

SEMI PV10-0716

TEST METHOD FOR INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) OF SILICON

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1 Purpose

1.1 Neutron Activation Analysis (NAA) is a highly sensitive method for multi-element quantitative and qualitative analysis of various materials.¹ In particular, it is an established method in the semiconductor industry for analyzing and qualifying poly-silicon (poly-Si), the feedstock for growing semiconductor grade single crystalline silicon (c-Si) as well as silicon wafers, regarding trace element contamination. The increasing demand for feedstock Si in the photovoltaic industry resulted in a higher volume of production of poly-Si and in developing alternative methods for purifying raw Si, resulting in materials that are generically called solar grade silicon (sog-Si) in the present Document. This material may occur in a variety of shapes, like chunks, powder, and granules.

1.2 The growing volume of production of poly-Si and sog-Si requires also an increase of quality control for these materials, for which Instrumental Neutron Activation Analysis (INAA) is one method of choice. INAA is an NAA where the analysis is conducted directly on the irradiated samples, in contrast to Radiochemical Neutron Activation Analysis (RNAA) where the irradiated samples are subjected to chemical separation for removing interfering species or for concentrating the radioisotope of interest.¹ Currently INAA is performed by laboratories using different irradiation sources and conditions, electronic equipment and preparation methods, and it is applied to a wide morphological variety of Si. Standardizing INAA for application to silicon will remove differences in the analytical approach and will establish a common reference for the analyses.

2 Scope

2.1 This Test Method covers the INAA of Si produced by chemical vapor deposition (CVD) or metallurgical purifying processes.

2.2 Samples to be analyzed may occur in single crystalline, polycrystalline, or multicrystalline form, as powder, granules, chunks, or wafers.

2.2.1 This Test Method refers to the analysis of the bulk of the materials. Analysis of the surface or surface near regions of samples may be performed according to the test method by additional sample preparation and avoiding carefully surface contamination during sample extraction, handling and preparation.

2.2.2 This Test Method does not refer to the analysis of thin amorphous, polycrystalline or micromorph Si films.

2.2.3 This Test Method is not intended for but may be applied to the analysis of samples of Si that were intentionally contaminated with high concentrations of specific elements after checking the impact on safety, limit of detection (LOD) and t_{w0} .

2.3 This Test Method covers only the activation of appropriate trace element nuclides by thermal or epithermal neutrons.

2.4 This Test Method is intended for analyzing a wide range of trace elements (see Appendix 1). This requires in general irradiation times longer than the lifetime of the decay of activated ^{31}Si and waiting times before performing the analysis until the activity of ^{31}Si has sufficiently decreased.

NOTICE: SEMI Standards and Safety Guidelines do not purport to address all safety issues associated with their use. It is the responsibility of the users of the Documents to establish appropriate safety and health practices, and determine the applicability of regulatory or other limitations prior to use.

¹ <http://www.wikipedia.org>

3 Limitations

3.1 Si with high concentrations of other elements may require specific attention regarding the level of tolerable radioactivity.

3.2 Only elements with isotopes that are converted in an appropriate radioactive nuclide by irradiation with neutrons can be detected by INAA (see Appendix 1). The nuclides of most elements lighter than Si have very short decay lifetimes after irradiation with thermal or epithermal neutrons. Their analysis is not covered by this Test Method, it requires different procedures.

3.3 High concentrations of As, Sb, and P may impact the LOD, depending on total neutron irradiation flux. P enhances the background in the entire γ -spectrum due to β -radiation, As and Sb also enhance the background of the γ -spectrum, but mainly in the energy range below their γ -lines. In addition, As and Sb may block the radiation counter because of their high activity. Following concentrations should not be exceeded for reliable determination of other elements: As, Sb < 1E13 at/cm³, P < 1E16 at/cm³ for best LOD, corresponding to As, Sb < 200 ppta and P < 2E5 ppta or As < 534 pptw, Sb < 844 pptw and P < 2.2E5 pptw.

NOTE 1: Analysis of samples with higher concentrations is possible, but impact on LOD and safety has to be taken in account. As, P, and to some extent Sb are used as dopants in the semiconductor industry and are intentionally added during crystal growth. Therefore, their concentration in an ingot can be estimated with sufficient accuracy. For completely unknown samples it is recommended to perform a preview INAA analysis with short irradiation time for assessing the concentration of potentially interfering elements.

3.4 The analysis of thin PV wafers is possible, but little bulk material may be left after removing the surface damage of such wafers. Sampling of several wafers may be required to achieve the mass necessary for analysis, depending on the LOD requested and irradiation time.

4 Referenced Standards and Documents

4.1 *SEMI Standards and Safety Guidelines*

SEMI C28 — Specifications for Hydrofluoric Acid

SEMI C35 — Specifications and Guideline for Nitric Acid

4.2 ASTM Standard²

ASTM D1193 — Standard Specification for Reagent Water

4.3 *ISO Standard*³

ISO 11929 — Determination of the Characteristic Limits (Decision Threshold, Detection Limit and Limits of the Confidence Interval) for Measurements of Ionizing Radiation – Fundamentals and Application

4.4 *Other Documents*

SEMI AUX027-0213 — Results of Round Robin for SEMI PV10, Test Method for Instrumental Neutron Activation Analysis (INNA) of Silicon

NOTICE: Unless otherwise indicated, all documents cited shall be the latest published versions.

