IAEA-TECDOC-512

# ANALYTICAL CHEMISTRY IN SEMICONDUCTOR MANUFACTURING: TECHNIQUES, ROLE OF NUCLEAR METHODS AND NEED FOR QUALITY CONTROL

REPORT OF A CONSULTANTS MEETING
ON THE NEED FOR INTERCOMPARISON AND REFERENCE MATERIALS
FOR CHARACTERIZATION OF SILICON
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN GAITHERSBURG, MARYLAND, USA, 2–3 OCTOBER 1987

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## FOREWORD

This report is the result of a consultants meeting held in Gaithersburg, USA, 2-3 October 1987. The meeting was hosted by the National Bureau of Standards and Technology, and it was attended by 18 participants from Denmark, Finland, India, Japan, Norway, People's Republic of China and the USA.

The purpose of the meeting was to assess the present status of analytical chemistry in semiconductor manufacturing, the role of nuclear analytical methods and the need for internationally organized quality control of the chemical analysis.

The report contains the three presentations in full and a summary report of the discussions. Thus, it gives an overview of the need of analytical chemistry in manufacturing of silicon based devices, the use of nuclear analytical methods, and discusses the need for quality control.

The meeting was organized by Dr. R.M. Lindstrom from the National Institute of Standards and Technology and Dr. R.J. Rosenberg from the Agency. Dr. R.M. Lindstrom acted as chairman of the meeting.

## *EDITORIAL NOTE*

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# INTRODUCTION

The development and production of silicon based electronic components require chemical characterization of materials in all stages, starting from the raw materials, and ending in the finished product. The analytical work includes determination of bulk concentrations and spatial distribution of both impurities and dopants, determination of the thickness and composition of thin films deposited on silicon etc. The high reliability demanded of modern semiconductor products requires an extensive programme of control. Frequently very low concentrations of impurities have to be determined. Therefore low detection limits and freedom of contamination are key requirements of the analytical work.

A number of different analytical techniques are needed and used. Among these several nuclear analytical techniques are of importance. Neutron (NAA), and charged particle activation analysis (CPA), Nuclear Reaction Analysis (NRA), prompt gamma activation analysis (PGAA) and Rutherford backscattering spectroscopy (RBS), being the most used ones.

The analytical problems involved are difficult and the quality requirements high. Often the quantitative calibration of non nuclear techniques is difficult. Few, if any, reference materials enabling unbiased control of the accuracy of the analytical procedures exist.

The Agency in co-operation with the National Bureau of Standards convened this consultants' meeting with the following objectives.

1. To get an overview of the analytical chemistry requirements in electronics industry and the analytical techniques used.

2. To find out the role of nuclear analytical techniques in this field.

3. To discuss the need of internationally organized quality control of the used analytical procedure.

The report contains three reports discussing the need for analytical chemistry in silicon electronics, analytical techniques used and analytical standards, and a summary report on the discussions on the need of quality control.

# NEEDS FOR ANALYTICAL CHEMISTRY IN SILICON ELECTRONICS TECHNOLOGY

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**Abstract**

Widespread needs for analytical and defect characterizations for quality control of raw materials, processes, and the environment for silicon device manufacture are discussed generally. Emphasis is focussed on acquainting the nuclear analytical chemist with existing challenges in trace characterizations for the electronics industry. Continuing opportunities are cited for analytical methods development, certification of new standard reference materials, and international collaborations in developing universally accepted analytical methods. Collaborative programs potentially suited for initiation by the International Atomic Energy Agency are mentioned.

