Combined EPMA, FIB and Monte Carlo simulation: a versatile tool for quantitative analysis of multilayered structures

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Abstract. Electron probe microanalysis and focussed ion beam milling are combined to improve the sensitivity and applicability of depth profiling quantification. With the nanoscale milling capabilities of the ion beam, very shallow bevels are milled by using a special preparation procedure to reduce any curtaining effect and minimize Ga ions implantation. A Ni/Cr multilayered specimen is used to evaluate the depth resolution. The best results are obtained by a well-focussed electron beam offered by a field-emission microprobe. A new evaluation algorithm is presented to quantify the structure in terms of mass thicknesses or if the density is known in terms of real thicknesses. The quantification procedure is based on Monte Carlo simulations where calculated $k$-ratios (calibrated X-ray intensities) are compared to the experimental ones to find the optimal structure. In comparison with an ion milled cross-section, the proposed bevel technique is more sensitive and provides more information about the material’s structure.

1. Introduction
Today, wavelength-dispersive (WD) and energy-dispersive (ED) detectors show excellent properties for highly sensitive measurements due to high peak to background ratios or high output count rates. By moving the beam step by step across small structures variations in the X-ray intensities are detectable although the dimensions of the structures are much smaller than the X-ray excitation volume. With the help of Monte Carlo simulations the local ionisation probability can be calculated in a virtual specimen, leading to the description of a three dimensional function. Laterally averaging this function gives the $\Phi(\rho z)$ function used in well-established quantification procedures for bulk, thin films and even multilayered structures [1]. However, conventional thin film analysis is mainly limited to layers containing elements, which are not present in the surrounding matrix, and limited to depths smaller than the mean free path of the characteristic X-rays [2]. To improve the sensitivity and applicability of depth profile analysis electron probe microanalysis (EPMA) can be combined with a destructive preparation technique, for instance, using a sputtering procedure. One possibility is an in-situ technique similar to Auger depth profile analysis, where X-ray intensity measurements and thin surface film removal by inert gas ions are alternated [2-4]. Another possibility is to scan the beam across the wedge of a sputtered crater. This requires the assumption of a laterally homogeneous sample. First attempts of the crater edge profiling EPMA were successfully applied to heat insulation coatings on glass [5]. The technique presented in this paper uses EPMA in combination with the...
focussed ion beam (FIB) milling. The first development steps have been presented earlier [6]. It has been shown that the FIB preparation technique delivers excellent properties due to the capability of its highly focussed ion beam to mill a precise, well-defined geometry [6]. This property makes the FIB preparation superior to all other sputtering based depth profile techniques and allows the determination of the depth scale by two independent ways. The aim of this work is to improve the depth resolution of this technique by reducing FIB artefacts and by using microprobes with better focussing optics [10] in order to extend the limits of depth profiling in EPMA. Finally, using a well-defined multilayered structure, the sensitivity and resolution of the proposed bevel technique are compared to those obtained from the measurements of a cross-section. In summary, the possibilities and limitations of the new method are evaluated based on the following points: (1) improvements of the FIB milling procedure, (2) theoretical considerations regarding the X-ray intensity profiles and depth resolution for the bevel geometry, (3) influence of the type of electron emitter and spectrometer on the depth resolution, (4) quantification of the multilayered structure, and finally (5) comparison to cross-section analysis.

2. Experiment
To test the technique a NIST certified multilayered sample was used [7]. It consists of nine alternating metal thin film layers, five layers of pure chromium with a thickness of 57 nm interlaced with four pure nickel layers with a thickness of 56 nm. The substrate consists of polished silicon. The thickness of each layer is defined with an uncertainty of 3 - 4 nm.

For the focussed ion beam (FEI Strata 205) preparation of the bevel, the coated wafer was cleaved and fixed on a holder in the vertical direction. The Ga ion beam was focussed on the cleavage plane with angles smaller than 1° relative to the surface of the coating. The bevels were milled by scanning the beam over an area of about 0.5 x 20 µm². The operating conditions were an ion accelerating voltage of 30 kV, an ion current between 300 and 1,000 pA, a dwell time of 1 µs, an overlap of 50 % and a total milling time between 10 and 60 min. The FIB prepared cross-section was performed in a similar manner except that the ion beam was positioned perpendicular to the coating’s surface and parallel to the cleavage plane. All the other conditions were kept the same as described above. For studying the curtaining effect a gas injection system for W deposition was used.

