Investigation of Room Temperature Oxidation of Cu in Air by Yoneda-XAFS

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Abstract. The structure of thin copper oxide layers which are formed on metallic Cu due to the exposure to air are investigated with Yoneda-XAFS and ReflEXAFS. The measured Yoneda-XAFS data were compared to quantitative model calculations in the framework of the distorted wave Born approximation (DWBA) assuming different model structures for the oxide layer. Yoneda-XAFS fine structure spectra measured for various different grazing angles show that the experimental data are best described by a model structure consisting of a duplex type oxide layer with an outer layer of CuO (tenorite) in direct contact with the gas atmosphere and an inner Cu_2O (cuprite) layer at the interface to the underlying Cu metal.

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INTRODUCTION

Oxide layers on Cu have been intensively examined with electrochemical and optical technique as well as X-ray and UV-photoelectron spectroscopy (XPS and UPS) and X-ray reflectivity measurements [1,2]. For the electrochemical oxidation of Cu in alkaline media, there is general agreement that the oxidation proceeds in two well separated steps: Starting from a reduced metal surface, first a thin Cu(I) layer, mainly consisting of Cu_2O is formed, while at higher potentials, a duplex type layer with a Cu(II)-oxide/hydroxide on top of the above mentioned Cu_2O layer is formed [1,2]. While the atomic structure of thermally formed, thick (about 100 nm thickness) oxide layers on copper has been examined with X-ray diffraction [3] and X-ray absorption spectroscopy [4], only little is known about the structure of thin passive films on Cu surfaces, which are formed due to the air exposure of Cu metal. XPS and surface sensitive EXAFS investigations have shown that the films are mainly composed of Cu_2O [4,5], but detailed structural investigations are still missing. We have therefore applied a combination of ReflEXAFS and Yoneda-XAFS [6,7] for a detailed study of the oxide layers formed on Cu in air at room temperature.

EXPERIMENTAL

The copper sample was prepared on smooth float glass substrates by DC-sputtering (700 V, 80 mA) in an Ar atmosphere of 1 Pa resulting in a film thickness of about 90 nm as determined by X-ray reflectivity (XRR) measurements. The investigated sample was exposed to air for 48 hours to allow a native copper oxide film of some few monolayers to form.

The presented X-ray experiments were performed at the X-ray undulator beamline BW1 at the DORIS III storage ring at Hasylab (Hamburg, Germany). A double-crystal monochromator with two flat Si(111) crystals was used. ReflEXAFS and Yoneda-XAFS data were collected at room temperature under ambient conditions. Incident and reflected intensities were measured by means of nitrogen- and argon filled ionization chambers. The incoming beam was collimated vertically to 120 μm and a second slit placed in front of the detector for the reflected intensities defined the acceptance angle for the ReflEXAFS and Yoneda-XAFS measurements to 0.04° and 0.10°, respectively.

RESULTS AND DISCUSSION

In Fig. 1 Yoneda-XAFS measurements from a Cu thin film after 48 h of exposure to air are presented for several different grazing angles α_i. According to the angular position of the Yoneda peak, the detector angle was set to $\alpha_f = 0.290°$.

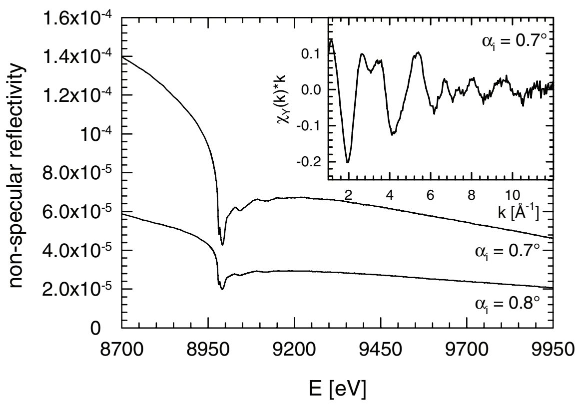

FIGURE 1. Yoneda-XAFS measurements of an air-oxidized Cu sample in the vicinity of the Cu-K edge for two different incidence angles as indicated and α_f =0.29°. The extracted fine structure $\chi_Y(k)$*k from the measurement at α_i = 0.7° is depicted in the insert.