## *1. Introduction*

Trace elemental analyses and defect characterization science have been traditionally important in the microelectronics industry. From the early stages of development of zone refined silicon for device fabrication to current technology exploiting epitaxially produced structures, characterizations of raw materials, processes, and completed devices have been vital for progress in very large scale integration (VLSI) technology. For example, a multitude of needs exist for quality control inputs during the multistepped chemical and physical processes required to produce the metal oxide semiconductor (MOS) device structure shown in Figure 1. Stringent quality controls are required for minimizing negative impacts of impurities in processing chemicals, and contaminants from the environment. Chemical and physical analyses are required during manufacture and during all phases of the life cycle of manufactured device products from development through accelerated life testing and following failure in field operation. At the development stage, characterizations are required to select optimum materials, and to establish specifications. To assure that selected commercially available materials adhere to established guidelines, additional analyses are preformed prior to manufacture. Assurance that raw materials and processing reagents of appropriate quality are selected beforehand, prevents predictable, unacceptable product yield losses during manufacture. Additionally, on-line monitoring of sensitive steps of chemistry intensive manufacturing processes provides real-time warnings of potential economically catastrophic process interruption due to the accumulation of detrimental impurities and reaction by-products.

Environmental controls for the fabrication of silicon devices are exceptionally well regulated and will not be discussed in this report. Needs for analytical methods to quality control raw materials, reagents and process chemicals will be emphasized. The status and reliability of current characterization methods will be assessed and areas presenting significant future challenges to characterization scientists are reviewed briefly.

