Synchrotron radiation-induced total reflection X-ray fluorescence analysis

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Synchrotron radiation-induced total reflection X-ray fluorescence (SR-TXRF) analysis is a high sensitive analytical technique that offers limits of detection in the femtogram range for most elements. Besides the analytical aspect, SR-TXRF is mainly used in combination with angle-dependent measurements and/or X-ray absorption near-edge structure (XANES) spectroscopy to gain additional information about the investigated sample. In this article, we briefly discuss the fundamentals of SR-TXRF and follow with several examples of recent research applying the above-mentioned combination of techniques to analytical problems arising from industrial applications and environmental research.

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1. Introduction

The ability of X-rays to undergo total reflection was experimentally discovered in the 1920s by Compton ([1] reprinted in [2]), who observed that the reflectivity of a flat target increased at angles below $\sim 0.1^\circ$. However, it took almost 50 years until Yoneda and Horiuchi [3] in 1971 realized that this effect could be used to enhance the sensitivity of X-ray fluorescence (XRF) analysis by putting the sample on the surface of such a flat reflector. Subsequently, this technique was refined by Wobrauschek in his PhD thesis [4] followed by several authors [5–8] and called “total reflection X-ray fluorescence analysis” (TXRF).

By 1954, Parrat had already used the angle dependence of the intensity of the (totally) reflected X-ray beam to investigate surfaces [9]. But the angular dependence of the fluorescence intensity for angles in the range of the critical angle of total reflection was first observed in 1983 by Becker et al. [10].

Today, TXRF is mainly used for non-destructive surface-contamination analysis in the semiconductor industry and for chemical-trace analysis, as it offers limits of detection (LDs) in the pg range for excitation with X-ray tubes and even in the fg region if synchrotron radiation (SR) is used. The effect of the angular dependence of the fluorescence intensity is used non-destructively to investigate surface impurities, thin surface layers and multi-layer structures and is called “grazing incidence” or “glancing incidence” (GI) XRF [11]. Recent reviews about TXRF and GI-XRF have been provided by Wobrauschek [12] and von Bohlen [13].

The use of SR is highly beneficial for TXRF and for angle-dependent XRF in general, because its properties (e.g., high intensity, linear polarization, small source size, and natural collimation) make it ideally matched to the requirements of these techniques. The first SR experiments were published in 1986 by Iida et al. [14] followed by results of several other authors [15–17]. A recent review on SR-TXRF analysis was given by Strel et al. [18].

The sensitivity of SR-induced TXRF (SR-TXRF) is several orders of magnitude greater than what can be achieved using conventional sources (e.g., X-ray tubes) [12,16,19–24]. Furthermore, if the SR is monochromatized with a high-resolution crystal monochromator, instead of a wide band pass system such as a multilayer, the technique can be extended to X-ray absorption spectroscopy (XAS) to gain chemical information on a specific element of interest [25–29]. Monochromatization results in a flux reduction of about two orders of magnitude, but it is still sufficient

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for X-ray absorption near edge structure (XANES) analysis at ppb level [25,26,30,31]. This allows an extension of XAS to:

- (1) the trace-element level in droplet samples where only small amounts are available [25,26]; and,
- (2) the investigation of thin-layered materials and implantations utilizing the GI-XRF set-up.

In the latter case, even extended X-ray absorption fine structure (EXAFS) analysis is possible, where the investigation of the fine structure of the absorption coefficient allows determination of parameters related to the local atomic structure of the sample. The combination of GI-XRF and EXAFS analysis therefore allows the characterization of the dopant in ultra-shallow implants, distinguishing contributions from the topmost and deeper regions. Over the past two decades, the combination of GI-XRF and XAFS analysis was successfully applied to various analytical problems and has been reviewed by several authors (e.g. [29,32–34]).

SR-TXRF has already demonstrated capabilities for ultra-high sensitivity that exceeds what can be done with conventional TXRF by several orders of magnitude. However, the advancements made in vapor-phase decomposition (VPD) TXRF have improved the effective sensitivity of this technique to compete with SR-TXRF. Furthermore, VPD-TXRF measurements can be performed within the semiconductor factory, making this the technique of choice for semiconductor-metrology applications. However, the collimation and the tunability of SR enables SR-TXRF to be used for XANES studies as described here, even EXAFS at the higher concentrations, as well as non-destructive depth-profiling studies. This is a promising aspect for future SR-TXRF

studies, as this allows chemical speciation at trace levels in and on surfaces, which is extremely difficult or even impossible to achieve with other techniques.

2. Fundamentals

2.1. TXRF analysis

As mentioned above, TXRF is mainly used for surface-contamination analysis in the semiconductor industry and for chemical-trace analysis, as it offers excellent LDs and simple sample preparation. In addition to studying substrates, such as silicon wafers, directly, small quantities of solutions or suspensions can be dried on sample carriers, which show sufficient optical flatness (e.g., silicon wafers, quartz or Plexiglas reflectors). During the drying process, the residue on the surface of the reflector forms a very thin sample. Subsequently the sample is excited under glancing angle (below the critical angle of total external reflection) and the emitted fluorescence radiation is collected by an energy-dispersive detector. Fig. 1 shows a typical experimental arrangement.

The main advantages of the TXRF set-up are the following.

- Due to the total reflection of the incident photons, only a very small part of the primary beam penetrates into the sample carrier. This leads to a dramatically reduced spectral background contribution, which originates from scattering on the substrate.
- The incident beam is totally reflected from the sample carrier and the sample is excited by both the incident and the reflected beam, resulting in a doubled fluorescence intensity.

Figure 1. (adapted from [21]). Typical experimental set-up for TXRF analysis.

- The extreme grazing incidence geometry allows the detector to be placed very close to the sample surface. This results in a large solid angle for the detection of the fluorescence radiation.

As a consequence, the sensitivity in TXRF analysis is very high and the LDs are improved by several orders of magnitude when compared to conventional XRF analysis. Furthermore, the angular dependence of the fluorescence radiation for angles in the range of the critical angle of total reflection can be utilized to investigate surface impurities, thin near-surface layers, and even molecules adsorbed on flat surfaces.

The theoretical basis for TXRF can be derived using formalisms analogous to the theory of light optics. In the following, we present only a brief summary, and details can be found in the references [21,35–37].