5 Terminology

5.1 Refer to the SEMI International Standards: Compilation of Terms (COT) for a list of the most current terms and their definitions.

5.2 *Abbreviations and Acronyms*

5.2.1 *ADC* — analog to digital converter

5.2.2 *CRM* — certified reference material

² ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Telephone: +1.610.832.9585, Fax: +1.610.832.9555, <http://www.astm.org>

³ International Organization for Standardization, ISO Central Secretariat, 1, ch. de la Voie-Creuse, CP 56, CH-1211 Geneva 20, Switzerland; Telephone: +41.22.749.01.11, Fax: +41.22.733.34.30, <http://www.iso.org>

5.2.3 *DI water* — deionized water

5.2.4 *INAA* — instrumental neutron activation analysis

5.2.5 *LDPE* — low density polyethylene

5.2.6 *LN₂* — liquid nitrogen

5.2.7 *LOD* — limit of detection

5.2.8 *MCA* — multichannel analyzer

5.2.9 *NAA* — neutron activation analysis

5.2.10 *PE* — polyethylene

5.2.11 *PFA* — perfluoroalkoxy

5.2.12 *PP* — polypropylene

5.3 Definitions

5.3.1 *ambient background* — radiation resulting from sources outside of sample recorded by detector.

5.3.2 *energy resolution* — width of peak in γ -spectrum at $1/e$ of its maximum.

5.3.3 *full-energy peak detection efficiency ε_p* — probability of detecting a γ -photon emitted by the γ -source, dependent on energy of γ -photon, distance between source and detector, and the shape of the source.

5.3.4 *irradiation capsule* — container in which sample is kept during irradiation.

5.3.5 *irradiation time t_{irr}* — duration of irradiation.

5.3.6 *lifetime $t_{1/2}$* — time after which a nuclide activity has decayed to 50% of its starting value.

5.3.7 *long time irradiation* — irradiation longer than short time irradiation.

5.3.8 *measuring time t_c* — duration of recording of γ -spectrum. An additional index i is used, such as t_{ci} with $i = 1, 2, \dots$ for several measurements.

5.3.9 *minimal waiting time t_{w0}* — time after end of irradiation until the activity of Si matrix has decayed to ≤ 1 MBq, typically $t_w \geq 36$ h.

5.3.10 *short time irradiation* — irradiation for a time $\leq$ maximum irradiation time allowed for PE foil.

5.3.11 *relative detector efficiency* — ratio of the peak area of the 1.33 MeV line of a calibrated ^{60}Co γ -source divided by the total source disintegrations during dead time corrected t_m to the efficiency of a 3×3 NaI(Tl) scintillation detector at 25 cm.

5.3.12 *relative intensity, of γ -ray peak* — probability of γ -ray peak occurring at decay of isotope.

NOTE 2: Unstable isotopes can emit γ -radiation with several well defined energies. The relative intensity denotes the frequency of γ -rays emitted with the different energies.

5.3.13 *waiting time t_w (sometimes also called decay time)* — time after end of irradiation until start of measurement. An additional index i is used, such as t_{wi} with $i = 1, 2, \dots$ for several measurements.

6 Summary of Method

6.1 The history of the sample is checked regarding potentially interfering trace elements and a decision regarding the necessity of a preview analysis is made.

6.2 The sample is prepared before irradiation according to its structure (chunk, granule, wafer or powder) and put in an appropriate container.

6.3 The sample is irradiated with thermal neutrons by an appropriate neutron source for a time as required for the intended LOD.

6.4 The sample is prepared after irradiation according to its structure.

6.5 A spectrum of the emitted γ -rays is taken.

6.6 The spectrum is evaluated with appropriate software and the concentrations of the impurities are calculated with the k_0 -method or by using the activation equation (see Appendix 2) after corrections for neutron flux variations, self-absorption, ambient background radiation, and set-up dead time were applied.

7 Interferences

7.1 *Sodium* — Due to the reaction $^{28}\text{Si}(n, p+\alpha)^{24}\text{Na}$, which is a reaction with fast neutrons, an apparent Na concentration may be measured that is higher as originally present in the sample. The effect of this interference depends on the irradiation source's neutron spectrum.

7.2 *Abundance of Isotopes* — Has to be known for the sample for being able to calculate the total concentration of an element in Si. Different isotopes of an element react differently with neutrons or not at all. Typically, calculations assume a natural abundance of isotopes.

7.3 *Peak Interferences* — Closely adjacent peaks in γ -spectra of nuclides of specific elements may overlap, inhibit the identification of the nuclide, and detrimentally impact the quantitative analysis. In such cases alternative lines, if present, should be used for the quantitative analysis. Identification of nuclides may be ascertained by correlating the peak area obtained by measurements performed after different waiting times based on the known lifetimes of the nuclides.

8 Ambient

8.1 *Laboratory* — Consisting of a part for chemical sample treatments and a part for the measurement apparatus. It has to be certified by local overseeing agency for handling radioactive materials.

