Chemical analysis of nickel silicides with high spatial resolution by combined EDS, EELS and ELNES

E Verleysen\textsuperscript{1,2}, H Bender\textsuperscript{1}, D Schryvers\textsuperscript{3} and W Vandervorst\textsuperscript{1,2}

\textsuperscript{1} IMEC, Kapeldreef 75, 3001 Leuven, Belgium
\textsuperscript{2} Instituut voor Kern- en Stralingsfysica, K. U. Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium
\textsuperscript{3} Universiteit Antwerpen, EMAT, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

E-mail: eveline.verleysen@imec.be

Abstract. The purpose of this study is to develop methodologies for the characterization of Ni-silicides by analytical TEM techniques. The measurements are performed in STEM mode to allow a good spatial resolution. Initial examination of the Ni-silicide phases is done by energy-dispersive X-ray spectroscopy (EDS). It is shown that quantification results with high accuracy and precision are obtained when a Ni-silicide reference layer is used as a standard, and an absorption correction is applied to the data. The EDS quantification results are then used as a reference for the quantitative electron energy-loss spectroscopy (EELS) analysis. It is shown that EELS analysis yields quantification results with high accuracy and precision, when the EELS data are treated with a model based approach. The EELS analysis is combined with a study of the Ni-L\textsubscript{2,3} near-edge structure (ELNES). The ELNES of the phases can be distinguished either visually or by calculating the branching ratio from the spectra with the model based approach. This paper shows that the different Ni-silicide phases can be distinguished with these EELS based methods. The accuracy and precision of the EDS and EELS results are compared.

1. Introduction
The continuous scaling in semiconductor technology has made accurate characterization of transistor components more challenging. Often, the main difficulty is to obtain both high spatial resolution and information on the chemical composition of the material. In this context, high resolution spectroscopic methods, such as EDS and EELS, play a crucial role in facilitating new materials integration and in the development of non-classical devices.

In this study, Ni-silicides are selected as a test-vehicle to develop quantitative methodologies for the accurate and precise characterization of transistor components. The Ni-silicide system consists of a wide range of different phases \cite{1}. These phases are formed in polycrystalline layers with generally small grain sizes. Since this makes it difficult to distinguish the phases based on their lattice spacings, it is essential to combine HREM studies with chemical analysis. In this paper the results of the characterization of the full range of Ni-silicide phases with EDS, EELS and ELNES are presented.

2. Sample preparation and experimental setup
Ni-silicide samples are prepared by rapid thermal annealing of a Ni-layer and a thin polycrystalline Si film, deposited on top of a SiO\textsubscript{2}/Si substrate. The temperature and thickness ratio of the Ni and Si-
layer are varied to obtain different phases. The samples are prepared for TEM by FIB lift-out. Wedge samples are used to study the effect of specimen thickness on the quantification results. EDS, EELS and ELNES measurements are carried out on a TECNAI F30 operating at 300keV, equipped with an EDAX detector and a Tridiem GIF energy filter. The measurements are performed in STEM mode with a spot size of 2 nm. To avoid beam convergence effects, a condenser aperture of 0.5 μm is used for the EELS measurements. To avoid saturation of the GIF, EELS spectra are recorded with an acquisition time that is five times shorter than the acquisition time of the EDS spectra. Additional ELNES measurements are performed at TU Delft on a TECNAI operating at 200 keV, equipped with a monochromator allowing an energy resolution of 0.2eV. These spectra are recorded in TEM mode.

3. Results and discussion

3.1. Quantitative EDS analysis
After initial qualitative examination, the EDS spectra are processed by removing the background, integrating the Si-Kα and Ni-Kα peaks and converting the integrated peak intensities to concentrations with the Cliff-Lorimer equation [2]. The k-factor in the Cliff-Lorimer equation is determined by a Ni-silicide standard: Ni$_{31}$Si$_{12}$, measured and processed under identical conditions as the unknown Ni-silicide samples. Since EDS recordings from various thicknesses of the samples indicate strong absorption of the Si-K peak, an absorption correction is applied to the data. The results of the quantitative EDS analysis are shown in table 1a. The estimated concentration ratios are presented, together with the expected concentration ratios [1] between brackets. The standard deviations from the N repetitive measurements at different thickness positions are shown. For the Ni$_3$Si phase, a possible variation in the Si/Ni concentration ratio between 0.295 and 0.325 is reported in the literature [1]. The accuracy is then expressed as a range calculated relative to these values.

3.2. Quantitative EELS analysis
The Si-K edge and the Ni-L edge are used for the quantifications. EELS spectra are processed using a model-based approach with the EELSMODEL program [3]. This means that a parametric model describing the expectations of the EELS observations is derived. The unknown parameters are estimated by fitting this model to the experimental spectrum, using a criterion of goodness of fit (maximum likelihood). The model is constructed from a background power law, a hydrogenic cross-section for the Si-K edge, a hydrogenic cross-section for the Ni-L edge with Gaussian peaks to model the white lines, and a convolution with the experimental low loss spectrum to simulate multiple scattering. Since the difference in energy loss is too large, it is not possible to record the Si and Ni core edges simultaneously. The results of the quantitative EELS analysis are reported in table 1b. It is shown that quantification results with a good accuracy and precision are obtained, except for the Ni$_3$Si phase. The reason for this is that the Si-K edge becomes very small and noisy for this phase. The accuracy is then expressed as a range calculated relative to these values.

