Surface and interface properties of cleaned and Ag–covered YBa$_2$Cu$_3$O$_{7-x}$ films

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Abstract

As–received YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) films are generally covered by approximately one monolayer of chlorine. Such YBCO films, which were first cleaned by annealing in oxygen or additionally by electron–stimulated desorption and subsequently covered with Ag at room temperature, were studied by using Auger electron (AES), low–energy electron energy–loss (LEELS), and photoemission spectroscopy (UPS). AES and LEELS signals of YBCO were detected even for *nominal* silver coverages Θ = 20 nm. This indicates that Ag overlayers grow extremely nonuniform. The formation of Ag islands is concluded from the coverage dependence of the AES lines of the substrate as well as of silver. For small Ag coverages, the Ag(MVV) Auger lines were found to be shifted by approximately −1.4 eV with respect to the Ag(350/355 eV) signals recorded with thick overlayers. On clean samples, we conclude the initial formation of Ag$_2$O up to $\Theta \approx 0.2$ nm and a growth of metallic Ag islands for $\Theta > 1$ nm only. On Cl–contaminated YBCO surfaces, a distinctly different behavior is observed. We infer an initial formation of AgCl which prevents an oxidation. Accordingly, energy losses caused by bulk–plasmon excitations in silver metal appear on YBCO:Cl samples already for $\Theta \approx 0.2$ nm. Our UPS data indicate that the Ag clusters show a polycrystalline morphology.

1. Introduction

Physics and chemistry of YBa$_2$Cu$_3$O$_{7-x}$ (YBCO) surfaces and interfaces are of special interest for microelectronic applications because it is desirable to integrate thin superconducting films and the required metallic connections into existing chip technologies. One of the metals, which seems to be most suitable for such electrical contacts, is silver since it was found to behave (nearly) nonreactive at the interfaces of YBCO single–crystals and ceramics [1, 2]. On the other hand, it was recently shown [3] that *as–grown* YBCO films are often covered by approximately one monolayer of chlorine which might, of course, influence the interface properties. Hence, it was the intention of this work to compare the results obtained with fundamental studies on cleaned but still Cl–contaminated and on clean samples which were covered by silver. It will be shown that few but significant chemical reactions of Ag occur which differ for Cl–contaminated and –decontaminated YBCO films.

2. Experimental

The YBa$_2$Cu$_3$O$_{7-x}$ films investigated in the present work were deposited at ISI, Forschungszentrum Jülich, by laser ablation on randomly oriented ZrO$_2$ substrates. They were inserted into our two–chamber ultrahigh–vacuum (UHV) system via a fast–entry lock.

Removal of carbon compounds from the sample surfaces was achieved by annealing for 2 h at 600°C in 1 bar of pure oxygen, followed by slow cooling to room temperature (RT), and reevacuation. Chlorine contaminations observed on all as–received samples were found to persist even after such O$_2$ anneals [3]. Almost clean surfaces were obtained by subsequent irradiation with 180–eV electrons impinging as 2.3 · 10^{20} particles per cm^2. Silver was evaporated from a Knudsen cell. The films were kept at RT and the background pressure did not exceed 5 · 10^{-10} mbar. The amount of Ag deposited was determined by using a quartz oscillator. In the following, *nominal* coverages Θ will be given which correspond to uniform Ag ad–layers.

All electron spectra were measured by using a cylindrical mirror analyzer equipped with a coaxial electron gun. AES and LEELS signals were excited by 3-keV and 150–eV electrons and were recorded as first and negative second derivatives formed by a lock–in amplifier, respectively. UPS was performed by using a He discharge lamp.

3. Results and discussion

3.1. Cleaned surfaces

A study of surface properties of as–received and cleaned YBCO films was previously reported [3]. Some of the findings are important for the present work and will thus be briefly described.

