Surface science in sub-seconds by a combination of grazing incidence geometry and QEXAFS

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Abstract. The feasibility of time resolved in-situ investigations of surfaces and thin film growth phenomena was explored by combining quick-scanning X-ray absorption spectroscopy with the grazing incidence geometry. Using a dedicated monochromator and an X-ray reflectometer, a time resolution of about 50 ms for a single spectrum is feasible. In-situ investigations performed during the sputter deposition of thin copper films demonstrate the capabilities of this approach.

1. Introduction

X-ray absorption fine structure (EXAFS) spectroscopy is a well established tool that can be used for the investigation of crystalline and non-crystalline condensed matter, and it provides accurate short range structure information such as bond distances, coordination numbers and the local atomic disorder [1]. While conventional transmission or fluorescence mode EXAFS is a bulk sensitive technique, it 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 the reflected X-ray beam only contains information about the near surface region of the studied samples [2-6]. If e.g. thin film growth phenomena are in the focus of interest, a fast data collection in the second or even sub-second range is required to study the structural evolution of the growth processes in detail. Recent experimental developments of the EXAFS technique have substantially improved the time resolution to about 50 ms for a single spectrum using an extremely fast scanning double-crystal monochromator [7-13]. Here we want to exploit the feasibility of time-dependent thin film growth studies using a combination of the grazing incidence geometry with the Quick-scanning EXAFS (QEXAFS) data collection. As examples, the reactive and non-reactive sputter deposition of copper are investigated.

2. Experimental details

All data presented here were recorded employing the QEXAFS monochromator installed at the SuperXAS beamline at the Swiss Light Source (Villingen, Switzerland) operated in the top-up mode with 400 mA of 2.4 GeV electrons [10]. The X-ray beam from the superbending magnet was vertically collimated on the QEXAFS channel-cut monochromator crystal using a bent mirror to improve the energy resolution and to increase the available flux, while a second toroidal 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]. More details of the monochromator system are described elsewhere [8]. The beam incident on the samples was further collimated by a slit system. All QEXAFS data presented here were recorded using an oscillating Si(111) channel-cut crystal and a 0.30° excenter disc, resulting in a scan range of about 500 eV at the Cu K-edge (8979 eV). The Bragg angle of the monochromator crystal was measured simultaneously with the acquired spectra using a recently developed fast angular encoder system [9]. Ar-filled ionization chambers were...
used as detectors for the incident and reflected X-rays, and a third ionization chamber was used to measure a reference Cu metal sample simultaneously with the actual thin film sample.

DC sputter deposition was performed in a miniaturized sputter chamber equipped with a magnetron source (55 mm diameter) and a resistively heated sample holder, which is depicted in Fig. 1. 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 system that is regulated by a gas-flow controller [14]. A turbomolecular pump (Pfeiffer TMU 071) enables a base pressure of typically less than $10^{-5}$ mbar, while the Ar-gas pressure was adjusted in the range of $2 \times 10^{-2}$ mbar during the thin film depositions on float glass substrates.

Figure 1. Photo of the opened cell used for the in-situ investigation of sputtering processes with the resistively heated sample holder, the float glass substrate and the thermocouples for the temperature measurements. The ionization chamber for the determination of the incident flux is visible in the back of the picture, while the beam stop used to absorb the non-reflected direct beam can be seen in the front left.

3. Results and discussion

In Fig. 2 selected reflection mode EXAFS spectra measured for a thin copper film (ca. 370 nm thickness) at the Cu K-edge are displayed for different scan speeds and an incidence angle of 0.25°. As can be seen, the quality of the spectra and the $k^2$-weighted EXAFS fine structure shown in the inset is not substantially affected if the scan speed is varied. Thus, we can demonstrate that a time resolution of about 50 ms for a single spectrum is feasible using the present setup at the SLS, and the study of thin film growth phenomena is possible on this time scale.