| Phase     | N | Ratio Si/Ni (expected) | St. dev. | Rel. prec. (%) | Rel. acc. (%) |
|-----------|---|------------------------|----------|----------------|--------------|
| Ni$_3$Si  | 15| 0.299 (0.295;0.325)    | 0.022    | 7.4            | 1.4;-8.0     |
| Ni$_{31}$Si$_{12}$ | 15| 0.389 (0.387)         | 0.027    | 6.9            | 0.5          |
| Ni$_2$Si  | 15| 0.501 (0.500)         | 0.028    | 5.6            | 0.2          |
| NiSi      | 15| 1.012 (1.000)         | 0.066    | 6.5            | 1.2          |
| Ni$_2$Si  | 15| 2.023 (2.000)         | 0.189    | 9.3            | 1.2          |

Table 1. Results of the quantitative analysis.

a) Results of the quantitative EDS analysis

| Phase     | N | Ratio Si/Ni (expected) | St. dev. | Rel. prec. (%) | Rel. acc. (%) |
|-----------|---|------------------------|----------|----------------|--------------|
| Ni$_3$Si  | 20| 0.264 (0.295;0.325)    | 0.052    | 19.7           | 10.5;18.8    |
| Ni$_{31}$Si$_{12}$ | 20| 0.395 (0.387)         | 0.022    | 5.6            | 2.1          |
| Ni$_2$Si  | 20| 0.494 (0.500)         | 0.058    | 11.7           | 1.2          |
| NiSi      | 20| 1.018 (1.000)         | 0.120    | 11.8           | 1.8          |
| Ni$_2$Si  | 20| 2.009 (2.000)         | 0.159    | 7.9            | 0.5          |

*Relative accuracy is defined as 100*(estimated value - expected value)/expected value, relative precision as 100*(St.dev.)/estimated value.
EELS results are compared to the EDS results in figure 1. It is shown that EDS and EELS yield comparable results for relative precision and accuracy. The acquisition time used for the EDS data is however five times larger than for the EELS data.

![Figure 1](image)

**Figure 1.** Comparison of a) EDS and b) EELS results. The straight line represents the expected concentration ratios. The y-error bars are given by \( \frac{t \cdot \text{Stdev}}{\sqrt{N}} \) where \( t \) defines the 95% confidence interval.

3.3. **ELNES analysis**

The EELS analysis is combined with a study of the Ni-L\(_{2,3}\) edge ELNES of each phase. The ELNES of the phases can be distinguished visually by looking at the anomalous intensity ratio of the Ni-L\(_2\) and Ni-L\(_3\) white lines (figure 2) [4]. This is most clearly visible in the spectra recorded with monochromator, since a far better energy resolution is obtained for these spectra. It is clear that the L\(_3\) peak becomes smaller relative to the L\(_2\) peak if the Si concentration increases. Also, changes in the tail of the L\(_3\) peak are visible. For the Ni\(_3\)Si, Ni\(_{31}\)Si\(_{12}\) and Ni\(_2\)Si phases, a shoulder is clearly visible. The NiSi and NiSi\(_2\) phases do not show this shoulder. The branching ratio, which is defined as the ratio of the area of L\(_3\) to the sum of the areas of L\(_2\) and L\(_3\), is extracted from the spectra by using the model based approach. The same model is used as for the quantitative EELS analysis, but the spectra are recorded with a smaller dispersion. The results are presented in table 3 and figure 3. It is clear that the Ni-silicide phases can be distinguished based on the difference in branching ratio. For the NiSi\(_2\) and NiSi phases the error bars overlap.

![Figure 2](image)

**Figure 2.** Visual comparison of the ELNES, after background subtraction and deconvolution with the low loss spectrum. a), b) and c) are measured with a monochromator.
Table 3. Results of the branching ratio calculations.

| Phase | N  | Ratio Si/Ni | Branching ratio | St. dev. |
|-------|----|-------------|-----------------|----------|
| Ni$_3$Si | 30 | 0.295-0.325 | 0.854           | 0.012    |
| Ni$_2$Ni$_3$ | 30 | 0.387       | 0.816           | 0.010    |
| Ni$_2$Si | 30 | 0.500       | 0.796           | 0.012    |
| NiSi  | 30 | 1.000       | 0.774           | 0.007    |
| NiSi$_2$ | 30 | 2.000       | 0.769           | 0.012    |

Figure 3. Results of the branching ratio calculations.

4. Conclusions
The results of the characterization of a wide range of Ni-silicide phases by EDS, EELS and ELNES are presented in this paper. It is shown that both the EDS and EELS methodologies yield accurate and precise quantification results. The EELS technique is more straightforward since no standard is needed, and it is not necessary to apply an absorption correction to the data. It is also shown that the Ni-L edge ELNES can be used for phase determination, either visually as fingerprint or by calculating the branching ratio from the white line intensities.

In future research, changes in the low-loss EELS spectrum of the different Ni-silicide phases will be studied. Also, the effect of high spatial resolution on the sensitivity of these methodologies will be tested. This procedure will be extended by combining the EDS and EELS methodologies with a quantification procedure based on HAADF-STEM contrast.

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