Application of high-resolution grazing emission x-ray fluorescence for material sciences

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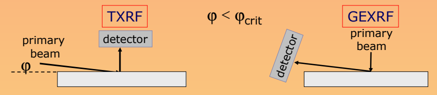
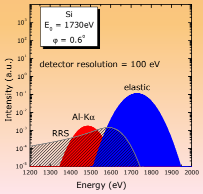
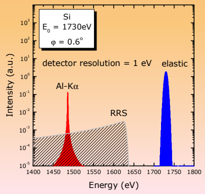
Motivation

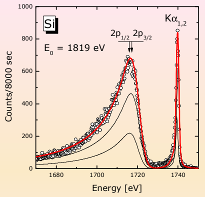
The application of the x-ray total reflection phenomenon combined with intense synchrotron x-ray beam offers new possibilities for measuring ultra low concentrations of light elements, e.g. aluminium, on Si surface [1]. The detection of Al on Si wafer by TXRF for photon energy below the K-edge of Si [2] is limited by the presence of resonant Raman scattering (RRS).
Can high-resolution grazing emission x-ray fluorescence (GEXRF) [3] be applied for Al detection in silicon?

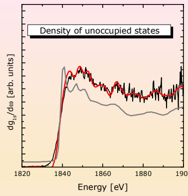






X-ray RRS in silicon



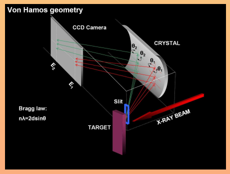


J. Szlachetko et al., Phys. Rev. A **75**, 022512 (2007)
J. Szlachetko et al., Phys. Rev. Lett. **97**, 073001 (2006)

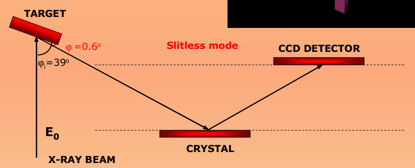
GEXRF high-resolution experiments (ESRF ID21)

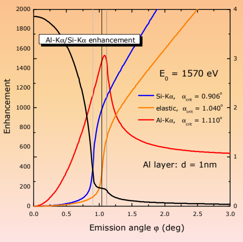
The x-ray resonant Raman scattering [4] and GEXRF high-resolution experiments were performed at the European Synchrotron Radiation Facility (ESRF) at beamline ID21.
The high-resolution spectra were observed by means of a von Hamos type bent crystal spectrometer [5].

Photon beam parameters (ID 21):
energy 1560–1895 eV, intensity 10^{10}–10^{11} photons/s,
energy resolution ~ 6 eV (two 20Å Ni/B_4C multilayers),
size 1 mm², horizontally polarized



von Hamos spectrometer:
- energy resolution: ~ 1 eV;
- ADP (101) crystal (2d = 10.642Å);
- Bragg angle: θ_B = 52°





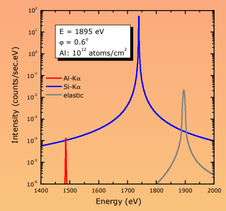
GEXRF intensity [6]:

$$I(\Delta x,\varphi) \sim \int_0^{\Delta x} e^{-2k\left[\mathrm{Im}\left(\sqrt{n^2-\cos^2(\varphi)}\right)\right]\cdot z}\,dz$$

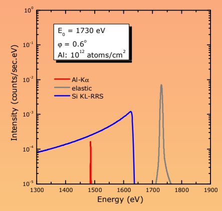
$$\mathrm{Enhancement} = \frac{\text{surface Al intensity}}{\text{bulk Si intensity}}$$

for $\varphi < \varphi_{crit} \sim \frac{1}{E_x}$

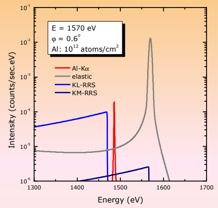
Optimization of photon beam energy



$E_0 > E_K(Si)$
background: Si-Kα tail



$E_K(Al) + \Omega_{2p}(Si) < E_0 < E_K(Si)$
background: RRS-KL

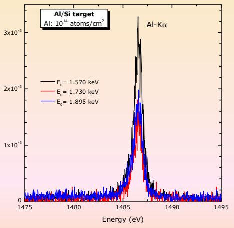


$E_K(Al) < E_0 < E_K(Al) + \Omega_{2p}(Si)$

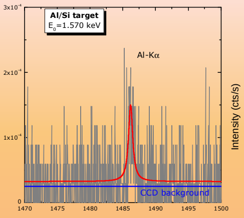
background: RRS-KM
elastic scattering
CCD background

