

Elemental composition and thickness determination of thin films by electron probe microanalysis

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Electron probe microanalysis (EPMA) applies to solid samples of homogenous (bulk) chemical composition and can usually not be applied to structures which are inhomogeneous in the micrometer range such as thin film systems down to a few nm. However, in combination with the established thin film software Stratagem, the thickness as well as the elemental composition of thin films on a substrate can be determined. This has been recently successfully demonstrated for Fe-Ni on Si and Si-Ge on Al₂O₃ thin film systems. For both systems five samples of different elemental composition and a reference were produced and characterised by inductively coupled plasma mass spectrometry (ICP-MS), Rutherford backscattering (RBS), and transmission electron microscopy (TEM) as reference values. Last year, a new and open-source thin film evaluation programme called BadgerFilm has been released. It can also be used to determine thin film composition and thickness from intensity ratios of the unknown sample and standards (*k*-ratios). In this contribution, we re-evaluated the data acquired for the Fe-Ni and Si-Ge systems using the BadgerFilm software package and compared the obtained elemental compositions and thickness values with the results of the Stratagem software and the reference methods. The conclusion is that the BadgerFilm software shows good agreement with the elemental composition and thickness calculated by Stratagem (mostly <2% for both composition and thickness) and with the reference values for two representative thin film systems (<1%–2% for composition and <10%–20% for thickness).

KEYWORDS

elemental composition, EPMA, film thickness, thin films

1 | INTRODUCTION

There are several published studies that prove the capability of electron probe microanalysis (EPMA), in both variants WDS (wavelength-dispersive X-ray spectroscopy) and EDS (energy-dispersive X-ray spectroscopy) detection modes, to determine accurately the elemental composition and thickness of thin films^{1–5} by employing the thin film analysis software package Stratagem.⁶ The Stratagem quantification algorithm was developed by Pouchou and

Pichoir, who initially made significant progress on building models for the standards based and standardless analysis of homogeneous bulk specimens.^{7,8} These models imply the description of the number of ionizations for different depths in the sample, which is called the ϕ (ρz) ionization depth distribution curve. Normally, for the calculation of the elemental composition of an unknown sample, the so-called *k*-ratios (or *k*-values) need to be determined, which are a common parameter for standard-based analysis. It is defined as the peak intensity ratio of a certain line *l* of a certain element *i* after background

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subtraction between the unknown sample and a standard sample, normalized to live time and beam current:

$$k = \frac{I_{i,\text{unknown}}}{I_{i,\text{std.}}}$$

For a pure element standard $0 \leq k \leq 1$. When the k -ratios are used, uncertainties in the atomic data such as the fluorescence yield of a certain X-ray line and experimental uncertainties such as the detector efficiency cancel out. Also, other over- or underestimated corrections which are applied to both, unknown and standard samples, reduce the errors and make the calculated results more reliable.

Pouchou and Pichoir also extended the models and developed methods to analyse thin films on substrates. In this case, different ϕ (ρz) curves need to be calculated for each film and the substrate. In addition, characteristic and bremsstrahlung fluorescence produced in one of the layers can significantly influence the X-ray excitation process in other layer(s), and these effects need to be taken into account. Using these models, it is possible to determine the film mass thicknesses (ρz , in $\mu\text{g}/\text{cm}^2$, or mass deposition) as well as the film(s) and substrate elemental compositions.⁹ By assuming a density of the film, the thickness can be extracted. It was demonstrated that the unconventional way of introducing the film thickness (an easily measurable parameter) into the software results in the overall film density.¹⁰ Particularly for porous films, this parameter is of particular relevance,¹¹ because if related to an assumed skeletal density of the material walls within the film, it will lead to the film porosity. The latter holds true under the assumption that the ϕ (ρz) model does not significantly deviates for this type of geometry (the model assumes 'solid' films), that is, the size of the pores is small enough.

In Stratagem, the k -ratios need to be provided. To improve the accuracy of the calculation of the chemical composition and thickness of the thin layer(s), k -ratios at different accelerating voltages shall be used. The reason for this is that at low acceleration voltages, where the electrons have a small penetration depth, the interaction volume is close to the surface and mainly interacts in the films. With higher acceleration voltages the interaction volume expands further into the sample and, therefore, further into the substrate. The k -ratios of elements only present in the film normally decrease with the accelerating voltage while the k -ratios of the elements in the substrate increase. Once having calculated the k -ratios from the measurements of the unknown and standard samples, the Stratagem algorithm starts fitting the provided k -ratios for different acceleration voltages simultaneously by calculating theoretical k -ratios using the ϕ (ρz) models. Several thin film material systems have been published as being successfully analysed with Stratagem with respect to the determination of their elemental composition and thickness.¹⁻⁵