To evaluate the depth resolution of the method the same sample was inserted into three different devices: a W-filament electron microprobe (Cameca SX50), a field emission (FE) microprobe (JEOL JXA8500F) both equipped with WD spectrometers, and a FE scanning electron microscope (SEM) (Zeiss Supra 40) equipped with an ED spectrometer (Thermo Fisher Scientific NSS 302). For all X-ray measurements an electron beam energy of 10 keV was taken. The other measuring conditions like the beam current and the measuring time per analysed point are shown in table 1. For calibration of the X-ray intensities pure standards were chosen. Line scans were performed along the bevel starting from the intact multilayered coating towards the uncovered substrate.

| Instrument         | Beam current (nA) | Measuring time (s) | Type of spectrometer          |
|--------------------|-------------------|--------------------|--------------------------------|
| Cameca SX50        | 100               | 10                 | WDS: PET for Si-Kα and Cr-Kα, LIF for Ni-Kα |
| JEOL JXA-8500F     | 50                | 10                 | WDS: PETJ for Si-Kα, LiF for Cr-Kα and LIFH for Ni-Kα |
| Zeiss Supra 40     | 1                 | 15                 | EDS                            |

Table 1. Measuring conditions used for the different instruments and detectors.
3. Advanced preparation of the FIB-bevel

To get the best depth resolution the angle of the bevel relative to the sample surface must be as small as possible. The interdependence between the angle and the depth resolution can be demonstrated by the following experiment. Bevels were milled under the same conditions with decreasing angle (step width was 0.5°). As can be seen from figure 1 decreasing the angle widens the uncovered layers. It is therefore obvious, that a better depth resolution will be achieved by a line scan across the bevel milled with a smaller angle. However, a limiting factor of the depth resolution is the curtaining effect. At very low bevel angles the milling process causes a pronounced smearing, which looks like a curtain (see figure 1). As a result, the sharpness of the interfaces is lost and the depth resolution worsens.

![Figure 1. FIB induced secondary electron imaging: top view of the milled bevel with decreasing angle from left to right. The specimen is a DRAM structure (STO/Pt/TiO₂/SiO₂ on a silicon substrate).](image)

Below a critical bevel angle the curtaining effect is unavoidable. The reason is the interdependence between the critical bevel angle \( \alpha_c \) and the divergence angle \( \beta \) of the ion beam. If the bevel angle approaches \( \beta \), a part of the ions, indicated by the red arrows in figure 2, digs into the surface of the bevel and causes an irregular removal of the material, which causes the curtaining effect. The question arises whether it is possible to decrease the critical bevel angle and thus reduce the curtaining effect. One possibility is decreasing the ion beam current but this means longer milling time and stability problems of the ion beam positioning.

![Figure 2. Schematic presentation illustrating the curtaining phenomenon. Due to the small bevel angle some ions are digging into the surface and causing an irregular removal of the surface material.](image)
Alternatively, a tungsten mask, a thin film deposited in-situ by the FIB, can be used. By shadowing a part of the ion beam, it decreases the divergence angle of the beam (see figure 3). The efficiency of the tungsten mask is illustrated in figure 4a where a bevel was milled under the same operation parameters with and without a tungsten mask. As a result, the tungsten mask minimizes the curtaining effect.

![Figure 3. Schematic presentation illustrating the influence of a tungsten mask to reduce the divergence angle of the ion.](image)

Furthermore, the curtaining effect can also be reduced by polishing the edge of the cleavage plane using the FIB before milling the bevel. In the polishing mode the ion beam is parallel to the cleavage plane and a low current of less than 100 pA is used. Polishing removes topographical irregularities and small oxide particles, which may interfere with the milling process. The advantage of polishing is clearly seen in figure 4b. The curtaining effect has almost disappeared from the bevel milled from a polished edge (left).

4. Theoretical considerations

4.1. Modelling of the experiment

Due to the relatively large information depth of EPMA the measured X-ray intensity profiles give no direct information on the desired concentration depth profiles. It was shown in a previous work [9] that, in principle, the X-ray intensity profiles can be calculated using Monte Carlo simulations [8]. For the calculations an experiment, which describes an in-situ depth profile technique, was simulated as follows: small amounts of the material are step by step removed from the specimen’s surface by ions and the X-rays of the interesting elements are measured, iteratively. This results in a distribution of
emitted X-ray intensities as a function of sputtered depth (in terms of mass coverage). After each sputtering step the ionisation depth distribution, $\Phi(z)$, is updated based on the structure of the residual material. This is necessary since changes in the elements present in the structure at each sputtering step may lead to large differences in interaction volume. To remove dependencies on fundamental and instrumental parameters intensities are calculated for bulk standards, i.e., the same calibration procedure as in an experiment. These calibrated intensities are described by the $k$-ratios ($I_{\text{unknown}} / I_{\text{standard}}$). Further details have been described elsewhere [9].

