Yoneda-XAFS with Area X-Ray Detectors

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Abstract. ReflXAFS is a well-known, surface sensitive method to investigate the structure of e.g. thin films. By a proper choice of incident and exit angles the Yoneda-peak, a distinct intensity maximum in the diffuse scattering, becomes visible. For multilayered samples, several Yoneda-peaks related to surface and interface regions may be observed. It is possible to utilize these peaks to measure the fine structure of an element inside the related surface and interface regions of a multi-layered sample. We will show that the use of 2D-area detectors allow the simultaneous measurement of the entire scattering pattern for each energy in an EXAFS spectrum, providing access to detailed in-situ structure information of the surface and interface regions in multilayered samples.

1. Introduction

Reflection mode X-ray absorption fine structure (ReflXAFS) is a well-known method for the determination of the chemical valence and the atomic short-range order around a chosen element of thin films and surfaces. A variation of the incidence angle allows a depth profiling of the sample. For incidence angles below the critical angle of total reflection this method is notably surface sensitive, whereas higher incidence angles lead to bulk sensitivity. In addition to the specular reflected beam, a second intensity maximum is present in the diffuse scattering pattern, firstly discovered by Yoneda [1]. The related scattering angle of this so called Yoneda-peak correlates with the electron density of the scattering materials and can also be utilized for XAFS experiments [2, 3]: By a proper choice of incidence and exit angles (see figure 1) multiple peaks related to the surface and interface regions of the Au/Bi bilayer sample used in this contribution can be found. This provides the possibility to measure the absorption fine structure of a chosen element in a chosen depth position inside a multi-layered sample [4, 5].

In general, a XAFS signal has to be measured with an accuracy of at least 0.1 % to provide reliable results. Due to the extremely low diffuse reflectivities of typically less than 10^{-4} even in the maximum of the Yoneda-peak a fine structure requires to be measured with an absolute precision of better than $10^{-5} – 10^{-6}$, which is very demanding from an experimental point of view. Successful experiments so far have been performed using ionization chambers as detectors and incidence as well as exit angles were defined by slit systems [2 - 5]. As a consequence, the different scattering peaks need to be measured sequentially, so that the data collection of a single sample may exceed several hours for a near edge structure (XANES) or even days for the extended fine structure, even if high intensity insertion device beamlines are used.

In this contribution, we will show the feasibility of Yoneda-XAFS experiments with improved area X-ray detectors to collect the entire scattering pattern including the specular reflection peak in one step (see figure 1), and therefore reduce measurement durations substantially with a comparable data quality.


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We will demonstrate that Yoneda-XAFS measurements in a wide energy range of about 1000 eV are feasible in less than one hour this way. Furthermore, due to the reduced acquisition times with the new experimental setup, real in-situ experiments of surface layers and buried interfaces become feasible by the combination of Yoneda-XAFS experiments with an in-situ heat treatment of the samples.

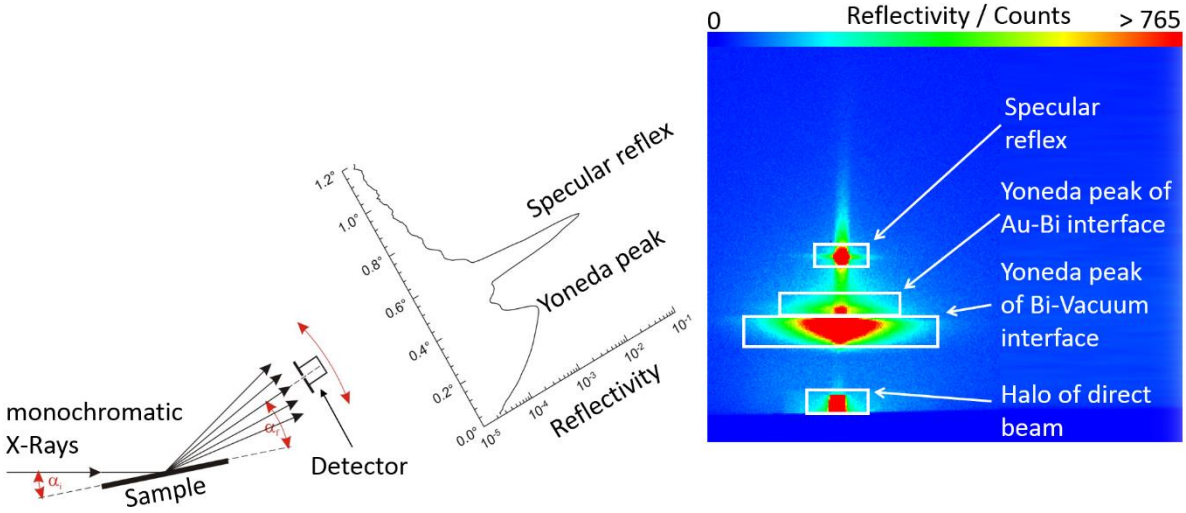


Figure 1. Left: Schematic layout of a Yoneda-XAFS experiment with ionization chambers as detectors. The different contributions in the scattering pattern need to be measured sequentially, extending the measurement durations by several hours. Right: The whole scattering pattern measured with an area X-ray detector for a single energy. The different peaks corresponding to the different interfaces inside a multi-layered sample (here: glass/Au/Bi) can be distinguished with a subsequent data analysis. The upper three white boxes show exemplary the regions of interest for a further data evaluation. Measurement durations were reduced substantially.

