ESRF	**Experiment title:** Depth Profiling of Al-implanted silicon by using the high-resolution grazing emission x-ray fluorescence (GEXRF) technique	**Experiment number**: MI 928
Beamline:	**Date of experiment**: from: 05.03.2008 to: 13.03.2008	**Date of report**: 23.02.2009 *Received at ESRF:*
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Report:

The combination of grazing emission x-ray fluorescence (GEXRF) [1,2] with synchrotron radiation and high-resolution detection of the fluorescence photons [3] has already proven to be successful to determine the concentration of low-level impurities on Si wafers (see report HE 2434). In addition the potential to perform 2D surface mappings of Si surfaces by using focussed x-ray beams was also shown (see report HE 2614). If one wants to go a step further and give a 3D map of impurities in Si, the problem of depth-profiling needs to be addressed. Depth profiles of impurities or dopants in Si wafers are indeed of prime importance in a variety of technological applications [4,5]. The depth profiling capability of the high-resolution GEXRF technique was probed in the present experiment. The measurements were performed at the ID21 beamline with Al-implanted Si wafers.

As shown in [7] the TXRF [6] and GEXRF geometries are equivalent but in GEXRF the experimental setup of TXRF [6] is reversed. In other words, in GEXRF the angle between the incoming beam and the target surface is standard (a few tens of degrees) but the sample fluorescence is measured at very small angles (~ 1 deg.) relatively to the sample surface. The angle of the grazing emission is chosen close to the critical angle. The latter depends on the energy of the measured impurity x-ray line. In the case of ion-implanted samples, the critical angle depends also on the substrate in which the ions are implanted because the dopant concentration is usually so low that the refractive index of the substrate remains unchanged. By tuning the exit angle below the critical angle, only the x-ray radiation due to evanescent waves propagating along the Si-vacuum interface can be observed. This makes the measurements sensitive only to a shallow surface layer about several tens of nanometres in thickness. Thus, the grazing emission geometry results in a relative enhancement of the characteristic fluorescence emission from the surface with respect to the fluorescence signal from the bulk of the substrate.

In the present experiment the sample fluorescence was measured by means of high-resolution using the von Hamos Bragg-type bent crystal spectrometer of Fribourg [8] equipped with an ADP (101) crystal. In this geometry the exit angle is determined with respect to the Bragg angle corresponding to the measured x-ray line and not by a double-slit system like in the standard GEXRF setup. The angular resolution is then mainly determined by the Darwin width of the crystal which is of the order of microradians and the apparent width of the beam spot on the target. Actually, as for small exit angles the crystal sees the entire irradiated target surface as a very narrow line, the angular resolution is preserved and an increased detection sensitivity is obtained. If in addition an adequate incident photon energy is selected (see Fig. 1), the high-resolution GEXRF technique allows the quantification of ultra low-level Al-impurities.

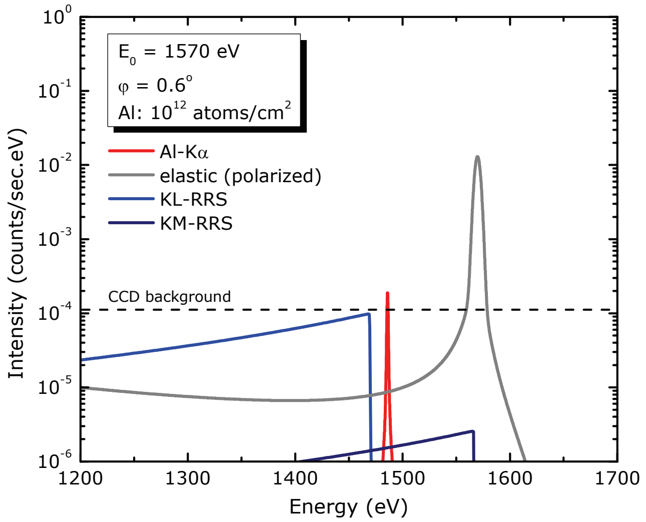

Figure 1: *By choosing an appropriate energy for the primary photon beam, the background in the region of the Al-Kα line can be substantially diminished. If the primary photon beam energy is just 20 eV above the Al K-edge the remaining background contributions result from the CCD noise, the elastic scattering of the primary photon beam and the Si KM-RRS.*

The exit angles for the Al signal were calibrated with the critical angle of the Si-Kα line which corresponds to 0.906 deg. in bulk Si. For each sample the intensity of the Al-Kα intensity was measured for 100 different exit angles. The measured angular profiles were found to change considerably with the concentration profile, i.e., with the implantation energy of the Al ions in the Si wafer (see Table 1).

