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Trace element analysis on Si wafer surfaces by TXRF at the ID32 ESRF undulator beamline

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Synchrotron radiation total-reflection X-ray fluorescence (SR-TXRF) has been applied to the impurity analysis of Si wafers using a third-generation synchrotron radiation undulator source. A lower limit of detectability (LLD) for Ni atoms of 17 fg (1.7×10^8 atoms cm^{-2}) has been achieved with an optical set-up based on an Si(111) double-crystal monochromator and a horizontal sample geometry. These first results are very promising for synchrotron radiation trace element analysis since we estimate that it is possible to lower the LLD by a factor of about 25 by employing appropriate optics and detectors. The use of a crystal monochromator opens new possibilities to perform absorption and scattering experiments (NEXAFS and X-ray standing-wave methods) for chemical and structural analysis of ultratrace elements.

Keywords: trace element analysis; surface contamination; X-ray fluorescence and reflectivity; grazing incidence; semiconductor applications.

1. Introduction

Surface-contamination characterization in the ultratrace range has a strategic importance on the metrology platform for future semiconductor development. Total-reflection X-ray fluorescence analysis (TRXRF or TXRF) is optimally suited for chemical identification and quantification of trace elements (see, for example, Prange & Schwenke, 1992). The measurement is surface-sensitive, non-destructive and reproducible. Furthermore, the technique offers mapping capabilities and the analysis is usually straightforward. Semiconductor industries have widely approved this analytical method for wafer contamination characterization. However, it appears that detection limits in the range of a few hundred femtograms, which are usually obtained for a limited number of elements with a rotating-anode source (Ladisich *et al.*, 1993), are not sufficient for imminent industry needs. The use of synchrotron radiation as an excitation source for TXRF has led to significant improvement of detection limits in the past few years. The advantages of synchrotron sources are high brightness, low angular divergence and linear polarization in the orbital plane, which improve the signal-to-background ratio. Furthermore, the X-ray energy tunability permits an optimal excitation of most elements. Therefore SR-TXRF might become an important R&D and process-control tool for semiconductor applications. Detection limits in the 10 fg range for medium-Z elements have been reported by several groups using bending magnets or wigglers at second-generation synchrotron radiation sources (Wobrauschek *et al.*, 1995; Pianetta *et al.*, 1995). A wide-energy band-pass approach based on multilayer monochromators and, in most cases, focusing optical elements has been used in order to increase the photon flux onto the sample. A monochromated beam is preferable to a white or filtered beam because it leads to a reduced background in the spectrum, improving the detection limits significantly.

In this paper we report an SR-TXRF test experiment using a third-generation synchrotron radiation undulator source and a basic optical set-up based on an Si(111) monochromator. The main aim of the study was to evaluate the lower limits of detectability (LLD) with an undulator beamline for future developments in surface trace element analysis, in particular for semiconductor applications.

2. Experimental

The experiment was carried out at the ‘SEXAFS and Standing Wave’ ID32 ESRF beamline (Comin *et al.*, 1997). Fig. 1 shows the experimental configuration used in this work. The beamline takes radiation from two undulators of 40 and 48 mm periods inserted in a high-β straight section. A basic optical set-up was used, consisting of an Si(111) flat double-crystal monochromator and collimating slits. No mirror or focusing elements were used. In order to reject undesirable high harmonics, the monochromator was strongly detuned. As a result, the diffracted intensity for the first harmonic was reduced by at least a factor of 5. The excitation energy was 10.5 keV. At the experimental station the beam, which is 1.8 mm wide and 0.8 mm high (FWHM), was collimated by 2 mm (H) × 80 μm (V) slits. The samples were mounted horizontally on a motorized goniometer head. A rotation stage with an angular resolution of 0.001° was used for the incident-angle adjustment. A Eurysis HPGe detector with reduced dead-layer, equipped with an 8 μm Be window, was placed almost along the polarized direction at about 70 mm from the beam footprint on the sample. The detection system observed the irradiated sample surface with an angle of a few degrees (~5°). In this case the attenuation inside the sample is negligible. A PTFE collimator of 40 mm diameter and 45 mm length with a central hole of 5 mm diameter was placed in front of the detector. The horizontal sample geometry is unusual for Si wafer SR-TXRF analysis because the detection of the fluorescence signal is not optimal. The beam path from the irradiated part of the sample to the detector may be long and therefore the solid angle of collection is small. However, it makes full use of the polarization effect and a good excitation of the sample is achieved. Further-

