National Institute of Standards & Technology

Report of Investigation

Reference Material 8095

$Si_{1-x}Ge_x$ Films on Si

This Reference Material (RM) is intended to provide a microanalysis reference standard for the semiconductor industry, primarily for secondary ion mass spectrometry (SIMS) analyses. A unit of RM 8095 consists of two 1 cm × 1 cm sections, each with a different film of $Si_{1-x}Ge_x$ on Si. The films have nominal compositions of 10 % (atom fraction) Ge in Si ($Si_{0.90}Ge_{0.10}$) and 25 % (atom fraction) Ge in Si ($Si_{0.75}Ge_{0.25}$). This Report of Investigation applies to serial numbers 8095-1 through 8095-5.

Reference Values: Reference values for the film compositions in mass fractions are provided in Table 1. Reference values are non-certified values that are the present best estimates of the true values. However, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may not include all sources of uncertainty [1].

Information Values: Information values for the Ge concentrations in atom fractions and atom fraction ratios are provided in Table 2. An information value is considered to be a value that may be of interest to the RM user, but insufficient information is available to assess the uncertainty associated with the value [1].

Expiration of Value Assignment: The reference values for **RM 8095** are valid indefinitely, within the uncertainty specified, provided the RM is handled and stored in accordance with the instructions given in this certificate (see "Instructions Handling, Storage, and Use"). Accordingly, periodic recalibration or recertification of this RM is not required. The certification is nullified if the RM is damaged, contaminated or otherwise modified.

Maintenance of RM: NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

The overall technical coordination for material procurement, processing and measurement activities was conducted by S. Turner, R.B. Marinenko, D.S. Simons, and J.A. Small of the NIST Surface and Microanalysis Science Division.

Reference and information value measurements and sample preparation were performed by R.B. Marinenko, D. Klinedinst, L.J. Richter, D.C. Meier, K.C.K. Scott, N.W.M. Ritchie, D.E. Newbury, S. Turner and E.S. Windsor of the NIST Surface and Microanalysis Division, R.L Zeisler, R.L. Paul, S.A. Rabb, L.L. Yu, and M.R. Winchester of the NIST Analytical Chemistry Division.

SIMS depth profile measurements were obtained by K.J. Kim, guest researcher in the NIST Surface and Microanalysis Science Division and by T. Büyüklimanli of Evans Analytical Group (East Windsor, NJ).

Statistical consultation for this RM was provided by S.D. Leigh of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this RM were coordinated through the NIST Measurement Services Division.

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INSTRUCTIONS FOR HANDLING, STORAGE, AND USE

Handling: The film side of the two RM sections is the polished, reflective side. These surfaces were cleaned by ultrasonification in acetone and isopropyl alcohol under clean room conditions prior to packaging. Immediately prior to use, dust particles should be removed from the surface with a pressurized duster.

Storage: When not in use the RM should be stored in its original container.

Use: To use these films as composition reference materials for SIMS, the Ge compositions in atom fractions and the atom ratios of Table 2 should be utilized. Note that the compositions of the films given in Tables 1 and 2 refer only to the portion of the films within 1.5 μm of the sample surface for the $Si_{0.90}Ge_{0.10}$ film and within 2.0 μm of the sample surface for the $Si_{0.75}Ge_{0.25}$ film.

PREPARATION AND ANALYSIS[(1)]

Material Source and Preparation: The films were prepared by chemical vapor deposition by Advanced Semiconductor Materials America (ASM America), Phoenix, AZ with nominal compositions of 10 % (atom fraction) Ge in Si ($Si_{0.90}Ge_{0.10}$) and 25 % (atom fraction) Ge in Si ($Si_{0.75}Ge_{0.25}$) on 20 cm diameter Si wafers. The nominal film thicknesses are 4 μm and 5 μm, respectively. The Si wafers were cut in half. One half of each wafer was sawed into 1 cm × 1 cm sections.

Homogeneity Testing: Spectroscopic ellipsometry of the uncut 20 cm wafer showed that the maximum lateral chemical homogeneity occurred within approximately a 5 cm radius around the wafer center. SIMS depth profiles showed that some changes occur in the films below 2 μm. Some details of the depth profile analyses are given in the Appendix and in reference 3. From these results it is recommended that the use of these films as reference standards be restricted to a depth no greater than 1.5 μm for the $Si_{0.90}Ge_{0.10}$ film and 2.0 μm for the $Si_{0.75}Ge_{0.25}$ film.

