ARXPS-STUDIES OF $\hat{c}$ -AXIS TEXTURED $\text{YBa}_2\text{Cu}_3\text{O}_x$ -FILMS

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$\text{YBa}_2\text{Cu}_3\text{O}_x$ sputter deposited cold on MgO grows in O_2 annealing epitaxially to a transparent, superconducting film with $T_c = 80$ K. The unscrapped surfaces of these films are smooth showing XPS lines changing with photoelectron take-off angle. This enhanced data base allows to separate the different chemical compounds (hydroxide, peroxide, carbonate, carboxyle, cuprate, graphite ...) and to obtain their spatial distribution. This yields the compounds, their amount and distribution making up the cinder growing with O_2 -anneal at internal and external surfaces. The cinder stoichiometry gives insights in the chemistry going on in O_2 annealing. Below the cinder the signature of $\hat{c}$ -axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_x$ is identified, showing that a Ba-oxide layer forms the stable surface. This coats insulating CuO_2 and Y-oxide layers yielding so an intrinsic dead layer.

1. INTRODUCTION AND EXPERIMENTAL RESULTS

Till now the superconducting perovskites protect themselves by extrinsic or intrinsic surface coatings against experimental studies such, as tunnel measurements or surface spectroscopy. ¹ Thus CLEAN surfaces are of crucial importance. But to characterize "CLEAN" the signature of "SCHMUTZ" must be known. This SCHMUTZ results as reaction cinder mainly from diffusion and chemical processes, like oxygenation or defluorination. ARXPS (angle resolved x-ray photo electron spectroscopy) is a method well suited to analyze the reaction cinder. ² This is because in ARXPS minor amounts (> 0.3 nm) of interface compounds and their spatial distribution are identified in a depth range of 5 to 10 nm with negligible radiation damage. ² The latter two properties are crucial, because perovskite grains are known to be coated by a O_2 -reaction cinder of about 1 to 5 nm mean thickness even after scraping, ¹ and because the perovskites are extremely radiation sensitive. ³

As a first step, the chemical compounds of the cinder and the cuprate have to be identified by ARXPS. This needs a fairly smooth surface with a layering of the chemical compounds. This was achieved by measuring unscrapped, smooth, highly $\hat{c}$ -axis textured $\text{YBa}_2\text{Cu}_3\text{O}_x$ films. ⁴ These films were prepared by dc magnetron or rf sputtering of O_2 -baked $\text{YBa}_2\text{Cu}_3\text{O}_x$ targets. The target and the substrate (MgO) were cool ($< 50^\circ$) to transfer Cu and oxygen effectively to the substrate. The sample was calcinated in 1 bar O_2 at 920°C (0.5h) and oxygenated at 750°C (3h). To identify contaminants, the film was UHV annealed at 500°C . To reduce the amount of graphite and carboxyles found at the surface an air anneal 24 h at 750°C was performed. ⁴

FIGURE 1
Ba 4 d doublets for 10° and 70° take-off angle fitted simultaneously for all data between 10° and 70° .

TABLE 1
Binding energies ^{6,7} and assignments

BE/eV		Assignment
87.2	1 Ba4d	Superconducting Cuprate
88.2	2 Ba4d	Cuprate surface
89.6	3 Ba4d	BaO_2 , BaCO_x ..
91.	4 Ba4d	Ba(OH)_2
156.2	1 Y3d	Superconducting Cuprate
157.3	2 Y3d	Y_2O_3 ...
158.6	3 Y3d	Y(OH)_3 , ..
284.	1 C1s	Graphite
285.	2 C1s	Graphite oxide
288.1	4 C1s	Carboxyle
289.6	5 C1s	Carbonate
529.1	1 O1s	O^{2-}
531.1	2 O1s	O_2^-
532.3	3 O1s	CO_x
533.9	4 O1s	$(\text{OH})^-$, H_2O

As shown in Fig. 1 and Ref. 4 the $\text{Ba}4d$, $\text{Y}3d$, $\text{Cu}1s$ and $\text{O}1s$ XPS lines show strong dependencies on photo electron take-off angle θ (against the surface normal) and on preparation. This increased data base yields by a simultaneous fit the binding energies and the angle dependence of their intensities $F_i(\theta)$.⁴ The stability of these fits is proven by successful fits after UHV and air anneal. To evaluate the stoichiometry and the spatial distribution quantitatively the fitted areas F_i as function of θ for Ba, Y, C and O are used.⁴ This yields the assignments summarized in Table 1.⁴ Because of the satellite problem so the integrated Cu 3s intensity is used, only.⁴