Auger measurements revealed that all films investigated were covered by approximately one monolayer (ML) of chlorine. While no C(272 eV) signal,
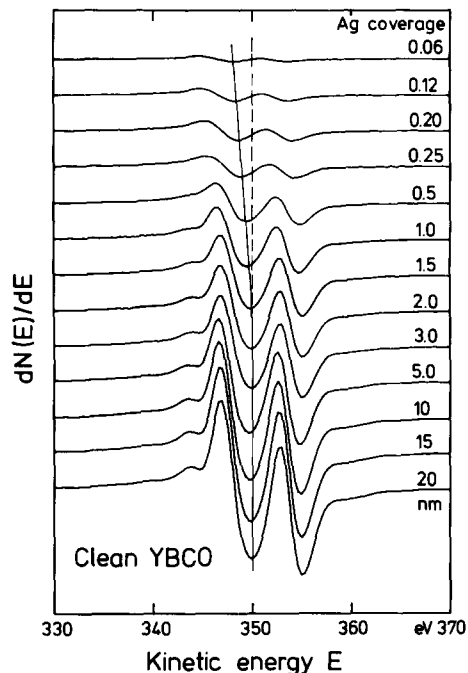
Fig. 1. Auger electron spectra obtained with a clean YBCO film which is covered by different amounts of silver. The chemical shift occurring at low coverages is outlined.

which is common for air–exposed surfaces, was observed after annealing of the samples in oxygen, the Cl(181 eV) line was found to be nearly unaffected by this often–used cleaning procedure. However, the chlorine contamination could be reduced to less than 0.04 ML by electron–stimulated desorption (ESD). Since it was demonstrated that such chlorine contaminations on as–grown YBCO films are not exceptional [3], we studied samples which were conventionally cleaned only and those which were additionally Cl–decontaminated.

Within the limits of experimental error, the bulk composition of the Cl–covered YBCO films resulted as 1 : 2 : 3 : 6.8. ESD–cleaning reduced the oxygen concentration at the surface. This result is confirmed by LEEL spectra which show an ESD–induced ener-

gy–loss of 4.4 eV which indicates the formation of the more oxygen–deficient tetragonal YBCO phase.

UPS studies performed with 21.2–eV photons revealed for Cl–covered YBCO films an intense Cl–like feature which is superimposed on a prominent intrinsic peak with a binding energy of 4.8 eV.

3.2. AES with Ag–covered films

Fig. 1 shows a series of Auger electron spectra restricted to the energy range of the silver MVV doublet. Their intensities increase as a function of nominal Ag coverage up to the maximum thickness $\Theta_{max} = 20$ nm. For $\Theta > 1.5$ nm, the characteristic energies of the $Ag(M_5VV)$ and $-(M_4VV)$ lines were recorded at 350 and 355 eV, respectively, and are in agreement with the AES standard data of silver. However, for lower coverages, the doublet is shifted to lower kinetic energies. No shifts were observed for the O(512 eV) and Cu(918 eV) signals from the
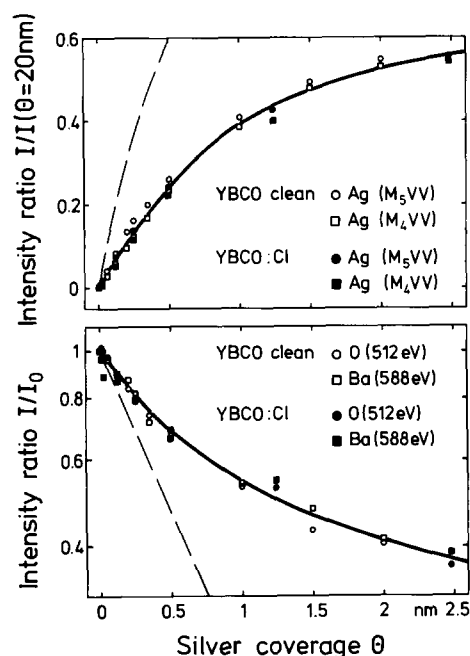
Fig. 2. Normalized intensities of specific Auger transitions recorded with clean and Cl–contaminated YBCO films as a function of silver coverage. The dashed curves were calculated as mentioned in the context of eqns. 1 and 2.

YBCO film as well as for the Cl(181 eV) line recorded with Cl–contaminated samples. All AES signals from YBCO were detected up to Θ_{max}.

Information on the growth mode of the silver overlayer was obtained by analyzing the AES signal heights as a function of Ag coverage. We performed

such measurements with Cl–contaminated (YBCO:Cl) and –decontaminated (YBCO$_{clean}$) samples. In Fig. 2a, the normalized intensities of the two Ag lines are shown and in Fig. 2b the relative heights of the O(512 eV) and Ba(588 eV) YBCO signals. Within the limits of experimental error, YBCO:Cl and YBCO$_{clean}$ data are identical.

