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Electron probe microanalysis of Ni-silicides at low voltage: difficulties and possibilities

E. Heikinheimo[1], P.T. Pinard[2], S. Richter[2], X. Llovet[3] and S.Louhenkilpi[1]

[1] Aalto University, Department of Materials Science and Engineering, P.O. Box 16200, 00076 Aalto, Espoo, Finland
[2] RWTH Aachen University, Central Facility for Electron Microscopy (GFE), Ahornstrasse 55, 52074 Aachen, Germany
[3] Universitat de Barcelona, Scientific and Technological Centres (CCiTUB), Lluís Solé i Sabarís 1-3, 08028 Barcelona, Spain

E-mail: erkki.heikinheimo@aalto.fi

Abstract. Interest in the use of EPMA at low voltage has grown considerably in recent years, mainly because of the availability of electron-beam instruments equipped with field-emission guns. However, EPMA at low voltage is marred by both experimental and analytical problems which may affect the accuracy of quantitative results. In the case of the analysis of transition elements, both the emission and absorption of X-rays are still poorly understood when they originate from electron transitions involving the partially filled 3d-shell. This is the case for the most intense Lα (L$_3$-M$_5$ transition) and Lβ (L$_2$-M$_4$ transition) lines. In this communication, we point out anomalies which appear to afflict the accuracy of EPMA of Ni-silicides using the Ni-Lα X-ray line and we discuss possible solutions.

1. Introduction

The incorporation of the field-emission (FE) gun into electron-beam instruments has stimulated the use of these instruments at low voltage and has opened up new opportunities for the characterisation of complex materials at a sub-micrometre scale. However, electron probe microanalysis (EPMA) at low voltage is marred by both experimental and analytical difficulties which may affect the accuracy of quantitative results [1-4]. On the one hand, at low energies, a surface layer several nanometres in thickness may represent a non-negligible fraction of the volume from which X-rays escape and therefore the influence of carbon contamination, surface oxidation, or the quality of the sample polish becomes crucial [1]. On the other hand, for most elements, conventional K-lines cannot be excited and therefore we have to rely on the use of L- and M-lines, which are less intense and more sensitive to chemical effects, especially below 1 keV photon emission energy.

Using conventional matrix correction procedures, quantitative analysis of the L-lines of transition elements is particularly problematic when the electron transitions involve the partially filled 3d-shell (M$_{4,5}$-subshells). This is the case for the most intense Lα (L$_3$-M$_5$ transition) and Lβ (L$_2$-M$_4$ transition) lines. Fialin showed that both the peak shape due to satellite emission and self-absorption of the Zn-Lα line emitted from Zn minerals largely depend on the electronic structure of these materials [5]. Pouchou illustrated the difficulties found when using the Ni-Lα line for the analysis of Ni aluminides [2]. The limitation of the use of the Lα- and Lβ-lines for the quantitative analysis of transition elements was recently discussed in a round-robin study [6], where participants analysed three steel

alloy samples at low voltage. The results showed an underestimation of Cr and an overestimation of Fe and Ni, with relative deviations from the expected values which amounted up to 30 - 40 %. Jonnard *et al.* [7] reported the results of another round-robin study of a metallic glass sample. The results obtained at low voltage using Lα-lines showed an overestimation of the Ni and Co content by 13 % rel. and 11 % rel., respectively.

Gopon *et al.* [8] showed that the use of the less intense Ll (L_3-M_1 transition) line, which does not involve transitions from the unfilled 3d-shells, may be a suitable alternative for the analysis of Fe-silicides at low voltage. Statham and Holland [9] also used the Ll-lines to analyse a high Cr-Ni steel. These authors concluded that it may be a route to improve quantitative analysis, although Cr-concentrations were found to be 9 % below expected values. Pinard *et al.* [10] used a similar strategy to re-analyse the steel alloy samples from Llovet *et al.*'s round-robin study [6] as well as other steel samples. Although good agreement was obtained for the major elements using the Ll-lines, the authors observed large discrepancies for the minor elements such as Mn (0.7 - 1.6 wt%) and Co (0.3 - 1.5 wt%). They were attributed to the low intensity of the Ll-lines and the presence of several interferences. It is therefore of great importance to further understand the quantification problem using the Lα-lines and to identify whether these difficulties are also found in other types of materials.