Implantation Energy [keV]	TRIM		Fit		R^2
	Centre [nm]	Width [nm]	Centre [nm]	Width [nm]	
1	3.65	1.92	4.09	1.92	0.836
5	10.9	5.74	9.36	5.68	0.993
10	18.7	9.57	18.5	9.53	0.996
15	26.1	12.6	23.3	12.4	0.996
20	34.2	16.7	32.7	16.5	0.993
25	42.3	19.5	43.3	19.6	0.995
30	50.3	23.4	56.5	24.1	0.983
50	83.7	35.6	82.1	35.3	0.980
100	172.8	61.9	169.1	61.1	0.985

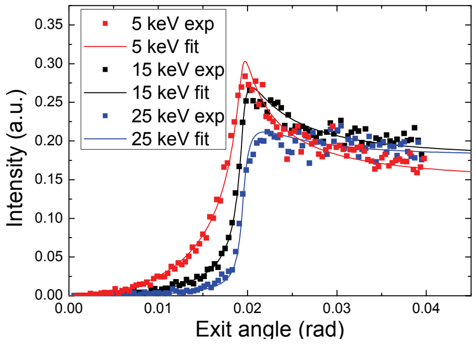

Table 1: *For each implantation energy the parameters of the Gaussian distribution (assumed for the depth profile of the Al impurities) were calculated (TRIM) and determined by fitting the experimental data (Fit). The correlation coefficient R^2 indicates how good the angular profile calculated with the fitted values agrees with the experimental data (see the figure juxtaposed to Table 1). As shown in the table, except for the implantation energy of 1 keV, the values are in reasonably good agreement.*

The depth profiles of the Al ions were extracted from the experimental data by fitting the measured angular distributions with theoretical curves that were calculated assuming Gaussian distributions for the profiles of the implanted Al ions. The choice of a Gaussian distribution was guided by theoretical calculations performed with the TRIM (**TR**ansport of **I**ons in **M**atter) software [9]. In the fitting procedure the centres and the widths of the Gaussian distributions were entered as free parameters. However, reasonable results were obtained only when adequate initial values were chosen for the fitting parameters. In addition the fits were found to be noise sensitive [10]. For this reason smoothing procedures had to be applied to the experimental data whenever the latter were too noisy. The centres and the widths of the Al distributions deduced from the fits were found to agree quite well with the values determined theoretically (see Table 1).

The ultimate goal of our project was to deduce the Al depth profiles from the experimental data without assuming any a priori knowledge about the distributions of the implanted Al ions. However, the inversion of the theoretical formula used to calculate the angular distributions is difficult and needs low noise levels as well as regularization methods [10]. We have therefore tried to deduce the profiles by numerical methods but until now the latter have been successful only for profiles corresponding to high implantation energies. In addition, the obtained concentration profiles were found to agree only qualitatively with the TRIM predictions, significant deviations being in particular observed for the concentrations close to the surface (see Fig. 2). This is, however, not really surprising since it is well known that surface concentrations determined from different depth profiling methods may scatter substantially [11].

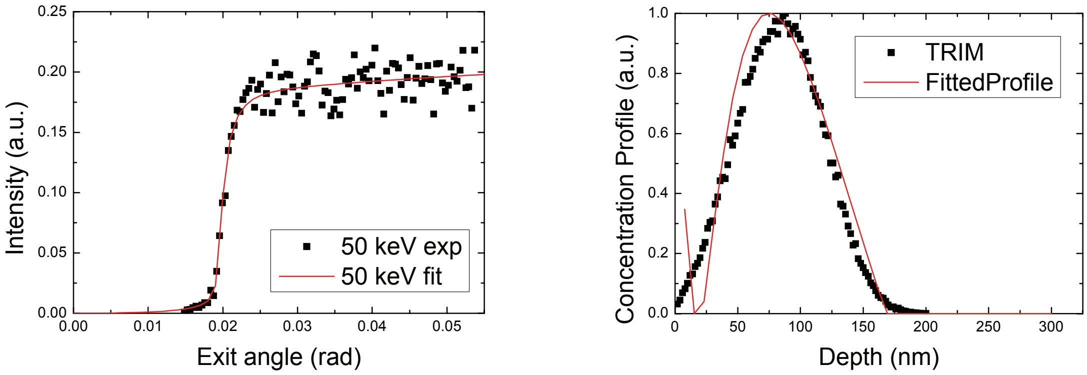

Figure 2: *Example of an Al concentration profile determined directly from the fit of the measured angular distribution (Fig. on the left) without any preliminary assumption for the shape of the depth profile. As shown on the right, the obtained concentration profile (red solid line) corresponds only quantitatively to the theoretical profile calculated with the TRIM program (full squares).*

To summarize, the experiment can be considered as successful since the capability of the high-resolution GEXRF technique to determine the depth-profiles of the implanted Al impurities could be clearly demonstrated. The data analysis, however, should be further improved in order to be able to quantify the samples without any a priori knowledge of the implantation energy. Finally, we would like to point out that the new technique probed in the present experiment with Al-implanted Si samples can be easily extended to other dopant or substrate materials.

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