Assuming a uniform ad–layer of thickness Θ, the AES intensities I of the substrate lines are attenuated as

$$I = I_0 \cdot \exp(-\Theta/\Lambda_{eff}) , \qquad (1)$$

and the adsorbate lines increase as

$$I = I_\infty \cdot \left[1 - \exp(-\Theta/\Lambda_{eff})\right] , \qquad (2)$$

where Λ_{eff} means the effective escape length of the Auger electrons considered. The dashed lines in Figs. 2a and b are obtained from eqn. 2 with $\Lambda_{eff}(350\ eV) = 0.56$ nm and eqn. 1 with $\Lambda_{eff}(550\ eV) = 0.66$ nm, respectively. Obviously, the recorded AES signals are incompatible with a layer–by–layer growth but indicate the formation of silver islands which do not completely overlap even at a nominal coverage of 20 nm. This finding agrees well with results of Meyer et al. [1] who deduced the formation of Ag clusters on YBCO single–crystals up to $\Theta = 9$ nm, the largest coverage from their x–ray photoemission data. However, Laubschat et al. [2] concluded a silver layer–by–layer growth from photoemission studies with ceramic YBCO samples.

Chemical shifts of the Ag(MVV) Auger lines were observed both, with clean and Cl–covered samples. The maximal shifts ΔE_{max} were evaluated as (−1.4 ± 0.2) and (−1.3 ± 0.3) eV, respectively, and are identical within the limits of experimental error. For small silver coverages, however, the data indicate some dissimilarities which are outlined in Fig. 3.

Schön [4] reported the chemical shifts of the Ag(M$_4$VV) Auger–transitions to be −1.4 eV for Ag$_2$O and −0.8 eV for AgO in comparison with Ag metal. Taking account of the increasing disruption of Cu–O bonds by Ag found with YBCO single–crystals for $\Theta < 0.8$ nm [1], these results suggest the formation of Ag$_2$O near to the interface of YBCO$_{clean}$ films, too. With such films, the initial shifts were found to be constant up to $\Theta = 0.2$ nm indicating a nearly complete oxidation to take place in this range of nominal Ag coverage. LEELS studies of Hockertz et al. [5] confirmed the occurrence of oxygen out–diffusion at RT from the bulk to O–depleted YBCO surfaces. Thus, similar processes might support the oxidation of small Ag islands. Hence, we interpret our results

on YBCO$_{clean}$ samples as an initial formation of Ag$_2$O, followed by lower oxidation states, and a metallic adsorption for $\Theta > 1$ nm.

With Cl–contaminated YBCO films, the initial energy shift was recorded only for $\Theta < 0.05$ nm while the Ag(350/355 eV) signals were obtained already with coverages $\Theta > 0.5$ nm. Thus, the Cl coating seems to cause a different chemical behavior at the
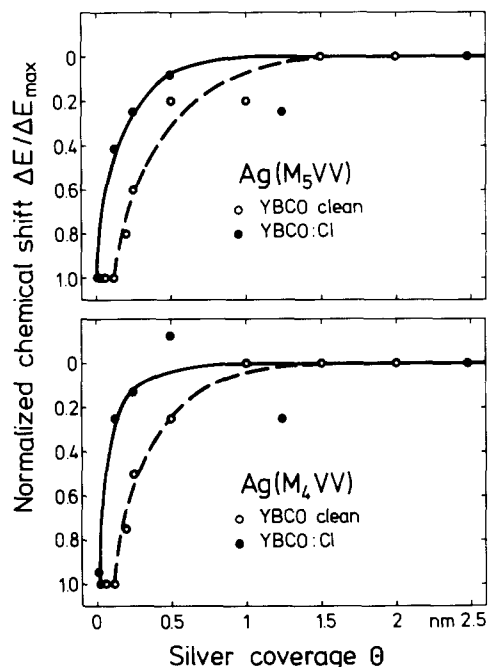

Fig. 3. Coverage dependence of the chemical shifts of AES Ag signals as observed with clean and Cl–contaminated YBCO films. Fig. 3a shows Ag(M$_5$VV) and Fig. 3b Ag(M$_4$VV) transitions.

interface. It was shown by König and Kirste [6] that metallic silver films stored in air for 1 – 2 weeks at RT became covered with AgCl. Apparently, silver chloride forms more easily than silver oxides. Therefore, we assume a formation of AgCl at YBCO:Cl interfaces. By considering the respective electronegativities, AgCl and Ag$_2$O should exhibit the same shifts of Ag AES–lines in comparison with pure silver. However, the AgCl seems to prevent an oxidation of the Ag clusters.

