ESRF	**Experiment title:** X-ray investigations of buried layers by means of non-specular grazing incidence XAFS	**Experiment number**: 20-02-718
Beamline: BM20	**Date of experiment**: from: 07.05.2013 to: 10.05.2013	**Date of report**: 11.12.2013
Shifts: 9	**Local contact(s)**: Carsten Baehtz	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dirk Lützenkirchen-Hecht* (dirklh@uni-wuppertal.de), Ralph Wagner*

Fachbereich C – Physik

Bergische Universität Wuppertal

Gauß-Str. 20, 42097 Wuppertal, Germany

Non-specular (diffuse) X-ray scattering is a method to obtain quantitative information of buried interfaces and multilayers: While the specular X-ray reflectivity provides information about the structures perpendicular to the surface of the sample (surface and interface roughness, layer thickness and density), diffuse X-ray scattering gives information on the in-plane and out-of-plane structure of the involved interfaces [1-3]. Combining diffuse X-ray scattering with X-ray absorption spectroscopy may give additional information such as the chemical valence and the local atomic environment of atoms which are located in surface and interface regions [4-6]. Making use of the angular correlation of the Yoneda-peak with the density of the X-ray scattering material (see e.g. [7] and Fig. 1), different interfaces can be selected by a proper choice of the scattering (exit) angles. Therefore, by measuring the X-ray absorption fine structure for well defined incidence and exit angles, it is possible to study the atomic short range order and the chemical state of a chosen element in a chosen depth position inside a multilayered sample [6, 8]. Due to the small diffuse reflectivities of typically less than 10^{-3} or 10^{-4}, the X-ray reflectivity fine structure has to be measured with an accuracy of at least 0.1% on this low intensity level, i.e. with an absolute precision of better than $10^{-5} – 10^{-6}$.

Successful experiments have so far been performed using ionization chambers as detectors, and incidence as well as exit angles were defined by slit systems [4-6, 8]. As a consequence the different diffuse scattering peaks have to measured sequentially, so that the data collection for a single sample may exceed several hours, even if high intensity wiggler beamlines are used. In the work described here, we want to investigate the feasibility of Yoneda-XAFS experiments using improved area X-ray detectors to collect the entire scattering pattern in parallel and employing a subsequent data analysis to separate the different contributions in the pattern. The present experiments were made using the Pilatus 100 K detector [9] at ESRF ROBL beamline BL20. Test sample was a Bi (20 nm)/Au (200 nm)-bilayer on a float glass substrate prepared by vacuum depostition. 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. Selected examples of collected patterns are shown in Fig. 1 for three different energies in the vicinity of the Au L_3 edge. As can clearly be seen, the intensity of the diffuse scattering strongly depends on the X-ray energy and the scattering angle, i.e. the diffuse scattering from the smaller exit angle (outer Bi-air surface) is not dramatically altered when the energy is scanned through the Au L_3-edge, while the pattern related to the larger exit angle (inner Bi-Au interface) dramatically drops down in this energy range (Fig. 1c).

