Grazing Emission X-Ray Fluorescence: Novel Concepts and Applications for Nano-Analytics

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Angle-resolved X-ray fluorescence spectroscopy gives access to elemental analysis of nanoscaled materials. The two main techniques of this method are grazing incidence X-ray fluorescence (GIXRF) and grazing emission X-ray fluorescence (GEXRF) spectroscopy. Principles of both techniques including main applications are discussed in this Review. The main focus lies on the description of GEXRF technique and its new analytical possibilities in the nano-world.

1. Introduction

Material scientists world-wide use basic X-ray fluorescence (XRF) spectroscopy techniques to quickly, reliably, and noninvasively analyze and quantify the elemental composition of their samples. Especially the minimal amount of sample preparation and the availability of commercial spectrometers made XRF an valuable option in the tool-box of the analyst. The progress in semiconductor industry, also demanding for increasingly sensitive analytical methods, led to the “nano-world” we encounter today. Quickly, new approaches in XRF methodology were required to handle the ever-lower detection limits, leading to total reflection X-ray fluorescence (TXRF), grazing incidence X-ray fluorescence (GIXRF) and grazing emission X-ray fluorescence (GEXRF) techniques. Indeed, the latter two not only give access to an integral quantification result in terms of mass deposition of the different elements but also enable in specific cases the reconstruction of elemental depth profiles in the nanometer scale. Such elemental depth profiles are of major importance for tailoring physical properties, e.g., of semiconductor devices by means of doping, buried interfaces in multilayers used as extreme ultraviolet (EUV) to soft X-ray optics or nanoparticles for catalysis, where the reactivity is dictated by their surface-to-volume ratio. It is noteworthy that the depth ranges probed by means of grazing XRF techniques allow bridging the gap between soft X-ray and electron-based probing techniques, which cover the first few nanometers below the surface, and standard X-ray-based techniques, which explore micrometer ranges. Hence, both GIXRF and GEXRF, are complementary to other nanoanalytical techniques for element-sensitive investigations of depth distributions within a sample. As GEXRF and GIXRF are X-ray probe-based techniques, an ultrahigh-vacuum environment is not mandatory; the electric and magnetic properties of samples can be disregarded and samples can be investigated under in situ conditions.

Although many articles, several review articles (e.g., refs. [1–5]) and textbook chapters,[6–10] are dealing with TXRF and some with GIXRF, literature on GEXRF is still scarce. However, GEXRF presents some unique advantages, such as the flexibility with respect to the excitation source or the detection scheme applied. With GEXRF, ionizing particles or polychromatic, noncollimated radiation can be used, which is especially beneficial for incoherent laboratory instrumentation. If an excitation spot at the micrometer scale is necessary, focusing optics can be applied. With respect to detection, the possibility to record angle-dependent intensity profiles of the XRF signal in a scanning-free manner not only increases spectrometer stability and efficiency but also elegantly allows the combination with chemical-sensitive X-ray absorption spectroscopy (XAS) or the analysis of nanoscaled 3D structures when using the energy-adjustability and superior brilliance of modern third-generation synchrotron facilities.

In Section 2 of this review on GEXRF, we will introduce the concept of angle-resolved XRF (ARXRF) measurements and focus on the process of data analysis for depth profiling. The extraction of actual depth profiles of a sample is an indirect procedure, e.g., by assuming a model of a sample and fitting the experimental curves, making the evaluation and interpretation of the measured data a crucial aspect. Furthermore, we discuss the concepts of GIXRF and GEXRF, where the depth-sensitivity is no longer solely based on the absorption of X-rays but interference effects due to reflection and refraction of X-rays must be considered. We will address the experimental differences between GIXRF and GEXRF and from there on stick to the field of GEXRF. Section 3 is dedicated to the development of GEXRF instruments concerning X-ray sources and detectors, highlighting the various pros and cons with respect to their fields of application. Finally, with the basic concepts discussed, we will show the various sample systems investigated and analytical
results obtained using GEXRF in Section 4. Thus, an insight into new analytical possibilities with GEXRF will be provided.

2. Angle-Resolved XRF

In standard XRF experiments, a sample is irradiated with X-rays, the energy of the incident photons being sufficient to remove a core electron from the elements to be analyzed. In the following relaxation process, the core hole at energy level \( E_0 \) is refilled by an electron from an upper shell of energy \( E_i \), leading to the release of energy \( E_i - E_0 \). This energy can be transferred to an Auger-electron or a secondary photon leaving the atom. Analyzing the energy of the emitted photon gives direct access to the emitting elemental species. The XRF production rate can be described by the Sherman equation. Here, all the fundamental physical cross-sections, probabilities, and attenuation processes are accounted for to predict the fluorescence intensity from a given sample composition based on tabulated fundamental parameters (FP) and setup geometry. This allows direct quantification of elemental mass depositions and/or concentrations based on measured XRF intensities, the so-called FP approach. As often the setup geometry and FPs are not known with sufficient accuracy, quantification is mostly performed by means of calibration using adequate and representative standards as samples and exploiting the nearly linear correlation between concentration or elemental mass deposition and XRF intensity within distinct limits. Either way, the measured signal originates from a specific volume limited by the lateral extension of the incident X-ray beam and the attenuation lengths of incident and fluorescence photons. Attenuation lengths are strongly energy and material dependent and range for hard X-rays typically from a few micrometers in metallic matrices to millimeters in organics. Thus, the investigation of nanoscaled materials is hardly possible because of insufficient spatial resolution and typically strong scattering background from the substrate material limiting sensitivities.

A prominent possibility to circumvent the mentioned challenges is to reduce either the angle of the incident (\( \psi_2 \)) or detected photons (\( \psi_1 \)) with respect to the sample surface. Here, Andermann and co-workers did some early investigations with respect to thin-film analysis in the soft X-ray range. The shallow angles reduce the information depth \( d_i \) according to Equation (1) and thus the scattering background originating from the bulk. In Equation (1), which is written for monochromatic excitation and a homogeneous sample, \( \rho \) refers to the sample mass density, and \( \mu_s \) and \( \mu_a \) to the attenuation coefficient of the sample for the incident photons of wavelength \( \lambda \) and fluorescence photons of wavelength \( \lambda_1 \), respectively.

\[
d_i = \frac{1}{\rho \mu_s} = \rho^{-1} \left( \frac{\mu_s}{\sin \psi_1} + \frac{\mu_a}{\sin \psi_2} \right)^{-1}
\]

If the incident angle \( \psi_1 \) of (sufficiently collimated) X-rays approaches the angle of total external reflection, no radiation except for an evanescent, exponentially damped wave penetrates the sample and propagates along the surface. Thus, there might be a non-negligible chance for X-ray absorption and creation of XRF in the vicinity of the surface. As penetration is confined to the evanescent wave (typically to below 3–5 nm), background signals from the bulk are suppressed. Furthermore, the coherent superposition of the incident and reflected X-rays can lead to an X-ray standing wave (XSW) pattern on the top of the surface or within a thin layer. The XSW is characterized by nodes and antinodes of local X-ray intensity reaching up to four times the intensity of the original beam. Both effects are the reason for superior limits of detection in TXRF, GIXRF, and (with a slightly different physical explanation) GEXRF for surface-near trace element quantification as compared with conventional XRF.