One starts with the interaction of an electromagnetic wave hitting the interface between vacuum and a medium with complex index of refraction, n , as shown in Fig. 2. The calculations are based on classical dispersion

theory and assume a perfectly flat interface between the two media. Although a real reflector surface shows a certain roughness on a microscopic scale, experimental results have shown that this approach gives good agreement with theory. For X-rays, medium 2 (the reflector material) has a smaller index of refraction than vacuum (or air), therefore the refracted beam is deflected towards the boundary (which is contrary to usual light optics).

An important aspect of TXRF is the interference of incident and reflected beams above the reflector surface. The superposition of the plane electromagnetic waves results in a variation of the intensity depending on the distance above the surface described as a standing-wave field. This is in contrast to standard XRF analysis where the intensity of X-rays is assumed to be constant in the vacuum and exponentially decreasing in the solid. To first order, in TXRF or GIXRF, the strength of the primary beam appears as a standing-wave field above the surface of the reflector with a periodic intensity

Figure 2. Optical paths of incident, reflected and transmitted beams at the interface of two media. The refraction index of medium 1 (usually vacuum or air) is larger than that of medium 2 (the reflector material).

Figure 3. (adapted from [38]). The interference zone (standing wave field) between the incident (E_0) and the reflected (E_R) plane waves with wavelengths λ showing nodes and antinodes with a period D .

variation (Figs. 3 and 4), whose period is a function of the angle of incidence and the wavelength of the radiation. The distribution of the nodes and antinodes above the surface (i.e. the radiation intensity within the wave field) is given by [21,38]:

$$I(\varphi_I, z) = I_0(1 + R(\varphi_I) + 2\sqrt{R(\varphi_I)} \cos(2\pi z/a - \phi(\varphi_I))) \quad (1)$$

Here, I_0 is the intensity of the primary beam, which is assumed to be constant. R is the reflectivity of the substrate, z is the height above the surface of the substrate and the argument of the cosine represents the phase difference of the incoming and reflected waves (the travel distance $2\pi z/a$ and a phase shift Φ). This phase shift occurs only in the region of total reflection ($\Phi = 0$ for $u_I > u_{\text{crit}}$) and is given by:

$$\phi(\varphi_I) = \arccos(2(\varphi_I/\varphi_{\text{crit}})^2 - 1) \quad (2)$$

Fig. 3 shows a sketch of the geometry – the prism-shaped volume defined by incoming and reflected beam is filled with nodes and antinodes each separated by distance D . For small angles, D is given by:

$$D = \frac{\lambda \sin(\varphi_I)}{1 - \cos(2\varphi_I)} \approx \frac{\lambda}{2\varphi_I} \quad (3)$$

In Fig. 4, examples of the intensity distribution above (and below) the reflector surface are displayed. As shown in Equation (3), D changes with the incident angle (and the energy of the incident radiation, which is assumed to be constant here). For an ideal surface (reflectivity = 1), the intensity varies between 0 and four times the intensity of the incident radiation (at nodes and antinodes) for angles below the critical angle of total reflection. For smaller reflectivity values ($R < 1$), the maximum intensity is decreased to values smaller than

the four-fold intensity of the primary radiation. Furthermore, it can be seen that the intensity below the surface follows the well-known exponential decay. However, as the boundary condition at the interface has to be satisfied, the intensity at the surface varies dramatically with the angle of incidence. This means that the penetration depth, defined as the depth where the intensity of the penetrating beam is reduced to $1/e$, also changes significantly with angle.

Since, the intensity of the fluorescence radiation emitted by atoms on or in the reflector surface is directly proportional to the field intensity of the standing wave, the angular dependence of the fluorescence radiation may be used to probe the elemental composition of the sample in depth and thus provide for non-destructive determination of concentration depth profiles as well as analysis of layered structures and of nanoparticles on the surface of the reflector.

The analysis of nanoparticles has resulted in further developments in the theoretical understanding of this phenomenon that we discuss in the next sub-section.

2.2. Angle-dependent TXRF or grazing incident XSW analysis and the influence of coherence length

The increasing interest in nanoparticles and related research during the past few years led to studies investigating the applicability of TXRF or grazing-incidence X-ray standing wave (XSW) measurements for the analysis of nanoparticles on surfaces. This method is also called XSW analysis because it utilizes the standing-wave field and the nodes and antinodes of the field intensity above the reflector surface (see Figs. 3 and 4).

Within the prism-shaped intersection volume comprising the region of overlap between the incoming and the reflected beam, the interference fringes show a

Figure 4. (from [12]). X-ray intensities above (within the standing wave field) and below a thick Si flat calculated for different angles of incidence. It can be seen that the dependence of distance D between nodes and antinodes is a function of the incident angle. Inside the medium, the intensity decreases as a function of the refraction angle. Calculated for Mo-K α radiation; the critical angle is at 1.8 mrad.

periodic intensity distribution normal to the surface ranging from 0 to a four-fold intensity increase relative to the primary radiation. If a (thin) sample is placed within this standing wave field, its atoms are excited and emit XRF according to the field-intensity distribution. By changing the angle of incidence (or the energy of the exciting radiation), the location of nodes and antinodes above the surface – and therefore inside the sample – is changed, allowing the selective excitation of different parts of the sample. For thicker samples [i.e. samples thicker than several node-antinode periods D (see Fig. 3)], the field intensity is averaged to give twice the intensity relative to the primary beam resulting in the well-known two-fold XRF intensity emitted by the sample in standard TXRF measurements utilizing a fixed angle of incidence.

A typical experiment is performed by collecting an XRF spectrum at each angle while tuning the angle of incidence with high accuracy and resolution (step size $\sim 0.001^\circ$) from 0 across the critical angle of total reflection. Each fluorescence spectrum is then analyzed by determining the intensities of the elements of interest (usually of the substrate element and the element or elements in the nanoparticle or layer). The resulting values are plotted *versus* angle to give the intensity profiles. From these profiles, the respective sample parameters (particle size, layer thickness) can be evaluated by an iterative fitting procedure on the basis of modeling calculations using the modulated intensity distribution above the reflector as an extremely fine dynamic ruler [11,21,39–41].