In this study, we have carried out systematic EPMA measurements on Ni-silicides in order to investigate the anomalies which appear to afflict the analysis of such materials using Lα-lines and we discuss possible solutions. The Ni-silicide system was selected for its simplicity as it consists of several binary compounds with a different composition and crystallographic structure. Furthermore, Ni-silicides play an important role in semiconductor technology, where methods for an accurate analysis of sub-micrometre Ni-silicide phases are needed.

The rest of the paper is structured as follows. Section 2 provides information on the experimental methods. In Section 3 we briefly discuss the theoretical calculations performed. We present and discuss the results of the different measurements and calculations performed in Section 4, and Section 5 concludes the paper.

2. Experimental method

The Ni-silicides were prepared by the diffusion-couple technique. The starting metals were bulk samples of Ni and Si (99.95+ purity). Diffusion couples were prepared by hot pressing the polished Ni and Si pieces together. The diffusion experiments were carried out by annealing the couples at 850 °C for 16 hours in a reducing atmosphere. Cross-sections of the diffusion couples, perpendicular to the interface, were cut, embedded in conductive resin, ground and finally polished.

The compounds Ni_5Si_2, Ni_2Si, Ni_3Si_2, and NiSi were identified by their different atomic number contrast in the backscattered electron image (figure 1) and quantified by conventional EPMA at 15 kV using the Kα (K-L_3 transition) line for both Ni and Si, pure Ni and Si metals standards, and the matrix correction algorithm XPP [11], as implemented in the microprobe software (table 1). The deviation (percent error) of the measured concentrations with respect to the nominal values is 1.9 % for Si and 0.4 % for Ni.

X-ray measurements were performed on three different instruments, namely a LEO 1450 scanning electron microscope (SEM) equipped with an INCA wavelength-dispersive X-ray spectrometer (WDS) at the Aalto University (Finland), a JEOL JXA-8230 electron microprobe at the University of Barcelona (Spain) and a JEOL JXA-8530F electron microprobe at the RWTH Aachen University (Germany). The aim of using different instruments (as well as operators, procedures, samples, etc.) was mainly to assess the reproducibility of the different measurements. The advantage of the FE microprobe (JXA-8530F) was the more reliable analysis of small NiSi-phases close to pure silicon. Furthermore, in the SEM the take-off angle is 30°, a much lower value than that of the two electron microprobes (40°). The use of the SEM-WDS reinforces confidence in the data as regards the influence of X-ray absorption effects on the analysis.
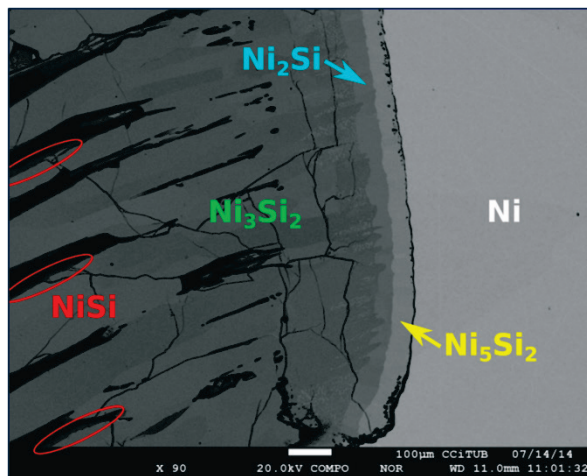
Figure 1. Backscattered electron image of the Ni-Si diffusion couple cross-section showing the different Ni-silicide phases.

Table 1*:* Nominal composition and results of EPMA analysis at 15 keV using the Ni-Kα and Si-Kα lines for the studied Ni-silicide phases. The EPMA analyses are the average of 10 measurements, with the corresponding standard deviation (at 1σ level) in parenthesis. Pure metal standards were used.