2.1. Depth Profiling

As mentioned earlier, a change in either the angle of incidence or detection leads to a variation in the information depth due to adapted path length of excitation and fluorescence radiation, respectively. Thus, when the information for quantification (the spectra) for various information depths (incident or detection angles) is available, the extraction of sample composition for distinct depth regions becomes feasible within specific limits, as will be discussed later. This principle is the basis of all discussed elemental depth profiling approaches with ARXRF. In practice, for a given sample, fluorescence count rates for various angles are recorded and plotted with respect to the varied angle. Figure 1 shows an example of calculated fluorescence intensities of a 100-nm-thick Fe layer sandwiched in Ga; the stack having a total thickness of 1 \( \mu \)m. We assume a rough interface such that refraction effects and interference of radiation can be neglected. As can be seen, the profiles not only change in intensity but also...
in shape. For increasing depth, the Fe Kα fluorescence (Figure 1, left) is quenched, especially for low angles, due to the increased absorption in the Ga on top. Also the shape of the Ga Kα profiles change. As the sensitivity of the method is especially large for elements close to the surface, the deeper the iron layer, the larger the signal of the gallium layer. Note that in the shown example the total mass deposition of the elements remains unchanged.

Thus, if the angular XRF profiles of a sample can be measured, it is possible to obtain information about the in-depth distribution of the elements by comparing the measurement with simulated intensities of a model sample. This of course implies, that a priori information about the sample is at hand and typically the results can be more specific, the more information is available. That means for the prior example if the principle structure of the sample is known to be a layer of Fe within a 1 μm thick Ga layer, it is relatively easy to fit the thickness and position of the Fe layer, assuming sharp boundaries. On the other hand, the real sample consist of several iron layers, incorporate iron–gallium diffusion layers or even elements not detected by the XRF measurement. Then, different sample compositions are possible, where even a rather strong change in structure leads to only minor changes in the angular profiles. This means that the back-calculation, i.e., the adaption of structural parameters to fit simulated fluorescence profiles to the measurement, is an ill-posed problems, which is one of the main challenges in elemental depth-profiling with ARXRF.

2.2. GIXRF and GEXRF

If an X-ray beam hits a smooth and flat sample surface at shallow angles ψ1, with respect to that surface, total external reflection can occur for ψ1 below the critical angle ψc, as the refractive index for any material is typically below 1 in the X-ray regime. In the case of a well-collimated, monochromatic incident beam, an XSW intensity pattern above the sample surface is formed due to interference with the reflected beam (Figure 2a, top). The nodes and antinodes are aligned parallel to the reflecting interface(s) with a distance of \( \frac{\lambda}{2 \sin \psi_1} \), λ being the wavelength of the incident radiation. The maximum intensity of the nodes will be four times the incident intensity due to the coherent superposition of the two electric-field amplitudes, provided that the reflection is 100%.

In 1954, Parratt described the calculation of the XSW field mathematically with an iterative approach, laying the foundation for the development of the quantitative description of grazing-angle XRR and fluorescence techniques.[23] In 1983, Becker et al. discussed the similarities between grazing-incidence and grazing-emission XRF based on the principle of microscopic reversibility.[24] The principle states that the electric field at any point in space P1 resulting from emission of a source at another point P2 is the same as at P1 if the source was at P1. Thus, in GEXRF geometry, the XRF intensity at the detector position originating from a point source in the sample can be calculated using the same formula as for the GIXRF geometry and using the fluorescence energy as incident energy. This means, the XSW field calculation based on the equations of Parratt[23] can be applied. The equivalency of GIXRF and GEXRF is demonstrated well by the respective equations used for primary fluorescence calculations for monochromatic X-ray excitation (see e.g., [25–27]).

\[
I_{\text{G}1}^{\text{GIXRF}}(\psi_1) = K(\psi_1) \int_0^\infty dz |E(\psi_1, z, \lambda)|^2
\]
\[
I(\lambda) A(\lambda, z, \psi_1) \rho(z) C(\lambda, z) \psi_{1h}^2(\lambda)
\]

\[
I_{\text{G}1}^{\text{GEXRF}}(\psi_2) = K(\psi_2) \int_0^\infty dz |E(\psi_2, z, \lambda)|^2
\]
\[
I(\lambda) A(\lambda, z, \psi_1) \rho(z) C(\lambda, z) \psi_{2h}^2(\lambda)
\]

In Equation (2) and (3), referring to GIXRF and GEXRF, respectively, \( I_0 \) is the intensity of a specific fluorescence line depending on the incidence and emission angles relative to the sample surface \( \psi_1 \) and \( \psi_2 \). \( K \) is a factor including the geometry and efficiency of the setup, the integral is taken over the sample depth \( z \) with 0 being the sample surface, \( E \) is the electric field of the XSW for either the excitation wavelength \( \lambda \) or the fluorescence wavelength \( \lambda_\text{fl} \). \( I(\lambda) \) is the excitation intensity, \( A \) is an absorption factor for the fluorescence (GIXRF) and excitation radiation (GEXRF), respectively, \( \rho \) the sample mass density, \( C(\lambda, z) \) is the concentration of the element i associated with \( I_0 \) and \( \psi_{ih} \).

Figure 2. a) Fe Kα GIXRF and b) GEXRF profiles calculated for a 10 nm thin Fe layer buried at 15, 25, and 35 nm within a Ga substrate (similar to Figure 1) excited with Cu Kα radiation. Zero roughness is assumed. The top sketches show schematically the interference phenomena appearing in (a) GIXRF and (b) GEXRF geometry in a single layer on top of a substrate. The digits in (b), top, indicate the number of reflections.
includes the absorption cross section, transition probability, and fluorescence yield (FY) for the fluorescence production. Thus, the differences in Equation (2) and (3) concern on the one hand the excitation for fluorescence radiation, which is either described by the XSW field for GIXRF or by the intensity of the incident X-rays attenuated by a factor A depending on the sample depth (for GIXRF, this factor is included in the XSW field calculation). On the other hand, in the case of GIXRF, a correction factor A for the attenuation of the fluorescence intensity must be applied, which is already included in the XSW field calculation in the case of GEXRF. Thus, if those damping factors A can be neglected (which is often the case due to the geometry), the main difference lies in the XSW field calculation once for the energy of the incident radiation (GIXRF) and once for the fluorescence calculation (GEXRF).

Although there are several software codes for the calculation of GIXRF profiles based on Equation (2), including fitting experimental data and retrieving structural information of the analyzed sample,[28–30] no published software for GEXRF evaluation is available for standard users so far (simple forward simulations are available online[31]). In principle, an integration of GEXRF profile calculation is straightforward. As mentioned, the XSW field calculation must be adapted, and the different absorption factors A must be considered. Interesting would also be the integration of alternative excitation functions for particles and electrons.

A probably more illustrative description for the interference effects appearing in GEXRF than the one based on the principle of microscopic reversibility is the following: From a microscopic point of view, in GEXRF geometry, first, an XRF photon is emitted by an atom in the sample. In principle, this photon can be emitted into all directions and if there was only one atom emitting radiation and nothing else, we would expect a homogeneous intensity distribution. But if there is a change in refractive index, the radiation must surpass, there is some finite chance for reflection. As shown in Figure 2b top, there could be several possible paths toward the detector for photons of a specific direction. This means in the framework of quantum physics, that the wave function of the photon, which propagates isotropically, can interfere with itself at the detector plane and modifies the possibility of detecting a photon. This is nicely visualized in the scanning-free GEXRF measurements shown later, where single photons are successively detected and the GEXRF profiles are slowly emerging with the reduction of statistical noise—just as in Young’s experiment with single photon or electron sources.

