



Analysis of elemental composition of $\text{Fe}_{1-x}\text{Ni}_x$ and $\text{Si}_{1-x}\text{Ge}_x$ alloy thin films by electron probe microanalysis and micro-focus X-ray fluorescence

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The present study reports on results of analysis of the elemental composition of thin films by electron probe microanalysis with energy dispersive (ED-EPMA) X-ray spectrometry in conjunction with the dedicated thin-film analysis software package Stratagem and by X-ray fluorescence in its version with a micro-focus X-ray fluorescence (μ -XRF) source attached to a scanning electron microscope (SEM). Two thin-film systems have been analyzed: $\text{Fe}_{1-x}\text{Ni}_x$ on silicon wafer and $\text{Si}_{1-x}\text{Ge}_x$ on Al_2O_3 substrate, in both cases the layers being grown to a thickness of about 200 nm by ion beam sputter deposition. Samples of five different atomic fractions have been produced and analyzed for each thin-film system. Moreover, reference samples with certified elemental composition and thickness have been also available. This study is part of an interlaboratory comparison organized in the frame of standardization technical committee ISO/TC 201 "Surface chemical analysis." Two laboratories have been analyzed by ED-EPMA (one laboratory standardless and one laboratory using both standardless and with standards variants) and one laboratory by μ -XRF (standardless and with standards). All the elemental compositions obtained with different methods are in very good agreement for the complete two sets of five samples each.

1 | INTRODUCTION

It was demonstrated in the past that electron probe microanalysis (EPMA) can be applied to determine accurately both elemental composition and thickness of thin films^{1–3} by using the dedicated software package for thin-film analysis Stratagem.⁴ The quantification routines were developed at the beginning of the 90s by Pouchou and Pichoir.⁵ Various film materials such as Cu, Au, Pt, Fe (also as a buried layer) deposited on Si, Ni-Cr on Gd-Fe-Pt magneto-optic alloys,⁶ pure metallic films of Pt and Ni,¹ binary alloys of Fe-Ni,² Pt-Ni-Co ternary alloy films,³ and pure carbon⁷ have been reported in literature as working successfully. The software can be applied also "conversely"; that is, by using the determined mass deposition of the film (in $\mu\text{g}/\text{cm}^2$) and feeding it with the film thickness, one can easily calculate the film

density, which for porous thin layers leads us to the true film porosity as an important and difficult to measure parameter.⁸ It should be noticed that gradients of the elemental composition in the depth of the thin layers cannot be distinguished by EPMA approach. For this purpose, depth profiling techniques or linescans over cross-sectioned samples should be applied.^{9,10}

The present study repeats measurements on an already tested system of Fe-Ni thin films on silicon^{2,11} and reports for the first-time results of analysis on Si-Ge thin films deposited on a nonconductive aluminum oxide substrate. Both thin-film systems have been chosen as samples of an interlaboratory comparison (ILC) organized in the frame of the standardization technical committee ISO/TC 201 "surface chemical analysis" under the lead of KRISS. The main objective of the ILC is to compare the results of atomic fractions of $\text{Fe}_{1-x}\text{Ni}_x$

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and $\text{Si}_{1-x}\text{Ge}_x$ alloy films obtained by different surface analysis techniques, such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) applied in the depth-profiling operation mode.¹² In the present paper, only the results obtained by EPMA and microfocus X-ray fluorescence (μ -XRF) are presented in detail. A complete report with the complete results of all the depth profiling techniques considered in the ILC is planned to be published at a later stage.

2 | MATERIAL AND METHODS

Five samples of different atomic fractions of each thin-film system, $\text{Fe}_{1-x}\text{Ni}_x$ on Si and $\text{Si}_{1-x}\text{Ge}_x$ on Al_2O_3 , have been grown by ion beam sputter deposition. Reference FeNi and SiGe films with well-known elemental composition and thickness have been also supplied for standard-based analysis. The size of all the samples prepared was 1 cm \times 1 cm. The atomic fractions of all the films including the references have been certified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) in the case of FeNi reference and Rutherford backscattering spectrometry (RBS) for the SiGe reference.¹²

EPMA measurements were performed in the two laboratories with (i) a Zeiss Supra 40 scanning electron microscope (SEM) having a Schottky field emitter and a Bruker XFlash energy dispersive X-ray spectrometer of type silicon drift detector (SDD EDS) (Lab #1) and (ii) a Hitachi SU6600 SEM equipped with a Bruker XFlash SDD EDS (Lab #2). The beam current has been measured with a calibrated external picoammeter. This is important for the standard-based quantification, as instabilities or offset (false indications) of the beam current constitute a significant source of measurement uncertainty that goes directly into the calculated elemental composition.

