ESRF	**Experiment title:** Investigation of the morphology of surface nanostructures by high-resolution grazing emission x-ray fluorescence.	**Experiment number**: MI-975
Beamline: ID21	**Date of experiment**: from: April 1st, 2009 to: April 7th, 2009	**Date of report**: Febr. 26th,2010
Shifts: 18	**Local contact(s)**: Dr. M. Salomé	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

J. HOSZOWSKA*, Département de Physique, Université de Fribourg, CH-1700 Fribourg, Suisse
J.-Cl. DOUSSE*, Département de Physique, Université de Fribourg, CH-1700 Fribourg, Suisse
W. CAO*, Département de Physique, Université de Fribourg, CH-1700 Fribourg, Suisse
Y. KAYSER*, Département de Physique, Université de Fribourg, CH-1700 Fribourg, Suisse
S. NOWAK*, Département de Physique, Université de Fribourg, CH-1700 Fribourg, Suisse
M. PAJEK*, Institute of Physics, Jan Kochanowski University, 25-406 Kielce, Poland
D. BANAŚ*, Institute of Physics, Jan Kochanowski University, 25-406 Kielce, Poland
J. SZLACHETKO*, E.S.R.F., F-38043 Grenoble Cedex, France
L. T. BACZEWSKI, Institute of Physics, Polish Academy of Sciences, 02-668 Warszawa, Poland

Introduction:

The effect of clustering of atoms in ultra-thin films deposited on the surface of materials is of great potential interest for future fabrication of semiconductor devices having desired optical, electronic and magnetic properties [1]. For deposited-film thicknesses of the order of an atomic monolayer the clustering may lead to the formation of islands, with quite narrow size distributions [2], which is an important aspect for nanotechnology. Such regular nanometer-scale structures are known to be formed in the Volmer-Weber or Stransky-Krastanow growth mode [1,3]. The increase of the number of atomic monolayers leads to the coalescence of islands and finally to the formation of a homogenous film [1]. The investigation of the morphology of such surface nanostructures – separated and joint islands – is of great importance for epitaxial nanotechnology, in particular, when it can be combined with the measurements of the lateral- and depth-distribution of atoms deposited on the surface.

In our experiment we have used the synchrotron radiation based grazing emission x-ray fluorescence (GEXRF) technique [4,5], using high-resolution for the detection of the fluorescence x-rays, to study the morphology of ultra-thin (few nanometers) layers. This novel high-resolution GEXRF technique [6-8], which was demonstrated to be a highly-sensitive method for investigating low-level surface impurities on silicon wafers [6,7], including the lateral 2D-mapping of the impurities [7] and their depth profiling [8], has also been reported to be useful in surface morphology studies [6].

The main objective of our project was to apply this novel method to the study of surface nanostructures by performing systematic high-resolution GEXRF measurements of samples with various surface morphologies, namely from well separated islands to a fully covering layer.

Samples:

Samples consisting of thin films of Al, MgO, Fe and Cr deposited on silicon substrates and a sample with Au islands on a Mo substrate were examined. The MgO, Fe, Cr and Au samples were prepared at the Institute of Physics, Polish Academy of Sciences, Warsaw, Poland, the Al ones at the Institute of Molecular Physics,

Polish Academy of Sciences, Poznań, Poland. The nominal thickness of most metal layers deposited on the silicon substrates was 5 nm. The morphology differences were achieved by a post-growth annealing of the samples and/or by changing the growth temperature of the layers. The morphology differences of the samples can be clearly observed in atomic force microscopy (AFM) pictures (see Fig. 1 and Fig. 2). The Au sample was prepared by depositing on a Mo substrate a wedge-like layer. This led to the creation on the Mo substrate of Au islands. Depending on the position on the sample surface, the density of the islands and the heights of the latter are different, whereas their transversal size is almost constant.

Experiment:

The experiment was performed at the ESRF beam line ID21, using the high-resolution von Hamos Bragg-type bent crystal spectrometer of Fribourg [9] for the detection of the sample x-ray fluorescence. The Kα x-ray fluorescence lines of Mg, Al, Cr and Fe as well as the Mα line of Au were measured as a function of the grazing emission angle around the critical angles θ_c. For such grazing emission angles the fluorescence from the substrate is limited to a very shallow (few tens of nm) near surface layer and is therefore strongly reduced [4,10]. This results in a high-sensitivity detection of the x-ray emission from the deposited layer. In order to fulfill the grazing emission condition $\theta < \theta_c$, the samples were tilted close to the direction of observation defined by the Bragg angle. For such a geometry the photon beam spot on the target is viewed by the crystal as a very narrow line, allowing thus a slitless operation of the spectrometer, which results in an increased detection sensitivity. The intensities of the x-ray fluorescence lines observed at exit angles around θ_c are strongly dependent on the morphology of the sample surface.