In the following, we will discuss some properties of GI- and GEXRF important for applications. Here, several aspects must be considered: Theoretical sensitivity, the necessity of coherence, geometric restrictions and their importance for spectrometer development—all in view of applications envisioned.

The main difference from a fundamental point of view between GI- and GEXRF (and the respective ARXRF geometries) is the path lengths and absorption of X-rays in the sample. In GIXRF, it is the incident radiation being strongly absorbed close to the surface due to large path lengths, while fluorescence radiation is usually detected at angles close to normal with respect to the sample surface, minimizing self-absorption. In GEXRF, on the other hand, the path length of the fluorescence radiation is large within the sample, leading immanently to more self-absorption within the sample as compared to GIXRF. In addition, the information depth in GIXRF is dominated by the excitation radiation, which means, that the efficiency of excitation is maximized. In GEXRF, on the other hand, many incident photons excite atoms beyond the information depth and do not contribute to the detected XRF intensity. Therefore, and especially if thin layers or elements close to the surface are analyzed, XRF signals in GEXRF are often lower than in GIXRF experiments (cf. the scales in Figure 2). However, the difference is usually not as strong as indicated in the simulation in Figure 2. The shallow incidence angles in GIXRF lead to an excitation footprint spreading over a wide sample surface. This footprint can be much larger than the detector field of view or the sample itself, reducing the number of excitation photons, effectively contributing to the detected XRF signal. In addition, laterally resolved studies with a resolution in the scale of a few micrometers are hardly feasible. As for GEXRF, the incident angle of the radiation allows for much more flexibility. It can be adapted depending on the sample system to maximize the efficiency, while keeping in mind the desired spatial and angular resolution. The actual sensitivity difference strongly depends on the applied X-ray source, setup, and sample system.

As for the excitation beam in GIXRF, spatial and temporal coherence must be sufficient to create the XSW field and make use of the interference effects.[32] Although this can be achieved easily and without too much loss of intensity at third-generation synchrotron facilities, it is a severe challenge for usually divergent and polychromatic laboratory X-ray sources. Here, slit systems and parallelizing and monochromatizing optics are applied at the cost of incident flux. In GEXRF geometry, the coherence limits apply to the XRF detection. Focusing optics can be used in the excitation channel, not only reducing easily the excitation footprint to the μm-scale but also rendering a larger angle of acceptance.

On the other hand, GIXRF setups are usually much more efficient with respect to the solid angle of detection. Typically, fluorescence is detected at close to 90°, allowing for extremely short sample-to-detector distances when using an energy-dispersive detector. For GEXRF setups, the spatial coherence requirements in the detection channel, i.e., angular resolution, substantially limit the solid angle of detection, which is only overcome in the scanning-free approach discussed later. The requirements on temporal coherence are met by the small natural line widths. Thus, no extra high-energy resolution detection is necessary, as long as the major fluorescence lines can be discriminated, which is often already achieved with energy-dispersive detectors. In addition, it also needs to be stressed, that only the GEXRF geometry allows for a completely static setup, while in GIXRF, the incident angle must be scanned due to the coherence restrictions.

Applications of GI- and GEXRF exist in both the soft and the hard X-ray range (examples will be given in the Applications section). The fundamental differences for the user are first of all the efficient excitation of the K-shell of low-Z and K- or L-shells of high-Z elements, respectively. Also, due to the larger scattering and absorption cross sections in the soft X-ray range, lower energies are typically preferable when dealing with nanomaterials, which in conjunction with the larger critical angle, hence reduced requirements on the angular resolution to be achieved, usually translates to increased efficiency. Note, for example, the different widths (inflection point to minimum) of 0.055° and
3. GEXRF Instrumentation

3.1. Excitation Sources

As mentioned earlier, GEXRF measurements can be performed with any kind of ionizing radiation, as the requirements on coherence are necessary in the detection channel rather than the excitation channel. Indeed, experiments using laboratory X-ray tubes and synchrotron radiation [24,27,36–38] and synchrotron radiation [39–42] electrons [33,43–45] or protons [46–48] can be found in the literature. The important characteristics of the source for GEXRF application are: availability and complexity, ionization cross-sections, focusing capabilities, and knowledge about the fluorescence generation function \(P(z)\), \(z\) being the sample depth. The latter is important for quantitative experiments and directly enters the formula for the fluorescence calculation (whole second line in Equation (3) when regarding X-rays and equivalent for particle excitation).

3.1.1. X-Ray Tubes

The first GEXRF experiments, i.e., observation and description of XRF modulation due to refractive index changes related to the sample, were performed to our knowledge by Becker et al. using a 1 kW fine-focus X-ray tube with Mo anode. [24] The authors measured and compared the angular profiles of a polycrystalline germanium sample in GEXRF and GIXRF geometry and concluded their equivalency, theoretically explained by the principle of microscopic reversibility. In the 1990s, most work in the field of GEXRF was done using a high power \((P > 1 kW)\) Rh [27,37,49,50] or Mo [51–54] anode X-ray tube, and only later, a few publications show the feasibility of more compact low power \((P < 1 kW)\) X-ray tubes, sometimes combined with polycapillary lenses [58,53,57]. Clearly, at the cost of simplicity, the high-power tubes allow for much more flux on the sample taking full advantage of the low brilliance necessary in the excitation channel (see Figure 3). However, for increased lateral resolution or angular resolution in a setup with short detector distance, microbeam excitation must be used. Then, the applicable source size of the X-ray generator is limited as well as the maximum available X-ray flux due to power density restrictions in X-ray tubes and low-power microfocus X-ray tubes might become competitive.

3.1.2. Synchrotron Radiation

In contrast to X-ray tubes, synchrotron radiation is less broadly available but offers some unique advantages. Indeed, the flux offered is unmatched by laboratory-based sources and moreover monochromatized radiation is usually provided which can be additionally tuned in energy. The energy tunability does not only allow to optimize excitation conditions for XRF radiation by profiting from the incident photon energy dependence of the photo-ionization cross-section but also to improve the background conditions due to elastic and inelastic scattering contributions or the presence of other XRF lines. The background conditions can be even further improved if the detection is realized in the minimum of the scattering cross-section for linearly polarized light, i.e., within the polarization plane and at 90° with respect to the incidence direction. In combination, these factors allow improving signal-to-background ratios and hence the detection limits. [58,59] Furthermore, synchrotron radiation sources deliver collimated radiation and focusing optics which can be easily combined with grazing emission setups to realize spatially μm-resolved measurements. It signifies a big step for elemental surface maps of contaminant or dopant distribution in terms of location and concentration. The feasibility of mapping in the grazing emission geometry was demonstrated in refs. [59-61]. At synchrotron radiation sources, GEXRF can be combined in
addition with XAS which allows to study, for example, the local electronic structure of implanted dopants.\textsuperscript{[62,63]} Synchrotron radiation sources enhances thus significantly the versatility of possible GEXRF applications.