8.2 *Operators* — Certified for handling radioactive materials according to local legislation.

9 Apparatus

9.1 Irradiation System

9.1.1 *Neutron Source* — Nuclear research reactor with constant flux of thermal neutrons. Sources differ in neutron flux and neutron spectrum. Preferably mainly slow, thermal neutrons with a small contribution of fast neutrons should be used. Typically neutron fluxes of appropriate reactors are in between $5\text{E}12$ and $2\text{E}14$ n/(sec cm²). The spatial flux variations of the neutron beam have to be known, then they can be taken into account. They impact the accuracy of the analysis results.

NOTE 3: The spatial flux variations at the irradiation positions are usually known to the operator of the reactor. If not known or in critical cases multiple radiation monitors can be used for probing the spatial flux variations.

9.1.2 *Irradiation Stage* — Specific to the irradiation source used.

9.2 Detector and Electronics

9.2.1 *γ -detector* — Intrinsic Ge detector or Li-drifted Ge detector (GeLi) cooled with liquid nitrogen, pre-amplifier included, for detecting γ -rays. The intrinsic efficiency of this detector for detecting γ -rays should be $>20\%$.

9.2.2 *Dewar Vessel* — For LN₂ for cooling detector.

9.2.3 *Electronics* — Consists of power supply for γ -detector, amplifier, ADC, MCA, PC.

9.2.3.1 *Power Supply for γ -detector* — Voltage according to detector used.

9.2.3.2 *Main Amplifier*

9.2.3.3 *ADC* — ≥ 12 bit

9.2.3.4 *MCA* — ≥ 4000 channels (stand-alone or board for PC).

9.2.3.5 *PC* — hardware and software interface appropriate for MCA.

9.3 *Balance* — Calibrated and certified, with accuracy $\leq 1\%$ of weight of 'sample', for determining the weight of the sample, the weight of the neutron flux monitor and for controlling stock removal by etching of sample.

10 Reagents and Materials

10.1 *Irradiation Capsule* — Typical Al, Al Mg, or high purity graphite alloy for long time irradiation, as provided by reactor, polymer for short time irradiation.

10.2 *Neutron Flux Monitor* — 99.9% Zr or better, for longtime irradiation, 99.9% Zr or 99.9% Au for short time irradiation, foil or wire.

10.3 *Hydrofluoric Acid (HF)* — Purity Grade 1 or better (SEMI C28).

10.4 *Nitric acid (HNO₃)* — Purity Grade 1 or better (SEMI C35).

10.5 *Water* — DI water according to ASTM D1193, type IV.

NOTE 4: Grade 1 quality, as well as DI water, are sufficient because impurity in the acid solutions are not radioactive or are only deposited on sample surface, which is removed before measurement of γ -radiation.

10.6 *Containers for Etching and Cleaning* — Inert with respect to acids used, not glass or silica, adapted to sample size.

10.7 *Sample Carriers* — Inert with respect to acids used, not glass or silica.

10.8 *Tweezers* — Preferably PFA; metal tweezers must not be used.

10.9 *Silica Container* — For powder and granular Si, size adjusted to irradiation capsule.

10.10 *Gloves* — For handling of radioactive samples one way, typically latex, for HF treatment of samples acid resistant gloves.

10.11 *Wash Bottle or Squeeze Bottle* — LDPE.

10.12 *Film Tube* — PE.

10.13 *Sample Bottle* — PFA or LDPE.

10.14 *CRM* — Appropriate for detector and distance of sample to detector.

10.15 *Liquid Nitrogen* — as commercially available.

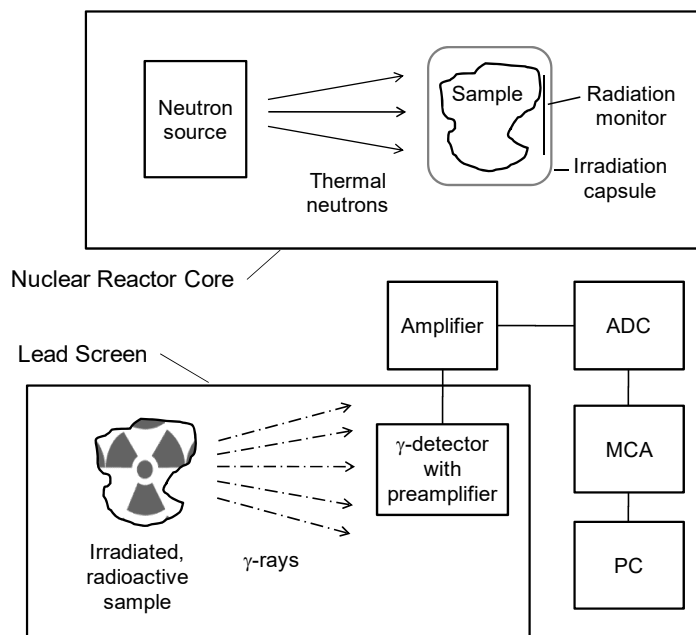


Figure 1
Schematic Set-up for Neutron Irradiation and γ -ray Detection and Counting