In order to avoid electrical charging under electron bombardment, the semiconducting SiGe films have made necessary application of copper tape onto their surface, contacting also the Al_2O_3 substrate and the SEM stage.

For the EPMA standard-based analysis, EDS spectra of the five unknown FeNi/Si and five unknown SiGe/ Al_2O_3 samples and the given FeNi/Si and SiGe/ Al_2O_3 reference samples (standards) with known chemical composition and film thickness have been acquired. Each sample has been measured at five different locations with an area of analysis of 100 $\mu\text{m} \times 100 \mu\text{m}$. In order to obtain more accurate results on the film composition and thickness, different accelerating voltages have been applied. For the FeNi/Si system, Lab #1 has used accelerating voltages of 15, 20, 25, and 30 kV, and Lab #2 has used 12, 16, 20, 25, and 30 kV; for the SiGe/ Al_2O_3 system, accelerating voltages of 15, 20, 25, and 30 kV have been selected by Lab #1, and 16, 20, 25, and 30 kV by Lab #2.

Net intensities of the X-ray lines of O K, Al K α , Si K α , Fe K α , Ni K α , and Ge K α have been determined after background removal and peak fit of the EDS spectra. The net intensities have been then used to calculate the k ratios as the basic input parameters for the calculation of the elemental composition of the thin layers according to the

quantification algorithm of the Stratagem software.^{4,5} The k -ratio is defined as the ratio of the net X-ray intensities of unknown and reference sample normalized to beam current and measurement live time.

It should be noted that for the analysis of the Al_2O_3 substrate, only the Al K α line has been evaluated in the analysis, due to the difficulties linked to the EPMA quantification of oxygen. Hence, the known stoichiometry of the Al_2O_3 substrate has been a priori defined in Stratagem; see Figure S1A,B in Supporting Information. For EPMA standardless analysis in Lab #2, only the net X-ray intensities of the EDS spectra of the unknown samples have been used, and theoretical k -ratios have been calculated.¹³ Finally, the k -ratios are input in the Stratagem software to calculate the film elemental composition and thickness; see Figure S1B in Supporting Information.

X-ray fluorescence (XRF) analysis can be used for the determination of elemental composition and thickness analysis of thin films as well. Here, a Bruker XTrace micro-XRF (μ -XRF) with a Rhodium anode, operating at 50 kV and 600 μA , has been used as attached to a SEM of type Jeol JSM 6490LV. A Bruker 6/30 SDD EDS has been used to collect the μ -XRF spectra. After background correction, the net peak intensities have been calculated using a peak-fit algorithm.

The information depth of μ -XRF data scales with the energy of the peak and can be much greater for high energy X-rays compared with the X-ray emission depths produced by the electron beam in the SEM.¹⁴ The X-rays focus on the sample by using a polycapillary optics,¹⁵ which has a spot size of 35 μm . For the standardless quantification by μ -XRF, a fundamental parameter (FP) approach has been used to calculate the film elemental compositions and their thicknesses.¹⁶ For standard-based analysis, the FP quantification of the reference samples with known film elemental composition and thickness has been used to calculate calibration factors.

3 | RESULTS AND DISCUSSION

An overview with the results of the standard-based and standardless EPMA/Stratagem and μ -XRF analyses of all five samples of different elemental compositions for both thin-layer systems, FeNi/Si and SiGe/ Al_2O_3 , is shown in Figure 1. Note the very good agreement (correlation) of all data with the reference values. Most of the relative deviations of the determined mass fractions for both systems are below $\pm 5\%$. If the good analysis results for the FeNi layers are expected, due to "simplicity" of the bimetal alloy system already tested in the past,^{2,11} the good quality of the results obtained for the SiGe/ Al_2O_3 thin-layer system is particularly valuable. In order to understand better the quality of the EPMA results for the example of the SiGe layer of "middle" composition, as determined by Stratagem, Figure S1 in Supporting Information illustrates the entire calculation sequence, starting with the definition of the reference sample (Figure S1A), over the input of the k -ratios for the individual X-ray lines (Figure S1B), followed by the representation of the good Stratagem fits of the measured k -ratios of the Si K α , Ge K α , and Al K α X-ray lines (Figure S1C); Figure S1D displays, after only three iteration steps, that the mass fractions of 27.36% for Si and 76.44% for Ge are