A typical simulation result is presented in figure 5. Kinks are visible at each interface. This is a characteristic feature of the method caused by the steep increase or decrease of the concentration at the interfaces. Consequently, the position of the interfaces can be easily identified. The amplitude of the step between two kinks in the $k$-ratio profiles is proportional to the mass coverage of each element. For instance, the increase of the Ni-Kα $k$-ratio is due to a successive excitation of the Ni layer with a simultaneous removal of the upper Cr layer (see figure 6). These results can be also used for the simulation of the bevel technique. In this configuration, instead of measuring X-ray intensities as a function of the sputtered depth, intensities are acquired along the distance of the bevel starting from the surface of the coating towards the substrate. In other words, each sputtering step of the in-situ depth profile technique is equivalent to a lateral step along the bevel. The increase of the Ni-Kα k-ratios on the bevel is equivalently due to a successive excitation of the Ni layers, but it is now caused by the movement of the beam along the uncovered structure from the upper Cr/Ni interface to the lower one. Kinks at each interface are also a characteristic feature of the bevel profile. Finally, it should be also pointed out that the similarities between the two techniques are only valid if a very shallow bevel, i.e., very small angles of about 1° or less, is considered.

![Figure 5](image1.png)

**Figure 5.** $k$-ratio profiles of Ni- and Cr-Kα versus sputter depth (proportional to the distance along a bevel) calculated by means of a Monte Carlo simulation.

![Figure 6](image2.png)

**Figure 6.** Schematic presentation of the bevel technique.
4.2. Definition of the depth resolution
To a first approximation, the k-ratio profiles can be considered as a convolution of the material’s structure with the X-ray excitation volume where the kinks correspond to the steep increase of the concentration at each interface. The differentiation of the simulated curves (figure 7) gives a better understanding of the actual concentration profiles and allows the determination of the depth resolution of the method. The differentiated k-ratio profiles show a similar behaviour as the concentration profiles, steep increases are visible at the interfaces. In a real experiment these steep increases are broadened due to the finite depth resolution of the method. Thus, the depth resolution can be quantified by the transition width, over which the measured signal drops from 84 % to 16 % of its original value.

![Figure 7. Profiles of the differentiated k-ratios (shown in figure 5) by the sputter depth.](image)

4.3. Quantification procedure
In the previous section the characteristics of the k-ratio profiles obtained from the combined FIB-EPMA method were studied using modelling. The next step is to extract from the data the chemical structure of the material. Two possibilities exist for the quantification of the chemical structure. First, a manual step by step procedure based on a thin film algorithm can be applied, where the multilayered structure is successively reconstructed starting with the determination of the composition of the substrate using the k-ratios at the lowest interface (kink). Then, using this composition and the k-ratios from the next interface (next kink) the thickness and composition of the next layer are calculated. This step is repeated until the composition and thickness of all layers are calculated. Further details are described in [6].

The second possibility is to use an automated evaluation procedure, where all the unknown parameters are simultaneously determined from the whole set of measured data. To be more precise in terms of a mathematical description let us define a parameter vector $\mathbf{P}$ consisting of the partial mass coverage $m_j$ ($j = 1\ldots N$) and a data vector $\mathbf{K}$ consisting of the experimental k-ratios $k_i$ ($I = 1\ldots M$). The data vector $\mathbf{K}$ is linked with the parameter vector $\mathbf{P}$ by a set of non-linear equations

$$k_i = f_j(m_1, m_2, \ldots m_j, \ldots, m_N)$$  \hspace{1cm} (1)

The aim is to find a solution $\mathbf{P}^*$, for which the Euclidian norm

$$\|k(P^*) - K^{exp}\|_2 \Rightarrow \min!$$  \hspace{1cm} (2)
or the deviation between $k(\mathbf{P}^*)$ and $K^{\text{exp}}$ is a minimum. Using a non-linear solver such as the Levenberg-Marquardt algorithm an optimized solution $\mathbf{P}^*$ can be iteratively determined from an initial value for $\mathbf{P}$.

