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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Test Method for Quantifying Tungsten Silicide Semiconductor Process Films for Composition and Thickness[1]

This standard is issued under the fixed designation F 1894; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative determination of tungsten and silicon concentrations in tungsten/silicon (WSi_x) semiconductor process films using Rutherford Backscattering Spectrometry (RBS).[2] (**1**) This test method also covers the detection and quantification of impurities in the mass range from phosphorus Å (31 atomic mass units (amu) to antimony (122 amu).

1.2 This test method can be used for tungsten silicide films prepared by any deposition or annealing processes, or both. The film must be a uniform film with an areal coverage greater than the incident ion beam (~2.5 mm).

1.3 This test method accurately measures the following film properties: silicon/tungsten ratio and variations with depth, tungsten depth profile throughout film, WSi_x film thickness, argon concentrations (if present), presence of oxide on surface of WSi_x films, and transition metal impurities to detection limits of 1×10^{14} atoms/cm^2.

1.4 This test method can detect absolute differences in silicon and tungsten concentrations of ±3 and ±1 atomic percent, respectively, measured from different samples in separate analyses. Relative variations in the tungsten concentration in depth can be detected to ±0.2 atomic percent with a depth resolution of ±70Å.

1.5 This test method supports and assists in qualifying WSi_x films by electrical resistivity techniques.

1.6 This test method can be performed for WSi_x films deposited on conducting or insulating substrates.

1.7 This test method is useful for WSi_x films between 20 and 400 nm with an areal coverage of greater than 1 by 1 mm^2.

1.8 This test method is non-destructive to the film to the extent of sputtering.

1.9 A statistical process control (SPC) of WSi_x films has been monitored since 1993 with reproducibility to ±4 %.

1.10 This test method produces accurate film thicknesses by modeling the film density of the WSi_x film as WSi_2 (hexagonal) plus excess elemental Si[2]. The measured film thickness is a lower limit to the actual film thickness with an accuracy less than 10 % compared to SEM cross-section measurements (see 13.4).

1.11 This test method can be used to analyze films on whole wafers up to 300 mm without breaking the wafers. The sites that can be analyzed may be restricted to concentric rings near the wafer edges for 200-mm and 300-mm wafers, depending on system capabilities.

1.12 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* The reader is referenced to Section 8 of this test method for references to some of the regulatory, radiation, and safety considerations involved with accelerator operation.

2. Referenced Documents

2.1 Terminology used in this document is consistent with terms and definitions as used in the *Compilation of ASTM Standard Definitions*, 8th ed ASTM, 1994, Philadelphia PA, USA, specifically for terms taken from the following ASTM standards:

2.2 *ASTM Standards:*

E 135 Terminology of Analytical Chemistry for Metals, Ores, and Related Materials[3]

E 673 Terminology Relating to Surface Analysis[4]

E 1241 Terminology of Semiconductor Technology[5]

3. Terminology

3.1 Numerous terms specific to RBS and ion stopping in solids can be found in the following references (**1, 2**)[2].

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 WSi_x—a tungsten silicide film characterized by a silicon/tungsten atomic ratio >2.00.

3.2.2 incident ions—He^+ or He^{++} ions with energy in the range of 2.25 to 2.30 MeV delivered to a sample surface from an appropriate ion source and accelerator system.

3.2.3 backscattered ions—Helium particles (charged or neutral) recoiling from atoms in a sample structure irradiated with a collimated beam of incident ions.

[1] This test method is under the jurisdiction of Committee F-1 on Electronics, and is the direct responsibility of Subcommittee F01.06 on Silicon Materials and Process Control.

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[2] The boldface numbers in parentheses refer to a list of references at the end of the text.

[3] *Annual Book of ASTM Standards*, Vol 03.05.

[4] *Annual Book of ASTM Standards*, Vol 03.06.

[5] *Annual Book of ASTM Standards*, Vol 10.05.

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3.2.4 RBS—Rutherford backscattering spectromerty, the energy analysis of backscattered ions for sample composition and depth profile.