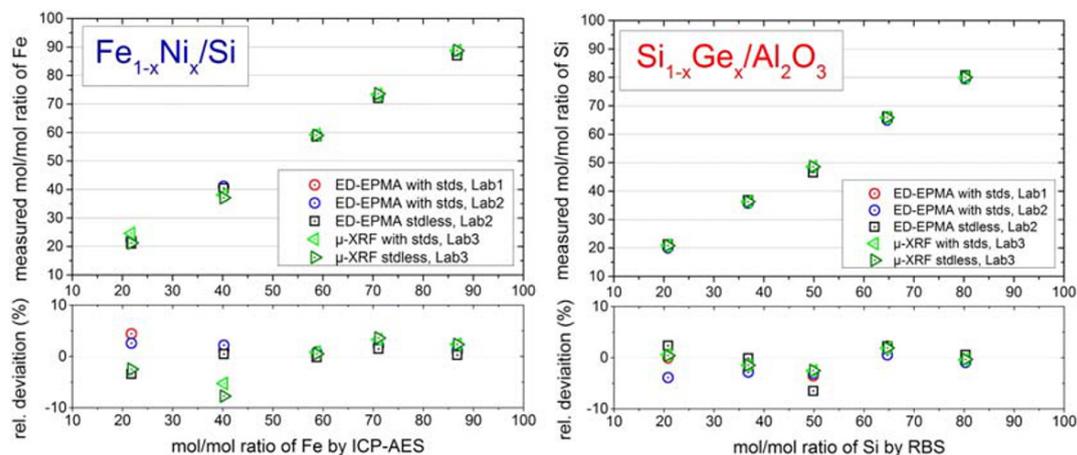


FIGURE 1 Mass fractions as result of the standard-based and standardless thin film analyses by electron probe microanalysis with energy dispersive (ED-EPMA)/Stratagem (Lab 1, Lab 2) an microfocus X-ray fluorescence (μ -XRF) (Lab 3, standardless and with standards) for the FeNi and SiGe films (in the ordinate) in dependence on the reference values of Fe (for FeNi layers) and Si (for SiGe layers) measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Rutherford backscattering spectrometry (RBS), respectively. In the lower panels the relative deviations to the reference values (from the abscissa) are displayed

calculated, this leading to a sum of molar fractions of 103.79%, which is an acceptable measure for the total mass fraction of the unknown SiGe layer (which ideally should be 100%). After normalization to 100%, the molar fractions become 48.05% for Si and 51.95% for Ge. This final result is visible in Figure S1F. Further, the mass deposition (in $\mu\text{g}/\text{cm}^2$) of the film is also calculated after the iteration sequence and can be represented as related to each X-ray line; see Figure S1E. The closer the points are, the higher the quality of the algorithm is. Once having the SiGe film mass deposition of $81.63 \mu\text{g}/\text{cm}^2$ and considering the film thickness, one can derive the film density. Conversely, assuming a film density (of $3.83 \text{ g}/\text{cm}^3$), the film thickness of 213.1 nm can be extracted from the mass deposition; see Figure S1E.

It should be noticed that this example has been shown in detail as the film with the largest deviations in both the sum of mass fractions (103.8 mass-%) and the film thickness. A complete overview of the measured film thicknesses for all the samples by means of all the methods (similar to the mass fraction results as in Figure 1) is given in Figure 2. Most of the relative deviations (in comparison with transmission electron microscopy [TEM] measurements) are smaller than $\pm 10\%$. The performance of both used μ -XRF versions (with standards and standardless) is slightly better than that of EPMA with energy dispersive (ED-EPMA). It should be noticed that the volume analyzed by μ -XRF is significantly larger than that of ED-EPMA. Thus, slight inhomogeneities in the film thickness (at same chemical composition) are more sensitively “caught” by ED-EPMA. Figure S2 in Supporting