Five sections from each wafer were selected from the region of maximum chemical homogeneity for electron probe microanalysis (EPMA) characterization. Quantitative chemical homogeneity of the films was tested with wavelength dispersive spectrometer (WDS) EPMA using thallium acid phthalate (TAP) and pentaerythritol (PET) crystals to acquire X-ray count data from the GeLα and SiKα peaks, respectively. Tests included 50 μm linear traverses in 2 μm steps, random point analyses, and nested design experiments in which 10 randomly-selected points were each sampled three times on each of the five specimens taken from the two film wafers. The nested design experiment was used to determine the within-specimen, between-specimen, and measurement heterogeneity uncertainties. The combined expanded heterogeneity uncertainty, $2\sigma_W$, for $Si_{0.90}Ge_{0.10}$ was determined to be 1.04 % mass fraction (relative) for Ge and 0.68 % mass fraction (relative) for Si; the combined expanded heterogeneity uncertainty, $2\sigma_W$, for $Si_{0.75}Ge_{0.25}$ was determined to be 0.94 % mass fraction (relative) for Ge and 1.48 % mass fraction (relative) for Si. A table with further details of the homogeneity testing results is given in the Appendix. Details of the testing procedures and analyses can be found in recent publications [2,3].

Quantification: The films were analyzed at 15 kV and 20 kV with WDS EPMA using the SiKα and GeKα X-ray lines [3] with PET and LiF crystals, respectively. Five points were sampled at 15 kV, and 10 points were sampled at 20 kV on each of five specimens from each film. Data were quantified with the Love-Scott II matrix correction procedure [4] using X-ray form factor, attenuation and scattering tables (FFAST) mass absorption coefficients [5]. Pure element wafers and a $Si_{0.86}Ge_{0.14}$ boule were used as reference standards. The characterization of the $Si_{0.86}Ge_{0.14}$ boule was reported [6] and the expanded overall heterogeneity uncertainty, $2\sigma_W$, was determined to be 0.92 % mass fraction (relative) for Ge and 0.81 % mass fraction (relative) for Si. The Ge composition was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and instrumental neutron activation analysis (INAA) to be 30.228 % mass fraction with an expanded uncertainty of the mean of 0.195 % mass fraction [6]. The Ge and Si concentrations calculated for both films are consistent at both 15 kV and 20 kV, and they are consistent using both the pure elements and the $Si_{0.86}Ge_{0.14}$ boule as reference standards. The mass balance for the two elements in the films is less than 100 % mass fraction. The reasons are not fully evident without further investigation. A short description of work done to investigate the lack of mass balance is given in the Appendix and further details are given in reference 3.

[(1)] Certain commercial equipment, instruments or materials are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Reference Values for Ge, Si and Total (Mass Fraction, in %)

Film	Si (mass fraction, %)[a]	Ge (mass fraction, %)[a]	Total (mass fraction, %)[b]
$Si_{0.90}Ge_{0.10}$	74.96 ± 0.67 (0.89 %)	22.80 ± 0.10 (0.44 %)	97.77 ± 0.68 (0.70 %)
$Si_{0.75}Ge_{0.25}$	53.50 ± 0.34 (0.64 %)	43.66 ± 0.21 (0.48 %)	97.16 ± 0.40 (0.41 %)[c]

[a] The reference values for Si and Ge mass fraction, in %, are a weighted mean of the results from EPMA obtained under four experimental conditions. The uncertainties for the elemental values are an expanded uncertainty about the mean with coverage factor 2, calculated by combining variance between experimental conditions [7-9] with a pooled variance across the four experimental conditions following the ISO Guide [10]. Relative expanded uncertainties are provided in parentheses. Uncertainties for data collected under each experimental condition are given in reference 3.

[b] The uncertainties for the total values are calculated from propagation of uncertainty. Relative expanded uncertainties for the total values are provided in parentheses.

[c] The uncertainties reported here are slightly different from those reported in reference 3 due to the recent adoption of an updated procedure for calculating uncertainties from different sources [7-9].

Table 2. Information Values for Ge (Atom Fraction) and Ge/Si Atom Ratio

Film	Ge (atom fraction)[a]	Ge/Si Atom Ratio[a]
$Si_{0.90}Ge_{0.10}$	0.1052 ± 0.0009 (0.90 %)	0.1176 ± 0.0012 (1.01 %)
$Si_{0.75}Ge_{0.25}$	0.2398 ± 0.0015 (0.61 %)	0.3155 ± 0.0025 (0.80 %)

[a] The information values for Ge atom fraction and Ge/Si atom ratio were obtained by normalizing the mass fraction values in Table 1. The Si and Ge mass fractions for a given film were multiplied by a common scaling factor so that their normalized mass fractions total 100 %. The normalized mass fraction ratios were divided by the atomic weight ratio of the two elements to obtain the atom fraction ratios and from these values the atom fractions of Ge for the two films were calculated. The uncertainties were obtained using a Monte Carlo procedure based on the mass fraction uncertainties of Table 1. The uncertainties are an expanded uncertainty about the mean with a coverage factor 2. Relative expanded uncertainties for the total values are provided in parentheses.

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Users of this RM should ensure that the Report of Investigation in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

APPENDIX

Depth Profiles: An example SIMS depth profile plot for a $Si_{0.75}Ge_{0.25}$ film specimen is given in Figure A1 below. Below 2 μm, gradual concentration changes occur. In the six $Si_{0.75}Ge_{0.25}$ specimens measured, the Ge/Si ratio increased by 2.9 % ± 0.9 % (1σ) at a depth interval of 3 μm to 4 μm relative to a depth interval of 0.5 μm to 2 μm. For the $Si_{0.90}Ge_{0.10}$ specimens, this transition was negative, 1.6 % ± 0.8 % (1σ) for a depth interval of 2 μm to 3 μm relative to a depth interval of 0.5 μm to 1.5 μm. Further details of analyses are given in reference 3.