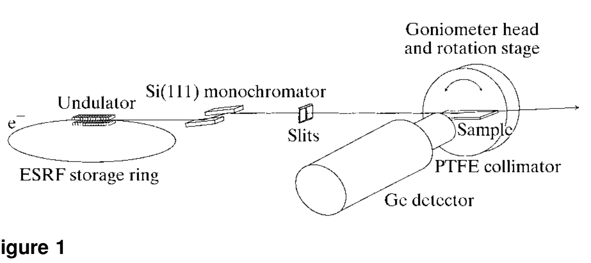

Figure 1
Schematic arrangement of the TXRF set-up using horizontal sample geometry.

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more, sample handling and mounting are simple. Measurements were performed in air under a laminar-flow hood providing an environment better than class 100. An Si wafer containing known amounts of Ca, Ti, Cr, Mn, Fe, Ni, Cu and Zn contaminants (see Table 1) was analysed. The contamination levels were determined using TXRF Rigaku standard equipment. Great care was taken in sample handling.

2.1. *Assessment of parasitic contributions*

The importance of the parasitic contributions due to experimental environment has been evaluated using a 'clean' (as received) Si wafer. The resulting fluorescence analysis is shown in Fig. 2. The top panel shows Cr, Mn, Fe, Co, Ni, Cu and Zn parasitic contributions. The scattered radiation from the sample excites the goniometer head which is situated in front of the detector (see Fig. 1). To lower this background, a shielding was achieved by placing an Re absorbing foil between the sample and the goniometer head. Rhenium *K* and *L* lines are not excited at 10.5 keV. Parasitic contributions are then strongly reduced except for Zn (see bottom panel on Fig. 2). Even though a part of the contribution may originate from the 'clean' sample itself and not from the experimental set-up, the background level is low enough to not have any influence on the results obtained with the contaminated Si wafer.

3. Results and comments

The TXRF spectrum over 2000 s measuring time for the calibrated sample is shown in Fig. 3. We notice that (i) due to the long air path, silicon fluorescence is totally absorbed and argon fluorescence from air is considerably attenuated, and (ii) due to the low solid angle of collection along the polarization direction and the low divergence of the incident beam, the contribution of the elastic peak is considerably limited. Consequently, we have an efficient detection of the fluorescence signal from contaminants.

The lower limit of detectability has been calculated using the formula (Bertin, 1975)

$$\mathrm{LLD} = 3(I_{\mathrm{BG}}t)^{1/2}c/I_N t,$$

where I_{BG} and I_N are background and fluorescence intensity (both in counts s^{-1}) and c is the concentration of the element to be analysed. Although the data were taken over 2000 s, LLDs have been calculated for a typical measuring time t of 1000 s in order to make comparison with other published works easier. The results are reported in Table 1. The minimum LLD is reached for Ni with 17 fg which corresponds to 1.7 × 10^{8} atoms cm^{-2} or 2.5 × 10^{-7} monolayer of an Si(100) surface. The limiting factors for low-*Z* elements (Ca, Ti) are air absorption, low cross section, low fluorescence yield and higher background due to *bremsstrahlung* contribution (Takaura *et al.*, 1995), and for high-*Z* elements (Zn, Cu) a higher background due to Compton contribution. The results are comparable with the best results obtained from second-generation synchrotron sources using the wide-bandpass approach (Wobrauschek *et al.*, 1995; Pianetta *et al.*, 1995). However, using appropriate mirror optics and detection system we estimated that it is possible to lower the LLD by about a factor of 25, *i.e.* below the femtogram range. Optics have not been optimized for this test experiment. As a result, only a small fraction of the photons delivered by the undulators have been used. Harmonic rejection and beam focus by means of a mirror will strongly increase the photon flux onto the sample. Additional gain in intensity can be obtained by using multi-element detectors located on both sides of the sample. Refinement of the geometry by changing the sample-to-detector distance and collimation diameter should also lower the LLD. Finally, we have to mention that the experiment was not carried out during the most powerful filling mode of the storage ring.