Preliminary results:

The intensity of the angular profile above the critical angle depends on the total amount of atoms deposited on the irradiated substrate surface but not on the layer morphology. The intensity differences observed above θ_c for Fe (up to 20%, see Fig. 1) and for Cr (about 10%, see Fig. 2) reflect thus deviations of the layer thicknesses from the nominal one (5 nm).

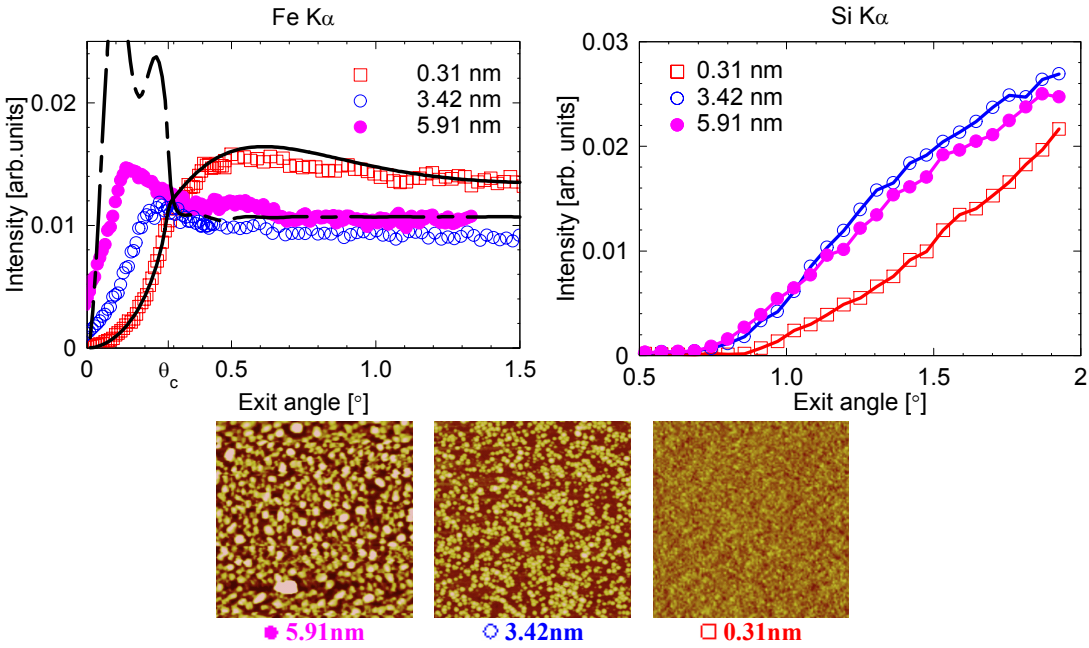

Figure 1: ***GEXRF angular profiles of three Fe samples having a nominal thickness of 5 nm and the rms of the roughnesses of 0.3, 3.4 and 5.9 nm, respectively (top left pannel). The angular profiles of the corresponding Si substrates are also shown (top right pannel), as well as the AFM pictures (1.5 µm scan size) of the three sample surfaces (bottom pannel). The theoretical GEXRF profiles calculated for an ideal 5 nm-thick plane layer (black solid line) and a single 300 nm x 30 nm island (black dashed line) are also depicted for comparison.***

Information about the morphology of the layer surface is provided by the shape of the angular profile below the critical angle. In particular information concerning the roughness of the sample surface can be gained

from the angular position of the first abrupt intensity increase. Indeed, as shown for Fe in Fig.1 and, to a smaller extent, for Cr in Fig. 2, the angular positions of the fast increase regions vary inversely with the rms roughness of the surface, in good agreement with the results of AFM measurements of the corresponding samples. For particle-like surfaces, the rms value of the roughness is only related to the height of the grains but not to the transversal dimensions of the latter. However, the grain size influences also the shape of the angular profile. Actually, profiles of samples whose surface consist of large size grains approach those corresponding to flat continuous layers. This explains why the differences between the angular profiles of the two Cr samples are less pronounced than those observed in the case of Fe, although the rms roughnesses of the two Cr samples were found to differ drastically (see Fig. 2).

As shown in Fig. 1, the morphology of the deposited layer is also reflected in the GEXRF angular profile of the substrate. As for the layer the threshold angle of the substrate fluorescence intensity varies inversely with the roughness of the layer. On the contrary, for angles above ~1°, the GEXRF intensities of the layer and corresponding substrate are found to be opposite. For a given sample, a higher fluorescence intensity for the layer corresponds indeed to a smaller intensity for the substrate. This is, however, not surprising since a higher layer fluorescence is related to a bigger number of layer atoms or a bigger layer thickness, which leads to a bigger absorption of the fluorescence x-rays from the substrate.