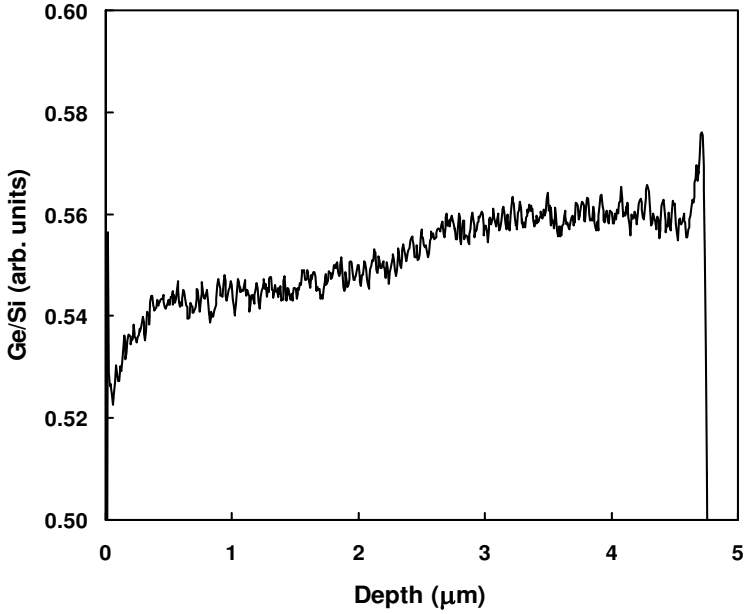

Figure A1. SIMS depth profile plot of Ge/Si ratio vs. depth for a $Si_{0.75}Ge_{0.25}$ film specimen. The ratio in this sample is constant to about a depth of about 2 μm and then increases by 2.9 % over an interval of about 1 μm after which it appears to remain constant down to the film-Si interface. The ratio change near the top surface is a SIMS-related artifact.

Homogeneity Results: A summary of homogeneity testing of the films is given in Table A1 below.

Table A1. Information Values for Expanded Heterogeneity Uncertainties in Relative % Mass Fraction[a]

	$Si_{0.90}Ge_{0.10}$		$Si_{0.75}Ge_{0.25}$	
	Ge Heterogeneity (mass fraction, %)	Si Heterogenetiy (mass fraction, %)	Ge Heterogeneity (mass fraction, %)	Si Heterogeneity (mass fraction, %)
$2\sigma_{SW}$[b]	0.70	0.46	0.68	1.32
$2\sigma_{PW}$	0.46	0.36	0.57	0.54
$2\sigma_{EW}$	0.62	0.36	0.38	0.40
$2\sigma_{W}$	1.04	0.68	0.94	1.48

[a] Ge was measured using the GeLα X-ray line with a TAP crystal; Si was measured using the SiKα X-ray line with a PET crystal.

[b] $2\sigma_{SW}$ is between-specimen expanded uncertainty, $2\sigma_{PW}$ is between-points expanded uncertainty, and $2\sigma_{EW}$ is the measurement expanded uncertainty. These uncertainty components were combined in quadrature to obtain the combined expanded heterogeneity uncertainty, $2\sigma_{W}$.

Mass Balance: The lack of mass balance in these films may be caused by physical characteristics, such as very small voids in the films, vacancies in the lattice, or a density that is different from the SiGe boule that was used as a standard. INAA, Auger spectrometry, and FIB SEM analyses were used to evaluate these possibilities. Impurities are known to be present. Traces of carbon and oxygen were observed in 2000s, 10 kV EDS spectra of both films, but these elements were also observed in EDS spectra of the pure Si and Ge wafers used as reference materials for the quantification. Oxygen (atom fraction > 10 %) and some carbon were detected on the surfaces of the films to depths from 3 nm to 6 nm with field emission Auger electron spectroscopy, and a NIST Monte Carlo [11] calculation determined that the amount of oxygen detected by Auger spectroscopy could be responsible for as much as a 1 % mass fraction loss of GeKα X-rays. No voids were observed in the FIB SEM work, so if present, they would be expected to be at the atomic level. Some work may be done in the future with the analytical electron microscope to investigate the structure of these films more fully. In addition to the possibilities cited above, elements may be present that could not be detected by EPMA. Hydrogen was eliminated as a major contributor to the mass discrepancy by INAA where each film was determined to contain a hydrogen concentration < 1 $\mu g/cm^2$. SIMS depth profiles obtained from Evans Analytical Group (East Windsor, NJ) of both films confirmed the INAA results. Surface concentrations of oxygen, carbon, and hydrogen decreased to 0.0002 atom fraction or less at 100 nm below the film surface, and both oxygen and carbon concentrations continued to decrease with depth.