Microsc. Microanal. 12, 318–321, 2006
DOI: 10.1017/S1431927606060405

Microscopy AND Microanalysis

Quantitative Thin-Film X-ray Microanalysis by STEM/HAADF: Statistical Analysis for Precision and Accuracy Determination

Aldo Armigliato,[1,*] Roberto Balboni,[1] and Rodolfo Rosa[1,2]

[1]*Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica e i Microsistemi (CNR-IMM), Sezione di Bologna, Via P. Gobetti 101, 40129 Bologna, Italy*
[2]*Dipartimento di Scienze Statistiche, Università di Bologna, Via delle Belle Arti, 41, 40126 Bologna, Italy*

Abstract: Silicon-germanium thin films have been analyzed by EDS microanalysis in a field emission gun scanning transmission electron microscope (FEG-STEM) equipped with a high angular dark-field detector (STEM/HAADF). Several spectra have been acquired in the same homogeneous area of the cross-sectioned sample by drift-corrected linescan acquisitions. The Ge concentrations and the local film thickness have been obtained by using a previously described Monte Carlo based "two tilt angles" method. Although the concentrations are in excellent agreement with the known values, the resulting confidence intervals are not as good as expected from the precision in beam positioning and tilt angle position and readout offered by our state-of-the-art microscope. The Gaussian shape of the SiKα and GeKα X-ray intensities allows one to use the parametric bootstrap method of statistics, whereby it becomes possible to perform the same quantitative analysis in sample regions of different compositions and thicknesses, but by doing only one measurement at the two angles.

Key words: analytical electron microscopy, Monte Carlo simulation, statistical analysis, silicon–germanium alloys

Introduction

Thin film X-ray microanalysis has benefited in the last decade from the availability in scanning transmission electron microscopes of both high angle annular detectors (STEM/HAADF) and more precise electron beam positioning, which allow better one-dimensional (1D) and two-dimensional (2D) drift-corrected elemental mapping to be performed. Moreover, instrumental parameters, such as the reproducibility of vertical movement of the sample and the precision of tilting, positioning, and readout, are now known with better accuracy. However, this does not necessarily imply, even in favorable specimens, that the precision and accuracy of the elemental concentrations is higher than in the past.

The aim of this work is to determine these parameters by a suitable statistical analysis of the film composition values obtained from a series of energy dispersive spectroscopy (EDS) spectra taken for different tilting angles in a uniform region of a Si-Ge thin film alloy. The Ge concentration and the local thickness values are deduced from the previously described Monte Carlo based "two tilt angles method" (Armigliato & Rosa, 1990; Armigliato, 1999), whereas the confidence intervals have been assessed by the so-called parametric bootstrap method (Armigliato & Rosa, 1990).

Received May 6, 2005; accepted April 4, 2006.
*Corresponding author. E-mail: aldo.armigliato@imm.cnr.it

Materials and Methods

$Si/Si_{1-x}Ge_x/Si$ heterostructures with two different Ge concentrations x have been deposited by chemical vapor deposition (CVD) on ⟨001⟩ silicon wafers. They will be henceforth referred to as SIGE1 and SIGE2, respectively. The Si-Ge alloy film, as well as the top layer cap silicon film (cap), are 100 nm thick in both samples. Prior to the Si-Ge deposition, a 1-μm-thick Si buffer layer was grown on the surface of the wafer to favor epitaxial growth of the Si-Ge film on the substrate. The fraction of Ge, x, was independently determined with great accuracy by Rutherford backscattering spectrometry (RBS) and amounts to $x = 0.127$ (SIGE1) and $x = 0.077$ (SIGE2).

Specimens were cross-sectioned for the thin film microanalysis measurements by a standard method involving sawing, gluing, mechanical lapping, and finally ion beam polishing to perforation by a Gatan PIPS miller. A 200-kV FEI Tecnai F20 FEG-(S)TEM, equipped with a high-angle annular dark-field (HAADF) detector, the TIA (Tecnai Interface Analysis) software, and an EDAX Sapphire detector