Recently, von Bohlen et al. [42] showed that the influence of the coherence length of the exciting radiation must be considered, as it significantly influences the standing-wave field above the reflector surface. When the finite coherence of the incident X-rays is taken into account, the number of nodes and antinodes in the intersection volume of the incident and reflected beam becomes limited. The volume right above the reflector

surface, which contains interference fringes, is therefore much smaller than the whole intersection volume and the height above the reflector surface to which a sample can be probed by the XSW method is dramatically reduced. The intensity distribution in the remaining (major) part of the intersection volume where no interference between incoming and reflected beam is possible then just consists of a constant two-fold intensity relative to the primary beam with no modulation as a function of angle (Fig. 5).

In their study, von Bohlen et al. [42] presented calculations performed for different coherence lengths and a set of samples modeled using various parameters, which show the influence of a finite coherence length on angular profiles of nanoparticles on a reflector surface. Since the longitudinal coherence length is a function of the source bandwidth ($\Delta\lambda/\lambda$) and the spatial (transverse) coherence length depends on vertical slit width and distance between slit and sample, the high flux and natural collimation of a SR source allows small slits (typically $<100\ \mu\text{m}$) and monochromators with high spectral resolution ($\Delta\lambda/\lambda \sim 10^{-4}$), dramatically reducing spatial and energy divergence, which, in turn, increases the longitudinal and transversal coherence lengths, thus enabling a wide range of nanoparticle sizes to be studied.

2.3. SR-TXRF analysis

Various X-ray sources can be used for TXRF analysis showing a multiplicity of properties. To demonstrate the advantages of SR as excitation source for TXRF, we show its influence on the LDs. The LD for XRF analysis is defined as follows:

$$LD = \frac{3 \cdot \sqrt{N_B}}{N_N} \cdot m_{\text{sample}} \quad \text{or} \quad LD = \frac{3 \cdot \sqrt{I_B}}{S} \cdot \frac{1}{\sqrt{t}} \quad (4)$$

where N_N and N_B are the net and background counts respectively, m_{sample} is the sample mass, I_B is the background intensity, S is the sensitivity (equal to net intensity I_N divided by the sample mass) and t is the

Figure 5. As Fig. 3 but considering the finite transverse coherence length of the X-ray beam causing $b < B$. Only a small volume close above the reflector surface contains interference fringes, the major part is filled by non-modulated double intensity of the non-interfering exciting and totally reflected X-rays ($\Rightarrow h < H$).

measuring time. It is obvious from Equation (4) that there are three possibilities to improve the LDs:

- 1) increasing the sensitivity S (I_N/m);
- 2) reducing the background; or,
- 3) increasing the measuring time, which is limited for practical reasons.

Net intensity I_N is proportional to the intensity of the exciting radiation. Using SR with its high flux is therefore advantageous in comparison to using X-ray tubes. A further increase in sensitivity can be attained by using a tunable excitation source, which enables adjustment of the exciting energy just above the absorption edge of the element of interest, resulting in optimized excitation conditions for this element.

Apart from using total reflection geometry to reduce the spectral background (and doubling the fluorescence intensity), another possibility to reduce the background is to decrease the scatter contributions from the sample itself by utilizing linearly polarized primary radiation [43,44]. Due to the anisotropic emission characteristics of the scattered radiation based on the classical dipole oscillator emission, it is advantageous to place a detector in such a position that only the isotropic emission of the fluorescence signal is detected – hence the combination of TXRF with polarized radiation leads to a lower background. Further, the use of monochromatic primary radiation improves the background conditions because only photons of one specific energy are scattered.

All these improvements can be accomplished when using SR. The intense beam with a continuous spectral distribution from photon energies in the infrared region to high-energy photons as well as the linear polarization in the orbit plane and its natural collimation are features best suited to excitation in total reflection geometry.

2.4. SR-TXRF-XAFS analysis

In past decades, a few experimental studies were performed utilizing the combination of TXRF and XANES, showing the applicability of the method to several analytical problems (e.g., [25,26,30,31]). As mentioned in the introduction, the motivation to utilize this powerful method is to extend XAS, and therefore chemical speciation, to samples that are available in small amounts (e.g., μL of solutions, ng of nanoparticles or aerosols, and thin films) and show elemental concentrations at the ppb level. However, it is well known that fluorescence acquisition of XAS spectra of concentrated samples suffers from self absorption, which causes damping and also broadening of the oscillations.

Some authors have performed quantitative speciation through analysis of XANES spectra by fitting them with analytical functions [45,46]. Another approach deals with corrections of the measured spectra to account for self absorption. Many authors have investigated self-

absorption effects in XAS using fluorescence acquisition depending on the angle of incidence and detection and have proposed correction models [47,48]. Due to irregular sample shape and the very shallow angle of incidence, these models are not applicable to TXRF. The extreme grazing incidence geometry used by TXRF enhances these self-absorption effects due to the extended path length of the incident beam in the droplet. This path length is equivalent to the penetration depth of the incident beam and is therefore energy dependent.

As the energy changes during a XANES scan, the volume where the fluorescence photons originate from varies. Higher absorption means a smaller excited volume and therefore less fluorescence intensity (and vice versa). Consequently, this leads to damping of the oscillations of the absorption coefficient above the absorption edge. The phenomenon is relevant at higher concentrations, such as would be used in the measurement of standards to have a good counting statistic in a relatively short measurement time. Any absorption of the fluorescence radiation within the sample can be neglected because it remains constant during an energy scan.

Recently, Meirer et al. [49] compared measurements with theoretical calculations to investigate the influence of self-absorption effects on TXRF-XANES analysis. The effect of the sample shape as well as the one of different concentrated droplet samples was studied. The experimental results showed clearly a linear correlation of the damping of the oscillations with the total mass of the samples. A simple Monte-Carlo algorithm was developed to simulate the self-absorption effect and the results showed good agreement with the measurements. Their work proposed a rather simple way to study *a priori* the absorption effects that will show up in TXRF XANES and allow the scientist to prepare the sample according to needs (measuring time, acceptable self absorption) of the experiment.

Based on these results, the same authors studied the applicability of the inverse TXRF geometry – the grazing exit (GE) set-up – to XANES analysis [50], because it was suggested that a normal incidence-grazing-exit geometry would not suffer from self-absorption effects in XAFS analysis due to the minimized path length of the incident beam through the sample. Their results proved this assumption and, in turn, confirmed the occurrence of the self-absorption effect for TXRF geometry. However, due to its lower sensitivity (one order of magnitude lower than for TXRF), it is difficult to apply the GE geometry to XAFS analysis of trace amounts (few ng) of samples. However, the self-absorption effect in the TXRF geometry decreases rapidly with smaller sample amounts, so it could be advantageous for future XAFS analyses to measure higher concentrated standard samples in a GE set-up and highly diluted samples in TXRF geometry.

