ESRF	**Experiment title:** Probing the possibility of improving the detection threshold of ultra-trace level Al impurities on Si wafer surfaces by grazing emission x-ray fluorescence	**Experiment number**: **HE-2434**
Beamline: ID21	**Date of experiment**: from: 14 March 2007 to: 21 March 2007	**Date of report**: 28.02.2008 *Received at ESRF:*
Shifts: 21	**Local contact(s)**: Dr Murielle SALOME	

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Report:

Introduction

In the reported experiment performed at the ID21 beamline a problem of detection of ultra low-level Al impurities in silicon was addressed by applying the high-resolution grazing-emission x-ray fluorescence (GEXRF) technique. Nowdays, a development of new methods of detection of Al impurities on the surface of Si wafer is one of the most important issue for further advancement of Si-based microelectronic technology. A sensitivity better than 10^9 atoms/cm^2 for detection of Al impurities on Si surface is presently needed, which will go further down in the near future. This can be achieved by combining the total reflection x-ray fluorescence (TXRF) method [1] with the preconcentration vapor phase deposition (VPD) technique to collect the metal impurities from the hole surface of the Si-wafer. In the reported experiment a new access to measure directly Al impurities onto Si wafers was tested by using the synchrotron radiation based high-resolution GEXRF technique [2, 3]. This novel approach offers unique new possibilities to study low-level Al-impurities on Si, namely, the low detection limits, a high-resolution x-ray detection, 2D-mapping capabilities due to narrow x-ray beam, and finally, a possibilities for depth profiling. In the performed experiment we have demonstrated that the proposed high-resolution GEXRF technique can be successfully used at the synchrotron radiation facilities giving new access to study Al impurities on Si surface.

Experiment

In this experiment we have measured the low-level Al impurities in several Si wafers, which were intentionally contaminated with Al in the range of 10^{12} - 10^{14} atoms/cm^2, by applying the grazing emission x-ray fluorescence (GEXRF) technique [2, 3]. The Al-Kα fluorescence x-rays excited by intense synchrotron radiation photon beam was measured with a high-resolution using a von Hamos diffraction spectrometer [4] having an energy resolution below 1 eV. The x-rays were measured at grazing emission angle $\varphi=0.6^0$, being below the critical angle $\varphi_c = 1.11^0$ for Al-Kα fluorescence line. Under this condition, the measured fluorescence x-rays were emitted from very top layer of the sample, which resulted in a substantial relative suppression of the Si-Kα fluorescence contributing to x-ray background for Al-Kα fluorescence line. The emission of Si-Kα fluorescence line for grazing emission conditions was further reduced by choosing the primary photon energy below the Si-K absorption edge. In this case the x-ray background for Al-Kα detection was mainly due to resonant Raman scattering (RRS), which was much weaker than Si-Kα fluorescence.

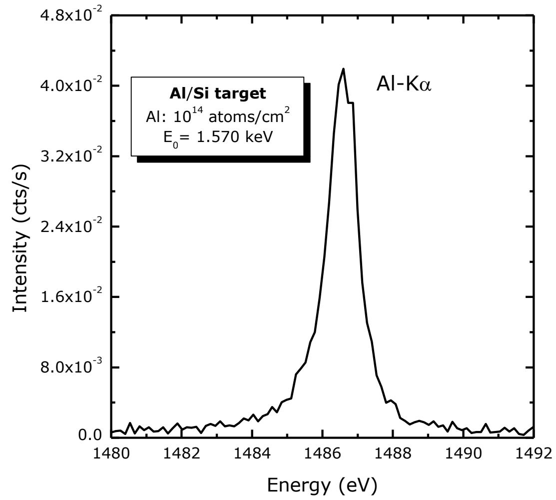

Fig. 1 Measured GEXRF spectrum of Al-Kα fluorescence line for Al-contaminated (10^{14} atoms/cm^2) Si wafer for photon beam energy 1570 eV.

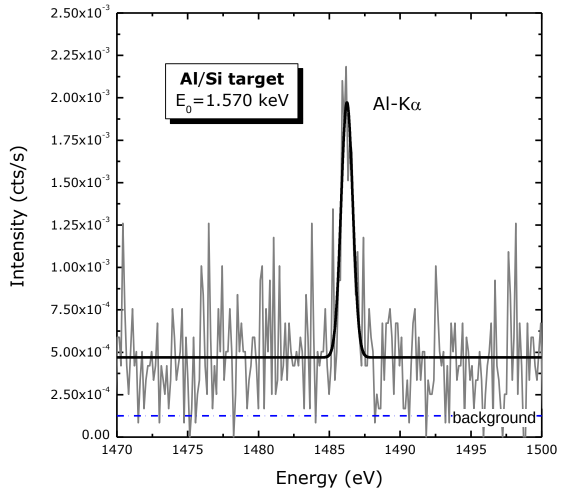

Fig. 2 Measured GEXRF spectrum of Al-Kα fluorescence line for a “clean” Si wafer for photon beam energy 1570 eV demonstrating a presence of about 10^{13} atoms/cm^2 Al-impurities on the surface. A level of a CCD background is shown on the figure.