### 3.1.3. Laser-Produced Plasmas

LPP sources overcome the power density limit of X-ray tubes by intentionally consuming small amounts of target material. This makes them appealing as high-brilliance sources of soft X-rays.\textsuperscript{[64]} Those sources are driven by a high-power laser creating a hot dense plasma on some target. Depending on the plasma parameters and target material, X-rays can be emitted from highly ionized or neutral atoms as well as Bremsstrahlung of high-energy electrons. In addition to the high brilliance of such sources in the soft X-ray range, a major difference to X-ray tubes is the pulsed operation, which in principle could be used for time-resolved studies in cycled systems. There had been some usage of LPP sources for GEXRF in the soft and tender X-ray range for the analysis of Al deposits on Si wafers\textsuperscript{[65]} or carbon–nickel multilayers.\textsuperscript{[66]}

### 3.1.4. Electrons

Light elements can also be analyzed with XRF spectroscopy after electron excitation, e.g., in a scanning electron microscope (SEM). The key advantage is that electron excitation allows limiting fluorescence excitation to the near-surface region, thus an efficient use of the exciting particles can be granted, whereas the application of shallow detection angles leads to a reduced background signal from the bulk (such as Bremsstrahlung of the electron beam). This is achieved due to the reduced information depth, which allows for an enhanced surface sensitivity.\textsuperscript{[67,68]} Another advantage is the preservation of lateral resolution when doing XRF analysis in an SEM. When using large detection angles, the XRF signal is recorded from the whole interaction volume, which can extend laterally up to the µm range within the sample substrate due to electron scattering. However, close to the sample surface, the interaction volume is still narrow and by using the GEXRF geometry, the signal reaching the detector can be limited to this region.\textsuperscript{[44]}

### 3.1.5. Protons

By irradiating a sample with MeV protons rather than electrons, the microbeam properties can be preserved because of efficient ion optics while the spectral background, and therefore limits of detection, are enhanced due to reduced Bremsstrahlung. However, also in particle-induced X-ray emission (PIXE), the analysis of light elements in the vicinity of the surface suffers from a large overall background contribution, which can be enhanced in the GEXRF geometry.\textsuperscript{[46,69,70]} The GEXRF scheme has also been applied to PIXE setups to enable depth-discrimination properties for the analysis of thin films and multilayers.\textsuperscript{[68,69,71]} A possible advantage of using protons for fluorescence excitation with respect to quantification is the fluorescence generation function, which can typically be assumed constant within the information depth.\textsuperscript{[48,71]}

### 3.2. Fluorescence Detectors

#### 3.2.1. Energy-Dispersive Detection

Silicon drift detectors (SDD), which have largely replaced Si(Li) detectors, are nowadays commonly available and offer a sufficient energy resolution to discriminate the XRF signals emanating from different elements within a sample. For GEXRF, this can be highly advantageous as this allows not only recording for each of the elements the angular intensity profile but it allows in principle also for a detailed analysis of the sample under investigation by combining the information of the different XRF lines monitored into a single model describing the sample. Note, however, that for each XRF line and each separate sample matrix in the sample structure, the optical constants need to be accurately known. The rather low energy resolution of energy-dispersive detectors does not automatically reduce the angular resolution as one might think, as the coherence requirements refer to the natural line width of the fluorescence radiation. A more separation of the various fluorescence lines is sufficient. Then, the contribution of the linewidth to the angular resolution is usually negligible and can be estimated from the variation of the critical angle over the linewidth of the studied XRF signal. In a first approximation, the relative change in the critical angle over the linewidth $\Delta \phi$ can be estimated by $\Delta \phi \approx \frac{\Delta E}{E}$, which is for example for the K lines of the 3d transition metals about $5 \times 10^{-4}$.

In the experiment, the angular intensity profiles can be recorded by either rotating the sample or by moving the detector, either on a circle centered on the sample investigated (to preserve a constant solid angle of detection) or in a linear motion perpendicular to the sample surface and starting from the sample horizon to above it. Independent of the approach selected, the XRF radiation is measured sequentially at different grazing emission angles, which can be assessed by geometrical means from the spatially resolved measurement. The quality of the measurement depends on the accuracy and the resolution of the positioning system. Indeed, a good angular resolution, i.e., of the order of a few hundredth degree or even better, is mandatory to resolve the different features in an angular intensity profile at least in the hard X-ray range. The required angular resolution depends on the XRF line energy and the specific sample under investigation; for example, the period of the interference fringes varies inversely with the energy of the XRF line and the layer thickness in the case of layered samples.\textsuperscript{[26]} However, the surface of the SDD is usually too large for the angular resolution required for GEXRF measurements such that slits are necessary in front of the detector in addition to a quite significant distance between the sample and detector. As a result, this factor, which is mainly responsible for the angular resolution achievable, reduces the solid angle of detection, hence the efficiency of a setup. In view of the achievable lowest limit of detection, this aspect was detrimental for a broader use of GEXRF for trace-element measurements.

#### 3.2.2. Wavelength-Dispersive Detection

The necessary collimation of the XRF radiation for GEXRF measurements permits a quite straightforward combination with
wavelength-dispersive setups without being further penalized by their small solid angle of detection compared with energy-dispersive detectors. Indeed, in a wavelength-dispersive spectrometer, the X-ray radiation subject to the measurement is inherently selected in terms of propagation direction by the dispersive element (crystal or grating) which discriminates the emitted X-ray photons by their wavelength. In GEXRF setups using energy-dispersive detectors, the collimation of the XRF signal to achieve an acceptable angular resolution is comparable to the angular acceptance of the diffractive gratings or crystals used in wavelength-dispersive setups such that the relative difference of the detection efficiency between both detection schemes is due to the reflectivity and surface of the diffractive element compared with the detection area of the energy-dispersive detector.

The main advantages offered by wavelength-dispersive setups are the energy resolution, which provides, for certain elements and emission lines, some sensitivity to chemical states, the discrimination capability for neighboring or energetically close-lying XRF lines such as the L-lines of mid-Z elements, good background rejection capabilities due to the physical principle of their energy discrimination and hence improved signal-to-background ratios, and finally their sensitivity toward low-Z elements. Indeed, the sensitivity to light elements was one of the main motivations to develop wavelength-dispersive GEXRF spectrometers as a complement to the grazing-incidence setups used for metallic contamination control. The initial works used a wavelength-dispersive setup based on slits, a dispersive element and a counting detector, which improved the discrimination capabilities of grazing XRF techniques in the low-Z range when using an X-ray tube or performing experiments requiring depth-resolution capabilities. This was followed by GEXRF measurements using a von Hamos crystal X-ray spectrometer with a position-resolved detector, to assess the detection limits of different elements when using synchrotron radiation and to realize depth-profiling applications.

3.2.3. Scanning-Free GEXRF

The possibility of recording an angular intensity profile in GEXRF without scanning through the sample or the detector positions was first demonstrated by means of an imaging plate in 1993 by Sasaki et al. The experiment was designed as proof-of-principle for detection of Kα fluorescence from a Zn monatomic layer in a Langmuir–Blodgett film on a Au substrate. The interferences in the grazing-emission XRF signal are nicely visible on the imaging plate (Figure 4). However, to get a quantitative measurement, the fluorescence profile had to be scanned additionally with an energy-dispersive Ge detector equipped with a slit. A following application was to acquire positional information about radioisotopes on the top of a reflecting surface by recording the interference pattern under grazing-emission conditions of the X-rays emitted during electron-capture processes.

Nowadays, and thanks to the recent developments in detector technology, scanning-free GEXRF setups are being realized with digital position-sensitive detectors. These detectors are advantageous compared to imaging plates in terms of sensitivity, signal-to-noise ratio, dynamic range and linearity in the intensity response. Moreover, some of this type of detectors can offer energy discrimination capabilities such that GEXRF data can be recorded at once for different elements.