	Nominal concentration (wt%)		EPMA analysis (wt%)		
Phase	Ni	Si	Ni	Si	Total
Ni_5Si_2	83.9	16.1	84.2 (0.2)	15.6 (0.04)	99.8
Ni_2Si	80.7	19.3	80.9 (0.2)	19.1 (0.05)	99.9
Ni_3Si_2	75.8	24.2	76.1 (0.2)	23.8 (0.09)	99.9
NiSi	67.6	32.3	67.9 (0.3)	31.7 (0.3)	99.6

Four series of measurements were performed on the four Ni-silicides. In all cases, when *k*-ratios were measured pure Ni and Si standards were used, and measurements were made at 10 different positions, with typical counting times of 30 s. The dispersing crystals were TAP crystals. Firstly, conventional EPMA measurements using the Ni-Lα and Si-Kα lines, pure Ni and Si metals standards, and the matrix correction procedure XPP, as implemented in the JEOL microprobe software, were performed at 6 keV. The beam energy of 6 keV was selected to reach a compromise between X-ray production efficiency and spatial resolution (a lower beam energy would not improve the spatial resolution because of the larger beam size) [3]. Secondly, Ni-Lα net intensities and *k*-ratios, extracted from peak-height intensity measurements, were collected for incident beam energies in the range 2 - 30 keV on all Ni-silicides and pure Ni. Although a different beam current was used at each accelerating voltage, it was measured before and after each measurement to diminish errors due to instrument instabilities. In the case of the SEM-WDS as well as the FE-microprobe, a peak search was also performed for each accelerating voltage and silicide. Thirdly, Ni-Ll *k*-ratios were acquired using the same procedure using a TAPH crystal (only on the JEOL JXA-8230 instrument). Finally, X-ray emission spectra around the positions of the Ni-Lα and -Lβ peaks at 2 and 30 keV were acquired using a Johann spectrometer with a 300 μm diameter exit slit in an attempt to ensure the highest spectral resolution. Measuring time was 7500 s per spectrum, with currents of 500 nA at 30 keV and

250 nA at 2 keV. The beam was defocussed to 5 µm. In order to minimize carbon contamination and its potential influence on peak shape changes [12], the sample was cleaned with plasma cleaner for 10 min prior to its introduction in the microprobe chamber.

3. Calculations

k-ratios for the different X-ray lines and studied compounds were calculated using the Monte Carlo (MC) simulation programmes PENEPMA [13] and MONACO [14], and the analytical model XPP [11], as implemented in the software DTSA-II [15].

Based on the general-purpose MC simulation package PENELOPE [16], PENEPMA simulates the transport of both electrons and photons using interaction models which combine results from first-principles calculations, semi-empirical models and evaluated databases (see Ref. [16] for details). In the case of photon absorption, which is non-negligible for soft X-rays, PENELOPE uses total cross-sections for photoelectric absorption from the Evaluated Photon Data Library (EPDL) [17]. By definition, the commonly used mass absorption coefficients (MAC) are directly proportional to the photoelectric cross-sections. PENELOPE simulates the emission of almost all known K-, L-, M- and N-lines, which include the Ll-line.

MONACO is a MC simulation programme of electron transport based on elastic and inelastic single scattering events calculated by using the Mott cross-sections and the modified Gryzinski cross-sections, respectively [13]. The mean energy loss is calculated by means of the Bethe formula and corrected by the energy losses of the single inelastic scattering events. It neglects any solid state structure. X-ray absorption is analytically computed from the conventional Beer-Lambert exponential relation using MACs from a selection of MACs from Henke [18] and Heinrich [19]. MONACO allows the simulation of the most commonly used X-ray lines, namely the Kα-, Kβ-, Lα-, Lβ-, Mα- and Mβ-lines.

DTSA-II is a multi-platform software package for quantitative EPMA where several correction algorithms and sets of fundamental parameters, including MACs, can be used. The implementation of the XPP model from Pouchou and Pichoir [11] was used for all analytical calculations. For the quantification of the Ni-Lα results, the MACs as defined in [14] were used. They consist of an experimentally determined MAC for Ni-Lα in Ni and MACs from Heinrich [19] for the rest of single-element materials. For the quantification of Ni-Ll results, the MACs from Chantler *et al.* [20] were used.