For the further data evaluation, the X-ray reflectivity R above the absorption edge is split into a smooth part R_0 and an oscillatory part ΔR with $R = R_0 + \Delta R$ and the reflectivity fine structure $\chi_Y = \Delta R(E)/R_0(E)$ [6,7] is calculated. In the insert of Fig. 1, k-weighted data for $\chi_Y(k)$*k are presented for α_i=0.70°. Although the absolute intensity of the measured Yoneda-XAFS data is approximately four orders of magnitude smaller compared to typical ReflEXAFS measurements, the data quality is comparable to that of conventional ReflEXAFS, and fine structure oscillations with very low noise are visible up to k > 10 Å^{-1}.

In Fig. 2, normalized magnitudes of the Fourier-transforms (FT´s) of several k-weighted Yoneda-XAFS data measured for two different glancing angles are presented. In addition, the FT´s of ReflEXAFS experiments of the same sample are also shown for different incidence angles, and both data sets are compared to the FTs of polycrystalline Cu, Cu_2O (cuprite) and CuO (tenorite) measured in transmission mode. Both the FT´s of the ReflEXAFS and the Yoneda-XAFS contain characteristics of metallic Cu as well as of Cu-oxide, i.e. the peak at about 1.5 Å radial distance corresponds to the first Cu-O neighbour distance, the peak at 2.15 Å corresponds to the first Cu-Cu neighbour of the metal and the peak at 2.75 Å corresponds to the first Cu-Cu distance in the oxide. For the ReflEXAFS data, the oxide contributions in the FTs decrease with increasing angle as can be expected due to the resulting increase of the X-ray penetration depth from about 2.7 nm for α_i=0.185° and z_0=25.4 nm for α_i=0.35°. In comparison to the ReflEXAFS data, the intensity ratio of the Cu-O coordination with respect to the first Cu-Cu peak is more pronounced in the FT´s of the Yoneda-XAFS data, because the diffuse scattering and thus the Yoneda peak originates from lateral inhomogeneities [8], which typically occur at surfaces or interfaces. In contrast, contributions of the bulk of the film have only negligible influence on this intensity (see, e.g. [8]).

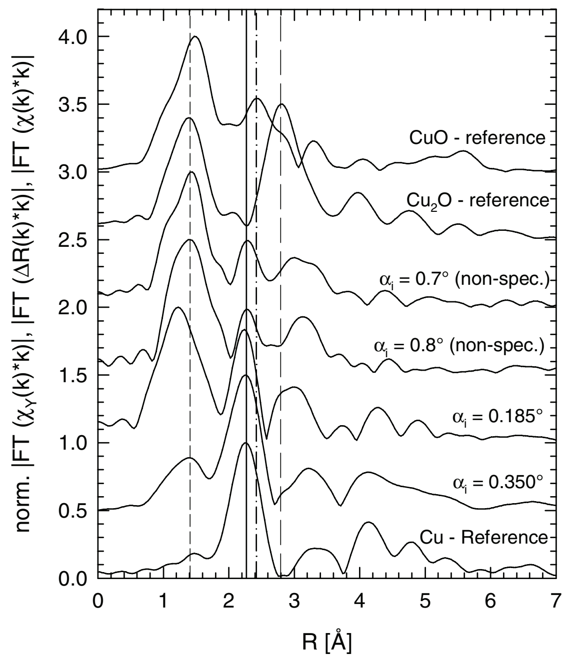

FIGURE 2. Normalized magnitude of the FT´s determined from ReflEXAFS measurements ($\Delta R(k)$*k, α_i=0.185° and α_i=0.350°) and Yoneda-XAFS experiments ($\chi_Y(k)$*k, α_i=0.7° and α_i=0.8°) of an oxidized Cu sample in comparison to transmission mode EXAFS experiments of Cu metal, Cu_2O and CuO ($\chi(k)$*k), respectively. The data are not phase-shift corrected. (k-range for the FT: 1.75 Å^{-1}≤ k ≤ 11 Å^{-1}, Hanning window function). The data are vertically shifted by 0.5 units.