In combination with SR excitation, the PILATUS detector was used for applications in the hard X-ray range. While being able to process a large photon count rate, no real energy-resolution is featured. Instead, an energy threshold can be set to omit counting low-energy photons, which helps in reducing straylight background and dark noise. The simultaneous detection of fluorescence photons with higher energies can possibly be suppressed by simultaneously adjusting the excitation energy of the synchrotron beam shortly above the respective absorption edge of the fluorescence line of interest. Also, the PILATUS detector features rather large pixel dimensions of 172 μm, enforcing large detector distances for the required angular resolution of typically below a few hundredths degree. Alternative hybrid pixel detectors exist (see e.g., refs. [84–86]), some of them commercially available, but have not been used for GEXRF analysis so far.

In laboratory setups, where photon densities on the detector are usually lower, charge-coupled devices (CCDs) have been successfully applied for scanning-free GEXRF measurements. Although those detectors are usually applied in an integrating mode, such that the information about X-ray energy is lost, they can also be applied in a single photon detection mode. In this case, on each recorded CCD frame, single photons must be distinguishable. Then, the intensity of the photon signal, which is proportional to the photon energy, and which is usually smeared over several pixels due to charge splitting, can be recovered by software algorithms. This approach provides real energy resolution and allows detection and discrimination of different XRF lines simultaneously, at least in the tendency to hard X-ray range. To date, the probably best-suited detector for scanning-free GEXRF with respect to pixel size (down to 36 μm), energy resolution (145 eV at Mn Kα) and frame rate (up to 1000 Hz) is the pnCCD, which has been used in the investigation of a C-Ni-multilayer in the soft X-ray range. However, for the soft X-ray range, novel sCMOS detectors are promising candidates for scanning-free GEXRF applications. The simple design and handling, fast readout (≥20 Hz) and low noise levels make them clearly superior to conventional CCDs in the single

![Figure 4. Schematic drawing of the scanning-free GEXRF setup used by Sasaki et al. The black lines labeled fluorescent X-ray interference (FXI) originate from Zn Kα of a monolayer of Zn in a Langmuir–Blodgett film on a Au substrate and are recorded with an imaging plate. Reproduced with permission. Copyright 1993, American Physical Society.](image-url)
photon detection mode, so that future application of those detectors can be expected.

Independently on the actual detection principle, the basic idea of scanning-free GEXRF is the dispersion of the angular scale along one dimension of a position-sensitive pixel detector. This approach allows acquiring the angular intensity profile of the XRF radiation in a single measurement at a fixed position of the setup components such that the reduced solid angle of detection per emission angle, which is required for reasons of angular resolution, becomes less detrimental. Compared to GIXRF, the major disadvantage, which is the lower detection efficiency in GEXRF setups, can hence be directly compensated for.\textsuperscript{[79]} Instability effects due to source intensity fluctuations or motor vibrations are avoided. The angular acceptance in the direction along which the emission angle is dispersed is defined by the individual pixels and no slit system is required. The XRF intensity is recorded simultaneously for all covered grazing-emission angles, eliminating any dead time due to motor movements. Especially beneficial seems the concept for laboratory instrumentation, thanks to the possibility to efficiently use the full flux of laboratory sources for XRF excitation on the one hand and the increased detection efficiency and the energy discrimination capabilities of modern detectors on the other hand.\textsuperscript{[38,57,66]}

In a scanning-free GEXRF setup, the covered range of grazing-emission angles, the angular resolution, and the solid angle of detection depend on the sample-to-detector distance, the pixel size in the dispersion direction as well as in the nondispersive direction and also on the footprint of the excitation radiation on the sample. The impact of the latter is usually negligible with respect to the aforementioned factors, but for smaller distances, it has to be regarded as well as the variation of the grazing-emission angle in the detector dimension perpendicular to the dispersion direction. An example of meaningful detector distances \textit{d} and their effect on solid-angle of detection \textit{Ω} and footprint size limits is given in Figure 5. A further factor which could broaden but can usually safely be neglected when assessing the angular resolution is the probed sample depth which varies with the grazing emission angle.\textsuperscript{[67]}

To compute the GEXRF profiles from the recorded measurements, the correct assignment of pixel positions to respective emission angles is crucial. Often, a calibration sample or an internal reference, e.g., the substrate signal if its modification by the material on top is negligible, is used to pinpoint a specific angle (as the critical angle) to a specific pixel position. Also the definition of the whole detector geometry by angle and distance measurements has been proven feasible\textsuperscript{[38]} and is useful if no reference is available. For large distances, the points of equivalent emission angles on the detector surface can be approximated by straight lines and XRF spectra can be created for pixel rows or rectangular areas. In this case, also the solid angle of detection of these areas is usually close to constant and does not distort the GEXRF profile, as in grazing-incidence XRF. However, this might not hold for short detector distances, and the calculation of the solid angle of detection for each angular region might become necessary.

In case of 2D position-sensitive detectors, the position sensitivity in both directions can be exploited to disperse the grazing-emission angles as well as the azimuthal angle, which is defined with respect to the axis contained within the surface plane and pointing toward the detector surface. This 2D information on the dependence of the XRF intensity on both angles is useful for investigations of structured surfaces in two or three dimensions, such as line gratings or periodic patterns of identical nanostructures, as already been shown by means of GIXRF.\textsuperscript{[94,95]}

4. GEXRF Applications

The main properties of GEXRF as compared to conventional XRF are 1) the drastically enhanced detection limits for elements in the vicinity of the sample surface \((10^{-9} - 10^{-11} \text{ g})\)\textsuperscript{[66,96,97]} as compared to conventional XRF \((10^{-6} - 10^{-8} \text{ g})\)\textsuperscript{[98]} and 2) the sensitivity with respect to the sample structure, or more precisely, to the changes in refractive indices within the sample.

In the following, we grouped the various applications of GEXRF measurements into three kinds. For the quantification of impurities on reflecting surfaces, mainly property (1) is exploited. Concerning the applications reviewed, only the standard method\textsuperscript{[8]} based on reference material or internal standards is used and an angular scan is performed merely to check for the best signal-to-noise ratio. Depth profiling of 2D structures as thin layers or multilayers is based on property (2) but with refractive index changes only in the direction normal to the sample surface. In contrast, for the analysis of 3D structures, e.g., nanoparticles or gratings, refractive index changes in two or three dimensions are important and also property (1) strongly contributes to the sensitivity, as the heights of the structures are often in the nanometer range.
4.1. Quantification of Impurities

With the application of GEXRF for trace analysis, it was hoped to overcome limitations of TXRF when analyzing light elements. Namely, energy-dispersive detectors in TXRF instruments featured insufficient discrimination properties below 5 keV, which could be overcome with wavelength-dispersive detectors. Indeed, investigations with such a spectrometer concept have been carried out for the analysis of (metal) contamination on silicon wafers,[55,58,59,97] trace metals in drinking water,[96] and trace elements in organic matrices.[99,100] In Figure 6, the example of GEXRF quantification on a "Jupiter" beer sample is shown. As for quantification, often a single intensity at a specific emission angle is used, the angle-dependent fluorescence intensity must be well known and controlled. The given standard deviations are calculated from three independent measurements and are probably explained by inhomogeneous sample deposition, which is not uncommon for dried residues (see later in the text).