Furthermore, DTSA-II was modified to allow the use of different MACs to correct for the absorption in both the unknown and standard samples. Notice that most EPMA correction programmes assume the same MAC for both corrections. Finally, using the libraries and databases within DTSA-II, an in-house programme was developed to derive empirical MACs from the EPMA measurements of the studied materials. This programme follows the method described by Pouchou and Pichoir [21] and is implemented in the software package XMAC [2], which was also used for comparison purposes. For a given X-ray line and sample, our programme considers the MAC of each absorber as a free parameter in the XPP model. The input values are experimental X-ray intensities measured at different accelerating voltages. The programme yields the MAC values which give the best fit between the experimental and calculated X-ray intensities.

4. Results and discussion

4.1. k-ratios versus energy (Lα)
The results of the analysis of the different Ni-silicide phases at 6 keV using the Ni-Lα line are tabulated in table 2. The deviation (percent error) of the obtained Ni concentrations with respect to the nominal values adds up to about 20 % - 30 % rel. This obviously throws serious doubts upon such results. Notice that only the Ni concentrations are overestimated, the Si values satisfactorily match the nominal concentrations as well as the measurements obtained at 15 keV (see table 1).

Table 2. Analysis of three of the silicide phases at 6 keV using the Ni-Lα and Si-Kα lines, Ni and Si pure metal standards and the matrix correction algorithm XPP, as implemented in the JEOL microprobe software.

	Nominal concentration (wt%)		EPMA results (wt%)		
Phase	Ni	Si	Ni	Si	Total
Ni_5Si_2	83.9	16.1	102.1	15.8	117.9
Ni_2Si	80.7	19.3	105.3	19.1	124.5
Ni_3Si_2	75.8	24.2	100.7	24.6	125.3

Figure 2 shows the experimental and calculated Ni-Lα *k*-ratios as a function of incident electron energy for the four Ni-silicides. There is good agreement between the experimental *k*-ratios measured on the three different instruments, which increases confidence in the data. The results obtained from the two MC programmes agree well with each other. The simulated results slightly differ from those obtained by XPP, especially at high energies. However, all calculated *k*-ratios differ greatly from the experimental values. The largely increasing differences with increasing beam energy suggest a problem with the absorption correction and seem to point to incorrect MAC values used in the calculations.
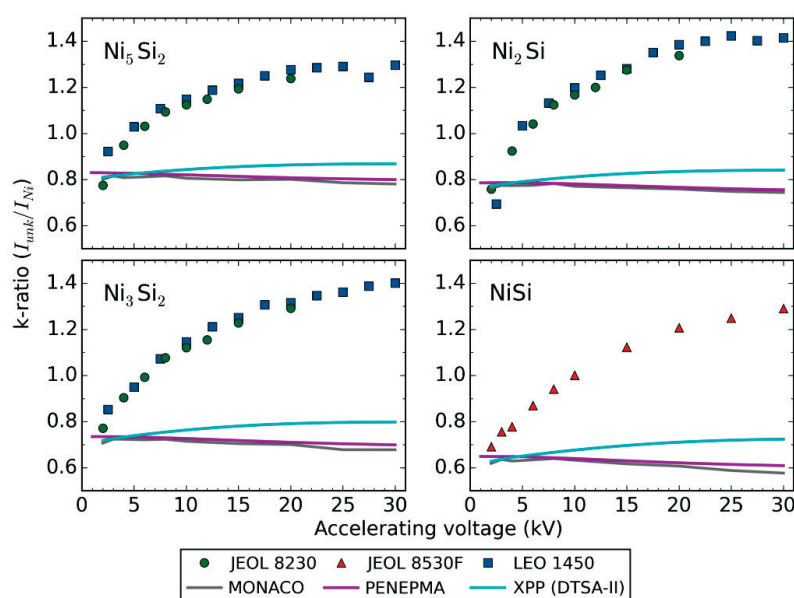
Figure 2. Experimental and calculated Ni-Lα *k*-ratios of four Ni-silicides as a function of accelerating voltage. Measurements were performed on 3 different instruments, as indicated in the legends. Calculations were performed with the MC codes MONACO, PENEPMA and the analytical model XPP using DTSA-II.