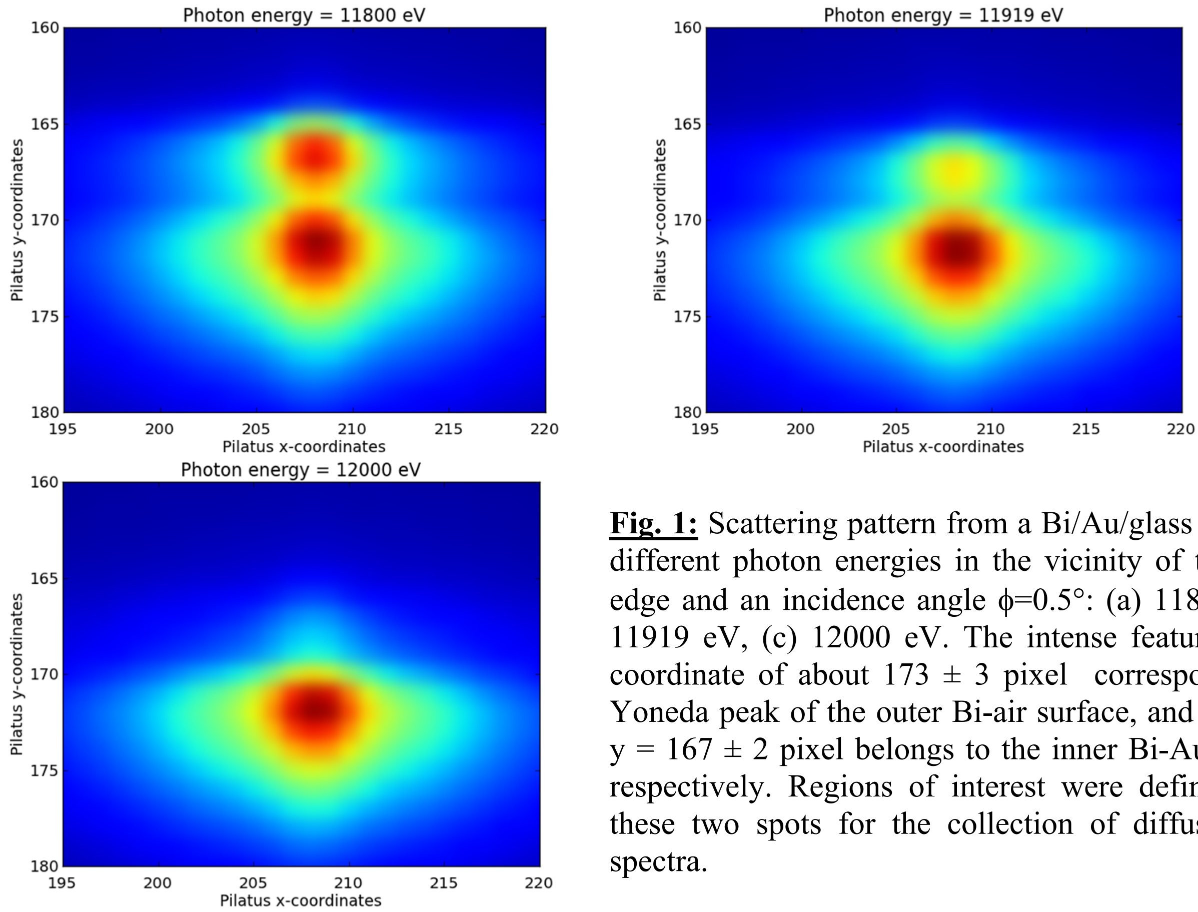

Fig. 1: Scattering pattern from a Bi/Au/glass sample for different photon energies in the vicinity of the Au L_3-edge and an incidence angle ϕ=0.5°: (a) 11800 eV, (b) 11919 eV, (c) 12000 eV. The intense feature at an y-coordinate of about 173 ± 3 pixel corresponds to the Yoneda peak of the outer Bi-air surface, and the spot at y = 167 ± 2 pixel belongs to the inner Bi-Au interface, respectively. Regions of interest were defined around these two spots for the collection of diffuse EXAFS spectra.

This behaviour is also observed in the EXAFS spectra calculated from these diffuse X-ray scattering profiles. As can be seen in Fig. 2, the intensity measured for the Yoneda-peak with the larger exit angle (smaller y-coordinate in Fig. 1) is always smaller compared to that related to the smaller exit angle (larger y-coordinate). While a distinct Au L_3-edge can be seen in the first Yoneda peak, no edge can be seen in the scattering related to the second feature. Furthermore, the Bi L_3-edge spectrum related to the first peak shows a fine structure similar to that of metallic Bi, while that of the second peak resembles that of Bi_2O_3 oxide. The qualitative interpretation of these observations is clear: The diffuse scattering related to the larger exit angle is related to the inner Au-Bi interface, where both elements are present in a metallic form.