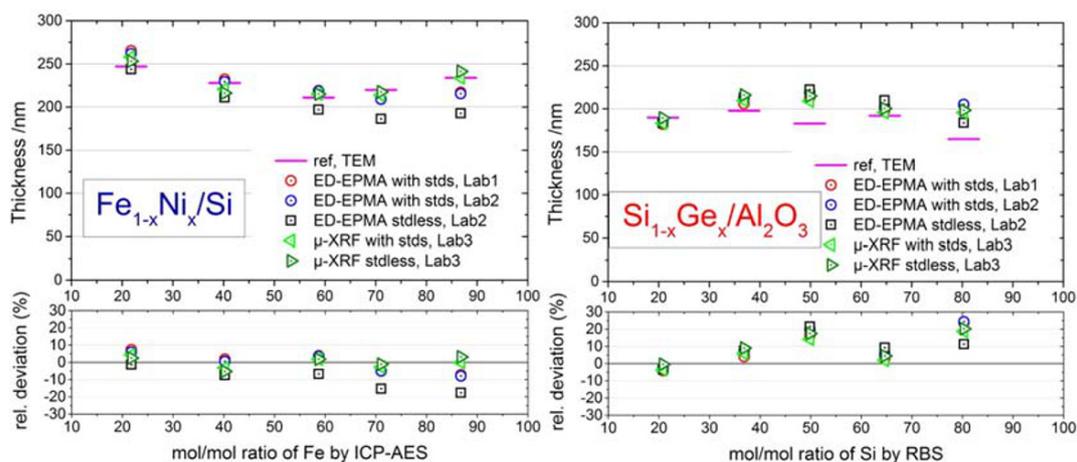


FIGURE 2 Film thickness as determined with standard-based and standardless thin film analyses by electron probe microanalysis with energy dispersive (ED-EPMA)/Stratagem (Lab 1, Lab 2) a microfocus X-ray fluorescence (μ -XRF) (Lab 3, standardless and with standards) for the FeNi and SiGe films. In the lower panels the relative deviations of the measured thicknesses to the reference values as measured by transmission electron microscopy (TEM) are displayed

Information illustrates such film inhomogeneities which can attain several nanometers as an example for the two reference films of the different layer systems.

According to an earlier systematic study of the measurement uncertainties on the model FeNi/Si thin-layer systems,^{2,11} a value of max. 3.0% has been estimated as the measurement uncertainty associated with the atomic fractions as calculated by the Stratagem approach. A similar value can be associated to the elemental composition calculated with the similar approach here for the SiGe/Al₂O₃ thin-layer systems.

As far as the μ -XRF elemental composition results are concerned, similar measurement uncertainties can be roughly estimated. Here, for example, the transmission function of the polycapillary optics may increase them up to $\sim 5\%$.^{14,15} Positively, no significant discrepancies are observed between standard-based and standardless results for both EPMA and μ -XRF.

4 | CONCLUSIONS AND OUTLOOK

The results of applying the thin-film analysis approach with EPMA linked to the dedicated software package Stratagem as well as with μ -XRF analysis attached to a SEM, on two thin-film systems, FeNi on Si and SiGe on Al₂O₃, are presented in this paper. Standard-based and standard-free results are shown for both methodical approaches (ED-EPMA/Stratagem and μ -XRF/SEM). The determined elemental compositions of all the layers (five different elemental compositions for both film systems) are in a very good agreement, this showing the performance of both approaches for such relatively simple thin-film systems (one layer only, two elements, well-defined substrates) with good homogeneity. It should be noticed that for the case of standard-based analyses with both methods, one reference layer sample for each system of well-known elemental composition and film thickness has been also available and accordingly considered in the analysis. Most of the relative deviations of the mass fractions as determined by all method combinations (ED-EPMA, μ -XRF, with standards and standardless) for both layer systems are below $\pm 5\%$. As far as the determined film thickness is concerned, most of the relative deviations (in comparison to TEM measurements) are smaller than $\pm 10\%$.

A detailed report including the data obtained by all the participants in the ISO/TC 201 ILC using also the other (depth profiling) techniques XPS, AES, and time-of-flight SIMS (ToF-SIMS) will be published soon.

ACKNOWLEDGMENT

Technical assistance from Mrs. Sigrid Benemann (BAM-6.1) is gratefully acknowledged.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Hodoroaba V-D, Terborg R, Boehm S, Kim KJ. Analysis of elemental composition of Fe_{1-x}Ni_x and Si_{1-x}Ge_x alloy thin films by electron probe microanalysis and micro-focus X-ray fluorescence. *Surf Interface Anal.* 2020;1-4. <https://doi.org/10.1002/sia.6834>