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RESONANT RAMAN SCATTERING IN SYNCHROTRON RADIATION BASED X-RAY FLUORESCENCE ANALYSIS

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Application of x-ray fluorescence (XRF) analysis for detection of low-level impurities in materials can be limited by the x-ray resonant Raman scattering (RRS) process. This effect is particularly important for detection of ultra-low concentrations of low-Z impurities in high-Z materials. In this case, the low-energy tail of strong fluorescence line of bulk material forms a "background" for detection of low-energy x-rays from the impurities. By tuning the primary x-ray beam energy below the absorption the strong x-ray fluorescence of bulk material can be eliminated, but instead, the x-ray Resonant Raman Scattering (RRS) structure appears limiting thus a sensitivity of the x-ray fluorescence technique for detection of low-Z impurities in the studied sample.

Well known example of this effect is a problem of detection of ultra-low concentrations of Al on the surface of Si-wafers, which have to be controlled below 10^{10} atoms/cm^2 level for future silicon-based microelectronic technology. It was demonstrated that in this particular case the resonant Raman scattering process limits a sensitivity of the total-reflection x-ray fluorescence (TXRF) technique [1] for detection of aluminum contamination on Si–wafer. In fact, in the TXRF method which uses semiconductor detectors, having energy resolution well above 100 eV, the Al-Kα fluorescence line is overlapping with RRS structure appearing for photon beam energies tuned below the Si-K-shell absorption edge to avoid an intense Si-Kα fluorescence. Consequently, the TXRF limits for detection of Al on Si surface are about 10^{12} atoms/cm^2 for optimized synchrotron radiation excitation conditions. Due to this limitation the TXRF method is usually combined with the vapor phase decomposition (VPD) technique enhancing by 2-3 orders of magnitude a sensitivity for detection of Al on Si-wafers.

In order to investigate new alternatives for detection of Al in silicon we have measured [2] with high-resolution the RRS spectra for Si and SiO_2 below the Si K-shell edge at the ESRF at beamline ID21. The high-resolution measurements were performed using a von Hamos Bragg-type curved crystal spectrometer [3]. In these measurements, which were performed at different photon beam energies tuned below the Si-K absorption edge, the x-ray RRS spectra were measured for the first time and the total x-ray cross sections for the at the $1s2p$ RRS process in Si and SiO_2 were obtained. In general, the experimental RRS cross sections are well described by the theoretical calculations based on the Kramers-Heisenberg approach. We have also demonstrated that from the measured RRS x-ray spectra the density of unoccupied states in silicon can be derived, giving thus similar information as one obtained by using the x-ray absorption techniques.

Guided by the results obtained for the RRS in silicon we have proposed to measure the ultra low level Al impurities on Si by using the high-resolution grazing emission x-ray fluorescence (GEXRF) technique, which is an "inverse" TXRF method. The results demonstrate that the high-resolution GEXRF method can be successfully applied for detection of low-level Al impurities in silicon. However, the further aspects of application of a high-resolution synchrotron radiation based GEXRF technique in material science will be discussed separately.

References

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