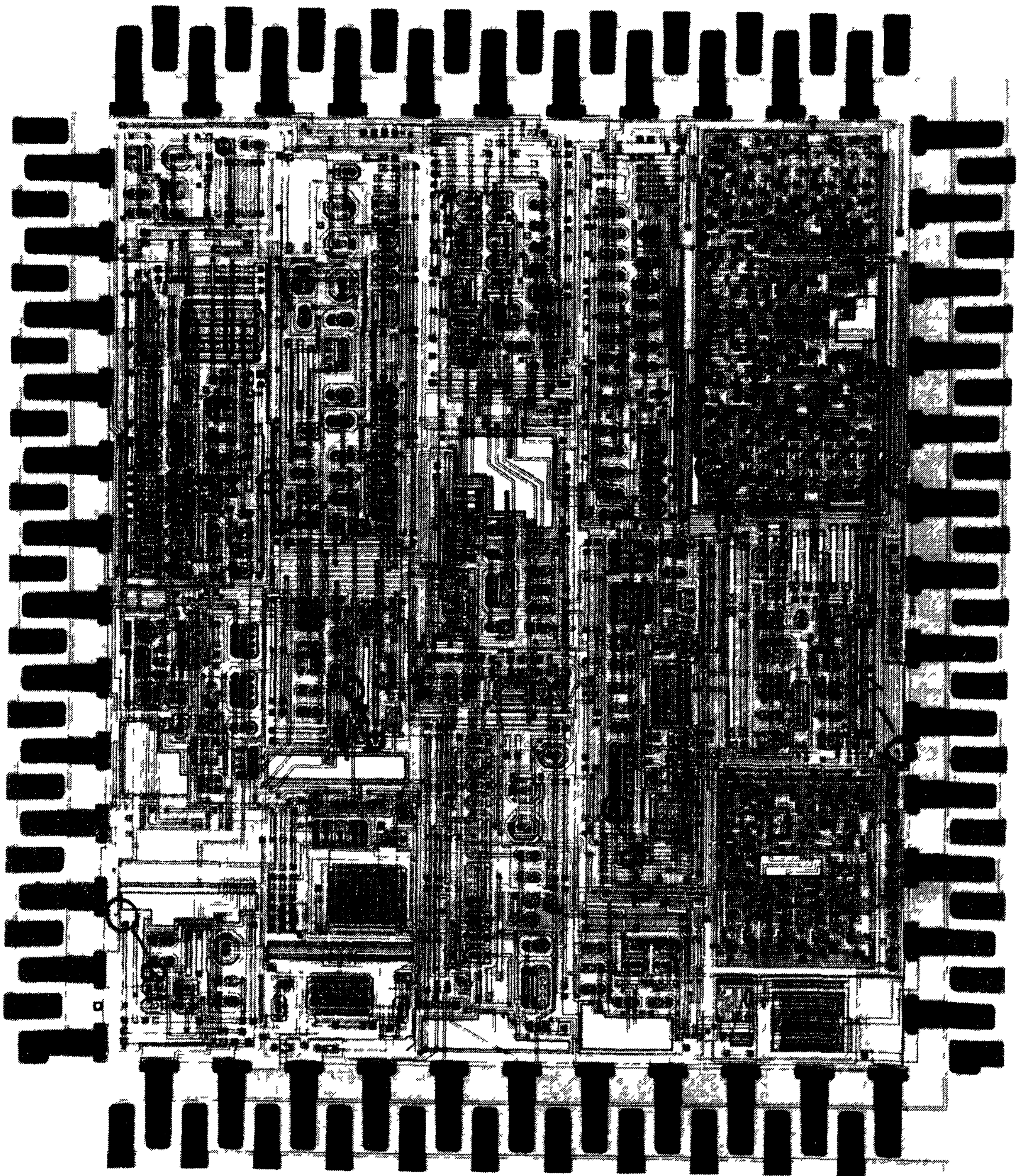

FIG. 1. VLSI Silicon Device.

For future development of universally accepted analytical methods for microelectronics, international collaborations can accelerate the rate of progress appreciably. Existing opportunities are cited for methods development and certification of standard reference materials where the International Atomic Energy Agency could be impactive. A specific focus of this report is to overview information that acquaints the nuclear analytical chemist with characterization needs in silicon microelectronics. High resolution surface and defect characterizations are not covered, since a companion paper treats these subjects in detail.

## 2. *Raw Materials*

Numerous materials are used in fabricating device structures. Some standard examples are given in Figure 2, which shows a cross section of the microcircuit pictured in Fig. 1. Silicon, contact materials and other metallizations generated by sputtering (PtSi, Au, Al, Ti), and dielectric materials of $SiO_2$ and $Si_3N_4$ generated by chemical vapor deposition (CVD) methods, are required to construct desired circuits. Obviously, the foundation of the technology depends upon the quality of single crystalline silicon wafers fabricated by liquid encapsulated Czochralski (LEC) growth from polysilicon melts. The extent to which the silicon industry controls the trace element purity of wafers is quite variable. No well characterized polycrystalline material is available as a standard reference material for raw material screening. Establishing specifications for detrimental trace impurities O, Al, B, Mo, W, V, Ti, C, Fe, P and other transition elements which are known to be effective killers of electrical carrier lifetimes is on-going [1].

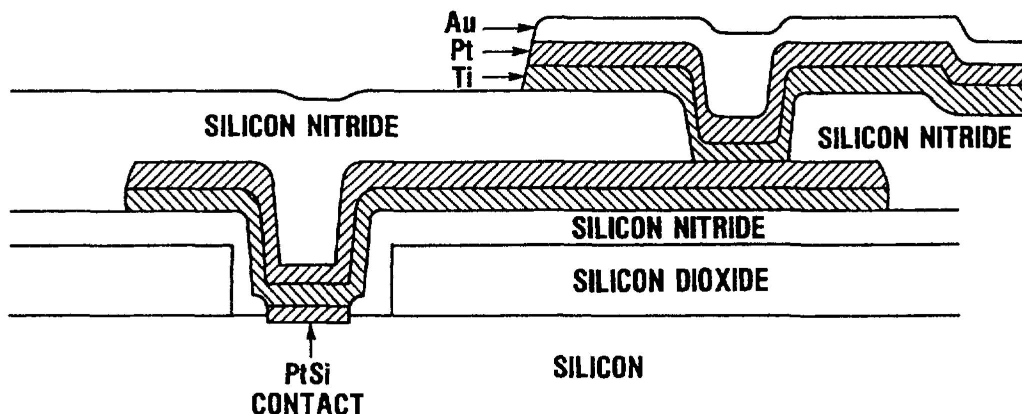


FIG. 2. Schematic of Cross Section of a Silicon MOS Device.

Contamination of the growing single crystal by impurities in fused silica crucibles in which the melt is contained must also be minimized. Thus monitoring of the purity of crucibles by activation analysis or other suitable methods is required [2]. Control of oxygen incorporation from dissolation of the fused silica crucible and atmospheric sources is also important to minimized propagation of catostropic precipitated oxygen defects on the one hand, [1] while incorporating sufficient interstitial oxygen to serve later for intrinsic gettering [3].