Recently, Moy and Fournelle¹² published a study and an open-source software package that is also based on the algorithms of Pouchou and Pichoir (PAP⁸), called BadgerFilm. Special care has been taken for the calculation of the Bremsstrahlung fluorescence. Instead of using the rather simple model described in PAP, a full calculation of

the ϕ (ρz) depth distribution algorithm was applied for every energy of the continuous Bremsstrahlung background which contributes to the Bremsstrahlung fluorescence. This program can analyse, besides homogeneous bulk specimens, also thin film systems on substrates. Further studies and refinements of the algorithm for thin film systems and application examples were also published recently by Moy and Fournelle.¹³ The data that need to be provided for the calculation of such thin film systems are the k -ratios of the constituent elements for one or more accelerating voltages.

In this contribution, we re-evaluated the data acquired for the Fe-Ni and Si-Ge systems using the BadgerFilm software package and compared the resulting elemental composition and thickness with the results of the established Stratagem software and other reference methods. It should be noticed that for this comparative study we have used the same measured k -ratios for both layers systems, as reported in Hodoroaba et al.¹⁴

2 | MATERIALS AND METHODS

Two types of layer systems were tested in this work: (i) $\text{Fe}_{1-x}\text{Ni}_x$ on Si substrate and (ii) $\text{Si}_{1-x}\text{Ge}_x$ on Al_2O_3 substrate. Both types of layers were grown by ion beam sputter deposition by KRISS, with five different nominal atomic fractions for each type of layer. For the quantification of the elemental composition and the thickness of the layers also a reference film system of each type of layer system was made available. The atomic fractions of all the films including the references were certified by ICP-AES (Inductively coupled plasma atomic emission spectroscopy) for the Fe-Ni reference¹⁵ and RBS (Rutherford backscattering spectrometry) for the Si-Ge reference.¹⁶ The thickness of all layers was measured by TEM after cross section sample preparation.

The measurements of the EDS spectra were carried out with a Zeiss Supra 40 scanning electron microscope (SEM) being equipped with a Schottky field emitter and a Bruker XFlash energy dispersive X-ray spectrometer of type silicon drift detector (SDD EDS). The primary electron beam current was measured with a calibrated external picoamperemeter. The knowledge of the accurate beam current value is crucial for the quantification.

Because the Al_2O_3 substrate with the Si-Ge film was electrically non-conductive, copper tape was used to contact the Si-Ge film over the side of Al_2O_3 substrate to the SEM stage and thus, avoid charging under electron bombardment.

As reported in Hodoroaba et al.,¹⁴ each sample of both sets of layer systems were measured at five different locations with an area of analysis of $100 \mu\text{m} \times 100 \mu\text{m}$. The following electron beam voltages were applied: 12, 16, 20, 25, and 30 kV for the Fe-Ni/Si system, and 15, 20, 25, and 30 kV for the Si-Ge/ Al_2O_3 system.

For the X-ray lines O K α , Al K α , Si K α , Fe K α , Ni K α , Ge L α the net intensities were determined after background subtraction. Due to the known large uncertainties of fundamental parameters of oxygen, the accurate quantification of the oxygen with EPMA is impossible. Hence, for the analysis of the Al_2O_3 substrate, only the Al K α line has

been evaluated in the analysis and the oxygen has been co-quantified by setting its stoichiometrically to Al.

As already described in the Introduction, the same k -ratios as measured and reported in Hodoroaba et al.¹⁴ for the two sets of thin film systems, $\text{Fe}_{1-x}\text{Ni}_x$ on Si substrate and $\text{Si}_{1-x}\text{Ge}_x$ on Al_2O_3 substrate, were used in this paper to compare the results provided by the BadgerFilm software package with those obtained by Stratagem.

3 | RESULTS AND DISCUSSION

Figure 1 shows the k -ratios exemplary for only one sample of each of the two series of layered systems: (A) $\text{Fe}_{88}\text{Ni}_{12}$ film on Si substrate with the Fe $K\alpha$, Ni $K\alpha$ and Si $K\alpha$ X-ray lines and (B) $\text{Si}_{65}\text{Ge}_{35}$ film on Al_2O_3 substrate with the Al $K\alpha$, Si $K\alpha$ and Ge $L\alpha$ X-ray lines. For the determination of the k -ratios, the reference layer systems provided by KRIS (Fe50Ni50 and Si50Ge50) have been used. It should be noticed the practically identical fits of the k -ratios for both software

algorithms Stratagem (solid lines) and BadgerFilm (dotted lines) for all the X-ray lines. Only for the substrate lines Si $K\alpha$ and Al $K\alpha$, the deviations between the two programmes reach a very few percent. The behaviour of the k -ratios fits for these two thin film systems as illustrated in Figure 1 is representative for all the other samples of different relative compositions.