3. Recent research

Recently, the trend in SR-TXRF has clearly changed from the hunt for LDs motivated by semiconductor industry to studies combining the advantages of TXRF with the possibilities offered by angle-dependent measurements and absorption spectroscopy. In the following, we present several selected studies that exploit the possibilities of such combined approaches.

As TXRF has become a routine analysis tool for surface inspection in semiconductor industry, many SR-TXRF studies have been motivated by problems related to semiconductor technology that address more specialized questions. In addition, TXRF has been applied to environmental research utilizing its excellent LDs, the simple sample preparation and the fact that only small sample amounts (in the μL range) are necessary in (SR-)TXRF analysis. We focus on studies in which TXRF has been used to address problems that go beyond the identification of surface elements and address the chemical speciation in particulate samples.

3.1. SR-TXRF analyses of metallic contamination on silicon wafers

For over 30 years, the device density of silicon chips has been increasing, leading to more stringent requirements for surface cleanliness. Metallic contaminations on the surface of Si wafers are known to be a serious limiting factor to yield and reliability of complementary metal-oxide semiconductor (CMOS)-based integrated circuits [51], as they can degrade the performance of the ultra-thin SiO_2 gate dielectrics that form the heart of the individual transistors.

In laboratory-based instruments, TXRF offers LDs down to the $5\text{E}9\text{ at/cm}^2$ [52]. When higher sensitivity is requested, monitoring is typically carried out by VPD of the native oxide layer and analysis by means of laboratory based TXRF and/or inductively coupled plasma mass spectrometry (ICP-MS) at the expense of the loss of the information relative to the location and the distribution of the contamination on the wafer [12,53–56]. To trace the source of the contamination, not only the distribution of the contamination is very valuable but also additional information on the chemical state of the element can be helpful. Understanding the chemical state is an important method to gain information on the source of contamination; if more metallic in nature, the contamination could be particles from wear or shearing of moving parts; or, if the metal is an oxide, corrosion may be taking place. Other species may indicate unexpected chemical reactions taking place.

Another important topic related to this problem is the wafer-cleaning process itself; to remove metal atoms from the silicon surface, in addition to particles and organics, various cleaning solutions are used, including

ultra-pure water (UPW) for rinse steps. Since cleaning solutions, especially UPW, can often be a source of contamination, it is vital to understand how metal species in solution interact with silicon surfaces.

In the following discussion, we present two studies in more detail to show the application of SR-TXRF to the analysis of surface residues on Si wafers that may originate from wafer handling or cleaning using contaminated UPW.

3.1.1. SR-TXRF-XANES analysis of iron contamination on a silicon wafer surface

Recently, Meirer et al. [57–59] investigated the feasibility of a SR-TXRF-XANES analysis to determine the chemical state of Fe contaminations on a silicon-wafer surface that should help in determining the true source of the contamination problem. This type of information is not readily accessible with standard laboratory equipment. The main purpose of the study was to test the method for a contamination issue as it appears in a microelectronic VLSI production fab.

An Si wafer from IBM laboratories showing surface contaminations in the $4\text{E}12\text{ at/cm}^2$ range for Fe has been investigated. The contamination was not intentionally prepared, but resulted from real contamination due to fabrication processes. SR-TXRF XANES measurements were performed at the bending magnet beamline L at HASYLAB using a modified micro-XRF set-up. This set-up allowed TXRF measurements with scanning capability. The wafer with 200-mm diameter was mounted vertically on a custom-made holder on a x,y,z, θ -stage in front of the side-looking detector to allow area scans and scans over the angle of incidence.

3.1.1.1. TXRF and angle-dependent XRF analysis. Prior to the SR-TXRF analysis, the sample was scanned using a laboratory TXRF wafer analyzer (Rigaku TXRF 300) to locate areas of interest showing high Fe concentrations. These areas were scanned at the synchrotron to find points with maximum Fe concentration. At these points, angular and energy (XANES) scans were performed to further characterize the Fe contamination. Fig. 6 shows the Ca and Fe distribution maps recorded in the laboratory (left, whole wafer) and at the synchrotron (right, marked areas A5, A7, A21). For maps recorded with SR-TXRF, the lateral resolution is determined by the size of the collimator of the detector (8 mm diameter) and the vertical beam dimension (1.6 mm). The maps of the elemental distributions for the other elements found on the wafer surface were used to double-check that the correct position of interest was found (e.g., the Ca map shown in Fig. 6). The angular scans and XANES analyses were performed at the positions labeled P5, P7 and P21. Furthermore, LDs of the set-up for Fe were determined by evaluating fluorescence spectra recorded at the points of interest for 100-s lifetime (LD100). The LD100 value was

calculated [see Equation (4)] using the quantification results of the analysis performed with the laboratory tool and was found to be in the range of 750 fg.

The results of the angular scans showed the typical angular intensity curve [60] of the Fe K α fluorescence, indicating that all contaminations at these points were

present as ‘thick’ residues on the wafer surface (i.e. samples thicker than several node-antinode periods of the standing-wave field above the reflectors surface) (see introduction). To give an example, Fig. 7 shows the angular profile recorded at point P5. For the given experimental parameters (exciting energy, angular range, slits) and using Equation (3), the thickness of the contamination can therefore be estimated to be not less than 1 μm . Considering a finite coherence length, this thickness can be somewhat smaller, but the contaminants were definitely not nanoparticles (i.e. $<100\text{ nm}$).

3.1.1.2. TXRF-XANES measurements. The authors compared two methods to extract the XANES spectra from the series of fluorescence spectra recorded at each energy:

- as commonly accepted, the XANES spectra were built summing all counts within the Fe-K α Region-Of-Interest (ROI); and,
- each fluorescence spectrum of the scan was fitted using the QXAS peak-fitting software package [61] and the calculated net intensities (fitted peak areas) were used to generate the XANES spectra.

This comparison was performed to make sure that method a) was acceptable for such low concentrations. The results revealed no significant differences between the scans generated in the two ways mentioned, except an increased signal in the low-energy range of the pre-edge region of the scan generated using the ROI method. This effect can be explained by a contribution of the scatter peak increasing the counts of the Fe-K α ROI at low energies far below the edge. However, as the signal-to-noise ratio was not improved using the peak-fitting method, the authors used the ROI evaluation.