The large differences observed between experimental and calculated *k*-ratios at 6 keV are consistent with the erroneous Ni concentrations measured at this energy. The error in the concentration would be undoubtedly worse at higher beam energies.

4.2. Absorption X-ray spectra

In order to shed light on the origin of the observed *k*-ratio discrepancies, X-ray absorption spectra around the L_2- and L_3-absorption edges were acquired on pure Ni and on the Ni-silicide samples. Absorption spectra were obtained from the ratio of two normalized X-ray emission spectra measured at low and high incident electron energy [22-24]. As shown by e.g., Chopra [24], absorption spectra obtained in this way are equivalent to X-ray absorption measurements using X-ray beams and thin foil absorbers.

The X-ray emission spectra from pure Ni obtained at 2 and 30 keV are presented in figure 3a. The Lα- and Lβ-lines represent radiatiave transitions of M_5-electrons to vacancies in the L_3-shells, and of M_4-electrons to vacancies in the L_2-shells, respectively. The spectra have been normalized to yield the same peak intensity for the Lα-line. For both the Lα- and Lβ-lines, the peak positions at 30 keV are shifted towards a lower energy with respect to those at 2 keV. The shape of the lines also shows a change, the high-energy side of the Lα- and Lβ-lines as they are lower at 30 keV than at 2 keV.
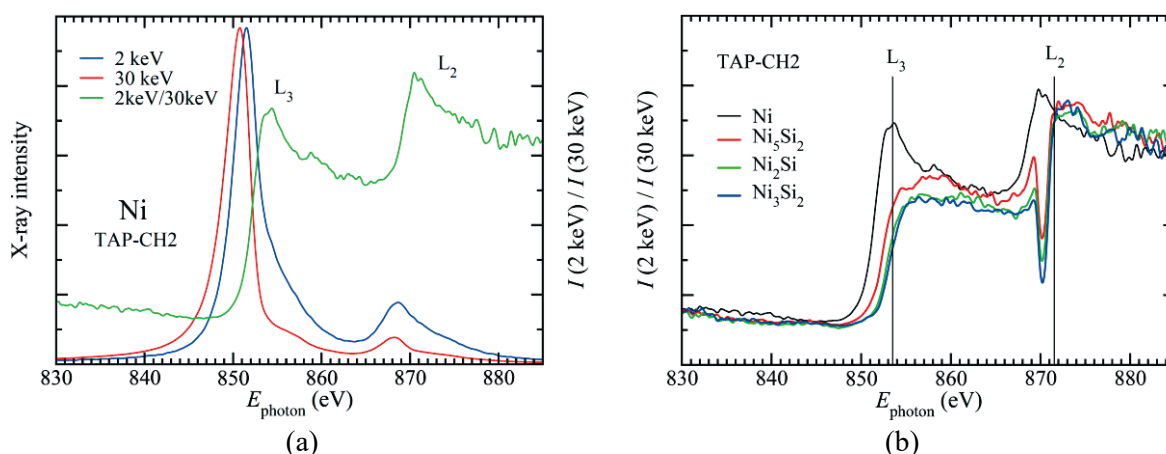
Figure 3. L X-ray emission spectra at 2 and 30 keV incident electron energy for pure Ni and $L_{2,3}$-absorption spectrum obtained from the ratio of the X-ray emission spectra at 2 and 30 keV (a) and X-ray absorption spectra of the Ni $L_{2,3}$-region for pure Ni and three Ni-silicides (b).

Figure 3a also shows the Ni $L_{2,3}$-absorption spectrum obtained from the ratio of the X-ray emission spectra at 2 and 30 keV. Two lines are observed just above the L_3- and L_2-absorption edges. These lines are generally referred to as white lines [24] or also as anomalous absorption [22]. White lines are believed to be associated with transitions from an inner-shell (in this case $L_{2,3}$-electrons) to an unoccupied level with a high density of states near the absorbing atom (in this case the 3d states). White lines are also known to depend on chemical bonding. As pointed out by Bonnelle [22], the changes in the shape and position of the Ni-Lα and -Lβ lines with increasing beam energy (see figure 3a) can be satisfactorily explained by the attenuating effect of the $L_{2,3}$-absorption spectrum on the natural Lα- and Lβ-line widths.

