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Physica B 357 (2005) 1–5

PHYSICA B

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Grazing incidence XAFS under non-specular conditions

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Abstract

The extended X-ray absorption fine structure technique (EXAFS) in the reflection mode under specular and non-specular conditions was used for the ex situ investigation of a sputter-deposited thin copper film on a float glass substrate. We prove the existence of a fine structure similar to EXAFS, which can be observed in the region of diffusely scattered intensities. It is shown that this new technique is surface sensitive for grazing angles above the critical angle of total reflection and an even higher surface sensitivity with respect to conventional reflection mode EXAFS can be achieved.

PACS: 61.10.Ht; 61.10.Kw; 81.05.Bx; 81.65.Mq

Keywords: EXAFS; Copper; X-ray scattering; Diffuse scattering; X-ray reflectivity; Atomic short-range order

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1. Introduction

Grazing incidence X-ray absorption spectroscopy (GIXAS) is a powerful tool for the study of surface and interface phenomena, such as adsorption [1], thin film growth [2], oxidation by gases [3], anodic oxide layer formation and passivation in aqueous media [4] and the formation of intermetallic phases [5]. GIXAS can give accurate information about the atomic short-range order (bond distances, coordination numbers and the local disorder) around a chosen element as well as its chemical valence [6]. The surface sensitivity is closely related to the penetration depth of X-rays, which amounts to a few nanometer for grazing angles below the critical angle of total reflection [7], and a variation of the incidence angle allows for a depth profiling of the samples. This is of high interest especially for layered systems such as oxidized surfaces or multilayers, where the element of interest may reside in several different sublayers. The theoretical treatment and the data analysis of GIXAS is much more complicated compared to

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doi:10.1016/j.physb.2004.11.007

conventional transmission mode X-ray absorption spectroscopy, since both the real part $\delta(E)$ and the imaginary part $\beta(E)$ of the complex refractive index $n(E) = 1 - \delta(E) - i\beta(E)$ contribute to the reflectivity fine structure as a function of energy. For layered sample systems additional contributions originate from the individual film thicknesses, densities and interface roughnesses. In order to include all these contributions, calculations of reflection mode GIXAS based on the Fresnel theory were performed in the past [5,8].

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 [9]. This peak can be related to lateral roughness features at the surface or the interfaces of the system under investigation. Its calculation is not possible in the framework of the Fresnel theory. More elaborate approaches such as the distorted wave Born approximation (DWBA) have to be used for modelling the experimental data [10–12]. Therefore, we conducted GIXAS under non-specular conditions, i.e. with the detector centred at the Yoneda peak position of the scattered beam.

In this contribution, we present the results of the first experiments employing GIXAS under non-specular conditions and demonstrate that this new mode of surface-sensitive GIXAS spectroscopy is a very promising tool for novel applications in surface science.

2. Experimental

We have chosen a thin copper film (thickness $\approx$ 90 nm) as a model system. The sample was prepared by DC-sputtering in an Ar atmosphere ($p \approx 1.5 \times 10^{-2}$ mbar) and float glass ($50 \times 20\,\text{mm}^2$) was used as substrate. If such a film is exposed to air, a copper oxide (Cu_2O) film of up to 10 nm thickness is formed at the copper (Cu) surface [13]. After preparation, the sample was exposed for 3 days to air to allow a native Cu_2O surface to form.

The experiments presented here were performed with synchrotron radiation of the X-ray undulator beamline BW1 [14] at the DORIS III storage ring at HASYLAB (Hamburg, Germany). A double-crystal monochromator with two flat Si(1 1 1) crystals was used. The GIXAS data were collected at room temperature in the vicinity of the Cu K-edge (8979 eV) under ambient conditions. Incident and reflected intensities were measured by argon and nitrogen-filled ionization chambers. 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 and non-specular case, respectively.

3. Results and discussion

Specular reflection mode GIXAS spectra of the sputtered Cu film are presented in Fig. 1(a) 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°. The increase of the absorption at the edge is in accordance with a decrease in the reflectivity. For the GIXAS data evaluation we split the X-ray reflectivity R above the absorption edge into a structureless background R_0 and an oscillatory part ΔR with $R = R_0 + \Delta R$. In this case, the reflectivity fine structure χ_R is given by: $\chi_R(E) = \Delta R(E)/R_0(E)$ (see e.g. Ref. [8]). The energy scale of reflectivity fine structure was converted into the electron wave number $k = \surd(2m/\hbar^2(E - E_0))$ and the spectra were Fourier transformed for the further data analysis. The peaks in the magnitude of the Fourier-transformed data correspond to the first few coordination shells in the vicinity of the absorbing atom. Owing to the photoelectron phase shift arising from the scattering processes, all peaks in these Fourier Transforms (FTs) are generally shifted to lower distances compared to the crystallographic distances [6]. In Fig. 1(b), the magnitudes of the FTs of the k-weighted fine structure data are presented. The FTs are normalized to the height of the peak at 2.55 Å. Comparing the FTs 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,