To perform chemical speciation of an unknown sample, XANES spectra are usually compared to spectra of possible reference materials. For a completely unknown sample, a reliable determination of the compound might be impossible and the investigator must be satisfied with a qualitative indication about the oxidation state of the element examined.

In the study presented, 10 common reference iron compounds were measured using the same experimental set-up [25] to be compared with the XANES recorded at the points of interest (high Fe concentrations). The number of standards measured was certainly a key factor in the trade-off between overall time of investigation and quality of the results or even success or failure. Table 1 presents the edge positions determined (first inflection point of the XANES spectrum) and the oxidation states of all measured standards and samples. The Fe oxidation states of the samples were determined by comparison with the standards.

The poor counting statistics for P7 and P21 due to the extremely low concentrations made doubtful the results of further investigations of the Fe compound on the

Table 1. Oxidation states and edge positions of standards and samples

	Compound	Edge position [eV]
FeS	Iron(II)-sulfide	7117
FeCl ₂	Iron(II)-chloride	7119
FeSO ₄	Iron(II)-sulfate	7119.5
Fe ₃ O ₄	Iron(II,III)-oxide	7119.5
FeC ₂ O ₄	Iron(II)-oxalate	7120.5
(NH ₄) ₂ Fe(SO ₄) ₂	Ammonium-Iron(II)-sulfate	7122.5
NH ₄ Fe(SO ₄) ₂	Ammonium-Iron(III)-sulfate	7123
Fe ₂ O ₃	Iron(III)-oxide	7123.5
Fe(NO ₃) ₃	Iron(III)-nitrate	7125
Fe ₂ (SO ₄) ₃	Iron(III)-sulfate	7126
Wafer at P5	Fe(III)	7125
Wafer at P7	Fe(II)	7121.5
Wafer at P21	Fe(III)	7124.5

Table 2. Results and fit parameters of the best fit for P5

	Fe ₂ O ₃ [%]	Fe(NO ₃) ₃ [%]	Fe ₂ (SO ₄) ₃ [%]	R-factor	chi-square
P5	26 $\pm$ 7	48 $\pm$ 8	26 $\pm$ 10	0.001424	0.1478

wafer surface. For P5, it was possible to perform linear combination fits to have an estimation of the composition of the Fe contamination. The three most appropriate standards (Fe₂O₃, Fe(NO₃)₃ and Fe₂(SO₄)₃) were used for a linear combination least squares fitting using all possible combinations (four) of these standards. The results and fit parameters of the best fit (best R-factor) are reported in Table 2 and shown in Fig. 8.

3.1.1.3. Conclusions. The authors could show that SR-TXRF in combination with XAS enabled XANES analysis of wafer-surface contaminations even in the pg region within a reasonable time frame (all measurements were performed within 48 h). The set-up allowed a spatially resolved multi-element analysis of the wafer surface. In addition, the type of contaminations (‘thick’ residuals on the surface) and the oxidation state of iron at three points could be determined. Due to the extremely low Fe concentrations and the limited measurement time, a satisfactory determination of the iron compound could be achieved only for one of the three points (P5) showing the (unexpected) presence of iron nitrate and iron sulfate. All these investigations were done non-destructively using the same experimental set-up.

3.1.2. Nucleation and growth of copper nanoclusters on Si surfaces from UPW solutions

Given the importance of aqueous solutions employing UPW in semiconductor processes, it is important to understand the effect of low levels of metal contamination in these solutions. One such study by Singh et al.

[30,62,63] used a number of SR techniques to study trace-copper (Cu) contamination of silicon-wafer surfaces from deoxygenated and non-deoxygenated UPW solutions – in particular, to understand the role that dissolved oxygen plays in the deposition mechanism.

Since Cu is a fast diffuser in silicon and can quickly reach active device areas [64], it is particularly important to understand Cu contamination from UPW solutions. For Cu contamination during the wet cleaning process, there are two alternative reaction pathways depending upon the pH value of the solution. In lower pH solutions, it is expected that Cu ions are electro-

chemically reduced and deposited on the surface as metallic particles [65]. Conversely, in higher pH solutions, Cu ions are precipitated and included in the oxide layer as a metal oxide/hydroxide [66]. Since UPW has a neutral pH, both reaction mechanisms are available for Cu deposition, so it is expected that other factors (e.g., amount of dissolved oxygen) play an important role in the deposition of Cu on silicon surfaces from UPW solutions.

Experiments were predominantly done at Beamline 6-2 at the Stanford Synchrotron Radiation Laboratory (SSRL), utilizing SR-TXRF, angle-dependent XRF (GIXRF) and

Figure 10. (from [62]). Cu surface concentration as measured by SR-TXRF versus the Cu solution concentration of the contaminated UPW. The samples immersed in deoxygenated water are represented by circles while the samples immersed in non-deoxygenated water are plotted with squares.

TXRF-XANES. From these techniques and atomic force microscopy (AFM) measurements, it was determined that the deposition of Cu varied greatly between oxygenated and deoxygenated solutions. Evidence of metallic Cu-cluster formation on the silicon surface in Cu-contaminated deoxygenated UPW was demonstrated, and the nucleation and the growth of these clusters were explored in more detail.

3.1.2.1. TXRF and angle-dependent XRF analysis. For this study, silicon [100] samples were cleaned and

etched to prepare a clean, hydrogen-terminated surface. Subsequently, the samples were immersed in either deoxygenated or non-deoxygenated UPW solutions contaminated with a Cu concentration in the range 0.01–1000 ppb while holding the dipping time constant at 300 s.

The concentration of the surface Cu contamination generated by this process was determined by measuring these samples with SR-TXRF for a standard counting time of 1000 s. For this measurement time, the authors reported extrapolated LDs of $8.9\text{E}7 \text{ at/cm}^2$ (LD1000) for

Figure 11. (from [62]). Angle scan measurements on silicon samples that were immersed in non-deoxygenated and deoxygenated UPW solutions contaminated with 100 ppb Cu, respectively. The sample immersed in deoxygenated UPW solutions shows evidence of particle growth and a fit indicates that the sizes of the particles are approximately 16.1 nm. However, the sample immersed in non-deoxygenated UPW has a profile indicative of a thin surface layer.