3.2.5 normal angle detector—a detector situated at an angle between 160 and 180° from the forward trajectory of the incident ion.

3.2.6 grazing angle detector—a detector situated at an angle between 90 to 130° from the forward trajectory of the incident ion beam.

4. Summary of Test Method

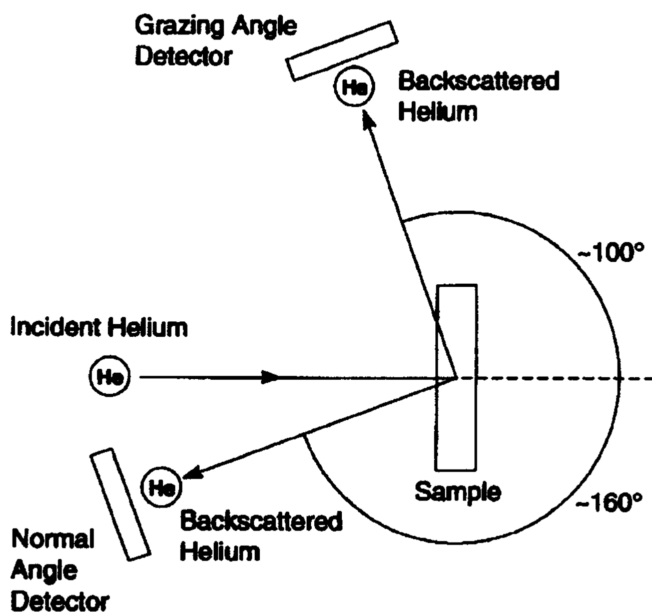
4.1 Fig. 1 shows a schematic of the measurement technique. A collimated beam of alpha particles (He^{++}) is incident on the sample surface. A fraction of the incident ions are scattered out of the specimen with backscattered energies corresponding to the atomic presence of elements in the sample at corresponding depths.

4.2 Spectra of the energy of backscattered ions are acquired at normal and grazing angle detectors for a measured quantity of integrated ion charge on the sample. The grazing angle detector is movable in order to maintain appropriate depth resolution for films of various thicknesses. The grazing angle detector position is chosen to provide a wide tungsten signal (increasing depth resolution) without causing an overlap of the tungsten and silicon signals. The normal angle detector is held fixed to provide accuracy and reproducibility over many months.

4.3 The spectra are analyzed for film composition and thickness using standard software packages. Requirements on the parameters used in software are enumerated in Section 13.

5. Significance and Use

5.1 This test method can be used to ensure absolute reproducibility of WSi_x film deposition systems over the course of many months. The time span of measurements is essentially the life of many process deposition systems.



NOTE 1—The grazing angle detector is movable to improve depth resolution of the WSi_x films.

FIG. 1 Schematic Diagram of RBS Experimental Arrangement

5.2 This test method can be used to qualify new WSi_x deposition systems to ensure duplicability of existing systems. This test method is essential for the coordination of global semiconductor fabrication operations using different analytical services. This test method allows samples from various deposition systems to be analyzed at different sites and times.

5.3 This test method is the chosen calibration technique for a variety of analytical techniques, including, but not limited to:

5.3.1 Electron spectroscopy for chemical analysis (ESCA or XPS),

5.3.2 Auger electron spectroscopy (AES),

5.3.3 Fourier transform infrared red spectroscopy (FTIR),

5.3.4 Secondary ion mass spectrometry (SIMS), and

5.3.5 Electron dispersive spectrometry (EDS) and particle induced x-ray emission (PIXE).

6. Interferences

6.1 Since RBS is a measurement of the energy loss suffered by energetic helium atoms from atomic masses, the interference of signals results if two or more atoms in the same layer have roughly the same atomic number (*Z*). The separation of atomic numbers necessary for detectable, independent signals varies depending on the mass range of the element in question (**1**). Masses in the range of $120<Z<200$ interfere with the signal from tungsten in a 1500Å WSi_x film.