Table 1
Concentrations of the calibrated Si wafer and lower limits of detectability.

Measuring time: 2000 s.

Element	Concentration (pg)	Net intensity (counts)	Background (counts)	LLD (fg)
Ca	67.9	26390	2799	578
Ti	19.2	18446	1415	166
Cr	0.5	996	665	57
Mn	0.3	789	641	45
Fe	4.5	14061	557	32
Ni	0.4	1763	383	17
Cu	1.5	8506	1354	27
Zn	14.4	102923	2671	31

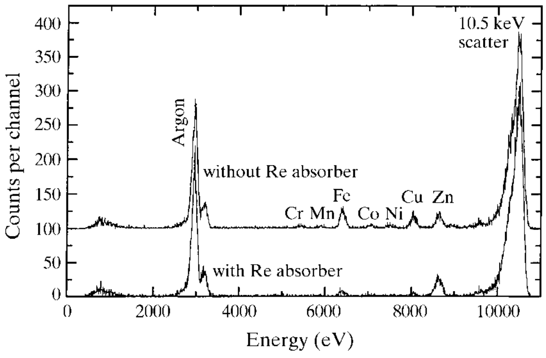

Figure 2
Assessment of parasitic contributions: TXRF spectra of a clean Si wafer.

A change of the geometrical arrangement can also be considered to lower the LLD. Very recently, examination of sample geometry effects has been reported by Görgl *et al.* (1997) employing bending-magnet radiation and multilayer structure for monochromatization at the L Hasylab beamline. They showed that the geometrical arrangement with the sample mounted vertically gave the best LLD. A factor of 6 between the vertical and horizontal arrangement has been observed. Although the

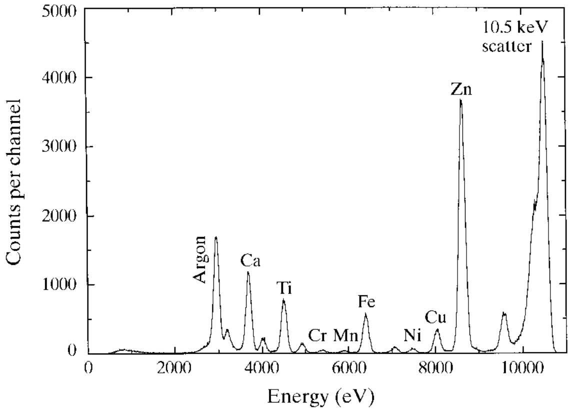

Figure 3
TXRF spectrum of a calibrated Si wafer (measuring time: 2000 s).

results of their examination are closely related to the exact geometry and the characteristics of the X-ray source, a similar effect may be expected in our case.

The use of a crystal monochromator instead of a multilayer structure for monochromatization opens new possibilities to study surface trace elements at an ultralow level. Chemical information about the contaminant may be obtained by performing X-ray absorption experiments (NEXAFS) under grazing-incidence geometry (Greaves, 1991). X-ray standing-wave methods might be applied either in a highly asymmetric case (Afanas'ev *et al.*, 1992) or in an in-plane configuration (Jach & Bedzyk, 1993) for structural investigations.

4. Conclusions

This test experiment demonstrated the capabilities of performing ultratrace-element analysis with a third-generation synchrotron radiation undulator as an excitation source. The horizontal sample geometry and air environment gave good results for medium-Z elements. Lower limits of detection should be easily obtained with a better optical set-up. However, in order to make such low detection imits truly useful for any experiment, contributions from parasitic signals must be as low as possible and great care must be taken in sample handling. In particular, it is known that contamination may originate from the detector itself.

New high-brightness synchrotron radiation sources such as ESRF, APS or SPring-8 provide the possibility of performing structural and chemical characterizations of femtogram materials. These sources are also promising for semiconductor applications and, in that sense, SR-TXRF developments are under way at the ESRF.

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