Focused beam total reflection X-ray fluorescence with low power sources coupled to doubly curved crystal optics

Z.W. Chen\textsuperscript{a,}*, N. Mail\textsuperscript{b}, F.Z. Wei\textsuperscript{a}, C.A. MacDonaldb, W.M. Gibson\textsuperscript{a}

\textsuperscript{a}X-ray Optical Systems, Inc. East Greenbush, NY 12061, United States
\textsuperscript{b}Center For X-ray Optics, State University of New York, University at Albany, United States

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Abstract

A focused beam total X-ray fluorescence technique was developed based on doubly curved crystal optics. This technique provides good detection sensitivity and spatial resolution for localized detection of surface deposits. Compact low power X-ray sources were used to demonstrate the benefit of the X-ray optics for focusing Cr K\textsubscript{\alpha}, Cu K\textsubscript{\alpha} and Mo K\textsubscript{\alpha} radiation. The detection capability of the focused beam total reflection X-ray fluorescence system was investigated with dried droplets of calibrated low concentration solutions. Detection limits at the femtogram level were demonstrated.

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1. Introduction

As the dimension of integrated circuits become smaller and smaller, the thickness of the gate oxide is being reduced to a level where it has become necessary to control the process to virtually atomic levels. With oxide thickness less than 10 nm, surface metal impurities can have deleterious affects on the oxide properties. Metals such as Ti, Ta, and Cu can be deposited on the surface at any number of processing steps ranging from wet chemical etching to ion implantation. Many processing steps involved in fabricating an integrated circuit are actually cleaning steps designed to remove metal contamination. As the feature size is reduced, the level of acceptable metal contamination is also decreased. More sophisticated experimental techniques are required to detect these contaminants with high sensitivity and low detection mass limits [1].

For environmental measurements, the detection of As, Hg, Cd, Pb, and other contaminants is required with high sensitivity. The discovery of arsenic in groundwater in several countries has aroused widespread concern over the last couple of years.

Total reflection X-ray fluorescence (TXRF) is a technique that provides quantitative elemental information for contaminants on surfaces. TXRF exploits the property that at very low incidence angles, an X-ray beam can be totally reflected from a flat surface so that the beam penetration into the substrate is reduced to the order of ~5 nm thickness. Due to this small penetration into the substrate, scatter as well as excitation of substrate atoms is reduced, which results in low background. Furthermore, X-rays reflected from the substrate can also excite surface contaminants, effectively doubling the effective X-ray flux.

High sensitivity has been achieved with TXRF using synchrotron sources [2–4]. Rotating anode laboratory sources have also been used for TXRF, but with limited sensitivity for local contaminants due to smaller X-ray flux on the sample.

The use of doubly curved crystal (DCC) optics to collect and focus X-rays from a large solid angle increases the usable flux from a laboratory source [5]. Doubly curved crystal optics typically have toroidal shape and provide a
point focusing for one wavelength with a small X-ray source [6]. The Bragg condition for the designed wavelength is satisfied over the whole crystal surface which gives two-dimensional focusing of X-rays. The flux density on local contaminants increases by orders of magnitude and very low detection limits can be achieved. This point-to-point Johan geometry is shown in Fig. 1. The diffracting planes of the crystal are parallel to the crystal surface. If the focal circle containing a point source S and the image I has radius \( R \), the crystal surface has a radius of curvature of \( 2R \) in the plane of the focal circle and a radius of curvature of \( r = 2R \sin^2 \theta_{\text{Bragg}} \) in the perpendicular plane, with the radius, \( r \), centered on segment SI. X rays diverging from S, and incident on the crystal surface at angles within the rocking curve of the crystal will be reflected efficiently to point I. The monochromatic flux density at the focal point for a DCC-based system is several orders of magnitude greater than that of conventional systems with higher power sources and similar source to object distances [7]. By comparison, the Von Hamos [8,9] geometry has cylindrical bending profile and it is designed for the dispersion of multiple wavelengths. For a given wavelength, only a narrow line on the Von Hamos crystal surface can provide reflection. Therefore the collection solid angle of Von Hamos geometry is a few orders of magnitude less than DCC optics. The increased flux due to the high capture angle into the two dimensional focus yields a very high sensitivity for local contaminant detection. The ability to therefore use low power sources allows portability or in situ, online process control.

2. Experiment

Focused beam TXRF measurements were carried out using the doubly curved crystal (DCC) optics. The focused beam TXRF setup, shown in Fig. 2, consists of a point X-
ray source, a doubly curved crystal (DCC) optic and a detector. The DCC optics were Si (220) for Mo Kα1, Si (111) for Cu Kα1, and Ge (111) for Cr Kα1. The DCC optics specifications are listed in Table 1. The DCC optic was mounted on two translation stages transverse to the X-ray beam and placed at the designed focal distance from the source spot. Source to optic alignment was performed with a large area image intensifier coupled to a CCD camera. The camera was placed at the 2θBragg angle at a distance of 250 mm from the optic to intercept the diffracted image. The DCC optic was moved along the transverse directions to the beam to obtain a uniform bright image of the beam, which implies that the source is reasonably aligned.