6.2 The detection limits of atmospheric elements (fluorine, nitrogen, oxygen, and carbon) in WSi_x films are 5 to 15 atomic % due to interference between the signals from these elements and signals from substrate silicon, silicon oxide, silicon nitride, or polysilicon layers that may be present in the sample structure.

6.3 The accuracy of this test method may be degraded by nonuniformity or interface roughness of the WSi_x film. Roughness of the surface or interfaces of the sample degrades the low energy edge of the tungsten and silicon and reduces the accuracy of the theoretical modeling used to describe the interfaces.

6.4 Energy of the incident ion beam and detector resolution directly impact the quality of the acquired experimental spectra. A lack of resolution due to the poor control of either of these parameters degrades the accuracy of the depth profiling of the tungsten in the WSi_x film.

6.5 It is necessary to restrict the beam current on samples to <80 nA. Currents in excess of this for most detection apparati may result in signal pile-up in the detector electronics and degrade the accuracy of the measurement.

7. Apparatus

7.1 *RBS Instrument*, consists of a source for a monoenergetic, well-collimated beam of helium ions (He^+ or alpha particles). This source typically is comprised of an ion source, accelerator, and energy-momentum selector magnetic sector. The analysis of general RBS data is optimally performed for an incident ion beam energy of 2.0 to 2.4 MeV. The data acquisition is performed in an evacuated (pressure $<1\times10^{-5}$ Torr) end chamber that is equipped with necessary data acquisition electronics. Data acquisition and analysis should

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proceed with the use of applicable software.

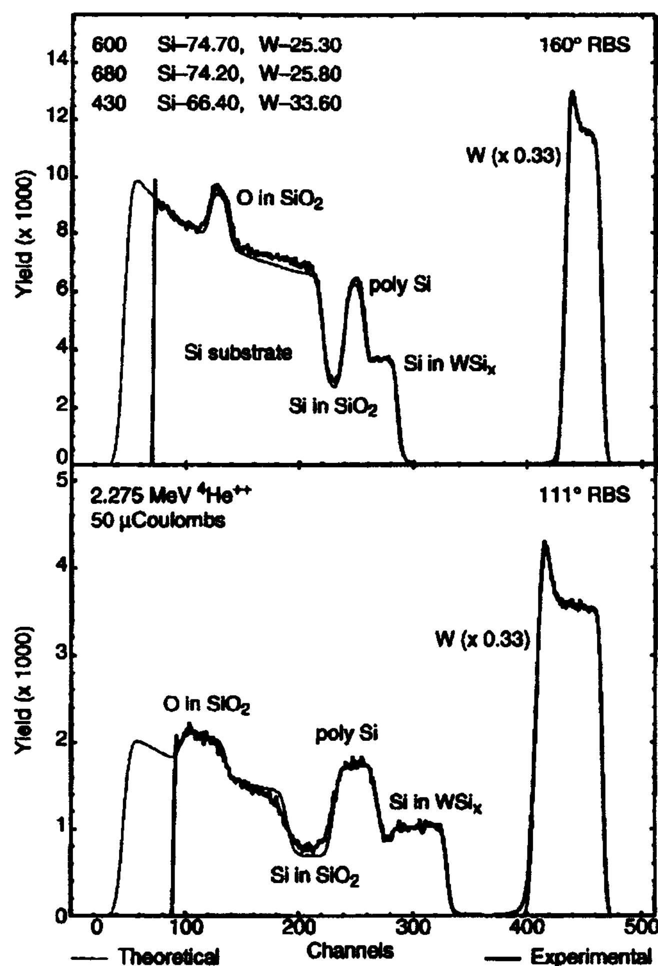
7.2 The energy of the collimated alpha particle (He^{++}) ion beam is restricted to the range of 2.25 to 2.30 MeV. The helium ions have a range of ~3-5 µm in the sample although only collisions occurring in the top ~1.5 µm result in a backscattered event detectable at the normal angle detector. This depth is limited to <1 µm for helium atoms backscattered toward the grazing angle detector. The detectors are silicon surface barrier detectors.

