Grazing incidence XAFS under off-specular conditions

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Grazing incidence X-ray absorption spectroscopy (GIXAS) is a powerful tool for the study of surface and interface phenomena and gives accurate information about the atomic short range order around a chosen element as well as its chemical valence. The surface sensitivity is closely related to the penetration depth of X-rays, which amounts to few nm for grazing angles below the critical angle of total reflection, and a variation of the incidence angle allows for a depth profiling of the samples. In the simplest case the theoretical treatment is based on the Fresnel theory [1]. When the intensity distribution of X-rays which impinge onto a surface under a angle larger than the critical angle of total reflection is considered, a second well defined peak (“Yoneda peak”) appears for exit angles close to the critical angle in addition to the specularly reflected beam [2]. This peak, resulting explicitly from lateral heterogeneities which occur typically at surfaces or interfaces, can not be calculated in the framework of the Fresnel theory. More elaborate approaches such as the distorted wave Born approximation (DWBA) have to be used for data modeling [3, 4]. Using an asymmetric scattering geometry, i.e. with the detector centered at the Yoneda peak in the scattered beam, a new detection mode for grazing incidence X-ray absorption spectroscopy is demonstrated here. This technique offers the unique advantage of combining the chemical selectivity of X-ray absorption spectroscopy with the sensitivity to lateral heterogeneities of diffuse surface X-ray scattering [5].

In this study, we investigated the structure of a thin (thickness ≈ 90 nm) Cu-film on a float glass substrate which was prepared by DC-sputtering. If such a film is exposed to air, a copper oxide film of up to 10 nm thickness is formed at the copper surface. After preparation the sample was exposed 3 days to air to allow a native copper oxide surface to form. The experiments described here were performed at the X-ray undulator beamline BW1 [6] using a Si(111) double crystal monochromator and N2- and Ar-filled ionization chambers as detectors for incoming and scattered intensities. The incident X-ray beam was collimated vertically by a 120 µm slit. The acceptance angle of the detector is equal to 0.04° and 0.1° for the specular und non-specular case, respectively. Specular reflection mode GIXAS spectra of the sputtered copper film are presented in Fig. 1a for different grazing angles. Increasing the grazing angle to higher values causes an increase of the penetration depth of the X-rays from about 3-4 nm at 0.185° to more than 100 nm at 0.35°. In Fig. 1b, the magnitudes of the Fourier-Transforms (FT’s) of the k-weighted fine structure data are presented. Comparing the FT’s with each other, distinct differences can be observed, especially for the height of the peak at about 1.5 Å radial distance. Assuming the presence of a thin oxide layer on top of the sample, this behaviour can simply be understood by the fact that the relative contribution of the underlying Cu-metal increases with increasing glancing angle and that of the oxide surface layer decreases accordingly.

**Fig. 1:** Specular reflection mode XAFS spectra of a sputtered Cu-film at the copper K-edge (8979 eV) for several grazing angles. (b) Normalized magnitudes of the Fourier-transforms of the k-weighted fine structure function extracted from the reflectivity data of Fig. 1a.
The spectra of the off-specular detection mode - with the detector centered at the Yoneda peak in the scattered beam - are presented in Fig. 2a. Similar to EXAFS, fine structure oscillations in the spectra of the diffusely scattered X-rays are visible. For further data processing we used the same method to extract the fine structure out of the spectra as for the specular data. In the insert of Fig. 2b the k-weighted reflectivity fine structure extracted from the scan at \( \alpha_i = 0.7^\circ \) is presented. Although the absolute intensity of the measured non-specular spectra is approximately three orders of magnitude smaller than in the specular case, fine structure oscillations with very low noise are visible up to 10 Å\(^{-1}\). The normalized magnitudes of the Fourier-Transforms of the k-weighted fine structures are shown in Fig. 2b. Comparing the FT's of both measuring modes one can see distinct differences. The peak at about 1.5 Å radial distance corresponds to the first Cu-O neighbour distance of the Cu\(_2\)O, 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 neighbour in the oxide. Since the Cu-Cu peak in the oxide data at 2.75 Å is not fully reproduced in the FT's of the reflectivity data, the structure of the surface oxide-layer is supposed to be highly disordered or even amorphous. The height of the Cu-O coordination with respect to the first Cu-Cu peak is a measure for the sensitivity to the oxide in the uppermost copper oxide layer. It is remarkable that this coordination is more pronounced in the Fourier-transform of the non-specular data than in the specular case: While both peaks have similar intensities in the specular case, the Cu-O peak of the off-specular data has twice the intensity of the Cu-Cu metal peak. This can be explained as follows: The specular reflectivity laterally averages over the sample, while the off-specular signal results explicitly from lateral heterogeneities. Thus the bulk of the Cu film appears to be laterally homogeneous and the diffuse off-specular scattering results from the heterogeneity associated with the oxide layer. This diffuse scattering contribution should therefore directly involve the fine structure of the oxide more strongly than the underlying copper. Therefore the oxide is much more pronounced in the diffuse scattering fine structure than in the specular signal and a higher sensitivity concerning to the top oxide layer was achieved.

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References