2. Experimental details

The Yoneda-XAFS experiments were conducted at the MRH endstation of the bending magnet Rossendorf beamline BM20 at the ESRF [6]. The synchrotron radiation beam was focused by two mirrors and monochromatized by a double-crystal Si(111) monochromator. Incident intensities were measured with a fluorescence screen and a nitrogen filled ionization chamber respectively, whereas reflected intensities were measured with the Pilatus 100 K 2D-area X-ray detector from Dectris [7]. A vacuum chamber with a sample heater was used as sample stage. The measurements and the in-situ sample heating were performed under vacuum conditions of about 10^{-7} mbar. Test sample was a Bi (20 nm)/Au (200 nm)-bilayer on a float glass substrate prepared by physical vapor deposition. The entire scattering pattern was evaluated for each energy while scanning across the Au L_3 (11919 eV) and the Bi L_3 (13419 eV) absorption edges for different temperatures and incidence angles.

3. Yoneda-XAFS experiments

For the bilayer sample we used in this experiment, an incident angle of $\Phi = 0.7\,°$ was chosen. The resulting scattering pattern is shown on the right side of figure 1. From top to bottom four peaks are observable and can be related to the specular reflection, the Au-Bi interface Yoneda-peak, the Bi-air interface Yoneda-peak and the remaining halo of the direct beam, which got mitigated by a lead plate, respectively. The diffuse scattering intensities were evaluated from these two Yoneda-peaks for room temperature, and during a heat treatment at 120 °C. The regions of interest (ROIs) for the data evaluation were carefully set after completing the measurement taking all scattering pattern of a single EXAFS

scan into consideration. This way small shifts of the Yoneda-peak with the energy were properly compensated. The intensities in the different ROIs (see figure 1) were integrated for each pattern and plotted for the corresponding energies. The resulting EXAFS spectra at the Au L_3- and the Bi L_3 absorption edges are shown in figure 2. Comparing the spectra at the Au L_3-edge at room temperature it can clearly be seen, that there is a distinct absorption edge in the case of the Au-Bi interface. This feature is absent in the Bi-air surface, due to the lack of gold atoms at the outer surface in its as-deposited state. The bismuth L_3-absorption edge at room temperature on the other hand is present in the Bi-air surface as well as in the Au-Bi interface spectrum. This is well expected, because the bismuth layer forms the surface as well as the interface.