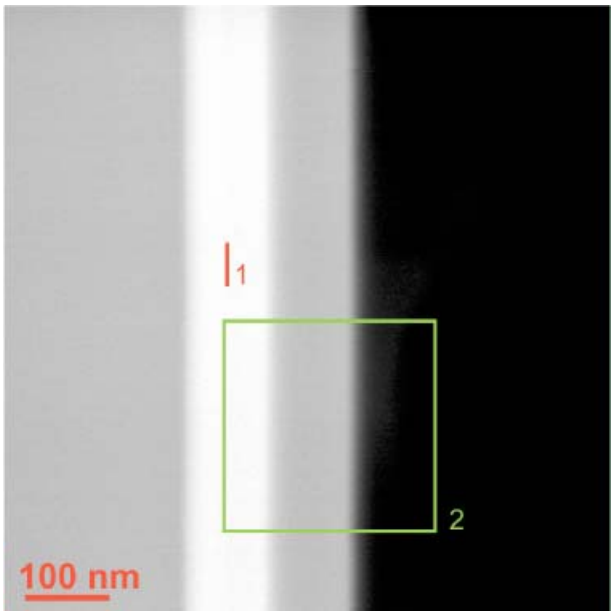

Figure 1. Cross-sectional HAADF/STEM image of the SIGE1 Si/$Si_{1-x}Ge_x$/Si heterostructure ($x = 0.127$). The regions where the 10 spectra were acquired at each angle of tilt and the square image detail chosen for antidrift correction are labeled (1) and (2), respectively.

were employed for X-ray microanalysis of the heterostructures. Drift-corrected multiple acquisition of X-ray spectra in the same area of the specimen was performed, using an electron spot of about 1 nm in diameter. For the application of the two tilt angles method the sample was tilted about an axis parallel to the ⟨001⟩ direction normal to the wafer surface in the 5°–20° range off the ⟨110⟩ orientation. The sample temperature was kept at 100 K, by using a Gatan LN_2-cooled double-tilting holder in order to reduce contamination.

Results and Discussion

Figure 1 shows a cross-sectional TEM image of one of the investigated Si-Ge heterostructures. From left to right the sequence corresponds to the top part of the 1-μm silicon buffer, the 100-nm Si-Ge film, and the 100-nm silicon cap.

Analytical Results from the Two Tilt Angles Method

The so-called two tilt angles Monte Carlo method described in previous papers (Armigliato & Rosa, 1990; Armigliato, 1999) is based on the convergence of the ratio between the experimental intensities of the SiKα and GeKα lines at two different tilt angles. We have acquired four series of 10 spectra each in the chosen sample area (e.g., that in Fig. 1) at four different angles of tilt (φ) toward the detector (5°, 10°, 15°, and 20°). The case $\varphi = 0°$ was not considered, due to the shadowing effect of the specimen holder, which is due to the relatively small elevation angle of the EDS detector in the Tecnai microscope (14.73°). Due to the geometry of the combination microscope–spectrometer, the takeoff angle is just 14.73° + φ, that is, it ranges from 19.73° up to 34.73° in our experiments. For each couple of angles φ_1, φ_2 we have determined the net X-ray intensities I_i^j (with i = SiKα and GeKα, $j = \varphi_1$ and φ_2) and calculated the ratios $R_j^m = I_1^j/I_2^j$. The next steps are (1) the generation by a MC code of two sets of corresponding computed ratios of X-ray intensities $R_j^c(C;t)$ as a function of Ge concentration C (at.%) and thickness t (nm) and (2) the minimization of the difference $|R_j^c(C;t) - R_j^m|$, to obtain the point estimates $\hat{C}$ and $\hat{t}$.

For each couple φ_1, φ_2 this procedure allows one to plot in a $(C; t)$ plane two curves corresponding to the two tilt angles. Their intersection yields the required $\hat{C}$ and $\hat{t}$ values (see also Armigliato & Rosa, 1990, for more details), obtained considering all possible (i.e., 100) measured ratios from the two sets of intensities.

The results for both samples are reported in Table 1. Note that the errors $\hat{\sigma}_C$ and $\hat{\sigma}_t$ associated to $\hat{C}$ and $\hat{t}$, respectively, represent one half of the 68% confidence intervals.

To discuss these results, we note an effect already reported in our previous papers (Armigliato & Rosa, 1990; Armigliato, 1999), namely, that the characteristic curves do not yield an intersection for all the couples. On the other hand, we have found that the availability of a large number of intersections, which is related to the quality of the whole experimental procedure, results in more precise analytical values, without impairing the accuracy of the resulting Ge concentration data. Therefore, we restricted further analyses to the couples 5°–20° and 10°–20° for sample SIGE 1 and to the couples 5°–15° and 5°–20° for sample SIGE 2, because they yield the greatest number of intersections. Figure 2

Table 1. Estimates and Associated Errors of Ge Concentration C (at.%) and Thickness t (nm) for Both Samples, Obtained by the Two Tilt Angles Method[a]

RBS ($C \pm \sigma$)	Local thickness by STEM and PEELS ($t \pm \sigma$)	Monte Carlo two tilt angles method				
		Angles couple	$\hat{C}$	$\hat{\sigma}_C$	$\hat{t}$	$\hat{\sigma}_t$
12.7 ± 0.3	STEM: 540 ± 50	5°–20°	12.5	0.9	500	230
	PEELS: 490 ± 100	10°–20°	12.7	1.0	410	260
7.7 ± 0.5	STEM: 440 ± 30	5°–15°	7.8	0.6	480	260
	PEELS: 530 ± 100	5°–20°	7.5	0.4	470	280

[a]Angle couples: 5°–20° and 10°–20° for SIGE1, 5°–15° and 5°–20° for SIGE2. The experimental C and t values are also reported for comparison.