Figure 3b shows a comparison of the Ni $L_{2,3}$-absorption spectra obtained for Ni, Ni_5Si_2, Ni_2Si and Ni_3Si_2. The white lines are less visible for the Ni-silicides when compared to pure Ni. This suggests that the absorption of Ni-Lα X-rays (E = 851.47 eV) by Ni atoms bonded to Si atoms is lower than for Ni atoms bonded to Ni atoms. The L_3-absorption edge of Ni shows a shift towards higher energy for the Ni-silicides, with respect to that of pure Ni. The drop in intensity observed at 871 eV near the L_2-edge for the Ni-silicides is due to a 2nd-order Bragg reflection of the Si-Kα which is stronger in the 30 keV spectrum.

It therefore appears that the increase of Si concentration in the Ni-silicides decreases the absorption of Ni-Lα X-rays by Ni atoms. As the Ni concentration decreases, the total absorption of Ni-Lα X-rays by Ni atoms decreases following the linear combination of the weighted mass absorption coefficients. However, in the case of Ni-silicides, the chemical bonding between Ni and Si atoms seems to eliminate, or at least to reduce, the anomalous absorption of Ni-Lα X-rays by Ni atoms. Absorption in the Ni-silicides is consequently lower than expected by the conventional matrix correction procedures. This effect can be one explanation for the large discrepancies between the experimental and calculated *k*-ratios (figure 2) and for the experimental *k*-ratio values above 1.

As discussed by Jarrige *et al.* [25], the electronic structure of Ni-silicides is governed by the interaction of the almost "discrete" Ni d-valence states with the "continuum" of Si p-states, which depends on the environment of the Ni and Si atoms. As a consequence, the absorption coefficient, which is proportional to the density of unoccupied states, also depends on the considered compound.

4.3. Empirical MACs
In order to quantify the different absorption behaviour of Ni-Lα X-rays by Ni atoms in the Ni-silicides, empirical MACs were experimentally determined from EPMA measurements. Indeed, for a given X-ray line and material, it is possible to obtain a MAC value by considering it as a free parameter in the EPMA correction procedure and then fit the predictions of the model to relative X-ray intensities measured as a function of beam energy (or take-off angle) [21]. Obviously, this empirical MAC is expected to give reliable results only in combination with the considered model and other experimental conditions such as the spectral resolution of the spectrometer used (in the case of peak height measurements).

We have developed our own programme which allows determination of the MAC for the absorption of one or several X-ray lines by atoms of different elements within materials of known composition by using the XPP model [14].

Figure 4 shows both the experimental and fitted Ni-Lα intensities as a function of beam energy for Ni and Ni_3Si_2 (figure 4a) and the experimentally determined MACs for the Ni-Lα absorption by Ni atoms in Ni and the Ni-silicides as a function of Ni concentration (figure 4b). The agreement between the measured and fitted intensities is excellent (figure 4a). The MACs for the different Ni-silicides are significantly lower than that for pure Ni, as illustrated in figure 4b. Tabulated MACs for a given X-ray line and absorbing atom are normally supposed to be independent on the concentration of absorbing atoms and thus should have a constant value (horizontal line in figure 4b). The qualitative trends observed in the X-ray absorption spectra for Ni and the Ni-silicides (figure 3b) are confirmed by the experimentally determined MACs values.

Table 3 tabulates the MAC for Ni-Lα and -Ll X-rays in Ni from different, widely used MAC compilations. The MACs based on EPMA measurements (Pouchou and Pichoir [11] and this study), are larger than those from the other compilations, most probably because the former account for the enhanced absorption of Ni-Lα in Ni.

4.4. Improved k-ratios using the measured MACs
In order to take into account the anomalous absorption behaviour of the Ni-Lα line, the *k*-ratios were re-evaluated using the experimental MACs. To this end, the DTSA-II programme was slightly modified to allow the use of a different MAC (of the same element) for the unknown and standard.