7.3 The majority of the incident alpha particles are implanted in the specimen. A fraction of the incident ions are scattered out of the specimen with backscattered energies corresponding to the presence of elements in the sample at corresponding depths. Fig. 2 shows sample spectra acquired from a sputter deposited WSi_x film on a polycrystalline Si/SiO_2/single crystal silicon structure at a 160° (normal angle) detector and a 110° (grazing angle) detector.

7.4 Spectra at the normal angle and grazing angle detectors are acquired for a measured quantity of charge. The grazing angle detector is movable in order to maintain appropriate depth resolution for films of various thicknesses. The grazing angle detector position is chosen to provide a wide tungsten signal (increasing depth resolution) without causing an overlap of the tungsten and silcon signals. The normal angle detector is held fixed to provide accuracy and reproducibility over many months.

7.5 The grazing angle detector spectrum must be acquired with the sample surface fixed with respect to the incident ion beam. The fixed orientation is performed with the sample normal aligned parallel with respect to the incident ion beam. The spectra from the grazing angle detector are used to measure an accurate depth profile of the tungsten in the film. Since the grazing angle detector is sensitive to surface layers, accurate information for layers deeper than ~3000Å is not obtainable from the grazing angle detector spectrum.

7.6 The normal angle detector spectrum is acquired with the sample orientation manipulated in a way that prevents ion channeling in any single crystal layers or substrates. This is referred to as a “random” orientation. The signal from the random orientation is thus normalizable from sample to sample and allows quantitative comparison of the WSi_x films on multiple samples.



NOTE 1—The detector angle setting can be found in the upper, right legend of the figures. The contributions from each element and layer is highlighted on the figures. This sample exhibits significant tungsten enrichment at the WSi_x/poly silicon interface, The theoretical model (upper, left legend of top spectrum) is read as layer thickness (Å), element, and atomic concentration. The model shown is for the WSi_x film only. The substrate structure is Si/SiO_2/poly silicon.

FIG. 2 Spectra From the Normal and Grazing Angle Detectors

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7.7 Since there is essentially no sample degradation due to data acquisition, suitable reference sample can be cleaved from any previously analyzed sample. This reference sample can then be used as a statistical process control (SPC) sample for periods ranging from several to many months, depending on the size and uniformity of the film on the reference sample. This sample should be used for reproducibility evaluation only and should not substitute for periodic system calibrations.

7.8 Sample preparation may be performed in ambient conditions. Care should be taken to avoid introducing impurities to the surface of samples other than unavoidable adsorbed atmospherics.

8. Hazards

8.1 This test method employs a particle accelerator. All necessary and recommended safety precautions for the operation and maintenance of the particle accelerator and support electronics and power supplies should be observed.

8.2 The reader is directed to pp. 366 to 374 and Appendix 16 of Ref (**2**), and included references therein, for guidance and recommendations in the considerations to safety and regulations when operating a particle accelerator.

9. Sampling

9.1 Sampling, or data acquisition, must be performed for sufficient charge intergration units (typically, μC) to ensure good signal to noise statistics. No predetermined charge intergration value can be used since signal to noise varies depending on detector active surface area, sample film thickness, and sample film roughness. For the measurement of a 1500 Å WSi_x film using detectors of 50 mm^2 active area, a charge integration of 40 μC per spectrum has been found to be sufficient for accuracies stated in 1.3, 1.4, and 1.8.

9.2 There is no "cross-talk" of data for samples mounted close to each other in the data acquisition system. As such, the number of mounted samples from which data can be acquired is limited only by the capabilities of the sample holder, incident ion beam spot size, and the data acquisition software.