The samples were prepared in a clean room by placing calibrated 2 μL droplets of a given concentration, typically 5–200 ppb, using a microdropper onto a 50 mm diameter silicon wafer. Several microdroppers were calibrated by measuring the mass of pure water droplets. The sample was dried in a controlled enclosure. After the droplet dried, a localized film of the sample was formed on the silicon surface. These samples mimic wafers with localized contaminants as well as providing a technique for sampling of multiple liquids. The mass of the contaminants on the silicon wafer surface was in the range of 10–400 pg. The intentionally contaminated silicon wafer was mounted on one rotation and three translation stages and placed at the optic output focal position, parallel to the adjustable slit between the optic and the sample, as shown in Fig. 2. The purpose of the slit was to restrict divergence in the scattering plane to less than the critical angle. An energy sensitive silicon drift detector (SDD) was placed close, ~4 mm, from the vertical wafer surface in order to maximize the collection solid angle (and hence sensitivity).

The measured output spot widths of the beam were 45 and 100 μm along the X and Y directions, respectively, so the beam spread on the silicon wafer held at grazing incidence in the beam direction is 45 μm/tanθin=25 mm, where θin, the incident angle, was less than the critical angle. The critical angles are 0.1° for the molybdenum and 0.35° for the chromium sources. The illuminated path on the wafer is thus 100 μm × 25 mm for the molybdenum source. The sample area would be limited by the detector viewing field which is 8 mm; however, the actual dried spot area was less than 3 mm in diameter. Thus less than about 10% of the beam from the optic was illuminating the sample at incident angles less than the critical angle for the molybdenum source and less than 35% for the chromium source.

The transverse X position and the incidence angle were roughly optimized by using the CCD camera. The reflected and the incident beam images could be distinguished by placing the camera far away, at 150 mm from the sample. Once the X position and angle were roughly optimized, a silicon drift detector with 50 mm² sensitive area was placed

<table>
<thead>
<tr>
<th>Parameters</th>
<th>DCC optics</th>
<th>Photon energy, keV</th>
<th>θBragg, deg</th>
<th>Input focal distance, mm</th>
<th>Output focal distance, mm</th>
<th>Convergent angle, ϕ, deg</th>
<th>2R, r, mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (220)</td>
<td>17.5</td>
<td>10.6</td>
<td>120</td>
<td>120</td>
<td>4</td>
<td>650</td>
<td>22.17</td>
</tr>
<tr>
<td>Si (111)</td>
<td>8.0</td>
<td>14.2</td>
<td>150</td>
<td>150</td>
<td>9</td>
<td>611</td>
<td>36.88</td>
</tr>
<tr>
<td>Ge (111)</td>
<td>5.5</td>
<td>20.5</td>
<td>120</td>
<td>120</td>
<td>14</td>
<td>342</td>
<td>42.01</td>
</tr>
</tbody>
</table>

Fig. 3. Si fluorescence intensity from a silicon sample versus incidence angle from three different DCC optics each corresponding to a different X-ray energy: (a) 5.4 keV, (b) 8.0 keV and (c) 17 keV. The critical angle for reflection from silicon for 5.4 keV is 0.35°, for 8 keV is 0.22° and for 17 keV is 0.1°, at the position of the vertical dotted lines.

Fig. 4. Fluorescence intensity as a function of Y position for a localized sample with 1000 pg Cu and 100 pg Pb on a silicon wafer, collected in 10 s.
4 mm from the sample to collect the fluorescence spectrum. The silicon wafer was then optimized in \( X \) position and scanned along the \( Y \) direction, to find the exact location of the sample. Once the \( Y \) and \( X \) positions of the sample were optimized, an angular scan was performed to optimize the incident angle. A typical plot of Si fluorescence versus incident angle is shown in Fig. 3. After optimization of position and angle the fluorescence spectrum was collected.

Based on the spectrum and the known concentration of the elements in the sample, the absolute minimum detection limit (MDA) was obtained by [10].

\[
MDA = 3m \frac{\sqrt{BG}}{S} \times \sqrt{\frac{t_c}{t_{1000}}},
\]

(1)

where \( m \) is the mass of each element, \( S \) is the fluorescence signal counts, \( t_c \) is the counting time, \( t_{1000} \) is the standard collection time of 1000 s, and \( BG \) is the background counts, so that \( \sqrt{BG} \) is the background fluctuation. The MDL, detectable concentration of impurity in original water sample, was obtained for each element by replacing the \( m \) with concentration, \( c \).