### 2.1 *Wafer Characterization*

Wafer scale characterizations are important for the minimization of device yield losses. Standard types of characterizations are listed in Table 1. Automated, nondestructive, imaging techniques are required for wafer scale monitoring. Several types of

commercial instrumentations are now available to perform some of the characterizations listed in Table 1. For the future the industry needs integrated analytical systems providing three or more of the most important wafer scale characterizations. In addition to these characterizations, many other physical methods have been developed for wafer or device characterizations at various stages of manufacture (Table 2).

TABLE 1. WAFER SCALE CHARACTERIZATIONS

| |
|---|
| Etch Pit and Dislocation Defect Densities |
| High Resolution SEM Inspection |
| Photoluminescence Detection of Crystalline Quality and Strain |
| Sheet Resistance |
| Radial Interstitial Oxygen Distribution |
| Radial Precipitated Oxygen Distribution |
| Radial Carbon Distribution |
| Trace Element Content and Distribution |

TABLE 2. PHYSICAL METHODS FOR TRACE ELEMENT CHARACTERIZATION AND DETECTION OF DEFECTS

| | |
|---|---|
| Cathodeluminescence | Hall Effect Measurements |
| Capacitance Spectroscopy | Photoconductivity |
| Dark Leakage Current | Resistivity Ratio |
| Deep Level Transient Spectroscopy | Thermally Stimulated Currents |
| Electron Beam Induced Currents | |

Although these methods are used widely throughout the industry and provide uniquely valuable information, virtually no reference standards, certified standardization, or calibration methods have been developed. Since each practitioner essentially establishes his/her own approach to calibration, cross- or intercomparisons of data is not possible. The exception is the case of boron density determinations in silicon by resistivity. A classic nuclear method, $\alpha$ track counting, has been used to calibrate the resistivity technique [4].

### *2.2 Sputtering Targets and Other Materials*

Other essential starting materials for silicon device technology include sputtering targets of Al, Au, Ti, Pt, W, silicides of Pt, Ta, and Ti, dielectrics of silicon dioxide and silicon nitride, and polyimides, encapsulants such as silicones, epoxies, ceramics,

glass sealants, and planarization agents. Each material can have uniquely detrimental impurities or beneficial dopants and consequently must be characterized accordingly. Sputtering target materials must be stoichiometric and/or homogeneous on the microscale. Electron and laser emission microprobe methods are used widely with significant success [5]. Impurity content and stoichiometry of targets must be controlled to achieve necessary conductivity. For example tantalum silicide must be $TaSi_2$ and the slightly Si rich material is preferred over $Ta_5Si_3$, which oxidizes easily. Oxygen impurities are detrimental and other impurities Fe, Al, Cu, B, Cr, Mo, Ti and W must be well controlled. Induction coupled plasma atomic emission methods have been developed for this purpose [6].

Aluminum is an important metallization material. Its trace element purity with respect to Na, Cu, U and Th must be assured. Nuclear methods are well suited for this task. Neutron activation for purity analysis and fission track counting for uranium determination are particularly attractive [7,8]. A well characterized aluminum standard reference material would be a welcomed product for the semiconductor industry.

In addition to purity of sputtering targets for device fabrication other quality control issues during fabrication of these film layers include correct thickness, controlled composition, etch rate, crack resistance, purity and stoichiometry to control resistivity, and physical and mechanical properties. For example, silicon nitride layers have important applications as a dielectric with several superior properties to silicon dioxide. Stoichiometry and composition acutely affect etch rates, dielectric constant and refractive index. Its compositional and microscale homogeneity have been well characterized by nuclear methods. 14 MeV neutron activation methods have been reported for determination of Si, N and O in the material, while the microscale homogeneity of N distribution in materials made by plasma, CVD and ceramic methods were determined by proton track counting [9]. The basis for the two methods is shown schematically in Figure 3. Bulk nitrogen is determined by counting positron anilation gamma rays at 0.511 MeV. Alternatively, nitrogen in the surface (upper 3 microns) of a sample is determined by detecting protons in a cellulose nitrate detector placed in intimate contact with the sample during thermal neutron irradiation.