In this experiment the x-ray background from the x-ray RRS process, studied for Si in our earlier experiment at ID21 [5, 6], which limits a sensitivity of the GEXRF method, was studied in details. For x-ray photon beam energy just above the Al-K (1560 eV) edge, but no more than 100 eV which is the binding energy of L-shell electrons in silicon, the Si KL-RRS feature appears even below the Al-Kα fluorescence x-ray line, making this measurements free of Raman scattering “background” from Si RRS for L-shell electrons. In this case only two orders of magnitude weaker (3%) RRS for M-shell electrons contributes to the Raman x-ray background. For this reason, we have used three photon beam energies in order to investigate such three different regimes of setting the detection limits for Al impurities, namely, when the x-ray background is dominated by i) the Si-Kα fluorescence emission (E=1895 eV), ii) the KL-RRS x-rays (E=1730 eV), and iii) the KM-RRS x-rays (E=1570 eV). In the experiment the elastically scattered photons, which contribute additionally to the x-ray background, were substantially suppressed by the linear polarization of the photon beam combined with an appropriate experiment geometry and the Bragg angle near 45^0 [6].

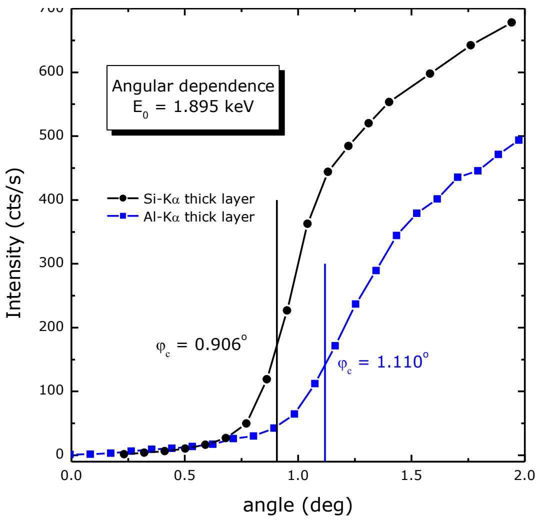

Fig. 3 Measured emission angle dependence of GEXRF intensity of Al-Kα and Si-Kα fluorescence lines for thick Al and Si samples for photon beam energy 1895 eV.

Results

The high-resolution GEXRF experiments were performed for several Al-contaminated and technologically "clean" Si wafers (see Figs. 1 and 2). In these experiments the x-ray spectra of Al-Kα and Si-Kα fluorescence lines were measured for different emission angles close to the critical angle. Additionally, the Al-Kα fluorescence line was measured for a thick Al sample (see Fig. 3) for normalization of the data. From the measurement of intentionally Al-contaminated (10^{14} atoms/cm^2) Si wafer (Fig.1) a detection limit of GEXRF technique was estimated to be 10^{12} atoms/cm^2 for direct measurement. This result shows that by combining the present synchrotron radiation based high-resolution GEXRF method with the preconcentration VPD technique, introducing an enhancement factor 10^5, an ultimate sensitivity of 10^7 atoms/cm^2 for detection of Al on Si can be reached. In the present GEXRF experiment we have observed about 10^{13} Al atoms/cm^2 on a "clean" Si wafer (Fig.2). From the measured dependence of the GEXRF intensity on the emission angle it was found that Al impurities are located on the surface of the wafer. This result demonstrates a capability of the GEXRF technique for depth profiling of impurities, which we plan to study in more details in the future. Finally, we have found that a sensitivity of the GEXRF method was limited in the present experiment only by the CCD background (~ 10^{-4} counts/s) (Fig. 2), which was not related to the photon beam. Concluding, we have demonstrated in this experiment that the high-resolution GEXRF method combined with synchrotron radiation excitation is a high-sensitivity x-ray spectroscopy technique for investigation of ultra low Al impurities in Si wafers. The results obtained were presented at two international conferences [7, 8] and a letter (in preparation) containing main results will be submitted to the Physical Review Letters.

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