Quick-Scanning QEXAFS in grazing incidence: Surface science in sub-seconds

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Abstract. Quick scanning X-ray absorption spectroscopy was combined with the grazing incidence geometry for the time resolved in situ investigation of surfaces and thin films. The results demonstrate that a time resolution of about 50 ms for a single spectrum is feasible using a dedicated monochromator. In-situ investigations performed during the sputter deposition of thin gold films demonstrate the capabilities of this new approach.

1. Introduction

Many important physico-chemical phenomena such as e.g. catalysis, the oxidation or corrosion of materials by gases and liquids and coating procedures are taking place at the surfaces of materials. All of those processes are strongly time dependent, so that fast surface sensitive in-situ probes are necessary to study those phenomena. The X-ray absorption fine structure (EXAFS) spectroscopy is a well established tool that can also be used for studies of non-crystalline solids or liquids, and it provides accurate short range structure information such as bond distances, coordination numbers and the local atomic disorder [1]. EXAFS can be made surface sensitive by using the grazing incidence geometry: For incidence angles below the critical angle of total reflection the penetration depth of the X-rays amounts to only few nanometers, and thus the reflected X-ray beam only contains information about the near surface region of the studied samples [2-6]. Here we have combined the grazing incidence geometry with the Quick-scanning EXAFS (QEXAFS) method [7]. Recent experimental developments of QEXAFS instrumentation have substantially improved the time resolution reliably to about 50 ms for a single spectrum [8-13]. Here we will show for the first time that thin film growth by sputtering can be studied in situ on a sub-second timescale by combining the Quick-scanning EXAFS technique and the grazing incidence geometry.

2. Experimental details

The reflection mode QEXAFS spectra were recorded using the QEXAFS monochromator installed at the SuperXAS beamline at the Swiss Light Source (Villigen, Switzerland) [10]. The basic setup and the monochromator system are described in detail elsewhere [8]. The storage ring was operated in the top-up mode with an electron beam of 2.4 GeV at about 400 mA. The X-ray beam from the superbend magnet was vertically collimated on the QEXAFS channel-cut monochromator crystal to improve the energy resolution and to increase the available flux, while a bent cylindrical mirror behind the monochromator focused the beam onto the sample, resulting in a spot size of 100 µm x 100 µm and a flux of about 10^{12} photons/s at the position of the sample [10]. The beam incident on the samples was
further defined by a slit system. All QEXAFS data presented here were taken using a Si(111) channel-cut crystal and a 0.30° excenter disc (see [9] for details), resulting in scan ranges of about 750 eV at the Au L\textsubscript{3}-edge (11919 eV). The Bragg angle of the monochromator crystal was measured simultaneously with the acquired spectra using a specially developed fast angular encoder system [9]. N\textsubscript{2}- and Ar-filled ionization chambers were used as detectors for the incident and reflected X-rays. A gold metal foil placed between the second and a third ionization chamber was measured simultaneously to the actual sample as a reference. DC sputter deposition was performed in a miniaturized sputter chamber equipped with a magnetron source (55 mm diameter) and a resistively heated sample holder [14]. The cell has two large area Kapton windows for the incident and reflected X-rays, electrical feedthroughs for the resistive sample heater and the temperature measurements, and a gas inlet that is regulated by a gas-flow controller. The cell is evacuated by a turbomolecular pump (Pfeiffer TMU 071) that enables a base pressure of typically 10\textsuperscript{-5} mbar, while the Ar-gas pressure was adjusted in the range of 2x10\textsuperscript{-2} mbar during the thin film depositions on float glass substrates.

The continuously collected spectra were separated, averaged, calibrated and normalized by in-house software tools [11]. The further reflection mode XAFS data analysis included a background subtraction and the extraction of the reflectivity fine structure \(\Delta R(E)\) by using the Athena software which is part of the IFEFFIT EXAFS data analysis software [15]. In contrast to conventional transmission or fluorescence mode EXAFS, both the real \(\delta(E)\) 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 depending on the grazing angle and the photon energy \(E\). Furthermore, for a thin film on a substrate, the presence of surface and interface roughness may change the distribution of the X-ray absorbing species within the penetration depth of the X-rays. Thus the respective contributions are affected in the detected reflectivity EXAFS signal, so that reflectivity EXAFS data cannot simply be analyzed using standard routines (see e.g. [1, 6]). If the X-ray penetration depth is larger than the film thickness, the absorption can not be directly extracted from the measured reflectivity EXAFS spectra. For the extraction of short range order structural information, the measured data have to modeled on an ab-initio basis [4, 6, 16]. Here we have calculated the reflectivity using the Fresnel theory and the Distorted Wave Born Approximation (DWBA) including surface and interface roughness [6]. The input parameters of these calculations, especially the film thickness and the roughness parameters, were refined until the results matched closely with the experimental data.

