ESRF	**Experiment title:** Application of the high-resolution grazing emission x-ray fluorescence (GEXRF) technique for low-level impurities detection in silicon.	**Experiment number**: HE-2614
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Report:

The production of ultra clean silicon wafers is one of the most important issues for Si-based microelectronic technology. Presently, the level of metallic impurities on silicon wafers can be directly controlled down to 10^{10} atoms/cm^2 by using the x-ray tube based total reflection x-ray fluorescence (TXRF) technique [1-3]. Lower detection limits can be provided by conjunction of the TXRF method with the vapor phase decomposition (VPD) technique that collects the impurities from the whole Si-wafer surface [4]. The TXRF-VPD method gives a sensitivity gain of two to three orders of magnitude. According to the International Technology Roadmap for Semiconductors [5] a sensitivity below the level of 10^9 atoms/cm^2 for transition metals on Si surface is needed. The application of the TXRF method combined with intense synchrotron x-ray sources offers best possibilities for measuring very low concentration of impurities on Si surfaces. Using the synchrotron x-ray beams, a sensitivity level of 10^8 atoms/cm^2 for direct detection of Cu was achieved [6]. However, the synchrotron radiation based TXRF technique, which employs the grazing incident geometry, cannot benefit from the available micro-focused x-ray beams in order to perform high-spatial resolution 2D surfaces mapping. Also in standard TXRF arrangements, low-resolution semiconductor detectors are usually used, which limits in some cases the elemental analysis of impurities. Therefore, further development of new direct techniques to measure metallic impurities on Si wafers is still a challenging problem. In this context, the application of the synchrotron based grazing-emission x-ray

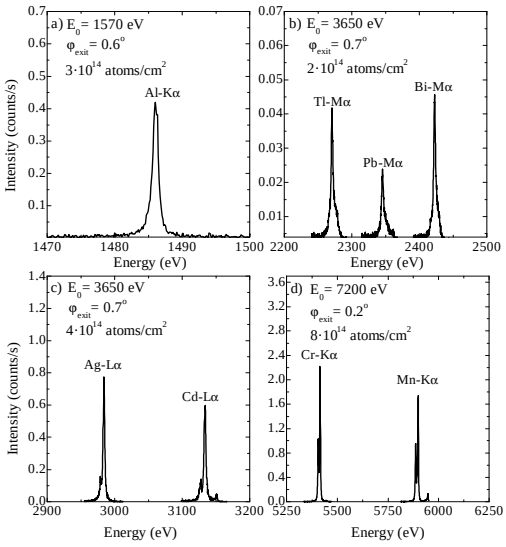

Fig.1 Examples of measured x-ray fluorescence spectra for K, L, and M series by means of high-resolution GEXRF method.

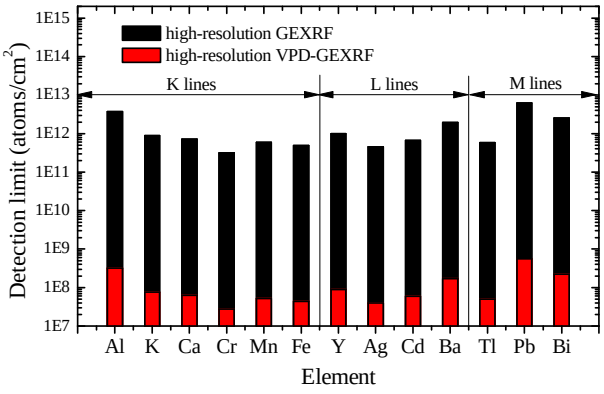

Fig.2 Determined detection limits for high-resolution GEXRF method (black bars). Estimated lowest detection limits for high-resolution VPD-GEXRF technique are shown by red bars.

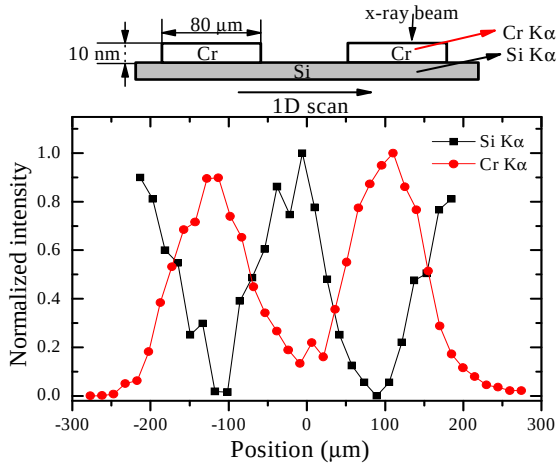

Fig.3 Result of 1D scan across layered Cr on Si sample, for Cr Kα (red) and Si Kα (black) fluorescence lines performed at grazing-exit conditions.

fluorescence (GEXRF) technique for measuring x-ray emission lines of Si-wafer impurities is an alternative.

In the GEXRF technique, which is a kind of inverse of TXRF, the excited x-ray fluorescence is observed at a small grazing emission angle ($\varphi<\varphi_c$) being close to the critical angle [7-9]. Such geometry results in a relative enhancement of the characteristic fluorescence emission from the surface with respect to the substantially suppressed fluorescence signal of bulk substrate. In order to maintain a good enough angular resolution for fluorescence x-ray detection, a double slit system between the target and detector was usually employed [10-12]. Due to that the detection efficiency of the GEXRF method was strongly diminished in comparison to the TXRF technique. In consequence, the GEXRF method was not commonly used for low-level elemental quantification.