Once having the k -ratios fitted as in Figure 1 for all the samples, the elemental composition and thickness of all the thin films of the two film system sets could be calculated by the BadgerFilm software. Figure 2 displays the mass fractions for the series of Fe-Ni (A) and Si-Ge (B) films as calculated by Stratagem (in red) and by BadgerFilm (in blue) in dependence on the reference values of Fe (A) and Si (B), respectively. The relative deviations between the results given by the two software packages are insignificant (as shown in the upper panels in Figure 2), smaller than 1%–2%, with only one exception of $\sim 9\%$ higher Si concentration for the $\text{Si}_{20}\text{Ge}_{80}$ film. It should be noticed that the overall measurement uncertainty resulted from the measurement at five locations on each sample, background subtraction,

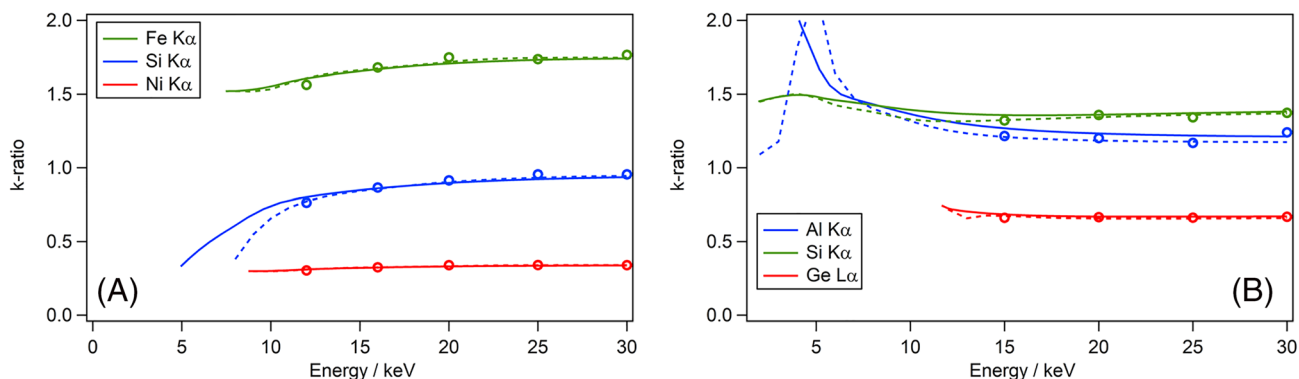


FIGURE 1 Examples of k -ratios in dependence on the acceleration voltage for the two layer-systems: (A) $\text{Fe}_{88}\text{Ni}_{12}$ film on Si substrate with the Fe $K\alpha$, Ni $K\alpha$ and Si $K\alpha$ X-ray lines and (B) $\text{Si}_{65}\text{Ge}_{35}$ film on Al_2O_3 substrate with the Al $K\alpha$, Si $K\alpha$ and Ge $L\alpha$ X-ray lines. The k -ratios resulted from the measured X-ray intensities related to the reference sample Fe50Ni50 film on Si substrate (in panel A) and to the reference Si50Ge50 film on Al_2O_3 substrate (in panel B) are displayed as circles, the StrataGEM fitted curves are shown as solid lines and the BadgerFilm fits are shown as dotted curves.

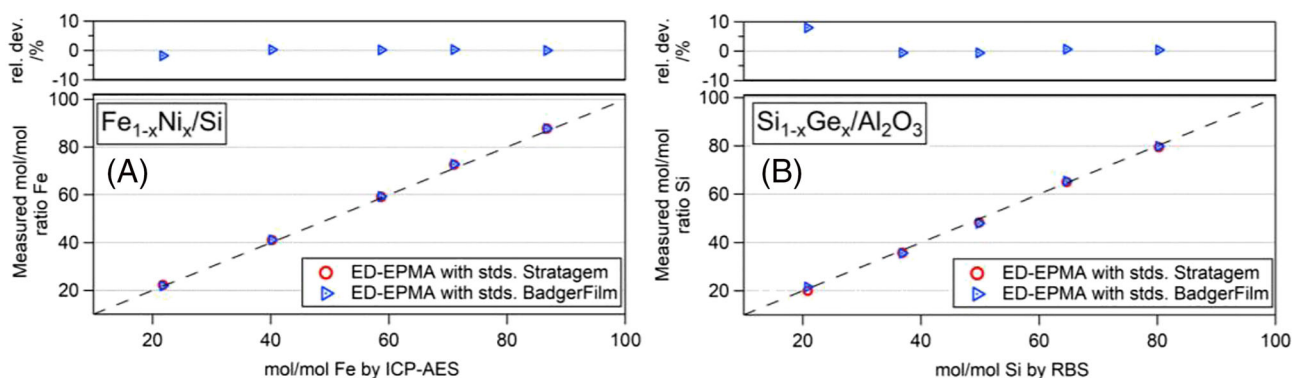


FIGURE 2 Mass fractions for the series of (A) Fe-Ni and (B) Si-Ge films as calculated by Stratagem (in red) and by BadgerFilm (in blue), from the same measured k -ratios, in dependence on the reference values of Fe (for Fe-Ni layers in panel A) and Si (for Si-Ge layers in panel B) measured by ICP-AES and RBS, respectively. In the upper panels the relative deviation between the values obtained with the two software packages are displayed.