Figure 12. (adapted from [30]). Cu K XANES spectra taken in transmission for reference samples of Cu, Cu₂O, and CuO. Each of these reference samples represents Cu in a different oxidation state. Also shown in dots is the XANES for the silicon sample dipped in 2% HF, spiked with 100 ppb Cu.

the set-up. Fig. 9 shows the SR-TXRF spectra recorded for the silicon samples that had been submerged in 10 ppb and 100 ppb Cu-contaminated UPW solutions.

The Cu surface concentrations of the samples were calculated from the SR-TXRF spectra using the fundamental parameters method [67] (i.e. by evaluating the Cu peak intensities and comparison with a reference sample, in this case a standard Si wafer with known surface concentrations). The results of this quantification are shown in Fig. 10, where the surface concentrations for the contaminated silicon samples are plotted as a function of Cu concentration in solution for both deoxygenated and non-deoxygenated UPW.

Figs. 9 and 10 clearly show that the amount of Cu deposited on the silicon surface strongly depends on whether the UPW has been deoxygenated or not. Below

concentrations of ~15 ppb, more Cu is deposited for non-deoxygenated solutions, but this trend is reversed for concentrations above this value, suggesting a different mechanism for Cu deposition. These findings were further confirmed by AFM measurements performed on selected samples, showing that samples immersed in deoxygenated UPW had particles on the surface at greater density and size (diameters were determined to 16.6 nm) than samples submerged in non-deoxygenated UPW, where Cu is predominantly deposited via precipitation into the surface oxide layer.

While the AFM measurements are useful to measure individual particles sitting above the surface, it is impossible to probe the distribution of impurities that may exist as atomically dispersed species or as a thin layer beneath the surface. In TXRF, this is possible by

Figure 13. (adapted from [63]). Cu K-edge XANES spectra are shown for silicon samples dipped in deoxygenated (right) and non-deoxygenated (left) UPW solutions that were contaminated with 100 ppb Cu. The overall fits are plotted as the solid line.

Figure 14. Fractional contributions for the XANES fits.

evaluating the fluorescence intensity as a function of incident-beam angle; moreover, by using TXRF, the average over a large number of particles is measured and that is useful to determine particle sizes at low concentrations where the particle density is low. Here, such measurements indicated that particle growth in deoxygenated UPW solutions occurs readily.

In Fig. 11, the Cu fluorescence intensity is plotted as a function of the angle for samples immersed in 100 ppb Cu-contaminated UPW. As can be seen, the sample prepared in non-deoxygenated UPW has a profile indicative of atomically dispersed Cu near the surface, where the maximum in fluorescence intensity occurs at the critical angle of 0.16° . However, the sample immersed in deoxygenated UPW has a fluorescence maximum at 0.1° suggesting that Cu particles are present on the surface. A fit of the angle scan for the deoxygenated sample was conducted by using a concentration profile representing particles (spherical caps) sitting on a thin surface layer extending beneath the surface. Further details regarding the concentration-profile model used for this fit are available [62]. The results of this fit indicated the presence of nanoparticles with a mean diameter of $16.1 \text{ nm} \pm 0.3 \text{ nm}$, agreeing well with the AFM measurements.

It was suggested that these differences in Cu deposition occur because, in non-deoxygenated UPW solutions, the growing oxide uses most of the nucleation sites preventing Cu clusters from nucleating. However, in deoxygenated UPW, the oxide grows more slowly allowing for Cu to nucleate mainly as metallic particles. To further confirm this hypothesis, XANES analyses were performed to determine whether Cu is present as an oxide or metal.

3.1.2.2. TXRF-XANES analysis. Fig. 12 shows the Cu 1s absorption spectra of the Cu reference samples (Cu, Cu₂O and CuO) having the oxidation state 0, I, and II, respectively. Also plotted in Fig. 12 is the Cu metal on

silicon sample that was created by intentionally contaminating a clean silicon wafer in 2% HF spiked with Cu at a concentration of 1000 ppb. Since reductive deposition dominates in low-pH solutions, it would be expected that any Cu deposited in 2% HF would be metallic in nature [68]. This is confirmed by the XANES spectrum, which clearly shows that the metal on silicon sample resembles the Cu metal foil spectrum.

Fig. 13 shows the Cu 1s absorption spectra of silicon samples that were contaminated in deoxygenated and non-deoxygenated UPW solutions with an intentional Cu concentration of 100 ppb. Using the reference samples shown in Fig. 12, least squares fits were made using the WinXAS program [69] to determine the percentage contribution of Cu metal, Cu(I) oxide, and Cu(II) oxide.

From these fits of the X-ray absorption spectra, it was determined that the Cu deposited onto the silicon sample surface for the deoxygenated solution was mostly metal in character. By contrast, the Cu deposited onto the silicon sample surface for the non-deoxygenated UPW solutions comprised less Cu metal and more Cu oxides. This provides further evidence that, in the absence of dissolved oxygen, Cu species in UPW solutions will deposit reductively onto the silicon surface, resulting in surface species that are mostly metallic in character. However, the presence of dissolved oxygen inhibits reductive deposition and Cu species are predominantly incorporated into a growing oxide, resulting in surface species that are more oxide in character.

Fig. 14 shows the results of the fits performed for all measured samples, summarizing the percent contributions of Cu metal, Cu(I) oxide and Cu(II) oxide to each fit. From these results the following conclusions can be drawn.

- (1) Samples immersed in deoxygenated solutions have greater metal content, which increases with solution concentration, suggesting that metallic Cu can freely deposit on the surface.

- (2) The corresponding non-deoxygenated solutions had surface species that were a mixture of Cu oxides and metallic Cu, indicating that the presence of dissolved oxygen increases the rate of oxidative deposition for Cu, while inhibiting the reductive deposition of metallic Cu.
- (3) For the samples immersed in solutions containing only 15 ppb Cu, the differences between deoxygenated and non-deoxygenated samples were minimal as both samples have large amounts of Cu oxides, in addition to some Cu metal, implying that, even in the absence of dissolved oxygen, the Cu concentration in the solution is just not high enough to allow for the growth of metallic Cu particles. These results agree well with the data shown in Fig. 10, where the surface concentration for samples submerged in deoxygenated UPW solutions exhibited a precipitous drop when the Cu concentration in the UPW solution was less than 15 ppb.
- (4) This effect is even more pronounced for the samples immersed in UPW solutions with 5 ppb Cu, as these samples had surface species that were predominantly Cu(II) oxide, with some metallic species that are most likely Cu particle embryos, which are unstable in solution.