3. Results and discussion

The total reflection condition and absolute incident angle can be verified by measuring the Si fluorescent intensity from a Si wafer versus incident angle. The Si fluorescence X-rays from a clean wafer as a function of the incident angle for DCC focused beams of three different X-ray energies, 5.4 keV, 8.0 keV, and 17.5 keV, are shown in Fig. 3. The plot for each energy has a steep slope as the angle is increased above the critical angle. Below the critical angle total reflection occurs and the silicon fluorescence, which requires penetration of the incident radiation into the wafer, is minimized. The well-defined critical angle is a good indication of the energy and angular quality of the DCC beams. The fluorescent intensity from the silicon surface was higher for the low energy source due to the higher characteristic X-ray intensity, high cross section at energies near the ionization energy, the larger collection solid angle...
due to the larger Bragg angle and the larger size of the slit due to the higher critical angle.

3.1. Measurement with Mo source

A number of samples with ionization energy less than the Mo characteristic energy line Ka1 at 17.5 keV were analyzed using a Mo source. These samples were silicon wafers with lead, platinum, arsenic, copper, and tantalum surface deposits with different controlled concentrations.

3.1.1. Lead and copper

Samples made from a solution that the film which formed after the 2 µL droplets dried contained 10–100 pg lead and 100–1000 pg copper were analyzed. The fluorescence intensity scan versus sample location is shown in Fig. 4. The copper and lead contaminants were highly localized on the silicon wafer substrate surface. The majority of the contaminants were concentrated within a few hundred micrometers. This shows the capability of this focused beam TXRF technique to investigate the spatial distribution of the contamination. The angular scan of Fig. 5 shows that the signal peaks are high for incidence angles less than the critical angle. This indicates that the contaminants were purely surface contamination. The spectrum taken for an incidence angle of 0.4 mrad, approximately one fourth the critical angle, is shown in Fig. 6. At this incident angle the Si Kα peak from the substrate is low. The peak near 17.5 keV is due to scattering of the incident Mo Kα1 radiation. The copper signal is high compared to the lead signal due to the higher concentration of copper. Calcium and sulfur contaminants were also seen in the sample. The spectrum of the spot from a pure water drop on a silicon wafer was also collected for comparison and, as seen in Fig. 7, shows very low background, with some sulfur contamination from the water and argon from the air.

The sensitivity of the focused beam TXRF system and the absolute minimum detection limits, MDA, for Cu and Pb, scaled to a standard collection time of 1000 s, computed from Eq. (1), is listed in Table 2. The number of atoms in the MDA was also computed. The corresponding minimum detection limit, MDL, was calculated in parts per trillion (ppt) by weight in the original 2 µL water droplet.

### Table 2

<table>
<thead>
<tr>
<th>Elements</th>
<th>Pb</th>
<th>Ta</th>
<th>Pt</th>
<th>Cu</th>
<th>As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity, CPS/pg</td>
<td>1</td>
<td>0.03</td>
<td>0.1</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>MDA, fg</td>
<td>35</td>
<td>240</td>
<td>210</td>
<td>140</td>
<td>25</td>
</tr>
<tr>
<td>MDA, no. of atoms</td>
<td>3×10⁵</td>
<td>8×10⁵</td>
<td>6.6×10⁵</td>
<td>13×10⁵</td>
<td>2×10⁶</td>
</tr>
<tr>
<td>MDL, ppt by weight</td>
<td>17</td>
<td>120</td>
<td>105</td>
<td>70</td>
<td>12</td>
</tr>
</tbody>
</table>

The counting times were different for the listed elements but are converted to a standard collection time of 1000 s. The MDA is also shown as the number of atoms and the MDL as the parts per trillion by weight in the 2 µL water droplet.
Pb and As in the droplet was below 20 ppt. Such low detection limit is due to the drastic improvement of the flux density of the beam using the focusing DCC optic.

3.1.2. Lead and platinum

A 2 μL drop from a 200 ppb by weight solution of platinum was placed on a silicon wafer. A 2 μL droplet from a 200 ppb lead solution was placed on top of the wet platinum droplet. This yielded 400 pg of Pt and 400 pg Pb. The Pt and Pb signal intensity versus transverse displacement of the silicon surface is shown Fig. 8a. The sample scan shows two peaks for the platinum signal, because the drop with lead displaced the platinum to the outer edges as shown in Fig. 8b. The measurement shows that the focused beam TXRF using DCC optics provides a spatial resolution of 50–100 μm. The TXRF spectrum of the mixed Pb and Pt sample is shown in Fig. 9. Small concentrations of S, Ca, and Cu were also identified. The Si Kα peak at 1.7 keV and Compton scattering at 17.5 keV are both low compared to the lead signal. The system sensitivity and detection limit for this lead sample is consistent with the 100 pg lead sample.