Figure 5 shows a comparison of the new evaluated *k*-ratios (labelled "Measured MAC") with the previously obtained *k*-ratios ("Original MAC") and the experimental data as shown in figure 2 for Ni_3Si_2. Although the new *k*-ratios are closer to the measured values, large differences still remain. This suggests that other anomalies may be taking place, most probably involving X-ray emission. Pouchou [2] suggested that for Ni aluminides the probability of the Ni 2p-3d radiative transition also depends on the structure of the valence band (e.g., on chemical bonding, which implies addition or removal of valence electrons). Hence, the assumption that the radiative transition probability is the same for the unknown and the standard may no longer be valid. Unfortunately, an explanation of the

dependence of the radiative transition probability on Si concentration in the case of Ni-silicides is not at hand. Furthermore, as discussed by Bonnelle [22], the intensity of an electron transition also depends on the density of states and the local partial density of Ni 3d-states largely depends on the composition of the Ni-silicide [25].
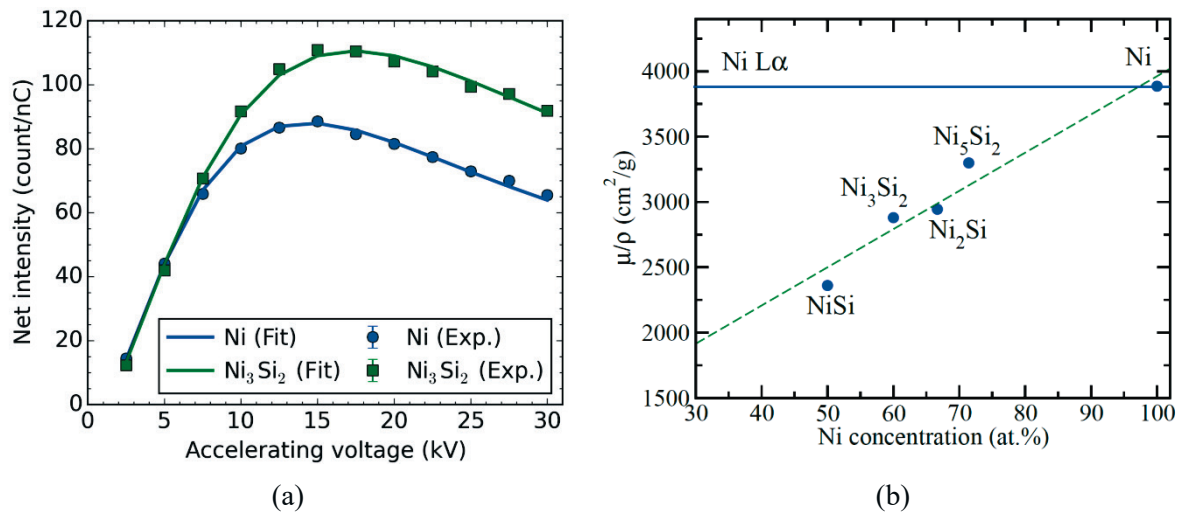
Figure 4. Experimental and fitted Ni-Lα intensities for pure Ni and Ni_3Si_2 (a) and Ni-Lα MAC by Ni atoms in pure Ni and four Ni-silicides as a function of Ni concentration (b).

Table 3. MACs for Ni-Lα and -Ll X-rays in Ni taken from different compilations (in cm^2/g). For the compilations for which the X-ray lines are not detailed, the MACs have been extracted at the photon energies of 851.47 eV (Lα) and 742.72 eV (Ll).

| Source	Lα	Ll
Henke *et al.* (1985) [18]	1,819	-
Henke *et al.* (1993) [25]	1,802	2,402
Heinrich [19]	1,806	2,426
Cullen *et al.* [17] – EPDL	1,654	2,225
Chantler *et al.* [20] – FFAST	1,697	2,255
Pouchou and Pichoir [11]	3,560	-
This study	3,998	-

4.5. k-ratios using the Ni-Ll line and conventional MACs
One solution to the quantification problems of Ni-silicides at low voltage is to use the Ni-Ll line, as has already been suggested by [8-10]. The Ll-line, with an energy of 742 eV, is far from the $L_{2,3}$-absorption edges, and corresponds to a radiative transition (L_3-M_1) that does not involve the unfilled 3d-shell.