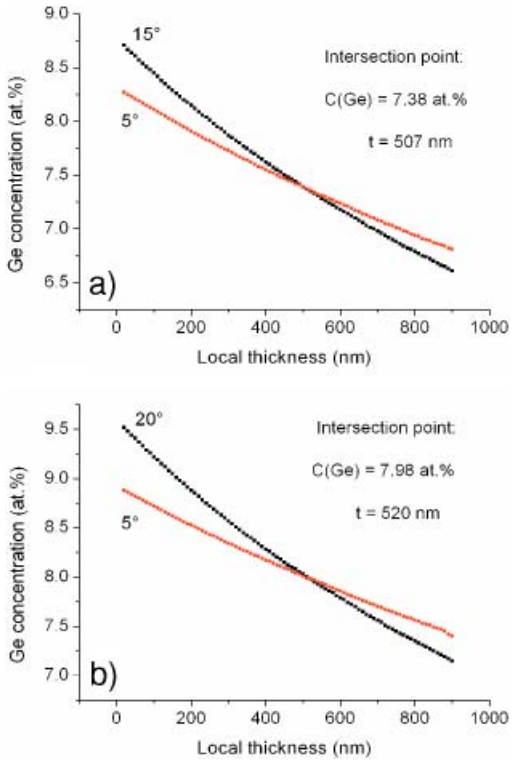

Figure 2. (C, t) characteristic curves generated by the two tilt angles method in SIGE2 for the couples 5°–15° (**a**) and 5°–20° (**b**). The intersection points yield the Ge concentration and the local sample thickness simultaneously. Note the close agreement between the two (C, t) couples of values.

reports, as an example, two pairs of the characteristic curves for the two couples of angles, relative to sample SIGE 2.

For comparison, the C(Ge) values obtained by RBS are reported, together with the thickness deduced from two experimental techniques available for these rather thick samples, namely, the electron energy loss spectrometry and the effect of projection of an inclined interface, which is visible in STEM/HAADF images upon tilting about an axis parallel to the interface plane. The former method exploits the electron energy straggling effect, which gives rise to a broad background under the plasmon peaks, whose maximum occurs at an energy loss E_p much higher than the most probable energy loss $E_m = 19.6$ eV in silicon. The thickness is deduced from the relation $t/\lambda = E_p/E_m$, where λ is the mean free path for inelastic scattering (Egerton, 1996). The projection effect method simply consists of measuring the width of the interface projected onto the screen plane in the STEM image, then dividing it by the tangent of the tilt angle (e.g., for a 4° tilt, the thickness is 14.3 times the projected width). Table 1 shows that the concentration values are in excellent mutual agreement, whereas the thickness value also agrees well with the rather broad distribution found by the two tilt angles method.

Table 2. Relative Errors of the Measured Intensities at 5°, 10°, and 20° Tilt Angles (Sample SIGE 1)

Tilt angle	$\Delta I(\text{SiK}\alpha)/I(\text{SiK}\alpha)$	$\Delta I(\text{GeK}\alpha)/I(\text{GeK}\alpha)$
5°	0.014	0.057
10°	0.010	0.047
20°	0.010	0.068

Analytical Results from the Bootstrap Method

By means of the parametric bootstrap method, it is possible to assign confidence intervals to to $\hat{C}$ and $\hat{t}$ with only one measurement at each one of two tilt angles.

The procedure starts with the collection of an experimental X-ray intensity couple I_i^j, performed at two tilt angles φ_1 and φ_2 in a single point of the sample; then, from a Gaussian with mean I_i^j and variance $(\hat{\sigma}_i^j)^2$, a large number $B = 1000$–$10{,}000$ of virtual intensities measurements for SiKα and GeKα, at φ_1 and φ_2, is generated. The above procedure is applicable because the measured intensities are Gaussian shaped, as has been verified by applying normality tests to the measured intensities. Finally, B ratios R_j^b are computed and the two tilt angles method is applied, in order to obtain the distributions (and hence the confidence intervals) of C and t that minimize the B difference $|R_j^b(C;t) - R_j^m|$.