Figure 2. Cu K-edge reflection mode EXAFS data measured from a sputtered thin Cu film with a thickness of about 370 nm in a pure Ar gas atmosphere for $\phi=0.25^\circ$ incidence angle. A float glass held at room temperature ($T = 25^\circ C$) was used as substrate. Different scan speeds were selected as indicated. The extracted $k^2$-weighted reflection mode fine structure data $\Delta R(k) \cdot k^2$ are compared in the inset. Single spectra are shown. Data are shifted by 0.1 units for clarity. The $\Delta R(k) \cdot k^2$ of a model calculation for a pure Cu film is also shown for comparison.
As an example of an in-situ measured deposition process, reflection mode QEXAFS spectra (incidence angle $\phi=0.225^\circ$) collected during the sputtering of a thin copper film on a glass substrate are presented in Fig. 3. The measurements were performed with 5 Hz oscillation of the channel-cut monochromator crystal, i.e. 100 ms for each spectrum, and only some selected spectra are shown during the initial stages of deposition. The displayed data were obtained by averaging over 10 subsequent spectra recorded in one direction, i.e. a total of 1 s data collection time. Due to the fact that the critical angle of total reflection for glass is only about 0.2°, the measured reflectivities $R(E)$ are small at the beginning of the experiment. However, $R(E)$ continuously increases when more Cu is deposited on the glass. By comparison with the data in Fig. 2, it can directly be deduced that the increased substrate temperature and the small amount of oxygen which is added to the Ar sputter gas have a substantial influence on the film properties. According to the use of purified Ar as sputter gas, the data in Fig. 2 fit nicely to a calculation of the reflection mode EXAFS for a model system consisting of a 370 nm thick Cu metal film at 25°C with a surface roughness of 1.5 nm on a glass substrate with 0.5 nm roughness [6], suggesting evidence for the presence of a pure Cu metal film. Such a simple fit cannot be done for the data presented in Fig. 3: Due to the presence of oxygen in the sputter plasma, the formation of Cu-oxides - i.e. Cu$_2$O and CuO - is very likely in this situation in parallel to a metallic Cu deposition [15]. This is supported by the increased white line intensities at about 8990 eV photon energy, which are characteristic for the copper oxides, in contrast to the double peaked structure of Cu metal [16].

![Figure 3](image.png)

**Figure 3.** Reflection mode Quick-scanning EXAFS data measured during the sputter deposition of copper on a heated float glass substrate ($T = 120°C$) in an Ar + 0.1% O$_2$ atmosphere for an incidence angle of 0.225° (pink lines). The data were measured with 5 Hz, and 10 subsequent spectra were averaged. The data are presented in a window of the analysis software [11], which enables the calculation of reflection mode EXAFS data on the basis of a layer model including surface and interface roughness [6]. Fits to the experimental data are shown in blue. See text for more details.

It has to be mentioned that the measurement conditions for the presented experiment are quite difficult: Due to the low reflectivity of the uncoated glass substrate which amounts to less than 0.08 prior to the copper deposition, the intensity in the second and third ionization chambers are very small at the beginning of the experiment. Thus a high amplification of the 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 deposited Cu layer increases by more than a factor of 10 to values of about 0.9 in the pre-edge region of the Cu K-edge, so that a significantly smaller current..
amplification is required in order not to exceed the maximum output current of the current amplifiers. Since the current amplification currently cannot be changed in the course of fast experiments in a satisfactory way without an interruption of the data collection and a loss of spectra, its value has to be selected prior to the start of the experiment on the basis of the maximum signals that are measured during the entire experiment.

The data in Fig. 3 are displayed as a screen-shot of the newly developed quick-EXAFS analysis software [11], which also enables a semi-automatic fitting of the measured data. The software needs all the geometric parameters of the reflectometer, i.e. the size of the sample, slit sizes, the distances from the sample to the detector, the aperture of the detector, and the incidence and exit angles. Furthermore, a model structure has to be defined, and the indices of refraction of the materials in the sample and the substrate have to be supplied [5, 6]. Fit parameters are the actual composition of the sample, the layer thickness and the surface and interface roughness, which may change in the course of a film deposition process. In the case of the experiment presented in Fig. 3, the measured data cannot be fitted satisfactorily using Cu metal alone. However, assuming a mixture of Cu-metal, Cu$_2$O and CuO [15], the measured reflection mode EXAFS data can be modelled satisfactorily, suggesting a much more complex film structure under reactive sputtering conditions compared to the deposition in pure Ar. Due to the clean sputter deposition conditions in a high-vacuum apparatus, other species than Cu, Cu$_2$O and CuO are rather unlikely. This approach is supported by the observation that the film thickness derived from the fits linearly increases with time with a slope of ca. 0.3 nm/s - such a behavior may be expected from the stable deposition conditions with a constant discharge current.

4. Conclusions and outlook
The feasibility of fast time-resolved in-situ investigations of thin film growth processes by a combination of quick-scanning EXAFS and the grazing incidence geometry was assessed. Our results show that it is possible to measure reflection mode EXAFS data of thin films with some nanometers thickness with an excellent data quality on a timescale of 50 ms for a single spectrum. 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 roughness scaling behaviour of the growing films. Detailed values will be presented in a subsequent publication.

The application of this new EXAFS technique seems to be promising also for the investigation of oxidation or corrosion processes, where the surface structure and composition may dramatically change as a function of time in the course of a corrosive attack.

Acknowledgements
We acknowledge the Swiss Light Source for beamtime and M. Nachtegaal for his excellent support at the SuperXAS beamline. Furthermore we would like to thank J. Just for his help at the beamline, and the BMBF for financial support under project no. 05K10PX1.

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