3.1.2.3. Conclusions. It was demonstrated that the deposition of Cu onto silicon surface from UPW solutions is strongly influenced by the presence of dissolved oxygen. TXRF measurements revealed that there is a critical concentration threshold, above which the amount of Cu deposited in deoxygenated UPW solutions was greater than that of non-deoxygenated UPW. Below this concentration threshold, the reverse is true and the Cu deposited is less for deoxygenated solutions. These differences suggest that the deposition mechanisms are influenced by the presence of dissolved oxygen and that reductive deposition occurs predominantly in deoxygenated UPW, while oxidative deposition primarily occurs in non-deoxygenated UPW. In addition, by measuring the Cu fluorescence as a function of the angle of incidence, the presence of Cu particles on the silicon surface was revealed for samples immersed in deoxygenated UPW, which was further confirmed with AFM images. Since reductive deposition would result in the plating of metallic Cu onto the silicon surface, the presence of particles confirmed that reductive deposition occurs in deoxygenated UPW. Finally, the chemical state of the deposited Cu was determined using XANES analysis. Samples immersed in deoxygenated UPW had a high metal Cu content, demonstrating that reductive deposition is the principal mechanism for deposition, while samples immersed in non-deoxygenated UPW had a high Cu(I) and Cu(III) oxide content, indicating that most of the Cu deposited on the silicon surface was incorporated into the oxide.

3.2. SR-TXRF analyses of atmospheric aerosols

Understanding the effects of aerosols on human health and global climate requires not only a detailed understanding of sources, transport and fate of atmospheric particles but also knowledge about their physical and chemical properties. An analysis of aerosols should therefore provide information about size and elemental composition of the particles. Furthermore, it might be helpful or even necessary to get information about the chemical state of a specific element of interest present in the particles.

Cascade impactors are devices designed for size-resolved sampling of particles according to their aerodynamic diameter. The particles can be directly collected on collector plates, which, in turn, can be used as reflectors for TXRF analysis (e.g., silicon wafers, Plexiglas or quartz carriers). TXRF analysis is especially suitable for the investigation of aerosols because it allows non-destructive multi-element analysis of trace and ultra-trace amounts (ng) of most elements. Multi-element analysis is one of the most appropriate tools for deriving fingerprints of different sources of fine particulate matter and hence enables the origin of air pollutants to be traced. If SR is used as excitation source, the sampling time (i.e. the time needed to collect the aerosols with the impactor) can be diminished because even smaller total sample masses (in the fg region) can be analyzed. This enables more precise time resolution of atmospheric events. Furthermore, the application of SR allows XANES measurements to gain chemical information about a specific element of interest. The oxidation state of elements is of relevance for their environmental impact, as the toxicity [e.g., Cr(III)/Cr(VI), As(III)/As(V)] or environmental activity [e.g., Fe(II)/Fe(III)] of an element may differ considerably depending on its oxidation state. Here, another advantage of SR-TXRF analysis is that the aerosols can be measured directly after collecting them on the reflector surface, so additional sample preparation, which could influence the chemical state of the sample, is unnecessary.

In the following, we present two studies that used SR-TXRF to analyze aerosols with special emphasis on A) high temporal resolution and B) the oxidation state of Fe present in the particles.

3.2.1. Analysis of airport-related aerosol particles with high time resolution using SR-TXRF

Groma et al. [70] reported the analysis of impactor-collected aerosols to monitor local air pollution. Urban air-quality research is an important part of environmental science, since air quality has a strong effect on human health. The air quality at airport areas is of increasing interest due to the dynamic growth of air traffic. The most critical pollutant here is fine particulate matter (PM_{2.5}) (i.e. particles with aerodynamic diameters smaller than 2.5 µm) – originating from the emissions of

aircrafts, ground-handling vehicles and passenger-related cars [71]. There is strong evidence that PM_{2.5} causes more severe health effects than particles with larger aerodynamic diameters [72]. Another reason why the study focused on aerosols with smaller-sized particles (0.25–4 µm aerodynamic diameter) was that larger particles naturally occur at lower concentrations (particles/m³). To allow statistically significant evaluation of these larger particles, longer sampling times would have been required – preventing measurements with a time resolution in the range of aircraft movements. However, the possibility to perform a multi-element analysis with a high temporal resolution (≤ 20 min) was an important point for the investigation of the aerosols to identify potential particle sources, so short collection times were necessary, and required special instrumentation and a highly sensitive analytical technique. Size-fractionated aerosol samples were collected on silicon wafers using a seven-stage May cascade impactor and were analyzed by means of SR-TXRF using the set-up installed at beamline L at HASYLAB, Hamburg, Germany [25,73]. This approach allowed quantitative determination of ultra-trace concentrations (pg/m³) of most elements from samples collected for less than 20 min, while retaining the full size resolution of the impactor. The sampling and trace-element analysis were performed at airport sites (Budapest Airport) near sources which show high spatial and temporal variability.

3.2.1.1. Results. Elemental concentrations in the samples were calculated based on the SR-TXRF fluorescence spectra using Cr as internal standard. LDs achieved for 20-min sampling time ranged from ng/m³ for the light elements (Al, Si) to pg/m³ for the medium Z elements (Rb and Sr) in the present matrix (see Table 3). The LDs were calculated for 100 s measuring time (LD100).

Aerosols were collected at three different sites at the airport (runway, Terminal 2 (high traffic) and Terminal

1 (low traffic)) in four different size fractions and were analyzed with respect to the elemental composition of each size fraction. The quantification of the elements found in the samples was performed using the fundamental parameter method [67] (internal standard: Cr). To trace the particle sources, the results of the quantification were discussed in three different aspects:

- (i) magnitude of concentration values at different sites;
- (ii) typical elements at different sites; and,
- (iii) size distribution.

The data confirmed facts that were previously expected for typical suburban areas, besides results that showed special characteristics of airport-related aerosols. Aerosols originate from long-range transport, city plume and from local sources, which showed large variability at the airport, since aircraft, ground-supporting vehicles and passenger cars have to be taken into account. The emission characteristics are all different and can be used to identify the sources.