Trace analysis with X-ray excitation was also carried out with energy-dispersive detectors in compact spectrometers, but only a few proof-of-principle studies on 10 μm Ga solutions[55] and certified bovine liver[56] are published. Substrates with a periodic structure were proposed to enhance the sensitivity.[101] Furthermore, trace analysis using electron or proton excitation usually showed qualitatively superior background and detection limits in GEXRF conditions as compared to XRF detection at large emission angles[45,68,102,103] but did not include a thorough quantification. Of course, if analyzing e.g., particles or particle inclusions with electron excitation, it has to be considered that the complexity of the excitation function (the second line in Equation (3), which is rather easily described for X-ray excitation) can introduce severe uncertainties.

A main issue arising for trace element quantification, also for proton or X-ray excitation, where the excitation function is usually rather well-known or even constant, originates from the sample itself. In this regard, Kuczumow et al. attest the GEXRF method serious problems arising for quantification of spin-coated light element contamination[104] and it can be stated that in general substrate and sample preparation need careful consideration.[105] In short, topological and matrix effects are said to be more pronounced in GEXRF due to the prolonged paths of the detected photons within the sample than in other XRF geometries. Therefore, reliable quantification may only be assured for simple, mono-compound contaminants. However, similar problems arise also for TXRF and GIXRF quantification studies, where the long path length refer to the incident beam with an energy above the analyte absorption edge. For these methods, specific sample preparation techniques are currently surveyed within the COST ACTION CA18130[106] to overcome some of those issues and also quantification with GEXRF could benefit from the expected results. Also, knowledge about FPs of light elements is constantly improving,[107,108] which might help in future quantification studies.

Compared to grazing-incidence techniques, detection limits similar[58,59] or one order of magnitude lower[109] were reported. An experimental comparison between TXRF and GEXRF with plate beamguide devices showed, however, that for most elements TXRF presents better detection limits, the difference being of up to one order of magnitude. On a theoretical basis, similar detection limits are expected,[110] the lower detection efficiency of GEXRF setups being expected to be partially compensated by their better signal-to-background ratio with respect to TXRF and GIXRF setups. Other factors to be considered are the photon flux and, especially when focusing optics are used, the photon density on the sample. Indeed, preconcentration techniques of contaminants allows in principle to improve the sensitivity of a GEXRF setup more than the sensitivity of a TXRF or GIXRF setup, as in a GEXRF setup, the irradiated area of the sample surface is smaller than in TXRF or GIXRF setups.[58,59] If the residue of the droplet used for preconcentration fits the irradiated area in a GEXRF setup, the enhancement factor for a GEXRF setup is larger than for grazing-incidence setups.

Figure 6. Grazing-emission XRF profiles of a dried beer sample diluted in galantine on a polycarbonate carrier. The graph shows the strong dependence of the fluorescence signal on the emission angle. Note the change in the critical angle due to the fluorescence line energy. Quantification was carried out by adding an internal standard solution (containing Sn, Sb, or Ga) to the sample before drying and using fluorescence intensities at the isokinetic angles (φi/√2). Results are displayed in the table and compared to inductively coupled plasma atomic emission spectroscopy (ICP-AES) quantification. Adapted with permission.[99] Copyright 1999, Elsevier.

Comparison of results for beer

| Analyte | GEXRF (μg ml⁻¹) | ICP-AES* (μg ml⁻¹) |
|---------|----------------|-------------------|
| Na      | 51 ± 10        | 64 ± 1            |
| Mg      | 102 ± 14       | 78 ± 2            |
| K       | 410 ± 50       | 507 ± 16          |
| Ca      | 53 ± 8         | 38 ± 2            |
| Zn      | <0.015         | 0.020±0.002       |
| Pb      | <0.06          | >0.025            |

*ICP-AES analyses were performed using a commercial JY24 instrument (Jobin Yvon, Longjumeau, France). a tHSD (P=0.99; f=4) = 4.604.
4.2. 2D Samples

4.2.1. Depth Profiling

Probably one of the most promising features of GEXRF (and GIXRF) is the possibility for nondestructive elemental depth profiling with depth-resolving capabilities from the subnanometer to several 100 nm range. The method is not only sensitive to sample composition, but as showcased in Section 2 ARXRF, it is also sensitive to (buried) mass depositions (layer thickness times density) or, if interference effects are present, layer thicknesses, densities, and roughness. Therefore, one of the main application fields is the characterization of thin films. For this purpose, the XRF intensity dependence on the grazing-emission angle has to be measured and fitted with a model of the sample. Following this approach, surface oxidation was studied on pure metals[26,37,111–113] or thermally treated alloys[41,114,115] and nano-films were characterized with respect to composition, film thickness, density, and roughness.[37,51,54,116,117] Furthermore, when studying an interface, additional virtual layers in the sample model used in the back-calculation process can be included, allowing a variation in their composition and/or thickness, to account for possible intermixing at the interface. In this way, GEXRF delivers nondestructive access to the analysis of buried interfaces and diffusion processes.[50,74,118–120] An example is given in Figure 7. Here, Monaghan et al. investigated silicon oxynitride films fabricated with different annealing times. By fitting the GEXRF profiles with a sample model including a virtual silicon nitride layer at the SiO$_2$/Si interface, the authors found a total amount of about $10^{13}$ atoms cm$^{-2}$, which increased with annealing time.[50]

Models used for the calculation of layers or multilayers are provided in refs. [26,27,121-123] and these can be adapted toward fitting experimental GEXRF intensity profiles. Other than that, formalisms used for GIXRF calculations, such as the matrix formalism introduced by Parratt,[23] can be used and adapted toward GEXRF by modifying the energy of interest via the principle of microscopic reversibility as stated in ref. [24]. The numerical calculations can be expanded by roughness models using a distorted wave Born approximation[242] or stack of virtual layers with varying density.[126]

Especially strong are interferences in the GEXRF profiles of multilayer samples consisting of a periodic structure of 2–3 distinct layers and with 15 to several hundred periods. Those kinds of structures are used for EUV or soft XRR and thus feature thicknesses of single layers from several nm to the sub-nm range. The strong interference effect is due to Bragg reflection of the fluorescence photons, which yields rather direct information about layer thickness from the interference angle and interface quality (combination of roughness and interlayer diffusion) from interference contrast. As many equivalent layer periods contribute to the same interference pattern, the samples might be especially suited for laboratory spectrometers with even low-power X-ray tubes or proton excitation[48,57] but complementary synchrotron radiation work is as well being realized.[116]

A similar interference enhancement was used by Tsuji et al. on purpose in a rather original application:[127] the intensity of the Ni-K$_\alpha$ line of a Ni layer deposited on a thick Pt layer was enhanced by sandwiching it with C layers. The angular intensity profile was found to depend strongly on the thickness of the C layers. In principle, this method could thus also be reversed to detect indirectly low-Z layers.