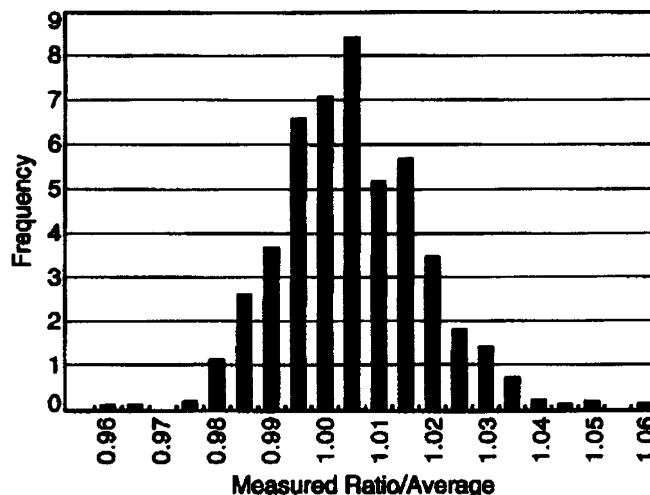
10. Specimen Requirements

10.1 Test Specimens must be uniform films with an area larger than the incident ion beam. The sample surface and interfaces between adjacent layers should be relatively smooth.

11. Calibration Standards

11.1 Results from RBS are quantitative without standards. As such, there are no NIST standards for RBS measurements. The RBS instrument is periodically calibrated against a bismuth implant reference sample (**4, 5**). This sample has been measured by various RBS instruments and found to contain a bismuth implant of 4.8(±4 %) × 10^{15} Bi atoms/cm^2.

11.2 Reproducibility of the RBS measurement is ensured through a statistical process control (SPC) program. The SPC program measures a WSi_x sample 2 to 3 times weekly for various film properties. These properties must lie within tight reproducibility limits for the instrument to be in control (see Fig. 3, Fig. 4). The spectra are also inspected for anomalies that cannot be measured quantitatively.



NOTE 1—The distribution demonstrates the stringent reproducibility capable of a controlled RBS instrument.

FIG. 3 Frequency Distribution of Measured Silicon/Tungsten Ratios From a Series of SPC Samples Covering >30 months

12. Measurement Procedures

12.1 Ensure that the instrument is in control as indicated by the most recent acquisition and analysis of a spectrum from the SPC sample. Any significant change in system electronics or beam energy warrants the acquisition and analysis of new SPC data.

12.2 Mount the sample(s) on a conducting sample holder and place in acquisition chamber. Evacuate acquisition chamber to at least 1×10^{-5} Torr or better. Absolute vacuum should be $<5\times 10^{-6}$ Torr or better.

12.3 Choose the appropriate grazing angle detector setting (see 7.3, 7.4, and 7.5). Record the settings of the normal and grazing angle detectors, the total charge intergration, the energy of the incident ion beam, and the sample orientation for each experimental spectrum.

13. Calculation and Data Reduction

13.1 Assemble the random orientation, normal angle and the channeled (or fixed), grazing angle detector spectra. Set the calibration parameters for each spectrum according to the location of the front edge of the silicon and tungsten signals. This also sets the energy conversion (keV/channel) of the spectra.

13.2 Experimental spectra are iteratively fit by a theoretical model. Variations of the theoretical model in number of layers, thickness of layers, and concentrations of elements in a given layer are performed until a theoretical model that adheres to the features of the experimental spectrum and represents a feasible physical structure of the film is obtained. A depth profile generated from the theoretical model is then produced. The grazing angle detector spectrum yields the most precise depth resolution of the tungsten and silicon. The normal angle detector spectrum yields the most accurate layer thicknesses and silicon/tungsten ratios.

13.3 For standardization of this test method, it is strongly recommended that the stopping power coefficients as determined by Ziegler and Chu (**3**) and reproduced in Table VII of