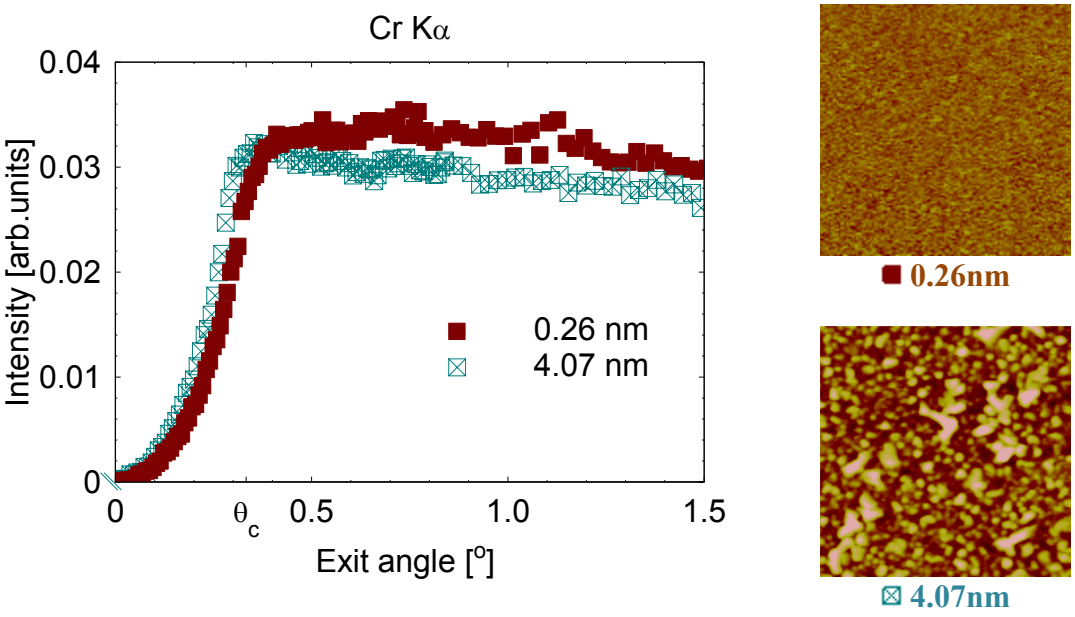

Figure 2: ***GEXRF angular profiles of two Cr samples (nominal thickness of 5 nm and rms roughnesses of 0.3 and 4.1 nm, respectively) and corresponding AFM pictures (1.5 µm scan size).***

The experimental angular profiles can be compared to theoretical predictions. For Fe calculations were performed for a uniform 5 nm thick layer and for a single island with a height of 30 nm and a length of 300 nm in the direction of observation. The results are depicted by black solid and black dashed lines, respectively, in Fig. 1. The theoretical curves were normalized so that they overlap with the experimental profiles at large angles. As shown, a fair agreement is found for the layer-like surface, whereas for the island strong deviations are observed below the critical angle. This is due to the consideration of a single island in the calculations, whereas the real sample consists of many close lying nanostructures. For this reason, we have started to develop a new numerical model permitting to consider many islands in the calculations. In this case not only the average size and height of the islands is of importance but also their average separation distance.

The data analysis of other samples (Al/Si, MnO/Si and Au/Mo) is still in progress.

References:

[1] N. Keiser, *Review of the fundamentals of thin-film growth*. Appl. Opt. **41**, 3053 (2002).

[2] Z. Gai et al., *Self-Assembly of Nanometer-Scale Magnetic Dots with Narrow Size Distributions on an Insulating Substrate*. Phys. Rev. Lett. **89**, 235502 (2002).

[3] I. Daruka and A. Barabási, *Dislocation-Free Island Formation in Heteroepitaxial Growth: A Study at Equilibrium*. Phys. Rev. Lett. **79**, 3708 (1997).

[4] H.P. Urbach, P.K. de Bokx, *Calculations of intensities in grazing-emission x-ray fluorescence*. Phys. Rev. B **53**, 3752 (1996).

[5] P. K. de Bokx et al., *Grazing-emission X-ray fluorescence spectrometry; principles and applications*, Spectrochim. Acta B **52**, 829 (1997).

[6] A. Kubala-Kukuś et al., *Observation of ultralow-level Al impurities on a silicon surface by high-resolution grazing emission x-ray fluorescence excited by synchrotron radiation*. Phys. Rev. B **80**, 113305 (2009).

[7] J. Szlachetko et al., *Application of the high-resolution grazing-emission x-ray fluorescence method for impurities control in semiconductor nanotechnology*. J. Appl. Phys. 105, 086101 (2009).

[8] Y. Kayser et al., *Depth profiles of Al impurities implanted in Si wafers determined by means of the high resolution grazing emission x-ray fluorescence technique*. Spectrochim. Acta B (in press).

[9] J. Hoszowska et al., *High resolution von Hamos crystal X-ray spectrometer*. Nucl. Instrum. Meth. Phys. Res. A **376**, 129 (1996).

[10] R.S. Becker, J.A. Golovchenko, J.R. Patel, X-*ray Evanescent-Wave Absorption and Emission*. Phys. Rev. Lett. **50**, 153 (1983).