2. ANALYSIS AND DISCUSSION

To identify the cuprate crystallites with $\hat{c}$ -axis perpendicular to the surface, we look for the strongest decreases in $F_i(\theta)$. Thus 1Ba, 2Ba and 1Y are identified with the cuprate, yielding $\text{YBa}_2\text{Cu}_{2.3}\text{O}_x$ as substrate for the cinder. Because $F_i(\theta)$ of 2Ba is slower decreasing with θ than 1Ba and 1Y, and because 1Ba is a signature of the superconducting cuprate⁶, we assign 2Ba to Ba-oxide being the stable surface⁵ of $\hat{c}$ -axis cuprate (see Fig. 2.. Underneath follows an insulating CuO_2 -plane, an Y-O-layer, a conducting CuO_2 plane, a metallic like Ba-O-CuO plane,... This explains⁴ the increase of angle dependence in the sequence 2Ba, 1Y and 1Ba.

The cinder adjacent to the cuprate has 2Y, 3Ba and Cu (40%) as metallic components. The differences in the angle dependencies are due to the fact that 3Ba represents, e.g., BaCO_x , BaO and BaO_2 . The peroxide forms an outermost layer, followed by BaCO_x underneath. At present, the exact composition of this Y-Ba-Cu-per-oxide-carboxide cinder cannot be given. The oxide cinder⁴ (Y_2O_3 , YBa_2CuO_2 ,²) forms an 1 nm thick coating of the cuprate followed by carboxyles (Ba-Cu) in a thickness of about 2 nm (Fig. 2). The carboxyles are mixed with hydroxides 3Y and 4Ba which disappear together with the 40-line by UHV anneal at 500°C. As outermost layer (oxidized) graphite ($\approx 1\text{nm}$) has been found (Fig. 2).⁴

In UHV anneal (5 h, 500°C) the changes in the XPS spectra indicate a work function increase of 0.7 eV and the loss of H_2O and OH groups (4Ba, 3Y, and 4O). In air anneal (24 h, 750°C) the XPS spectra change strongly:⁴ Graphite (factor 10) and carboxyles (~ 5) are burnt off BaCO_3 is reduced negligibly whereas BaO_2 grows dramatically, the cuprate, Cu- and Y-oxide retract from the surface.

The above results are the first reported on $\hat{c}$ -axis textured $\text{YBa}_2\text{Cu}_3\text{O}_x$ -films. By the Ba-O layer⁴ is surface is more stable than (a,b) surfaces which amorphize and CuO retracts yielding the 2-4-8 physe.⁵ The stability corresponds to the slower growth (x8) rate of $\hat{c}$ -surfaces layer by layer. The observed cinder⁴

is with 7 nm quite thin. This seems to be due to sputter deposition of O rich material ($\text{YBa}_2\text{Cu}_3\text{O}_6$) omitting so long-time oxygenation. The O needing only a short-time oxygenation. The O diffuses via (a,b) surfaces into the film leaving most cinder buried between the grains. For longer air anneal (24h, 750°C) the deterioration of the cuprate sets in. This deterioration may be via (a,b) surfaces, which below 450° are unstable against amorphization and insertion of CuO planes into the grains.⁵ We see this deterioration as retraction of the cuprate and as growth of BaO_2 .⁴ In general, the cinder contains such compounds, which are more stable and have a low vapor pressure at these temperatures. This explains the existence of Y_2O_3 , BaCuO_2 , BaCO_3 , BaO_2 or graphite in the cinder. But the occurrence of graphite in O_2 anneal needs further discussion. This graphite is caused by, e.g., CO_2 calcination via BaO as catalyzer. To reduce the amount of graphite and BaCO_x more effectively, the use of air is appropriate because of the $\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$ reaction as shown by our results.

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FIGURE 2

Sketch of a $\hat{c}$ -axis $\text{YBa}_2\text{Cu}_3\text{O}_x$ -surface coated by cinder growing with O_2 reaction time. The Ba-oxide surface layer indicates a stable but intrinsically "dead" surface coating of about 1 nm thickness.