For SIGE1 the relative errors on the measured intensities, deduced from the series of experimental spectra, are reported in Table 2. Note that for the GeKα X-ray line the relative errors are about 5%–7%.

By applying the parametric bootstrap with $B = 5000$ we obtained the results reported in Table 3, together with the results deduced from other techniques as in Table 1. It appears that the parametric bootstrap yields results in fair

Table 3. Estimates and Associated Errors of Ge Concentration C (at.%) and Thickness t (nm) for Both Samples, Obtained with the Parametric Bootstrap[a]

RBS $(C \pm \sigma)$	Local thickness by STEM and PEELS $(t \pm \sigma)$	Parametric bootstrap				
		Angles couple	$\hat{C}^*$	$\hat{\sigma}_C^*$	$\hat{t}^*$	$\hat{\sigma}_t^*$
12.7 ± 0.3	STEM: 540 ± 50	5°–20°	12.6	1.0	520	230
	PEELS: 530 ± 100	10°–20°	12.8	1.1	420	270
7.7 ± 0.5	STEM: 540 ± 50	5°–15°	7.9	0.6	480	240
	PEELS: 530 ± 100	5°–20°	7.6	0.5	460	280

[a]Angle couples: 5°–20° and 10°–20° for SIGE1, 5°–15° and 5°–20° for SIGE2.

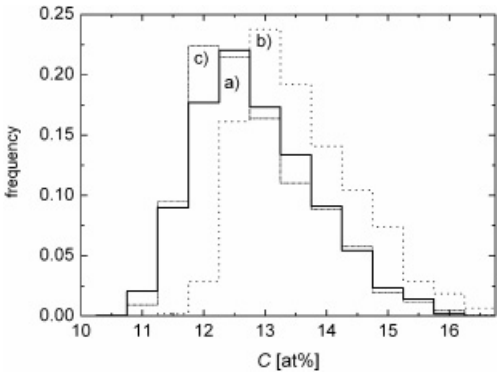

Figure 3. Frequency distributions of $\hat{C}^*$, obtained by the parametric bootstrap for three experimental intensity values and with the angle couple 5°–20°.

agreement with those obtained with 10 experimental measurements at each angle.

Figure 3 reports the frequency distributions of $\hat{C}^*$ for three experimental intensity values and with the angular couple 5°–20° (SIGE1). Note that the distributions are not normal shaped. We tested the method with different measured intensities, and, as expected, the exact values of $\hat{C}^*$ and $\hat{t}^*$ depend on the intensity values given as input, but the associated errors $\hat{\sigma}_C^*$ and $\hat{\sigma}_t^*$ stay the same. The data reported in Table 3 refer to the histogram labeled as a in Figure 3 (continuous line). For the b (dotted line) and c (dashed line) histograms, $\hat{C}^*$ are equal to 12.8 and 12.6, respectively, whereas $\hat{\sigma}_t^*$ are both equal to 1.0.

As a discussion of these results, we point out that the parametric bootstrap method represents a useful data elaboration procedure in practical X-ray thin-film quantitative microanalysis, because it allows the experimenter to deduce the film composition together with the associated precision and accuracy by performing a single spectrum acquisition at two different tilt angles with good counting statistics. This obviously shortens the time required for the experiment, which is an advantage in terms of the overall stability of the microscope–spectrometer combination.

Conclusions

This work demonstrates that quantitative thin-film X-ray microanalysis of Si-Ge alloys, performed with state-of-the-art STEMs, despite the better controlled experimental conditions, does not yield concentration values more *precise* (about 8% relative) than in the past. However, the *accuracy* is quite good (about 1% relative). This information is obtained from the application of the Monte Carlo based two tilt angles method to a series of 10 spectra acquired in the same area of the sample.

Moreover, the Gaussian shape of the experimental X-ray intensities enables the use of the parametric bootstrap method, once the confidence intervals are known from the previous procedure. The bootstrap results suggest that if one estimates once for all the precisions of the measured intensities in certain experimental conditions, one can assign with confidence concentrations and thickness errors to X-ray microanalysis experiments from just one X-ray intensity measurement (instead of 10), performed in the same experimental conditions at two tilt angles in different points of the sample.

References

Armigliato, A. (1999). Thin film X-ray microanalysis with the analytical electron microscope. *J Anal At Spectrom* **14**, 413–418.

Armigliato, A. & Rosa, R. (1990). Simultaneous determination of composition and thickness of thin films by X-ray microanalysis at 300 kV and Monte Carlo simulation. *Ultramicroscopy* **32**, 127–136.

Egerton, R.F. (1996). *Electron Energy-Loss Spectroscopy in the Electron Microscope*, 2nd ed. New York: Plenum Press.