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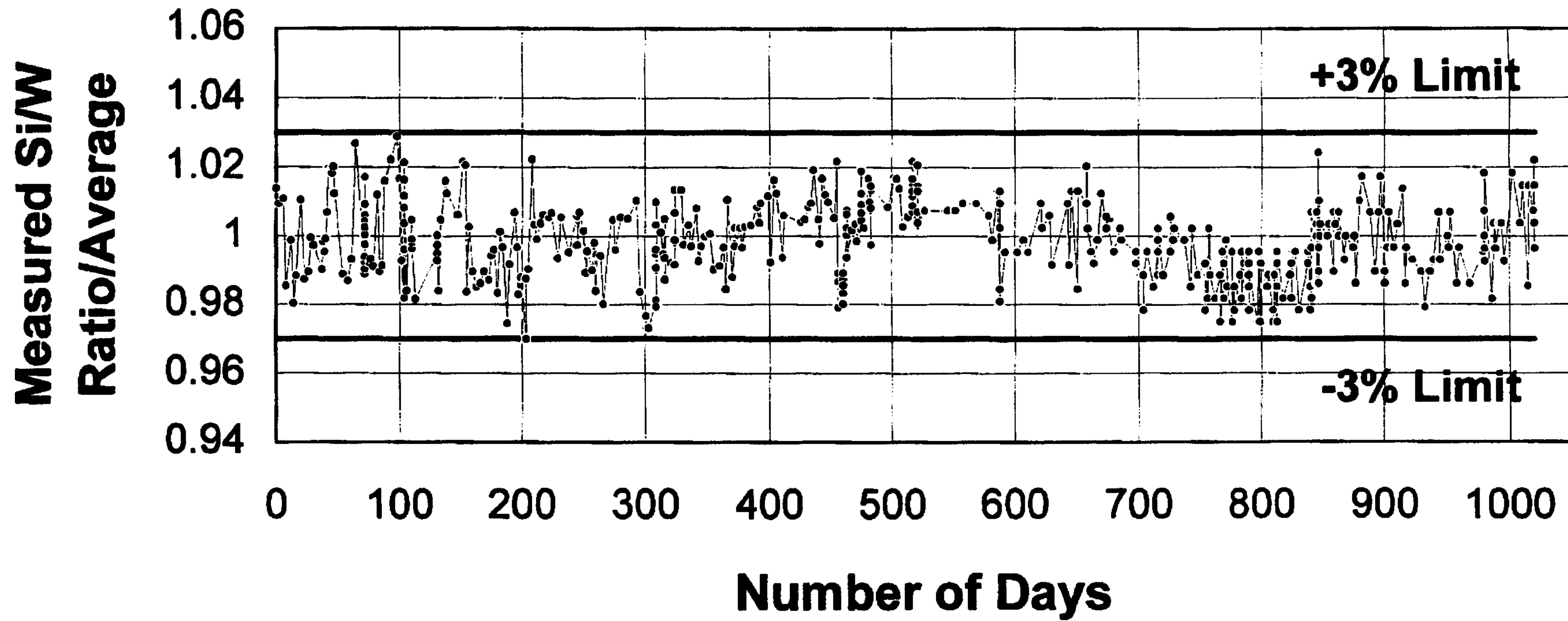

NOTE 1—Since the values were obtained from various samples with widely varying compositions, the ratios are normalized by originally measured silicon/tungsten ratios.

FIG. 4 Running Plot of Measured Silicon/Tungsten Ratios Obtained in an SPC Program.

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Chu, Mayer, and Nicolet (**1**) be used in the data reduction of the tungsten and silicon signal heights. This suggestion is made due to the near-universal recognition of and accessibility to the text as an RBS reference. The polynomial fit to the (**4**) helium stopping cross-section is reproduced here as follows:

$$\epsilon = A_0 + A_1E + A_2E^2 + A_3E^3 + A_4E^4 + A_5E^5 \quad (1)$$

for tungsten, where the coefficients are:
A_0 = 61.69
A_1 = 156.6
A_2 = 150.9
A_3 = 62.45
A_4 = 12.33, and
A_5 = 0.9421.

for silicon, where the coefficients are:
A_0 = 57.97
A_1 = 56.59
A_2 = 77.66
A_3 = 36.41
A_4 = 7.624, and
A_5 = 0.5995.

13.4 Subtract the minimum background of the 160° spectrum between the silicon and tungsten signals. Set the effective solid angle of the spectra by normalizing the theoretical model to the experimental spectrum at the tungsten signal. Determine the silicon/tungsten ratio from the 160° spectrum. Determine the depth profile of the tungsten from the grazing angle spectrum.