3. Results and discussion

In Fig. 1, the reflection mode QEXAFS spectra collected during the sputter deposition of a thin gold film on a glass substrate are presented for an incidence angle of \(\Theta=0.23^\circ\). Due to the fact that the critical angle of total reflection for glass is only about 0.2\°, the measured reflectivities are low at the start of the experiment. However, the reflectivity continuously increases during gold deposition. The measurements were performed with 10 Hz oscillation frequency of the channel-cut monochromator crystal, i.e. one single spectrum was measured within 50 ms. The displayed data were obtained by averaging over 10 subsequent spectra measured going up in Bragg angle, so that each spectrum contains the information measured during 1 s. It should be stressed that the measurements are technically very demanding: Due to the low reflectivity of the glass substrate, which amounts to less than 0.03, the intensity in the second and third ionization chambers are very small at the beginning of the experiment, i.e. prior to the gold deposition. Thus a high amplification in the used current amplifiers would be desirable in order to obtain a high quality signal with low noise. However, in the course of the deposition process, the reflectivity of the gold layer increases by more than a factor of 30 to values of about 0.9 in the pre-edge region of the Au L\textsubscript{3}-edge. Thus, at the end of the film growth, significantly smaller current amplification is required in order not to exceed the range of the current amplifiers. Since the current amplification can not be changed in the course of the experiment, its value has to be selected on the basis of the maximum signals that are measured during the entire experiment.
Figure 1. Reflection mode ($\Theta = 0.23^\circ$) QEXAFS data at the Au L$_3$-edge collected during the sputter deposition of a thin gold film on a float glass substrate at room temperature. The spectra (solid grey lines) were measured with 10 Hz oscillation frequency, 10 subsequent up spectra were averaged and displayed. Fits of the experimental data using the distorted wave Born approximation (DWBA) are shown as dotted black lines. The thickness of the gold layer of each simulation is indicated.

Distinct signatures of the Au L$_3$ absorption edge are already visible after only 2 s of sputtering, and well developed fine structure oscillations are detectable after a few seconds of deposition. Here the XANES features typical for metallic gold are clearly visible after about 5 s, corresponding to a film thickness of about 2.75 nm. With increasing film thickness, all the features in the spectra become more pronounced.

For a more detailed analysis of the experimental data, we have fitted the spectra assuming a polycrystalline thin gold film on the glass substrate. Using the $\delta(E)$ and $\beta(E)$ values extracted from a transmission mode EXAFS spectrum of a gold foil and tabulated data for the glass substrate [17], we have calculated the energy dependent reflectivities of the thin films by applying the DWBA. By a variation of the film thickness $t$, the vacuum side surface roughness $\sigma_1$, and the substrate side interface roughness $\sigma_2$, the experimental data can be modelled, and calculated reflectivity data are included in Fig. 1. In Fig. 2, the influence of the different parameters on the calculated spectra in comparison to the experimental data measured 9 s after the start of the experiment is shown. Single spectra measured in 50 ms are plotted, which hardly can be distinguished from the best fit results. As can be deduced from Fig. 2(a), a small variation of the film thickness ($t_f$) from 4.59 nm to 4.65 nm causes significant changes in the reflectivity spectra. For constant vacuum and substrate side roughness parameters, an increase of $t_f$ results in an overall increase of the reflectivity in the entire energy range, and thus, the best thickness value can be determined to be 4.62 nm in the present case. The Fourier-transformed data shown in the insert of Fig. 2(a) only show minor changes, namely a small increase of all peaks with increasing thickness. In Fig. 2(b) the influence of the vacuum side surface roughness on the calculated spectra is shown for a film thickness $t_f = 4.62$ nm. Obviously, the roughness mainly influences the post-edge region of the spectra, where the films with smaller roughness exhibit a larger reflectivity, and thus the influence of film thickness and roughness can be discriminated.

The increased edge jump also leads to slightly higher peaks in the Fourier-transformed data in the insert of Fig. 2(b) (see also [6]). The substrate side interface roughness only plays a minor role in the present case as the incidence angle $\Theta$ is significantly larger than the critical angle of the substrate, so only a small fraction of the impinging X-rays are scattered back to the surface and contribute to the signal measured in the detector [6]. As can be concluded from these plots, the calculated reflection mode EXAFS spectra are sensitively depending especially on the thickness $t_f$ and the surface roughness $\sigma$ of the deposited gold thin films, and thus, the determination of those parameters from the X-ray data measured in-situ during thin film growth is possible. This is also illustrated in Fig. 1, where the calculated reflectivity spectra are also shown, and the determined film thicknesses are indicated as a function of time. As can be deduced from this figure, the correct description of the X-ray data is possible from the initial stages of material deposition to the film growth on scales of several nm. This
is a unique capability – of course the film thickness and roughness may be obtained by other techniques. However there are only very few techniques that may be applied in-situ during sputtering, but non of those may also yield the atomic structure of the deposited films on a sub-second time scale.

Figure 2. Experimental reflectivity EXAFS ($\Theta=0.23^\circ$) data measured after 9 s of gold sputter deposition (full grey line) and simulated spectra with varying thickness and surface roughness parameters: (a) Variation of the thickness around $t_f=4.62$ nm. Vacuum side surface roughness $\sigma_1=11.2$ Å, substrate side roughness $\sigma_2=7.0$ Å. (b) Variation of $\sigma_1$ around 11.2 Å for $t_f=4.62$ nm and $\sigma_2=7.0$ Å. In the inserts, the Fourier-transformed data are shown (data are not phase-shift corrected; $k$-range for the FT: 2 Å$^{-1} < k < 9.8$ Å$^{-1}$).

4. Conclusions
The results have shown that a detailed investigation of thin film growth processes is feasible using a combination of quick-scanning EXAFS and the grazing incidence geometry. The measured data can be modeled quantitatively as a function of time using the Distorted wave Born approximation, yielding precise values e.g. for the thickness, roughness and the roughness scaling behaviour of the growing films. The determined values will be given in a detailed publication, which furthermore will also include the oxidation of thin films.

5. References
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