3.3. LEELS with Ag–covered films

In Fig. 4, we show LEEL spectra for successive Ag depositions on an YBCO:Cl film. For low coverages, only the well–known loss features of the uncovered sample [3, 5] were observed but not the energy loss of 4.4 eV which should, for example, indicate a withdrawal of oxygen from the YBCO interface as ex-

pected for a formation of silver oxides. Additional Ag–induced structures are detected for $\Theta > 0.2$ nm. Energy losses of 3.8 and 7.8 eV appear which are assigned to excitations of one or two silver bulk–plasmons. The bulk–plasmon energy of Ag metal was reported by Daniels [7] as (3.78 ± 0.02) eV. Our data
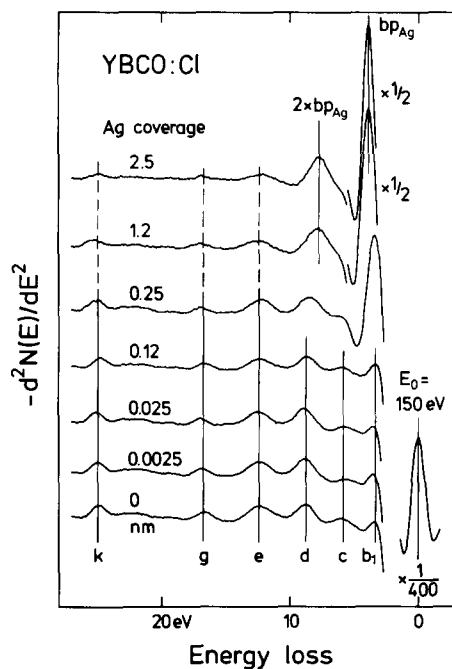

Fig. 4. LEEL spectra recorded after different Ag depositions on a Cl–contaminated YBCO film. The specific loss features are labeled as in previous works, e.g. [5].

are in excellent agreement with this value. We note that the plasmon energy–loss already occurs for $\Theta \approx 0.2$ nm. This indicates the existence of Ag clusters with metallic properties on YBCO:Cl even at low coverages. Moreover, the prominent losses of the YBCO substrate were still recorded at $\Theta_{max} = 20$ nm. This would be impossible with completely Ag–covered surfaces since Λ_{eff} of these electrons is in the order of 0.3 nm only.

3.4. UPS with Ag–covered films

Photoemission spectra obtained with He I radiation show, as previously reported [3], distinct differences between clean and Cl–covered YBCO samples. With large Ag coverages, the respective features were no longer observed because a broad Ag(4d) signal is superimposed in the entire range of binding energies between 3.5 and 7.2 eV. Even for the largest Ag coverages, $\Theta = 6$ nm, the YBCO–related structure at 8.8 eV was still found. This again proves island

formation. A comparison of the Ag valence–band structure recorded by us with spectra reported by others [8, 9] shows that our data fit well with those of polycrystalline silver.

4. Summary

Chemical, electronic, and morphologic properties of Cl–contaminated and of clean YBCO films covered by silver were investigated by applying AES, LEELS, and UPS. Previous studies indicated bulk $YBa_2Cu_3O_{6.8}$ composition up to the surface on Cl–covered films but oxygen–deficient $YBa_2Cu_3O_{6.5}$ on ESD–cleaned surfaces. Nevertheless, for small *nominal* Ag coverages, $\Theta < 0.2$ nm, the formation of Ag_2O seems to occur on clean but not on YBCO:Cl surfaces. Here, AgCl most probably forms which then prevents oxidation of silver. Up to the largest Ag coverage examined, $\Theta = 20$ nm, the growth of islands was found. It is assumed that the morphology of the overlayers is almost independent of a Cl–contamination and that on both types of samples the islands exhibit no preferential orientations.

Acknowledgements

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