13.5 The theoretical model assumes that layers in the WSi_x films are comprised of tungsten in WSi_2 (hexagonal) bonds and excess elemental silicon. This theoretical approach assumes that all tungsten is incorporated into WSi_2 bonds. The density of the WSi_x film is then an upper limit on the actual film density and generates a lower limit on the thickness. The RBS formulation arises from the relation that the product of the film thickness and film density is the fundamental unit of measurement (atoms/cm^2) in RBS. Film thicknesses determined by this approach have demonstrated accuracies to within 10 % compared to thicknesses determined from SEM cross-sections (**6**).

14. Report

14.1 Report the important experimental parameters with the following results:

14.1.1 Sample and laboratory identification,

14.1.2 Energy of the incident ion beam,

14.1.3 Angle settings of the normal and grazing angle detectors, and

14.1.4 Date of measurement (for traceability to SPC records).

14.2 Report secondary experimental parameters for archival purposes although not critical to presentation of results as follows:

14.2.1 Energy per channel calibration,

14.2.2 Surface elemental markers (channel numbers) for relevant elements,

14.2.3 Software name and version, and

14.2.4 Operator.

15. Precision and Bias

15.1 *Precision*—The precision of this test method is determined from step heights observed in the tungsten signal from numerous films. The accuracy of this test method is reinforced from the measurement of the bismuth implant "standard" (**4, 5**) and the stringency of the SPC program.

15.2 The accuracy of film thicknesses is based on comparison to SEM cleave and cross-section measurements (**6**). The SEM instrument is calibrated to NIST standards and provides basis for accuracy (see Annex A1 for details on the thickness determination).

16. Keywords

16.1 analysis of tungsten silicide; backscattering analysis; composition; metallization films; quantitative analysis; RBS; WSi_x

ANNEX

(Mandatory Information)

A1. EQUATIONS GOVERNING DENSITY CALCULATION OF WSi_x FILMS

A1.1 The atomic density (in units of atoms/cm^3) of a WSi_x film is calculated by assuming that the film is comprised of WSi_2 plus excess elemental silicon. The equation used to calculate the film density from the atomic concentration of each layer is as follows:

$$D_{WSi_x} = 3 \times f_w \times D_{WSi_2} + (f_{Si} - 2 \times f_W) \times D_{Si} = f_{WSi_2} \times D_{WSi_2} + f_{Si'} \times D_{Si}. \quad (A1.1)$$

A1.2 The density of a layer is related to the thickness of a layer because the product yields the areal concentration (in units of atoms/cm^2) of the elemental signals. The areal concentration is the fundamental unit measured in an RBS analysis.

A1.3 It is assumed that all tungsten is incorporated into WSi_2 unit cell. Thus, thicknesses determined from Eq A1.1 is a lower limit on the actual film thickness.

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(**1**) Chu, W. K., Mayer, Nicolet, *Backscattering Spectrometry*, Academic Press, New York, 1978.

(**2**) *Handbook of Modern Ion Beam Materials Analysis*, Ed. J.R. Tesmer and M. Nastasi, Materials Research Society, Pittsburgh, PA 15237 USA, 1995.

(**3**) Ziegler, J.F., and Chu, W.K. *Atomic Data Nuclear Data Tables*, Vol 13, 1974, p. 483.

(**4**) Cohen, C., Davies, J.A., Drigo A.V., and Jackman, T.E. *Nucl. Inst. Meth*, Vol 218, 1983, p.147.

(**5**) Davies, J.A., Jackman, T.E., Eschbach, H.L., Domba, W., Watjen, U., and Chivers, D. *Nucl. Inst. Meth*, Vol B15, p. 238.

(**6**) "Determination of Accurate Metal Silicide Layer Thickness by RBS", Kirchhoff, J.F., Baumann, S. M., Evans, C., Ward, I., Conveney, P., *Nucl. Instr. Meth* Vol B 99 pp. 476-478.

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