In this study, the authors could identify typical aircraft-related particles from extremely small sampling volumes. Special, aircraft-related particles were detected near the runway and showed high Cu concentrations due to aircraft-brake erosion. Size-fractionated sampling allowed determination of particles unrelated to airport combustion processes (e.g., aerosols of larger size fractions containing Ca, Ti and Fe due to resuspension). Furthermore, elements originating from wood-burning processes (e.g., S and K), which are connected to atmospheric transport, could be identified by comparing concentration magnitudes at different sites. This was possible due to the excellent features of SR-TXRF showing LDs in the range of pg/m³ for 20-min sampling time. This short collection time allowed study of temporal variation (e.g., due to aircraft landing and movement) of elemental concentrations in size-fractionated aerosols.

3.2.2. Characterization of atmospheric aerosols using SR-TXRF and Fe K-edge TXRF-XANES

In this study, Fittschen et al. [74] investigated the elemental composition of atmospheric aerosols using SR-TXRF and determined the oxidation state of Fe in the aerosols by means of Fe K-edge XANES in total reflection geometry.

For the same reasons mentioned in sub-section 3.2.1 above, this study focused on elemental determination according to the particle size with special interest in small aerosol particles [i.e. fine (PM₁₀) and ultra-fine dust (PM_{2.5})]. Furthermore the research focused on lead, which is known for its toxicity [75], and iron, which acts as a micro nutrient for phytoplankton, the basis of marine life.

Since the 1970s, abatement measures for Pb as additive in fuel led to reduced levels in the atmospheric environment [76]. Nonetheless, Pb is again object of

Table 3. Detection limits for 100-s measuring time (LD100) calculated for each element detected in the aerosol particles collected at airport sites

Element	LD100 (pg/m ³)
S	451.3
Cl	282.8
K	107.9
Ca	70.2
Ti	48.7
Cr	23.4
Fe	12.4
Cu	4.5
Zn	3.5
Se	2.6
Br	2.4
Sr	3.4
Pb	5.3

public discussion about its concentration in electronic devices and toys. Iron is the most abundant transition metal in atmospheric aerosols and is transported from the great land masses into the ocean. Iron oxides originating from the Earth's crust mainly contain Fe(III). For marine organisms, the uptake of Fe(II) is much easier than that of Fe(III), so a change in oxidation state is very important. As iron undergoes reactions in the atmosphere [77], it is likely that the oxidation state is different for various particle-size fractions. To achieve a high particle-size resolution, a 12-stage round-nozzle low-pressure Berner impactor covering the size range 16–0.015 μm (aerodynamic particle diameters) was used. The sampling time for the aerosols over the city of Hamburg was kept as short as possible to avoid oxidation of Fe during sampling and to test the feasibility of the method for analysis of aerosols collected during short sample times (<1 h), which enables the detection of changes that may occur due to day and night time and different meteorological conditions. The samples were analyzed at beamline L at HASYLAB, Hamburg,

Germany, using the SR-TXRF set-up with a vacuum chamber and a sample changer [25,73].

3.2.2.1. Results. In this study, the authors used an HP DeskJet 500C inkjet printer to apply a picodroplet containing the internal standard (160 pg Cobalt) onto the collected aerosol following a procedure described previously [78]. Using this internal standard, the elemental concentrations for each size fraction were calculated from fundamental parameters [67]. The Fe K-edge TXRF-XANES measurements were performed before that, to make sure that the application of the internal standard did not change the Fe species.

LDs for 100-s measuring time (LD100) were calculated for all size fractions. The LD100 mean value of all size fractions for Fe was found to be 11.5 pg/m^3 (1-h sampling time), which is in agreement with the results presented in sub-section 3.2.1.1. The LD for Pb (LD100 mean value of all size fractions) was determined to 10 pg/m^3 .

Figure 15. (adapted from [74]). Fe K-Edge TXRF-XANES spectra from 10 aerosol particle size fractions. In addition, the XANES of reference standards Iron(II)-sulfide (FeS), Iron(II,III)-oxide (Fe₃O₄) and Iron(III)-oxide (Fe₂O₃) are shown for comparison. The vertical line at 7123.5 eV indicates the edge position (first inflection point) of the Iron(III)-oxide standard.

The results of the quantification showed that traffic-related particles containing Zn and Pb occur in fine aerosols. The samples collected during night time showed lower concentrations of these elements so proving that Zn and Pb can be related to city traffic. Summation of Pb concentrations over all stages gave bulk elemental concentrations of 5 ng/m³ for samples collected during the day and 2 ng/m³ for samples collected during night. These concentrations are very similar to those reported by Groma et al. [70] (low traffic period) and are the same order of magnitude as the concentrations (1.6–90 ng/m³) determined during a large-scale campaign on post-abatement Pb levels in several urban and rural sites in Germany. In this campaign, the aerosols were collected over a time period of 24 h [79].

To learn more about the redox characteristics of Fe present in atmospheric particulate matter, its oxidation state was analyzed by Fe K-edge TXRF-XANES with respect to particle size. As several studies reported, Fe is photochemically reduced in the atmosphere, so it seemed possible that Fe(II) was enriched in specific particle-size fractions according to its generation. Total amounts of Fe found on the collection plates were low (500–900 pg) but sufficient for XANES analysis by comparison with different Fe standards. All measurements were performed in vacuum and repetitive scans did not show changes of the fine structure, confirming that oxidation of the samples did not occur during the measurements.

Fig. 15 displays the results of the XANES analysis showing that Fe was present in the oxidation state +3 (predominately in the form of Fe(III) oxide) in all collected aerosols and all particle-size fractions. This is in good agreement with other studies, which all found predominately Fe(III) in the aerosol particulates [80–82], although high amounts of Fe(II) were reported in rain and cloud samples [83,84].

4. Conclusion

A clear trend has become evident in the development of SR-TXRF analysis, due to its versatility. The excellent LDs of SR-TXRF can be readily used in combination with absorption spectroscopy, enabling XAS studies of samples available only in small amounts and/or at very low concentrations. Furthermore, samples applied to or naturally found on or in the surface of a reflecting substrate material can be characterized by angle-dependent measurements of their fluorescence. Recent studies have shown that SR-TXRF is especially suitable for analyses utilizing the standing-wave field on top of a reflector surface generated by the interference of incident and reflected beams.

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