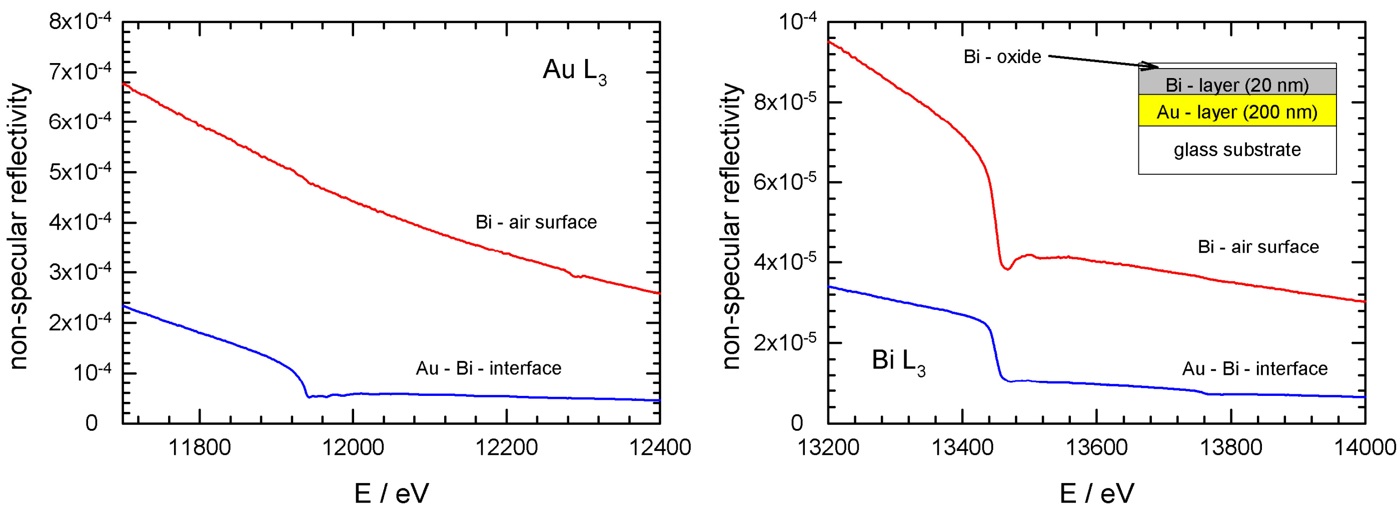

Fig. 2: Non-specular reflection mode EXAFS experiments at the Au L_3- and Bi L_3-edges for an incidence angle ϕ = 0.5° and exit angles according to the Yoneda peaks shown in Fig. 1. The inset depicts a model of the layer structure of the sample.

On the other hand, no gold is present at the outer surface of the bilayer, and thus no Au L_3-edge is observed for the smaller exit angle. Due to the chemical reactivity of Bi metal, the latter metal is oxidized at its air-side surface, forming a thin oxide layer of about 1-2 nm thickness [10], and accordingly, the X-ray absorption fine structure in the diffuse scattering reveals features similar to that of Bi_2O_3 (see e.g. [11]) due to strong contributions of the outermost surface to the scattered signals.

A detailed modelling of the measured data is currently in progress in order to determine the thickness of the Bi oxide layer at the surface. Furthermore, the possible formation of a gold-bismuth alloy at the inner interface should result in modifications of the EXAFS detected at the Yoneda peak at larger exit angles, and thus a very careful analysis is required to identify such interfacial phases. A more detailed publication is currently in preparation [12].

References:

[1] S.K. Sinha. J. Phys. III (France) 4 (1994) 1543.
[2] V. Holy, J. Kubena, I. Ohlidal, et.al. Phys. Rev. B 47 (1993) 15896.
[3] V. Holy, U. Pietsch, T. Baumbach. Springer Tracts in Mod. Phys. 149 (1999).
[4] P. Keil, D. Lützenkirchen-Hecht, R. Frahm. Europhys. Lett. 71 (2005) 77.
[5] P. Keil, D. Lützenkirchen-Hecht, R. Frahm. Physica B 357 (2005) 1.
[6] D. Lützenkirchen-Hecht, P. Keil, R. Frahm. Surface Sci. 601 (2007) 4232.
[7] J.-L. Cao, A. Solbach, U. Klemradt, et al. J. Amer. Ceram. Soc. 89 (2006) 1321.
[8] P. Keil, R. Frahm, D. Lützenkirchen-Hecht. Corrosion Sci. 52 (2010) 1305.
[9] P. Kraft, A. Bergamaschi, Ch. Broennimann, et.al. J. Synchrotron Rad. 16 (2009) 368.
[10] R. Atkinson, E. Curran. Thin Solid Films 128 (1985) 333.
[11] N. Jiang, J.C.H. Spence. J. Phys.: Condens. Matter 18 (2006) 8029.
[12] D. Lützenkirchen-Hecht, R. Wagner, C. Baehtz. J. Synchrotron Rad., in preparation.