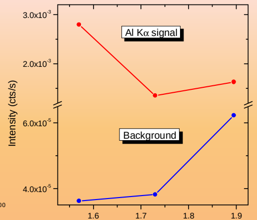
Note:
polarization effects (θ_B ~ 45°)
CCD noise (2×10⁻⁵ 1/s)

GEXRF results for Al impurities on silicon



The x-ray beam was tuned to energies of 1.895 keV, 1.730 keV and 1.570 keV in order to measure the fluorescence of Al Kα x-rays from intentionally contaminated Si wafers. In addition, the Al signal from «pure» Si wafer was recorded for «Raman free» conditions.





GEXRF detection limits for Al

Detection limit (1000 s):

$$C_{DL} = \frac{3\sqrt{N_{bckg}}}{N_{peak}}\frac{\sqrt{t}}{\sqrt{1000}}\cdot C$$

Deposited thin Al layer: $C \sim 10^{14}\frac{atoms}{cm^2}$

Surface Al contaminations in silicon: $C \sim 10^{13}\frac{atoms}{cm^2}$

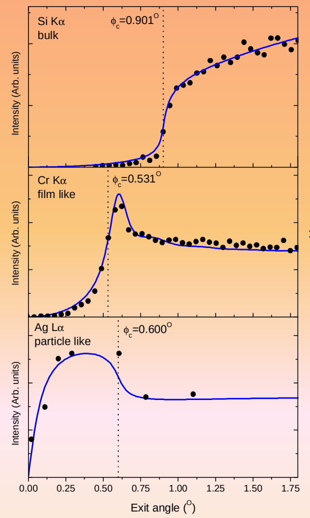
Measured detection limit: $\rightarrow C_{DL} \sim 10^{12}\frac{atoms}{cm^2}$

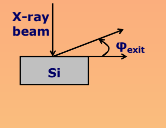
Extrapolated VPD-preconcentrated detection limit
for D = 300 mm Si wafer and d = 1 mm - beam diameter:

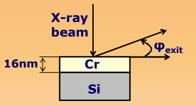
Enhancement factor: $\left(\frac{D}{d}\right)^2 \sim 10^5 \rightarrow C_{DL} \sim 10^7\frac{atoms}{cm^2}$

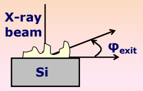
GEXRF angular dependences

The composition, density and thickness of the layers can be derived from the intensity evolution around the grazing exit angle.

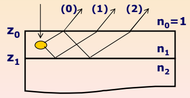


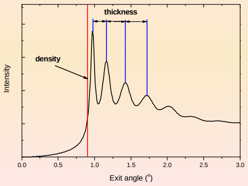






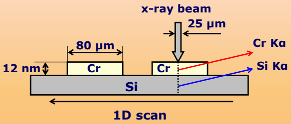
Interferences between the direct and reflected beams lead to a fringe pattern in angular distribution of the fluorescence intensity



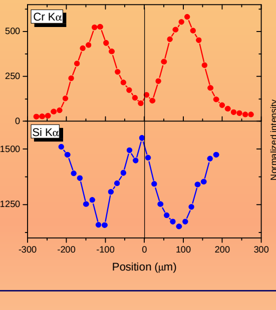


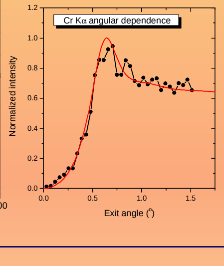
$$I(\theta) \approx \int_{z_1}^{z_0} |t_0|^2 Exp\left[-2\,\mathrm{Im}\,k_{z,1}(z_0 - z_s)\right] \times \left|\overbrace{\frac{1}{1-r_0^+r_1^-Exp[-2\,\mathrm{Im}\,k_{z,1}(z_0-z_1)]} + \frac{r_1^-Exp[-2\,\mathrm{Im}\,k_{z,1}(z_s-z_1)]}{1-r_0^+r_1^-Exp[-2\,\mathrm{Im}\,k_{z,1}(z_0-z_1)]}}^{\text{multiple reflections}}\right|^2 dz_s$$

2D mapping capabilities



In order to validate the 2D mapping capabilities of GEXRF method, a 1D scan was performed across a layered Cr/Si sample.





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