DOI: 10.1017/S1431927605507499
Microsc Microanal 11(Suppl 2), 2005
Copyright 2005 Microscopy Society of America

Quantitative Electron Probe Microanalysis of Si-Ge Reference Materials

R. B. Marinenko, S. Turner, D. E. Newbury, L. Richter, L. Yu, R. Zeisler, D. Simons
National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg MD 20899

Si-Ge alloy research materials are being characterized at NIST in cooperation with the semiconductor industry for use in the quantification of Si-Ge films used for components now being used in a multitude of high-tech devices. We have tested the macro- and micro-heterogeneity of SiGe single crystal boules and 4-μm thick films of SiGe on Si with wavelength dispersive electron probe microanalysis (WD-EPMA) and have determined that these materials would make good microanalysis standards [1]. The total expanded (k=2, 95%) Ge homogeneity uncertainty for five different specimens from a single-crystal SiGe14 (14 at. % Ge) boule was 0.9 % relative and for five specimens from each of the SiGe10 and SiGe25 films it was 1.3 % relative or less.

We are now quantifying these materials using EPMA and bulk techniques, namely, neutron activation analysis (INAA) and inductively coupled plasma-optical emission spectroscopy (ICP-OES). Results in % mass fraction (mf) of the bulk analyses compared to the nominal value for the SiGe14 boule are listed in Table 1. EPMA quantification of this binary system with EPMA is complicated by the large mass absorption coefficient (MAC) for SiKα line ($K\text{-}L_{2,3}$ transition) in the presence of Ge as well a significant range of values from the different MAC sources. The SiKα X-ray fluoresces the GeLα ($L_3\text{-}M_{4,5}$) line making this line difficult to use in quantitation especially at lower voltages where the GeLα line would be most useful. In addition, there are atomic number corrections for the GeKα X-ray line.

The need for homogeneous reference standards over a range of compositions between the two pure end members was clear in the M&M 2001 paper by Carpenter in which he described the use of α-factors from several data reduction procedures to determine the accuracy one could expect in the 20 keV analysis of GeSi alloys [2]. For our characterization work the GeKα line is more useful for quantification especially for the bulk specimens we are characterizing. Initial analyses with the GeLα line demonstrated little consistency in results from multiple excitation potentials (15, 20, and 25 keV), from different correction procedures, and from the GeLα and GeKα lines. The results reported here were calculated with Armstrong's correction procedure although the full PAP procedure was also used with similar results [3,4]. Either Heinrich's '86 ICXOM MACs or the combination of Henke's 85 and Armstrong's MACs (called LINEMU) were used and are indicated [5].

In Table 2 are the correction factors for the SiKα and GeKα X-ray lines taken from Armstrong's correction procedure using Heinrich's MACs at 15, 20, and 25 keV. There is no fluorescence correction in this system. The greatest correction is for absorption of the SiKα line that even at 15 kV is near the generally recommended lower limit of 0.70. There are atomic number corrections for the SiKα and GeKα X-ray lines, but the GeKα correction at 15 keV is only 5 % less than at 25 keV suggesting that this line can be used at 15 keV, a reasonable compromise excitation potential for simultaneous measurements of both lines.

The average % mf concentrations for SiKα and GeKα from WD-EPMA of 10 points from each of five specimens taken from the SiGe14 single-crystal boule are listed in Table 3 for three excitation potentials. The 15 keV results for Ge are most similar to the nominal composition and to the ICP-OES results in Table 1 and the total at 15 keV is about 100 %. For the 20 keV and 25 keV results, the Si and Ge concentrations are respectively about 1 % and 4 % greater than those determined at the lower excitation potential, and the Ge results are greater than the reported INAA values in Table 1. In the two columns on the right of Table 3 are the results of a mixed keV correction procedure for SiKα at 15 keV and GeKα at 20 and 25 keV. Results here are consistent with the 15 keV values.

https://doi.org/10.1017/S1431927605507499 Published online by Cambridge University Press

In Table 4 are the WD-EPMA average values from the analysis of 20 points on each of five different specimens from the SiGe10 and SiGe25 4-μm films on Si. Results are consistent for Ge at 15 and 20 keV as well as for the mixed keV correction. Totals are less than 100 %. This may be due to the film densities that may be less than that of the standards. Energy dispersive (EDS) analyses of the films are reported in the last two columns and are, at most, 3 % relative higher for the Ge in the SiGe10 film analyzed at 15 keV. Differences are primarily attributed to the use of different correction procedures since k-values determined from WDS and EDS data agreed to within 1 % relative.

References

[1] R. B. Marinenko et. al , Amer. Inst. of Physics (AIP) Conf. Proc. of ULSI 2003 Meeting, Austin, TX, (2003).

[2] P. Carpenter and S. D. Cobb, Microsc. Microanal. 7 (Suppl 2) (2001) 682.

[3] J. T. Armstrong, Electron Probe Quantitation, Plenum Press, NY (1991) 261.

[4] J. L. Pouchou and F. Pichoir, Electron Probe Quantitation, Plenum Press, New York (1991) 31.

[5] K. F. J. Heinrich, Proc. 11th Internat. Cong. on X-ray Optics and Microanal., Aug. 1986, London, CA.

Tables: All concentrations in % mf with relative expanded uncertainties in parentheses.

Table 1. Bulk analysis of SiGe14 boule.

SiGe14 Boule	Technique (# samples)	
Nom. Ge Comp	ICP-OES (2)	INAA (5)
29.61	29.73 (0.5)	30.35 (1.5)

Table 2. ZAF correction factors for anal. of SiGe14 boule with ele.stds.

keV	Element	Z	A
15	Si Kα	1.0629	0.7199
	Ge Kα	0.8040	1.0009
20	Si Kα	1.0605	0.5962
	Ge Kα	0.8273	1.0018
25	Si Kα	1.0596	0.4878
	Ge Kα	0.8424	1.0027

Table 3. Analysis of SiGe14 bulk alloy in % mf with element standards

Sample/ Ele,Line	Armstrong Correction/ LineMu MACs			Mixed keV Armst Cor/Hein'86 MACs	
SiGe14	15 keV	20 keV	25 keV	15, 20 keV	15, 25 keV
Si Kα	70.88(0.6)	71.35(0.8)	71.70(0.4)	70.56(0.6)	70.57(0.6)
Ge Kα	29.58(1.4)	30.79(0.4)	30.95(1.0)	29.49(0.4)	29.79(1.0)
Total	100.56	102.14	102.65	100.15	100.36

Table 4. Analysis of SiGe thick films with element standards

Sample/ Ele,Line	Armstrong Cor/LineMu MACs		Mixed keV (as in Table 1)	EDS Analysis	
SiGe10	15 keV	20 keV	15, 20 keV	15 keV	20 keV
Si Kα	75.94	75.72	76.75	76.41	75.87
Ge Kα	22.42	22.90	22.95	23.12	23.03
Total	98.37	98.61	99.70	99.53	98.90
SiGe25					
Si Kα	55.04	55.15	55.71	55.47	55.57
Ge Kα	43.80	44.14	44.16	44.56	44.54
Total	98.84	99.30	99.87	100.13	100.48

https://doi.org/10.1017/S1431927605507499 Published online by Cambridge University Press