Figure 6 shows a comparison of the measured and calculated *k*-ratios for the Ni_5Si_2- and Ni_3Si_2-phases, as a function of beam energy. The calculations were performed with PENEPMA and XPP (DTSA-II), using the MAC value from EPDL and FFAST database, respectively (table 3).
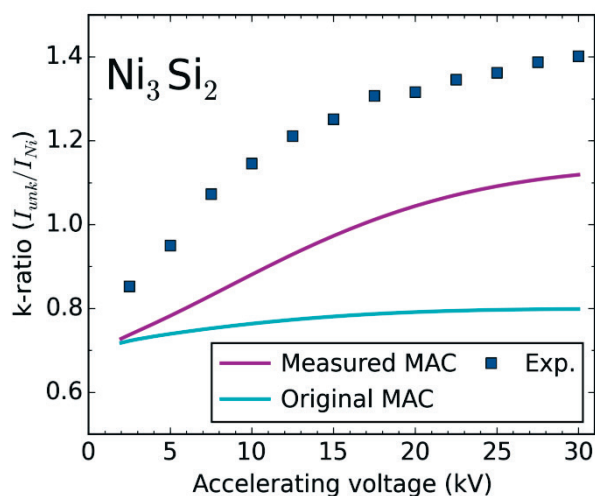
Figure 5. Experimental Ni-Lα k-ratios and calculated k-ratios using different MACs as indicated in the legends (see text for explanation).
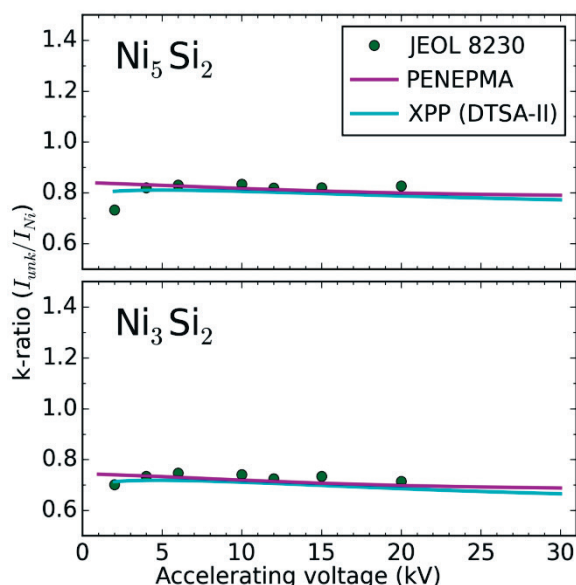
Figure 6. Experimental and calculated Ni-Ll k-ratios as a function of accelerating voltage.

It should be noted that Ll-line measurements are more challenging because of the much lower intensity of the Ni-Ll line when compared to the Ni-Lα line. Longer acquisition times and/or high beam currents are required which lead to problems due to contamination and other experimental issues [4]. The use of larger diffracting crystals or the simultaneous use of similar crystals in different spectrometers may help to mitigate such problems as demonstrated by the satisfactory agreement between the experimental and calculated k-ratios (figure 6). It should be noted that most matrix correction programmes do not allow the use of Ll-lines for quantification, since MACs are often tabulated only for the most widely used X-ray lines, namely the Kα-, Kβ-, Lα-, Lβ-, Mα- and Mβ-lines.

5. Conclusions

Systematic EPMA measurements on the Ni-Si system have been performed in order to illustrate the difficulties of using the Ni-Lα line for the quantitative analysis of Ni-silicides at low beam energy. In particular, we have shown that the behaviour of the Ni $L_{2,3}$-absorption spectra is very sensitive to chemical bonding. This means that the MACs of Ni-Lα due to Ni atoms in Ni-silicides depend on

Si concentration and they significantly differ from tabulated values. By using MACs empirically calculated from EPMA measurements, the deviation between the measured and calculated Ni-Lα k-ratios decreases, but the results are still far from being satisfactory. This suggests that X-ray absorption is not the only factor causing the anomalous behaviour of the Ni-Lα line in the Ni-silicides. We have finally shown that the difficulties in getting reliable accuracy for the above-studied compounds can be overcome by using the Ni-Ll line.

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