SYNCHROTRON RADIATION BASED MICRO X-RAY FLUORESCENCE ANALYSIS OF THE CALIBRATION SAMPLES USED IN SURFACE SENSITIVE TXRF AND GEXRF TECHNIQUES

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The x-ray fluorescence techniques, with widely used the total-reflection x-ray fluorescence (TXRF) method [1], offer unique possibilities to study the concentrations of a wide range of trace elements in various types of samples. These techniques can be used for detailed surface studies of different materials, including ultra-low concentration contamination, the lateral and depth distributions of elements in the micrometer and nanometer scales. TXRF method is commonly employed in the semiconductor industry for determination of contaminants on silicon wafer surfaces [1]. An alternative method to TXRF is the grazing emission x-ray fluorescence (GEXRF) technique [3]. In the GEXRF method the x-ray fluorescence is observed at a small, grazing emission angle below a critical angle, being usually lower then 1°, depending on the energy of the emitted characteristic x-ray. The grazing emission geometry results in suppression of x-ray fluorescence from the bulk material, which for grazing emission angles is limited to the evanescent x-ray waves propagating along the surface. In this way the x-ray fluorescence from the substrate is limited to the very shallow surface layer of about few nm, which results in a relative enhancement of the characteristic fluorescence emission from surface impurities with respect to emission from the bulk. The GEXRF is an "inverse" of the total reflection x-ray fluorescence (TXRF) method and both techniques have similar detection limits.

In a series of experiments performed at the ESRF beamline ID21 we have demonstrated that the grazing emission x-ray fluorescence (GEXRF) technique combined with synchrotron radiation excitation and high-resolution x-ray detection offers attractive possibilities for application of synchrotron radiation to study the distribution elements on the surface of materials in nanoscale [4]-[7]. One of possible application is determination of the low-level impurities concentration on silicon [4, 5].

Both TXRF and GEXRF techniques provide qualitative and quantitative results. Calibration procedure normally used involves placing a microdroplet ($\sim \mu$l) of the standard solution onto a silicon wafer. After evaporation of the solvent, the residual amount of elements on the wafer is used as a reference standard [4, 5, 8]. However, usually a distribution of residue material on the substrate surface is not known accurately and consequently, such calibration method is burdened with uncertainty whether the calibration sample is of the pure particle type, which is usually assumed for evaluation purposes, or whether forms a film type layer. In the latter case, the relationship between the elements concentration on the wafer surface and the resulting fluorescence intensity deviates from that of the particle case, and thus leads to invalid calibration factors.

In the present work the investigation of the lateral distribution of elements in the multielemental calibrating samples by using the synchrotron radiation based micro X-ray fluorescence is presented. The studies have been performed at the European Synchrotron Radiation Facility (ESRF) at the ID21 X-ray microscopy beamline. The goal of this project was the investigation of a uniformity of the elemental distributions and determination of the residuum morphology, especially in the context of application different temperatures in drying process. In data analysis the censoring approach [9] will be also applied. This statistical approach allows on the data corrections in case of the presence of "nondetects". i.e. the measurements in which the concentration is not measured directly due to the actual value of detection limit.

The performed investigation of the lateral distribution of elements in the multielemental calibrating samples combined with the application of the censoring approach to "nondetects" can results in substantial improvement of calibration procedures for surface sensitive TXRF and GEXRF techniques, used for determination of contaminants on semiconductor surfaces.

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