3.1.3. Arsenic and tantalum

A TXRF spectrum from a mixed solution of 400 pg As and 400 pg Ta is shown in Fig. 10. A spectrum from a mixed solution of 40 pg As and 40 pg Ta is also shown in Fig. 10 for comparison. Significant signal was observed even for the 40 pg sample. The system sensitivity and minimum detection limit for the deposited arsenic and tantalum, scaled to a standard collection time of 1000 s, is listed in Table 2. Again, an MDL for As in water at ppt levels were achieved. This demonstrates that this low-power focused beam TXRF technique could be among the most sensitive methods for As analysis in water.

3.2. Measurement with Cu source

The experimental setup for the copper source was the same as for the molybdenum source except a Si (111) DCC optic was employed. The beam was focused at a convergent
angle of 9° by the optic. Two samples, each with equal amounts of manganese and titanium, were analyzed.

The signal for 400 pg Mn and 400 pg Ti versus the transverse position, \( Y \), is shown in Fig. 11. The \( Y \) position scan of the titanium peak is much broader than the manganese peak. Several samples showed similar broadening and titanium tails, possibly due to low solubility of Ti in water resulting in deposition of the Ti as the water drop dried from the edges while the more soluble Mn stayed in the remaining water drop. The wider spread of Ti contributes to the relatively low Ti signal at the peak position compared to the Mn signal. The TXRF spectrum from two samples, one with 400 pg each of Mn and Ti and one with 40 pg each are compared on a log scale in Fig. 12. The system sensitivity and the minimum mass detection limit of Mn and Ti contaminants scaled to a standard collection time of 1000 s are listed in Table 2. The results in Table 3 were obtained by assuming that all the Mn and Ti content in the 2 \( \mu \)L droplet were within the beam. Obviously this is not true for Ti based on the distribution shown in Fig. 11. Therefore the detection limits obtained for Ti was a conservative number and it gives a upper value of the detection limits. The minimum detection number of atoms within the beam were also estimated and the results are listed in Table 2.

### 3.3. Measurement with Cr source

Measurements were repeated with a Cr tube and a Ge (111) optic. The fluorescence intensity from a silicon sample versus incident angle is shown in Fig. 3. The TXRF spectrum for a 200 pg titanium sample is shown in Fig. 13. The spectrum shows calcium contamination in the sample and Ar from the air. The sensitivity of the system and the minimum detection limit for titanium are listed in Table 4. A 200 pg sulfur sample was also analyzed. The fluorescence intensity versus transverse position plot is shown in Fig. 14. The minimum detection limit and sensitivity for sulfur is listed in Table 4. The background in the spectrum at the Ti and S peak positions with a Cr source are higher compared to that obtained with a Cu source because the strong Cr scattering peak, which contributes to the background because of a low energy tail, is closer to the measured energy. This could be reduced through the use of a liquid nitrogen cooled Si(Li) detector. The stronger Si fluorescence peak from the Cr source also contributes to the background in the electronic circuit. However these effects are more than compensated by the higher excitation cross sections for Ti and S with a Cr source compared to the higher energy sources.

### 4. Conclusions

Focused beam total reflection X-ray fluorescence (TXRF) measurements were carried out with low power sources using three doubly curved crystal (DCC) optics designed for Mo K\( \alpha \), Cu K\( \alpha \), and Cr K\( \alpha \) radiation. Minimum detection mass limits in the range 20–150 fg for localized contaminants were achieved for transition metals or heavy elements for a standard collection time of 1000 s using 10 to 50 W sources. The average sensitivity for this experiment was better than 1.0 cps/pg. The focal spot of these optics was on the order of 100 \( \mu \)m, which yields very high spatial resolution compared to conventional TXRF measurements. The focused monochromatic beam on the localized sample improves the sensitivity and minimum mass detection limit. The high spatial resolution makes it possible to scan the samples to determine the distribution of contaminants on the surface.

### Table 4

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ti</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPS/pg</td>
<td>1.3</td>
<td>1</td>
</tr>
<tr>
<td>MDA, fg</td>
<td>200</td>
<td>800</td>
</tr>
<tr>
<td>MDA, no. of atoms</td>
<td>(25\times10^8)</td>
<td>(150\times10^8)</td>
</tr>
<tr>
<td>MDL, ppt by weight</td>
<td>100</td>
<td>400</td>
</tr>
</tbody>
</table>

The MDA is also shown as the number of atoms and the MDL as parts per trillion by weight in the 2 \( \mu \)L water droplet.
References


