_{Ba,4d}(0)} = G(\varphi) \ \exp \left[\frac{d}{\lambda_{Ba,4d,surf}} \left(1 - \frac{1}{\cos\varphi} \right) \right] \qquad (4)$$

which enables us to determine the thickness d of the surface layer on top of the superconducting thin film. In deriving eq. (4), we assumed that the surface layer has a uniform thickness d and that in this layer the inelastic mean free path of the photoelectrons can be described by $\lambda_{Ba,4d,surf}$. In eq. (4), effects of surface roughness have been neglected.

3. EXPERIMENTAL

The YBCO thin film was prepared by a modified rf-magnetron sputtering technique. Experimental details are given in ref. 2.

The ARXPS experiments were carried out on a Kratos XSAM 800 spectrometer, controlled by a PDP 11 microcomputer, with a base pressure of 4×10^{-10} Torr. The photoelectron energy analyser acceptance angle was fixed at 9 degrees. The spectrometer was calibrated by measuring the Cu $2p_{3/2}$ XPS peak and the X-ray induced Cu L_3MM Auger peak on a clean, sputtered Copper sample using a Mg anode[3], and its linearity was checked.

The spectra were taken using the DS800 program[4]. Except for the sample tilt, all the measurements were done with the same instrumental settings. The

background subtraction, simulations and data analysis were done on a 80386/80387 personal computer. For background subtraction, we used the method of Shirley[5]. In all simulations, 100% Gaussians were used.

4. COMPOSITION OF THE SURFACE LAYER

In this report, typical XPS spectra taken on a high T_c superconducting $YBa_2Cu_3O_{7-\delta}$ thin film on a YSZ (100) single crystal are given. The film had a thickness of 10 nm and a $T_{c,zero}$ of 88 K. In studying films with comparable thicknesses on $SrTiO_3$ and MgO (100) single crystals no essential differences with the spectra shown here were observed. For the elements Y, Ba, Cu, O and C, ARXPS spectra were taken at photoelectron take off angles of 0,10,..,70 degrees, to obtain information about the distribution and chemical environment of these elements. For the elements, the spectra taken at take off angles of 0 and 60 degrees are shown in figures 1-6.
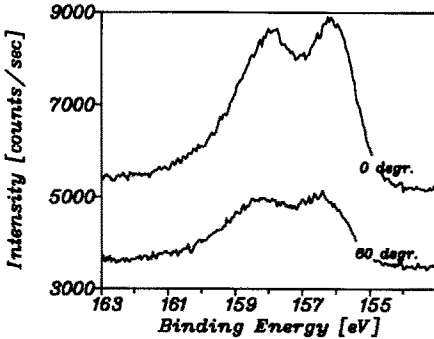

FIGURE 1
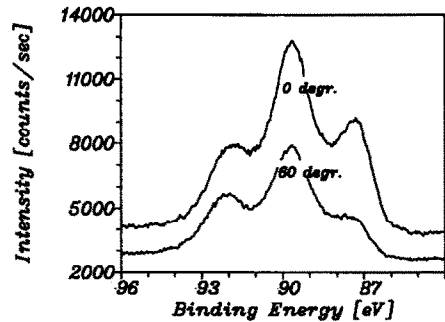Y 3d spectra, taken at 0 and 60
degrees take off angle

FIGURE 2
Ba 4d spectra, taken at 0 and 60
degrees take off angle

The Y 3d spectra, shown in figure 1, reveal that Y is present in one chemical state only: in the superconducting material beneath the non superconducting top layer.

In the Ba 4d and Ba 3d spectra, displayed in figures 2 and 3 respectively, clearly contributions of Ba in two different chemical states can be observed. The intensity of the high BE component increases when compared to the low BE component with increasing photoelectron take off angle, so the low BE component can be attributed to Ba in the superconducting material and the high BE component to Ba in the surface layer.
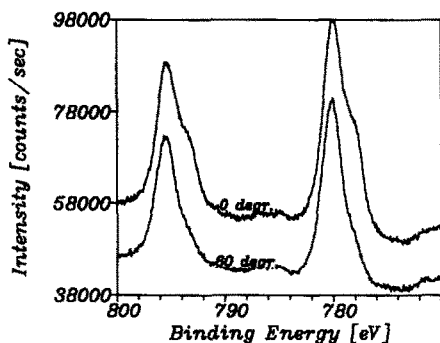
FIGURE 3