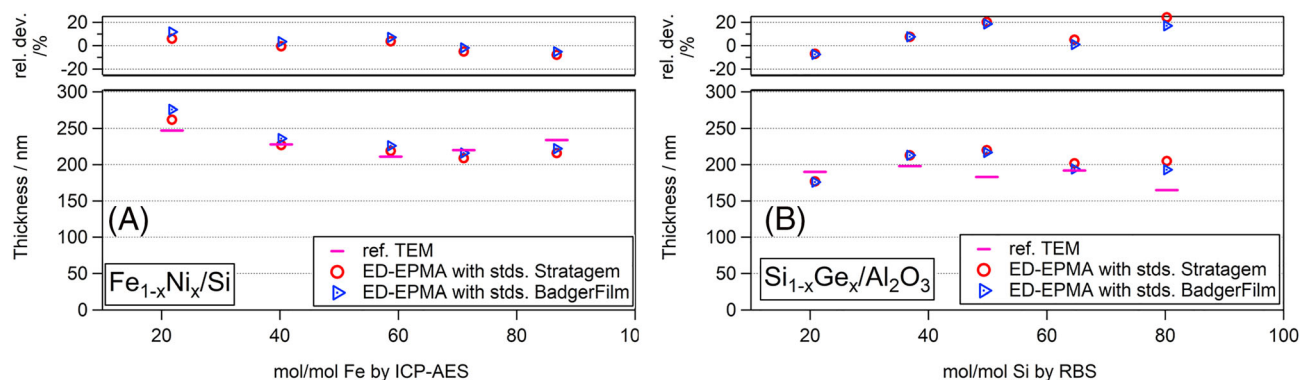


FIGURE 3 Film thickness for the series of (A) Fe-Ni and (B) Si-Ge films as calculated by Stratagem (in red), by BadgerFilm (in blue), from the same measured k -ratios, and as measured by TEM. In the upper panels the relative deviation of the calculated thicknesses to the reference values measured by TEM are shown.

Poisson counting distribution, beam current measurement (with the calibrated picoammeter), have been systematically evaluated as part of the CCQM study¹⁵ as being 3 at.-% (at a 95% level of confidence) for this type of layer material systems.

The film thickness for the same samples in Figure 2, as calculated by Stratagem (in red) and BadgerFilm (in blue), are shown in Figure 3. Additionally, the film thicknesses as measured by TEM after proper cross sectional sample preparation are also introduced in the two plots as reference values. Similarly, the relative deviations between the values calculated (from the same k -ratios) with the two software packages, BadgerFilm and Stratagem, are below 1–2%, as shown in the upper panels in Figure 3. As far as the agreement with the TEM reference measurements is concerned, relative deviations below 10% and for two Si-Ge samples around 20% can be reported. One explanation for the somewhat larger deviations for the film thickness calculated by both software packages relative to the TEM reference values can be due to the uncertainty of the introduced theoretical densities for each film (including the references). Another explanation would be the measurement of different samples of the same batch by EPMA and TEM, which might possibly have had different thicknesses.

4 | CONCLUSIONS AND OUTLOOK

In this paper the performance of the newly released thin film EPMA software BadgerFilm has been evaluated. Two representative sets of layer systems, who have been systematically characterised in the past, were considered: (i) five different relative concentrations of metal alloy $\text{Fe}_{1-x}\text{Ni}_x$ on Si substrate and (ii) a somewhat complicated one involving L X-ray lines and a nonconductive substrate: five different relative concentrations of semiconductor alloys $\text{Si}_{1-x}\text{Ge}_x$ on Al_2O_3 substrate. For each layer system a reference layer-substrate sample with known elemental composition and thickness was available. The results of the evaluation of the elemental compositions and film thicknesses by the BadgerFilm software, based on the same k -ratios, show an excellent agreement with the results calculated by the Stratagem

software: for both the calculated elemental compositions and film thicknesses, the relative deviations are below 1%–2%. Relative to reference values, both software packages show excellent agreement with respect to the elemental composition and deviations of 10% up to 20% for the film thickness.

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