With regard to continuously varying concentration profiles, the angle-dependent depth ranges covered by GEXRF for different typical semiconductor substrates is well suited to characterize the depth profiles resulting from ion implantations realized with energies in the (lower) keV-regime. In this energy range, the typical ion-penetration depths range from several tens of nanometers to at most hundreds of nanometers, which is in line with the depth ranges accessible by means of GEXRF. The tunability of the probed depth region with the grazing angle was hence applied to depth-profiling measurements of ion-implanted samples.[37,42,61] A peculiarity with depth profiling of dopant profiles where the concentration changes gradually is, however, that the local concentration needs to be low enough to neglect depth-dependent changes in the optical constants of the substrate; otherwise, the reconstruction of the depth profile would become nonlinear. Furthermore, during modeling of an angular intensity profile using, for example, an equation as stated in ref. [37], care has to be taken that the solution makes physically sense. The inversion problem itself is ill-posed[37] such that due to experimental and numerical errors either the use of regularization methods[128] or of the maximum entropy method was suggested.[129] Due to measurement statistics, most commonly, an analytical description of the implantation profile is selected to model the experimental data.[42,61,130]

4.2.2. Depth-Resolved Chemical Speciation

GEXRF and GIXRF can be combined with routes offering chemical sensitivity, e.g., fluorescence detected XAS which allows to...
probe the local and electronic environment of specific elements. Together with the angle-dependent probed depth range in the surface-near sample region, GEXRF and GIXRF allow thus for nondestructive depth-resolved absorption measurements.\cite{39,131,133} If a scanning-free GEXRF setup is used at a synchrotron radiation source, a very elegant way of depth-resolved chemical speciation due to XAS in FY mode has been demonstrated.\cite{62,81,82,132} Indeed, the combination of scanning-free GEXRF and XAS measurements allows decreasing the number of parameters which need to be varied sequentially with the incident energy solely. The XAS measurement is performed simultaneously for all grazing-emission angles covered. In general, the combination of GEXRF and XAS allows the differentiation of the absorption spectra originating from different integral sample depth volumes and provides thus access to depth-resolved chemical speciation studies. An example of such a study on a model for all solid-state lithium-ion batteries is provided in Figure 8. Using a PILATUS detector in a scanning-free GEXRF setup, fluorescence intensities of a LiCoO$_2$ electrode–solid electrolyte model interface are recorded while scanning the incident synchrotron radiation energy above the Co K edge. Each pixel row of the detector refers to a different XRF emission angle, and thus information depth. From the FY–XAS spectra in the various pixel rows, the shown EXAFS oscillations can be obtained.

In contrast to XAS studies conducted using GIXRF,\cite{131,133} the advantages offered by combination with GEXRF are a reduced sensitivity toward self-absorption effects\cite{134–137} and a more straightforward definition of the depth volume being probed. In GIXRF, the probed depth range is defined by the energy of incident X-rays, which is being varied in a XAS measurement, whereas in GEXRF, it is defined by the energy of the monitored XRF line, which is constant. Hence, in GIXRF, a combined variation of the grazing incident angle and the incident photon energy and an accurate knowledge on the energy-dependent optical constants is required to guarantee a comparable depth volume probed during a XAS measurement. Furthermore, in GEXRF, the extinction depth of the XRF photons is well below the attenuation length of the incident X-ray photons such that the detected XRF yield depends only on the absorption coefficient of the studied element.\cite{39} Hence, in GEXRF, the probed sample volume, i.e., the number of atoms contributing to the detected XRF yield, does not vary with the incident photon energy and depends solely on the grazing-emission angle selected. The ensuing insensitivity of fluorescence-detected XAS measurements realized in the grazing-emission geometry to self-absorption effects was experimentally confirmed by transmission XAS measurements on thin samples\cite{139} and in comparative XAS measurements in the GIXRF and GEXRF geometries on dried residues,\cite{63} although sample inhomogeneity has also to be accounted for when interpreting the observed differences. When considering the angular regime above the critical angle of total external reflection for the energy of the XRF photons, the probed depth volume for the different emission angles can be assessed by purely geometrical considerations.\cite{81,82,132}

### 4.3. 3D Samples

#### 4.3.1. Nanoparticles

In general, regardless of the excitation conditions, the benefit of GEXRF is that any background signal originating from the bulk volume of the substrate is suppressed. In the case of investigations of nanoparticles deposited on the top of a suitable surface for GEXRF investigations, the consequence is that the XRF signal emanating from the nanoparticles can be measured in principle at almost background-free conditions. Furthermore, the total external reflection on the substrate surface of the XRF photons emitted from atoms within the nanoparticles may interfere on their path toward the detector with XRF photons emitted directly toward the latter. Depending on the difference in the path length, constructive interference then provides in the optimum case a fourfold intensity increase instead of a twofold intensity increase expected for incoherent superposition of the XRF photons emitted via both possible paths. Here, a modulation by the substrate reflectivity may as well contribute to changes in the angular intensity profiles. In case the refractive index of the substrate for the energy of the XRF photons is known, the interference pattern in the angular intensity profile ranging from $0^\circ$ to the critical angle contains information on the size and shape of monodisperse, low surface density nanoparticle distributions without requiring information on the optical properties of the

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**Figure 8.** EXAFS features for different pixel rows (150–154) of the PILATUS detector for a model sample a) without interlayer and b) with Nb$_2$O$_5$ interlayer. Different behaviors at the interface (pixel row 150) can be seen. Reproduced with permission.\cite{82} Copyright 2011, Royal Society of Chemistry.
nanoparticles.\textsuperscript{[83]} It has to be mentioned, that GEXRF probes the ensemble of nanoparticles contained with the excitation beam at once such that averaged information is obtained. No statistics over individual nanoparticles is provided. For particle sizes of few nanometer only, it can be assumed that the atoms emitting the X-ray signal of interest are all in the same plane.\textsuperscript{[26]} For larger nanoparticles, the varying distance of the atoms emitting the XRF signal to the substrate surface cannot be neglected.\textsuperscript{[138]} Depending on the nanoparticle morphology, a varying cross-sectional area, i.e., a changing number of atoms emitting the XRF signal in the direction perpendicular to the substrate surface, has to be considered.\textsuperscript{[83]} It was noticed that the size range which can be most reliably investigated lies in the range between about 10 to above 100 nm,\textsuperscript{[138]} the lower limit being due to limited interference features in the angular intensity profiles, whereas the upper limit is given by the angular resolution of the detection system as the features in the angular intensity profiles get sharper with increasing particle size.\textsuperscript{[83]}

The restriction to low surface densities of nanoparticles is essential to neglect any absorption of the emitted XRF radiation within neighboring nanoparticles. The attenuation of the X-rays propagating at a grazing angle is, indeed, discussed in GIXRF for more regularly distributed nanoparticles.\textsuperscript{[139,140]} Moreover, it has been shown for GIXRF\textsuperscript{[141]} that the surface coverage can impact the angular intensity profiles, although the impact depends on the energy of interest for the grazing XRF experiment and the elemental composition of the nanoparticles. This aspect has to be kept in mind if accurate information on the nanoparticle morphology is to be extracted from the angular intensity profiles. Substrate edges may affect the measurements and data interpretation as well.\textsuperscript{[138]}

In the angular range above the critical angle of total external reflection, the X-ray intensity is proportional to the number of emitting atoms such that for calibrated instrumentation, which allows for quantitative measurements, the number of nanoparticles can be estimated when information on the nanoparticle morphology is at hand.

A further restriction mentioned was the monodispersity. As GEXRF probes the ensemble of nanoparticles contained within the volume where XRF radiation is excited, an average information on these nanoparticles is obtained. In case of deviations from a monodisperse size distribution, combinations of different particle sizes have to be considered in a weighted sum of the intensity profiles resulting from the different size contributions.\textsuperscript{[142]}

Particles and aerosols deposited on a surface or thin films on the top of a substrate have been investigated by means of GEXRF using electrons\textsuperscript{[103,138,143–146]} or with charged particles\textsuperscript{[46,68]} for the excitation of the characteristic fluorescence X-ray radiation. An example by Tsuji et al. is given in Figure 9, where an extended electron probe microanalysis (EPMA) instrument is used for the analysis of an aerosol particle on a Au film.\textsuperscript{[143]} The Au film suppresses the signal from the Si substrate and leads to an enhancement of fluorescence radiation at shallow emission angles, increasing the overall signal-to-background ratio. When using charged particles, these should be small compared to the mean free path of the ionizing particles used to grant a homogeneous excitation of the XRF signal within the nanoparticle volume. This allows then for a more straightforward analysis of the angular profiles recorded and hence a more reliable analysis of the nanoparticle size and shape can be realized.

