Investigation of saturation effects in TXRF using picodroplets

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In general Total Reflection X-Ray Fluorescence Analysis (TXRF) is known to allow a linear calibration typically using an internal standard for quantification. For small sample amounts (low ng region) the thin film approximation is valid neglecting absorption effects of the exciting and the detected radiation [1]. For high total amounts of samples, deviations from the linear relation between fluorescence intensity and sample amount have been observed (saturation effect) [2]. These are not directly linked to a loss of validity of the calibration with internal standard, but are certainly an obstacle to absolute quantification or external standard quantification.

The fluorescence intensity emitted by samples with different amounts of nickel (0.012-240 ng) was measured using Synchrotron Radiation induced TXRF (SR-TXRF) to determine the upper limit of sample mass where the linear relation between fluorescence intensity and sample amount is no longer guaranteed. The element nickel was chosen for this investigation because it is usually used as reference standard for calibration of TXRF Wafer analyzers in the semiconductor industry. The samples were produced by an Hewlett Packard (HP) prototype Thermal Inkjet Picofluidic System (TIPS) [3] which applied a pattern of droplets (30 pl) directly on the surface of Si wafers. Picodroplets were used for this investigation because a lower saturation effect was expected. After drying each sample consisted of many small residues on the wafers’ surface with an almost constant distance between each other. Dependent on the concentration of the printed solution each residue contained sample amounts in the pg-range (0.015-300 pg). The printed patterns were investigated with an optical microscope (Fig. 1+2) to determine the average droplet diameter of each sample.

<table>
<thead>
<tr>
<th>amount [pg]</th>
<th>diameter [µm]</th>
<th>amount [pg]</th>
<th>diameter [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0015</td>
<td>6.1 ± 2.1</td>
<td>15</td>
<td>16.0 ± 2.6</td>
</tr>
<tr>
<td>0.15</td>
<td>9.5 ± 1.7</td>
<td>75</td>
<td>29.6 ± 6.7</td>
</tr>
<tr>
<td>0.75</td>
<td>10.3 ± 1.4</td>
<td>150</td>
<td>36.6 ± 7.5</td>
</tr>
<tr>
<td>1.5</td>
<td>10.6 ± 2.4</td>
<td>300</td>
<td>40.9 ± 6.1</td>
</tr>
</tbody>
</table>

Table 1: Averaged diameter of the picodroplets

The results of the measurements will be compared with the results of measurements performed using laboratory X-ray sources and with those of a simulation program. Therefore SR-TXRF was used because a well known geometry and an exact definable beamsize are
necessary parameters for the simulation program. Furthermore only with SR-TXRF this broad range of sample amounts (12 pg – 240 ng) is measurable. 

SR-TXRF measurements were accomplished at the bending magnet beamline L of HASYLAB using the TXRF vacuum chamber equipped with a sample changer [4]. The Si(111) double crystal monochromator was used to get a well defined energy (9keV) and a low divergence of the exciting radiation which are desirable parameters for the simulation program. The fluorescence spectra were recorded using a Silicon Drift Detector (SDD) with an active area of 50mm².

It could be shown that in the case of picodroplet standard samples the relation between fluorescence intensity and sample amount is linear up to 10-12 ng Ni. At larger sample amounts deviations from the linearity occurred (Fig. 3). For single VPD microdroplets Hellin et al. [2] reported that the relation between fluorescence intensity and sample amount is only linear up to ~3 ng Ni. However, in this work much higher excitation energies were used emitted by laboratory X-ray sources (Mo and W tube) and monochromatized by a multilayer system. It can be assumed that saturation effects caused by self absorption of the incident radiation are larger for smaller energies as the absorption becomes stronger for exciting energies close to the absorption edge of the element of interest. The presented data shows that for picodroplet samples the range of linearity between fluorescence intensity and sample amount could be expanded even using lower excitation energy (9keV). This leads to the conclusion that picodroplet samples are very promising to be used as an external standard in future TXRF analyses.

References