The theoretical treatment and the data analysis of the Yoneda-XAFS is more complicated than that of conventional transmission mode X-ray absorption spectroscopy, since both the real and the imaginary part of the complex refractive index as well as the surface and interface roughness contribute to the off-specular reflectivity fine structure. Thus, besides the real and imaginary part of the refraction index, three more parameters for the complete description of the roughness, namely the rms-roughness σ, the lateral correlation length ξ and the Hurst parameter h, are needed. For the analysis quantitative model calculations in the framework of distorted wave Born approximation (DWBA, see e.g. [8]) were done, assuming two different models for the structure of the native oxide film. The first one consists of a simple Cu_2O-layer on copper while the second employs a multilayered duplex oxide layer consisting of a $CuO/Cu_2O/Cu$ structure. The needed complex refractive indices were extracted form transmission experiments of reference compounds by a Kramers-Kronig analysis. The results of these calculations are compared to the experimental data in Fig. 3.

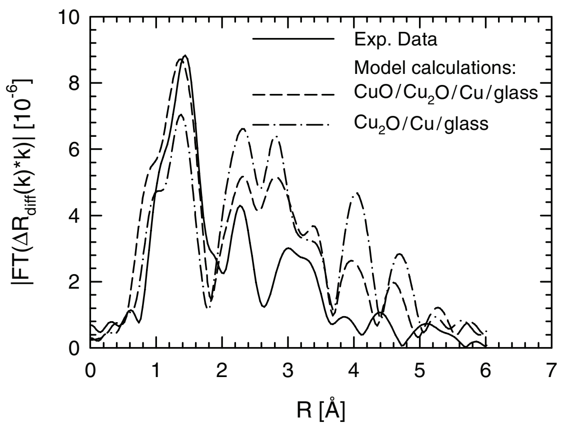

FIGURE 3. Fourier-transforms of k-weighted non-specular reflectivity fine structure data: Comparison of the experimental data (solid line) with model calculations assuming a single Cu_2O-layer (5.3 nm thickness) on copper (dash-dotted line) and a duplex layer consisting of a multilayered duplex oxide layer consisting of a CuO (1.3 nm)/Cu_2O (2.0 nm)/Cu structure (dashed line). The model calculations were performed in the framework of the DWBA. (The data are not corrected for phase shifts. k-range for the FT: 1.75 $Å^{-1} \leq k \leq 11$ $Å^{-1}$. Hanning windows.)

For the calculations, the surface and interface roughness of the oxides were set to 1.0 nm each, and the roughness of the inner Cu-substrate interface was set to 0.4 nm. The correlation length was set to 50 nm for all the oxide surfaces and interfaces, and 70 nm for the inner oxide-Cu metal interface. These values were obtained by analysing X-ray scattering data (detector and rocking scans) and agree qualitatively with ex-situ AFM investigations of air exposed, oxide covered Cu thin films [9]. The values for the Hurst Parameter were set to 1.0. In the case of the single oxide layer model, the best fit was obtained for a Cu_2O-layer thickness of 5.3 nm, while the duplex oxide layer model best fitted to the experimental data for 1.3 nm CuO on 2.0 nm Cu_2O on the Cu metal.

The position of the first Cu-O shell of the copper oxide and the first Cu-Cu shell of the copper metal can be reproduced very well by all the calculations. However, the intensity of the first Cu-O coordination is not described adequately assuming a single Cu_2O layer only. These model calculations suggest a considerably lower intensity of this peak, while on the other hand significantly higher contributions are resulting for both the Cu-Cu interaction of the metal substrate at 2.3 Å as well as for the Cu-Cu peak of Cu_2O at 2.8 Å. In contrast, assuming a duplex layer consisting of 1.3 nm CuO and 2.0 nm Cu_2O reproduce the intensity and the shape of the Cu-O peak correctly. In addition, although the total thickness of the duplex structure is smaller than that of the single Cu_2O layer, the intensity of the Cu-Cu peak of the metal substrate is significantly reduced in intensity, resulting in a closer fit of the experimental data. Further the reproduction of the intensity of the Cu-Cu peaks belonging to the oxide layer in the radial distance of 2.8 Å to ca. 3.6 Å is obviously improved.

CONCLUSIONS

We have presented Yoneda-XAFS investigations for air exposed Cu thin films. The comparison of the experimental data with those of model calculations strongly suggests the presence of a duplex type structure of the Cu-oxide (passive) layer with an outer CuO part of ca. 1.3 nm thickness and an inner Cu_2O layer of about 2.0 nm. The experiments suggest that especially the application of the Yoneda-XAFS technique is very promising for detailed structural investigations of surface phenomena such as electrochemical oxidation and reduction of metals or the study of corrosion resistant passive layers.

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