In experiment, we have combined the grazing emission geometry with the wavelength-dispersive spectrometer for detection of low-level impurities on Si surface. By exploiting the fact that the grazing emission angle φ_{exit} is determined by the direction of observation of x-rays defined by the Bragg angle θ_{Bragg}, the spectrometer can be operated in a slit-less mode. In such setup, the angular resolution of x-rays observed at a given exit angle is defined only by the crystal rocking curve of the crystal and is in the order of micro radians. Thanks to the slit-less operation the detection efficiency could be strongly improved. In fact for small exit angles, the crystal sees the entire irradiated target surface as a very narrow line. Moreover, for grazing emission angles tuned below critical angle of Si (i.e 0.906 deg), the x-ray radiation, which is due to the evanescent waves propagating along the Si/vacuum interface, from depths of few nanometers can be only observed.

As an example, the high-resolution GEXRF x-ray spectra for M, L and K series are shown in Fig.1, whereas the results obtained for the detection limits are shown in Fig.2. As it can be seen, the direct detection limits of the high-resolution GEXRF method are in the order of 10^{12} atoms/cm^2. We would like to emphasize that assuming the wafer to be 300 mm in diameter, a lowest detection limit in the order of 10^7 atoms/cm^2 for the high-resolution VPD-GEXRF method could thus be achieved (red bars in Fig.2).

The GEXRF method combined with micro-sized beams provide an unique possibility for performing surface sensitive 2D mapping x-ray measurements. In order to probe the mapping capability of the novel technique a 1D scan across a layered Cr/Si sample was performed. The variation of the fluorescence intensity as a function of the scan position is shown in Fig.3 for both the Cr Kα and Si Kα x-ray lines. For this measurement, the beam size was 25 µm, and the layered structure was scanned by moving the sample step by step along the beam direction with a step length of 20 µm. The fluorescence signal was recorded at exit angles of 0.7 degree for Cr and 1.2 degree for Si. As it can be seen from the graph, the evolution of the fluorescence intensity agrees rather well with the 80 µm width of the Cr layer. For the intensity of the Si Kα x-ray line, the result is similar but the intensity evolution is reversed. The effect of the absorption of the Si Kα x-rays in the 10 nm thick Cr layer is strong due to the small angle of

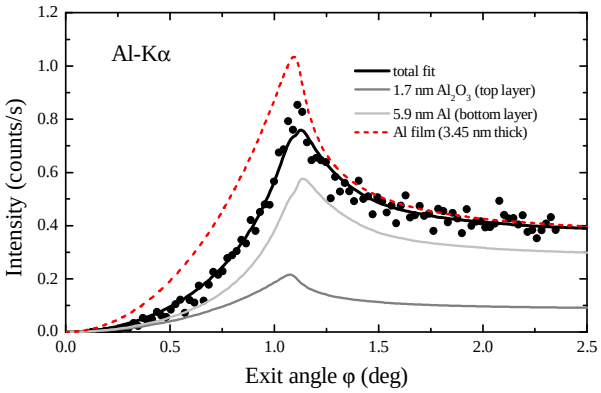

Fig.4 The measured intensity evolution around critical angle for thin Al layer is shown by black dots. The results of theoretical calculations assuming a uniform layer-like and island-like Al distribution on Si substrate are shown by red dashed and black solid lines, respectively

observation. At 1.2 degree, the path length of the Si Kα x-rays through a 10 nm thick Cr layer is indeed about 0.5 µm.

The GEXRF method gives also a unique possibility to study the thickness and composition of thin layered samples. The latter can be performed by the acquisition of the x-ray fluorescence signal for different exit angles being close to the critical angle. In order to demonstrate the capabilities of this technique the angular scan for ~10^{15} atoms/cm^2 of Al evaporated on Si substrate was performed. The result of measured intensity evolution of Al Ka line is shown in Fig.4 by black dots.

In order to determine the exact thickness of Al layer from measured intensities a separate GEXRF measurement close to the critical angle were performed employing the thick Al target. The measured intensities for both, thin and thick Al samples, were compared with the theoretical calculations described by Urbach and Bokx [8]. From this analysis, we have determined the Al layer thickness to be 3.45 nm. However, assuming a uniform film-like layer of Al on Si substrate, the theoretical curve (red dashed line in Fig.4) could not reproduce well the experimental data for exit angles below the critical angle. In fact, during the thin-film growth process, known as a Volmer-Weber process, the Al atoms form rather island-like structures instead of film-like layers [16, 17]. Indeed, assuming the island-like morphology the calculated theoretical curve (shown by black solid line in Fig.4) can reproduce satisfactory the experimental angular dependence. From the fit, we have found that the Al atoms forms the islands of 7.6 nm height. Moreover, in order to reproduce satisfactory the data an Al oxide layer was added in the computation. The latter, which is due to the natural oxidation process, has been found to be 1.7 nm thick.

To summarize, we have shown that by applying the high-resolution GEXRF technique very low levels of trace element concentrations on the surface of silicon wafers can be measured. We have also demonstrated that the GEXRF method is well suited for elemental 2D mapping, where the spatial resolution is given by the size of the x-ray beam. Finally, we have shown that the profile of the depth distribution of thin layer samples can be extracted from the measured intensity evolution around the grazing emission angle.

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