5. Results

5.1. Intensity profiles
X-ray intensity measurements of Ni-K\(\alpha\), Cr-K\(\alpha\) and Si-K\(\alpha\) were acquired along the milled bevels of the NIST Ni/Cr multilayered structure using three different devices and detectors: 1) Cameca SX50, 2) JEOL JXA-8500F, and 3) Zeiss Supra 40 (see figure 8).

In general, all the results show the periodic structure of the specimen as expected from the modelling (figure 5). The maxima and minima in each profile have approximately the same values, indicating the uniform thickness of the Ni and Cr layers. A different behaviour is observed for the first Cr maximum after the Si substrate (see figures 8b/8c). This corresponds to the situation where the electron beam is crossing the first interface of Cr/Ni multilayered structure. In other words, at this location the specimen consists in a thin Cr film on top of a Si substrate. Due to the lower atomic number of Si the intensity of backscattered electrons is lower, resulting in a lower emitted Cr-K\(\alpha\) intensity in comparison to the intensities emitted at the other interfaces.

The first Cr maximum is almost disappearing in the profile measured by the tungsten filament microprobe (figure 8a). Furthermore, in comparison to the predicted theory the oscillations are generally smaller and no kinks are visible at the interfaces.

Results from the FE microprobe (figure 8c) show stronger oscillations and kinks are clearly visible at the interfaces. Similarly, the ED $k$-ratio profiles measured by the FE-SEM (figure 8b) also exhibit pronounced oscillations, but the signal is noisier due to the lower intensity.

Both FE instruments deliver well-focussed beams with diameters smaller than 100 nm [10], whereas the tungsten microprobe offers larger beam sizes at the chosen operating conditions. These experimental results demonstrate the influence of beam size on the depth resolution of the combined FIB-EPMA method.

5.2. Determination of the depth resolution
The depth resolution of each instrument was determined using the aforementioned method of measuring the transition width from differentiated $k$-ratio profiles (figure 9). The depth resolution was determined at each interface. The averaged values are listed in table 2, in terms of mass coverages (first column), mass coverages corrected for the uncertainty of the standard (second column) and thicknesses in nm (third column). These values correspond to the depth resolution of FIB-EPMA under the chosen devices and operating conditions. As expected, the smaller beam diameter, produced by field emission instruments, improves the depth resolution of the FIB-EPMA method up to about a few nm.

Table 2. Depth resolution determined by different instruments in terms of mass coverages (first column), mass coverages corrected for the uncertainty of the certified standard (second column) and thicknesses in nm assuming the density of pure Cr and Ni (third column).

|                | $\Delta z /\mu\text{g/cm}^2$ | $\Delta z^\# /\mu\text{g/cm}^2$ | $\Delta z' /\text{nm}$ |
|----------------|-------------------------------|----------------------------------|------------------------|
| Cameca SX50    | 16.8                          | 14.2                              | 16.0                   |
| JEOL JXA-8500F | 8.6                           | 6.0                               | 6.7                    |
| Zeiss Supra 40 | 9.4                           | 6.8                               | 7.6                    |
Figure 8. Line scan measurements of calibrated Ni-Kα, Cr-Kα and Si-Kα intensities across a bevel at 10 keV performed by different instruments: a) Cameca SX50, b) Zeiss Supra 40, and c) JEOL JXA 8500F.
5.3. Quantification

For the quantification of the multilayered structure the measurements from the FE microprobe were taken. All the Cr-Kα and Ni-Kα k-ratios acquired along the bevel were used to create the data vector $K$ (eq. 1). The Si-Kα k-ratios were not used, since the only valuable information about the mass...
thicknesses is contained in the Cr-Kα and Ni-Kα profiles. The unknown parameters described by the structure vector $P$ are the mass thicknesses. The calculated $k$-ratios for the different X-ray lines and sputter depths ($K(P)$) were obtained by means of Monte Carlo simulations. A non-linear solver was used to solve eq. 2 and obtained the optimized solution $P^*$. The optimized thicknesses of each layer are presented in table 3 together with the relative errors. The relative errors are defined as the relative deviation between the nominal and calculated thicknesses. On average the errors correspond to the certification limits of the specimen which are in the order of 7% for Ni and Cr.