4.3.2. Structured Surfaces

In the case of random (i.e., nonperiodic) distribution patterns, the influence of neighboring particles is mostly disregarded, but in the case of regular arrays of structures with heights of few tens to hundreds of nanometers, and depending on the shape of the nanoparticles, additional refraction interfaces may have to be considered.\textsuperscript{[147]} The angular intensity profile may present different features which vary with the effective surface density of the arrays investigated.

In the case of well-ordered periodic distributions of particles or structures with lateral and vertical dimensions in the range of few tens to hundreds of nanometers and periodicities in the same range, such as line gratings or periodically repeating identical surface structures, GIXRF measurements showed a sensitivity of the angular intensity profile to the azimuthal orientation of the periodical arrays,\textsuperscript{[94,148]} as is exemplarily shown in Figure 10. This class of samples has until recently not been considered for GIXRF and GEXRF investigations such that novel modeling, computationally demanding approaches are required which take into consideration the surface distribution pattern in terms of height, width, and periodicity in particular. Indeed, calculation approaches of the X-ray standing wavefield based on ray-tracing,\textsuperscript{[149]} the finite element method\textsuperscript{[94,150]} or on many-beam dynamical diffraction theory\textsuperscript{[95]} were presented. Due to the 2D detection inherent to scanning-free GEXRF, recording the 2D

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Net intensities of Al K\(\alpha\), Si K\(\alpha\), K K\(\alpha\), and Ca K\(\alpha\) as function of exit angle for an atmospheric single particle collected on top of a flat Au film (=120 nm) deposited on a flat Si wafer. The excitation of the XRF signals was realized with an electron beam. The use of the Au film on the top of the Au film enabled a detection of Si K\(\alpha\) XRF without contribution from the wafer beneath. Interference effects can only be observed below the critical angle of the respective fluorescence line, whereas above the critical angle only the contribution emitted directly toward the detector contributes to the measurement signal. In this angular regime, a reliable quantification could be performed, whereas in the angular regime below the critical angle, the angular intensity evolution is dictated by the particle shape. Reproduced with permission.\textsuperscript{[143]} Copyright 1999, Elsevier.}
\end{figure}
angular-dependent XRF signals of such samples is straightforward and we expect future developments in this field of application.

4.4. Remarks on Quantitative Depth Profiling

Depending on the targeted accuracy of the GEXRF analysis, either for quantification of impurities, depth profiling or the analysis of structured surfaces, evaluation as compared to the measurement itself becomes (of course) arbitrarily complicated. Let us consider the example of depth profiling, i.e., fitting of a sample model to a (or several) GEXRF profile(s). Qualitative information can already be gained with respect to the present elements and with some experience in the technique, also about a rough structure: Which elements are rather close to the surface? What are roughly the length scales of probably periodic interfaces? What is the quality of the surface? and so on. Actually, this kind of information together with any available a priori knowledge is the starting point of building a sample model applied in following fitting approaches. As here some decent amount of expert knowledge is necessary, this might be one reason why only recently GIXRF (and GEXRF potentially) are becoming commercially available options for already existing spectrometers. Probably, we might see some development in this part using machine-learning algorithms for a “first model” estimation, helping to spread the application of GI- and GEXRF depth-profiling techniques.

5. Combination with Other Methods

To perform X-ray-in/X-ray-out 3D analysis, GEXRF (in contrast to GIXRF) can be coupled with micro-focus excitation. This has been shown with synchrotron sources for the analysis of thin-film electrodes, impurity detection and ion implants and with polycapillary lenses coupled to X-ray tubes for thin metal layers, biological samples and Japanese lacquerware. It has already been stated that GEXRF is also feasible with shallow incident angles, especially, if excitation efficiency of atoms in the vicinity of the surface are investigated and spatial resolution is less critical. Tsujii et al. showed in a number of publications how GEXRF and GIXRF can be combined and how the respective fluorescence profiles, now affected by interference effects in the excitation and detection channel, can be calculated and applied for analysis of thin films, layers, interfaces, and impurities. If the experiment and the calculation are well-controlled, this approach drastically increases depth sensitivity and background-rejection capabilities for surface near regions due to the more exhaustive dataset.

Furthermore, the flexibility in the excitation channel makes GEXRF suitable for complementary measurement modes using particle and electron excitation. It is rather straightforward to implement GEXRF as analytical tool in SEMs. The combined method has been applied to calcium carbonate particles exposed to nitric acid and to metal surfaces and atmospheric particles. Also, a reflection high-energy electron diffraction (RHEED) spectrometer was equipped with a Si(Li) detector for XRF detection at shallow emission angles for additional surface information and by using proton excitation, the elastically back-scattered protons of a multilayer have been recorded simultaneously to the GEXRF profiles.

Finally, there had been an interesting approach in combining GEXRF with atomic force microscopy (AFM). By means of a focused ion beam (FIB), a few µm large pinhole was drilled into the cantilever of an AFM and used for defining the incident X-ray spot on the sample. Shallow XRF detection was applied to increase the surface sensitivity for an yttrium oxide layer.

6. Conclusion and Perspectives

ARXRF spectroscopy is already a useful analytical tool for elemental characterization of nanoscaled materials. Both main techniques, GIXRF and GEXRF, facilitate the analysis of trace elements and elemental depth profiles in a noninvasive manner with low effort in sample preparation. In comparison to...
standard XRF analysis, these techniques exploit interference effects, thus, increasing fluorescence intensity and reducing background signal of the sample. This advantage has already been used to analyze contamination on wafers or within organic matrices, structural and compositional properties of metal (alloy) thin films, e.g., with respect to oxidation, interdiffusion in multilayers, implantation profiles, or nanoparticle shapes. Although a qualitative analysis is straightforward, quantitative analysis is still under development. For both techniques, quantification is more challenging than for standard XRF experiments due to requirements on control of angular axis and solid angle of detection. Also, sample preparation is an important factor for reliable quantification. The precision of depth profiling and quantification will increase with further knowledge in FPs and optical constants (especially in the soft X-ray range).

The focus of this review was laid on GEXRF as we see broader possibilities in experimental developments and, thus, applications. Compared to GIXRF, flexibility in excitation channel allows for more efficient excitation and/or lateral resolution in the μm range or below (e.g., with electron excitation). The novel scanning-free approach with modern detectors for GEXRF, SF-GEXRF, allows for static, compact spectrometers and combination with a variety of existing analytical tools (XRD, SEM, PIXE). A GEXRF extension of already existing laboratory instruments is straightforward, facilitating a broader analytical use. At synchrotron facilities, depth-resolved chemical speciation by combination with NEXAFS/EXAFS is feasible and experimentally less challenging compared with GIXRF.

Also, scattering and diffraction experiments already using 2D detectors seem to be a natural candidate for the combination with SF-GEXRF, providing meaningful sample systems and keeping in mind the different requirements on dynamic range. This could be the case, e.g., for periodically 3D-structured surfaces, where SF-GEXRF has a big potential if 2D ARXRF profiles are being exploited.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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