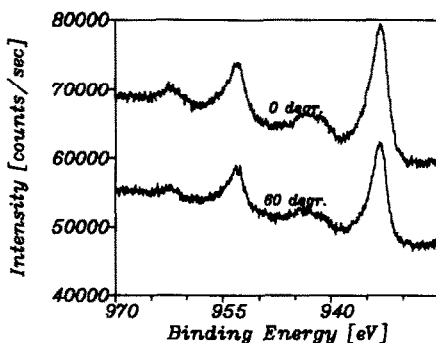Ba 3d spectra, taken at 0 and 60
degrees take off angle

FIGURE 4

Cu 2p spectra, taken at 0 and 60
degrees take off angle

For Cu, the 2p spectra are shown in figure 4. The ratio of the intensity I_{sat} and I_{main} of the satellite and main peak respectively decreases from 0.29 to 0.18 with increasing photoelectron take off angle, indicating a Cu II to a Cu I reduction in the surface layer. This is in good agreement with the observation of oxygen losses in the top layer, which will be shown below.

In the O 1s spectra, shown in figure 5, we observe, as in the case of Ba, features of O in two different chemical states. From their photoelectron take off angle dependence, the low BE component can be assigned to O in the superconducting material and the high BE component to O in the surface layer. We determined the ratios of the areas of the high and low BE components in the Ba 4d and O 1s features and found that in the surface layer the O atomic concentration has decreased by 30% when compared to the superconducting material.
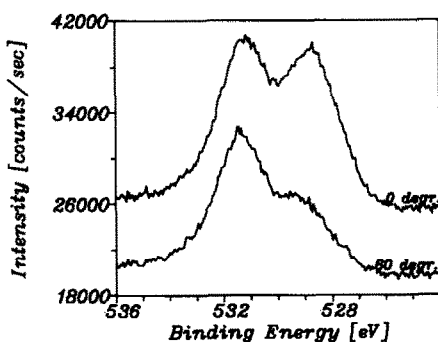

FIGURE 5

O 1s spectra, taken at 0 and 60
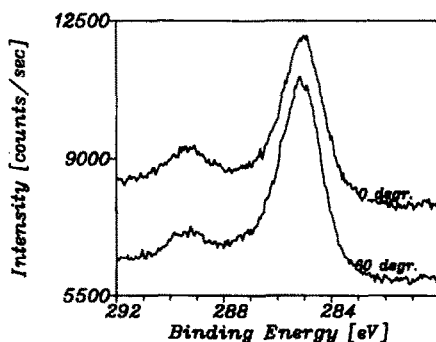degrees take off angle

FIGURE 6

C 1s spectra, taken at 0 and 60
degrees take off angle

In figure 6, the C 1s spectra are given. Clearly contributions of graphite and some carbonates near 285.0 and 289.5 eV respectively, can be observed. The intensity of the peak attributed to carbonates decreases when compared to the intensity of the graphite peak under glancing incidence, indicating that the surface layer is not ended by carbonates but by graphite. The carbon contaminations detected here are expected to be due to the transport of the film through ambient from deposition to the XPS analysis set up. Also contamination with moisture, leading to the formation of some hydroxides cannot be excluded.