**Table 3.** Thickness of each layer and relative deviation with respect to the certificated values.

| Layer n° | Type of layer | Thickness / nm | Rel. dev. /% |
|----------|---------------|----------------|--------------|
| 1        | Cr            | 60.0           | +5.2         |
| 2        | Ni            | 54.5           | -2.6         |
| 3        | Cr            | 56.1           | -1.6         |
| 4        | Ni            | 56.9           | +1.6         |
| 5        | Cr            | 56.3           | -1.1         |
| 6        | Ni            | 54.2           | -3.2         |
| 7        | Cr            | 50.3           | -11.7        |
| 8        | Ni            | 59.8           | +6.8         |
| 9        | Cr            | 52.5           | -7.9         |

To evaluate the potential influence of Ga implantation during the FIB preparation, the Ga-Lα intensity was acquired in the case of the tungsten microprobe measurements. For the calibration a GaAs standard was used. As a result, Ga-Lα $k$-ratios of less than 0.001 were detected at the chosen conditions (see figure 10). This corresponds to approximately less than 0.01 wt% Ga. Thus, FIB-induced Ga implantation can be neglected for the quantification of the above described multilayered structure.

![Figure 10](EMAS2015Workshop_IOPConf_Series_MaterialsScienceandEngineering_109(2016)012014_doi10.10881757-899X1091012014)
6. Discussion

6.1. Cross-section versus bevel technique

Another method to analyse a sample as a function of depth is to prepare a cross-section and performs a line scan across the prepared surface, ideally using a FE electron microprobe or FE-SEM to benefit from the smaller beam diameters (figure 11).

![Figure 11. Schematic presentation of the measurement across the cross-section.](image1)

In comparison to the bevel, the FIB preparation of a cross-section is generally easier, since the curtaining effect is less pronounced (figure 12). To directly compare the depth sensitivity of the two techniques, a cross-section was prepared from the same certified multilayered system from NIST (see section 2). A gold layer was sputtered on top of the structure for protection against ion etching during the FIB preparation. Intensity measurements of the Ni-Kα and Cr-Kα X-ray lines were acquired across the structure starting from the Si substrate (figure 13). The same operating conditions on the JEOL JXA-8500F FE microprobe were chosen as the ones used for the bevel technique, a beam energy of 10 keV and a beam current of 10 nA. A beam drift correction procedure was used. The normalized X-ray intensities are presented in figure 13. The comparison of these profiles with those on the bevel (figure 8c) reveals lower amplitudes in the X-ray profiles along the cross-section. In addition, the interfaces are more diffuse and their exact position is more ambiguous.

![Figure 12. FIB-induced SE image of the milled cross-section of the multilayered structure.](image2)
The quantification of multilayered structures based on X-ray intensity profiles across a cross-section is not established. Apart from the lack of analytical models to calculate the lateral X-ray ionisation distribution, the size and profile of the electron beam become crucial parameters. Assuming a Gaussian beam with a standard deviation of 50 nm and using the nominal thicknesses, simulations were performed using the Monte Carlo programme DTSA-II [11] to better understand the experimental profiles. The simulated profiles are shown in figure 14. To quantify a multilayered structure with unknown compositions and thicknesses, Monte Carlo simulations and a non-linear solver could be combined as presented in [12], albeit the very long calculation times.

Some conclusions can be drawn from the comparison between the bevel and cross-section techniques. It is more challenging to achieve an artefact-free FIB preparation of a bevel, a large milled area with an appropriate surface finish and a small bevel angle. However, this technique has the advantage to be less sensitive to the beam size and beam profile. No further measurement or assumption is needed for the beam diameter. Furthermore, the interfaces, layers and elements present in each layer can be directly determined from the experimental profiles. Finally, the quantification of an unknown multilayered structure based only on X-ray intensities acquired along the bevel can be done by a special thin film algorithm using Monte Carlo simulations and an optimisation algorithm [6].

7. Conclusion
This work shows the great potential of combining EPMA with the FIB specimen preparation. By improving the milling process to reduce curtaining effects (edge polishing or tungsten mask), low bevel angles were achieved. With the focussing capabilities of FE microscopes, a depth resolution of a few nanometres was obtained using the bevel technique. Using an optimisation algorithm based on...
Monte Carlo simulations, the multilayered structure of a reference test material was quantified with an accuracy for the layer thicknesses comparable to the certified values.

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