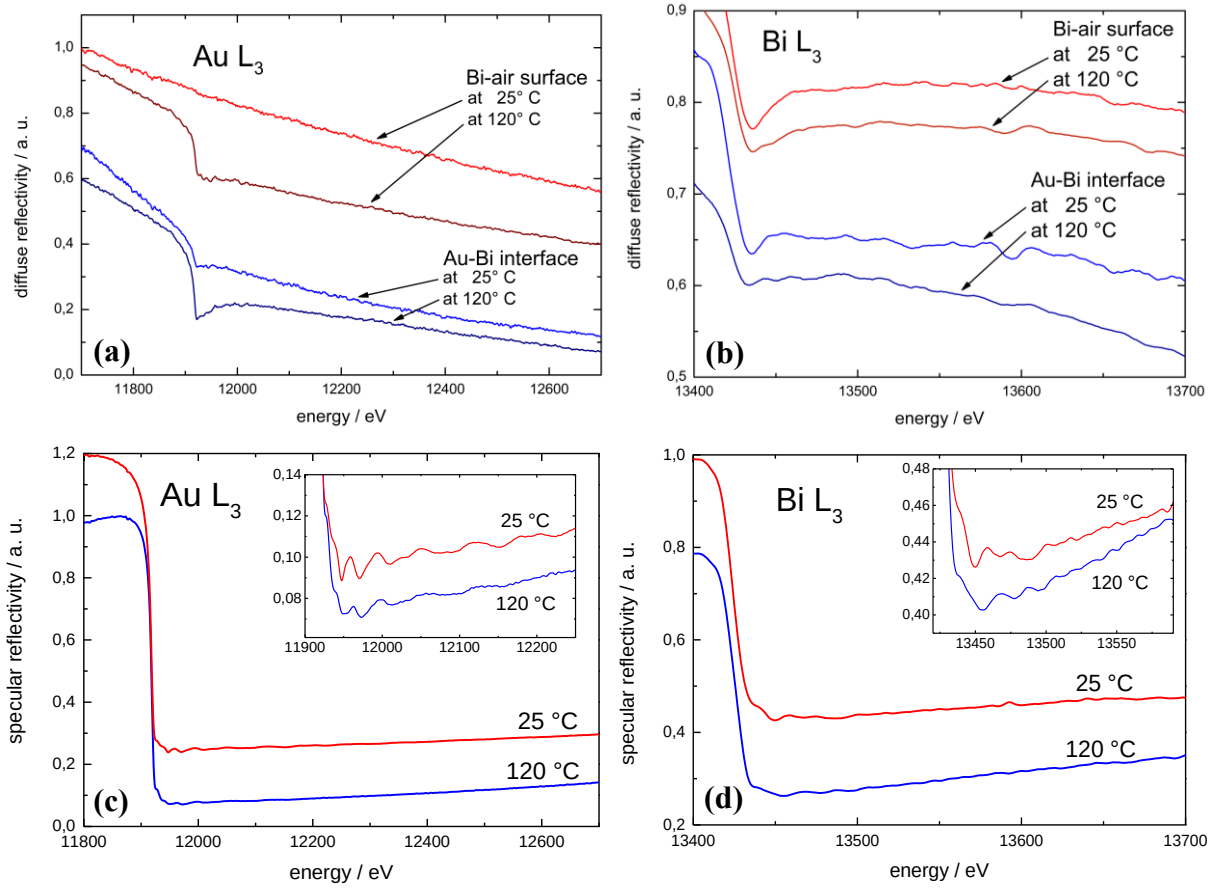


Figure 2. In-situ specular and diffuse reflection mode EXAFS experiments at the Au L_3- and Bi L_3-edges for an incident angle of $\Phi = 0.7$ °. The intensities in (a) and (b) were calculated from the corresponding Yoneda-peaks in the scattering pattern shown in figure 1 at room temperature, and during the heat treatment at 120 °C, respectively. The Au edge related to the outer Bi-air surface forms during the heat treatment due to diffusion of Au through the Bi layer, whereas an alteration in the XANES features at the Bi edge is visible during the heating process. The intensities in (c) and (d) are simultaneously calculated from the corresponding specular reflection peaks in the same scattering pattern as in (a) and (b). An alteration in the fine structure during the heating process is clearly observable and may give additional information about the alloy forming processes.

Heating the sample to 120 °C alters the absorption spectra significantly. As can be seen in the Au-Bi interface spectrum, the Au absorption edge gets more pronounced at 120 °C, which can be interpreted by an increased Au concentration in this sample region. An even more obvious alteration is observable

in the spectrum related to the scattering at the outer vacuum-side surface of the bilayer, which now is also showing a distinct gold absorption edge at 11919 eV and XAFS features as well. This alteration clearly indicates that gold atoms are present at the outer vacuum-side surface of the bilayer sample. It can be assumed that the Au got to the surface due to diffusion processes. A comparison of the fine structure to calculated spectra suggests certain differences to a simple metallic gold layer, i.e. the presence of an intermetallic AuBi-species is very likely [8]. The Bi absorption edges on the other hand do not show such a simple behavior during the heating process at 120 °C. The Bi-air surface does not seem to show any alteration, although a small change in the fine structure of the inner Au-Bi interface is observable. This may indicate that the alloy formation process already started in the Au-Bi interface region, but the concentration of gold atoms in the outer surface is not yet sufficient to observe an alteration in the Bi structure.

A more detailed analysis of the collected data is very demanding and currently in progress. Especially the data processing is getting optimized to enhance the data quality and thus clearly differentiate the fine structure from the noise. A subsequent, careful analysis of the EXAFS may give additional information on the formation of a gold-bismuth alloy in the interface or surface region of the sample. Due to the simultaneous measurement of the entire scattering pattern, a further source of information may also be the measured specular reflection mode EXAFS (see figure 2 (c) and (d)) and thus it should be included in the modelling for a more detailed description of the sample and the alloy formation process.

4. Conclusion

Due to the utilization of an area X-ray detector like the Pilatus 100 K and the resulting, significant time saving, we were able to perform in-situ Yoneda-XAFS measurements for the first time. The resulting data clearly show an alteration in the EXAFS spectra determined from the interface and surface regions of the sample during the heating process. This indicates the diffusion of gold atoms from the inner gold layer to the outer bismuth layer surface and it can be assumed that an alloy formation process is taking place at the Au-Bi interface region.

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