5. THICKNESS OF THE SURFACE LAYER

As described in section 2, absolute ARXPS measurements enable us to determine the thickness of a surface layer accurately. For this, we measured the function $G(\varphi)$, as defined in eq. (3) on a clean sputtered Si sample. The result is given elsewhere[1]. To obtain the intensities of the Ba in the superconducting material, we simulated the Ba 4d spectra, taken at 0,10,..,70 degrees take off angle. In the simulations, of which a result is shown in figure 7, two doublets each consisting of two Gaussians were used. The dotted line represents the Ba 4d doublet at 87.3 eV of the superconducting material, the dashed line at 89.3 eV the Ba 4d doublet of Ba in the surface layer. The doublet splitting equaled 2.58 eV and the intensity ratio of the Ba $4d_{3/2}$ and Ba $4d_{5/2}$ lines was taken to be 0.7. The sum of these two Ba lines is given as a solid line. The results show that the measured Ba 4d spectra can be simulated perfectly by two Ba lines, belonging to Ba in two different chemical states.
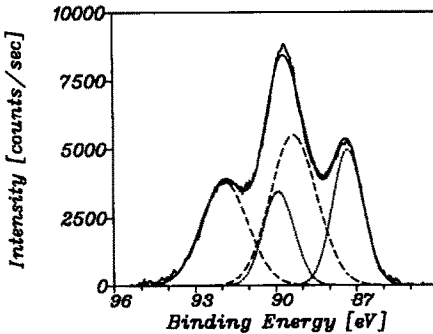

FIGURE 7
Simulation of the Ba 4d spectrum, taken at 0 degrees take off angle. For a description: see section 5
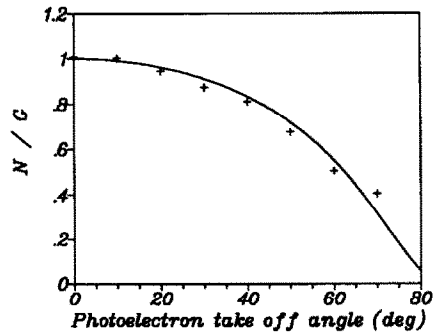
FIGURE 8
Absolute ARXPS measurements. For a description, see sections 2 and 5, "+" indicates measurements, the solid line is the result of the fit

In figure 8, the intensities of the Ba 4d low BE component (see figure 7), normalized to the intensity at normal take off angle and divided by the measured function $G(\varphi)$, are given. When these measurements, indicated with "+", are fitted with a modified Levenberg-Marquardt fit procedure[6], we find:

$$d = (0.60 \pm 0.05)\ \lambda_{Ba,4d,surf}\ (\pm\ 8\%),\ \text{residue } S = 0.002.$$

The residue S and the confidence limits have been calculated using the variance-covariance matrix[7].

6. DISCUSSION

When the XPS spectra in this report are compared with earlier results[8], it can be concluded that the quality of the surface of the $YBa_2Cu_3O_{7-\delta}$ thin films greatly improved, and this quality will be of crucial importance in further research on multi layer structures of high T_c superconducting $YBa_2Cu_3O_{7-\delta}$ thin films.

With our assignment of lines in the XPS spectra to elements in superconducting material, covered by a non superconducting surface layer, we can simulate our XPS spectra perfectly. Other results[9] confirm our assignment. The XPS spectra in this report show that the surfaces on the $YBa_2Cu_3O_{7-\delta}$ thin films are of high quality.

Using absolute ARXPS film thickness measurements, we find that the surface layer on $YBa_2Cu_3O_{7-\delta}$ thin films has a thickness of 0.60 $\lambda_{Ba,4d,surf}$. For $\lambda_{Ba,4d,surf}$ a value can be taken from the literature[10] and we can estimate the thickness d to be 10.5 $\pm$ 0.9 Å ($\pm$ 8 %).

7. CONCLUSIONS

In this report, we studied the surface layer on c-axis oriented high T_c superconducting $YBa_2Cu_3O_{7-\delta}$ thin films. In the Y 3d feature, no chemical shift has been observed, indicating that Y is present in one chemical state only. In the Ba 3d and Ba 4d features, we found contributions of Ba components in two different chemical states. These two Ba lines were assigned to Ba in the superconducting $YBa_2Cu_3O_{7-\delta}$ material and to Ba in a non superconducting top layer. Also in the O 1s feature, two O lines appear, one belonging to O in the $YBa_2Cu_3O_{7-\delta}$, and one belonging to O in the top layer. In the surface layer 30 at. % O is missing. The ARXPS experiments show that the stable surface of c-axis oriented high T_c superconducting $YBa_2Cu_3O_{7-\delta}$ thin films is the Ba-O plain, above the Y and that the superconducting film is covered with a non

superconducting top layer with a typical thickness of 1.1 nm, containing Ba- and Cu-oxides and, due to transport through ambient, graphite, some carbonates and hydroxides.

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