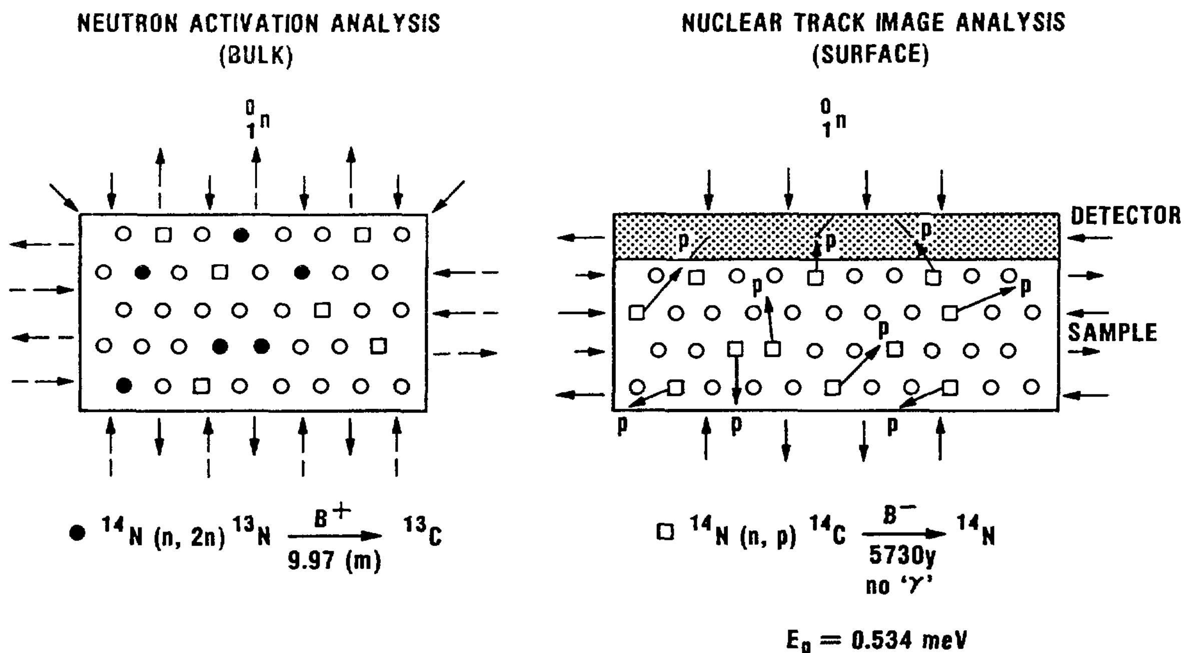


FIG. 3. Nuclear Methods For Determining Nitrogen.

TABLE 3. FILM MATERIALS FABRICATED BY CVD TECHNIQUES

| | |
|---|---|
| Silicon Dioxide | Tungsten Silicide |
| Silicon Oxynitride | Borophosphosilicate Glass |
| Silicon Nitride | Phosphosilicate Glass |
| Tantalum Silicide | |
| Titanium Nitride | |

Following exposure of the detector the regions damaged by energy deposition during the passage of the proton are exposed by chemical etching to visualize the proton tracks, which are then counted by optical microscopy. Track density versus concentration calibration plots are used for quantitative analysis.

Borophosphosilicate silicate glass (BPSG) deposited by CVD methods has important microelectronic applications including dielectric insulation of gate interconnects from metallization, gettering of Na and other rapidly diffusing ions, viscous flow planarization, and passivation overcoating. During VLSI fabrication the composition of BPSG must be controlled to within a few tenths of a percent in order to match melt flow characteristics of the glass with the conditions and temperature of processing. Glasses with boron levels covering the range 3.94 to 7.60% have been analyzed by induction coupled plasma atomic emission, analysis (ICP-AES) and used subsequently as comparison standards for X-ray fluorescence [10]. Excellent agreement for the determination of boron in the same series of glasses has been accomplished also by prompt gamma neutron activation analysis [11]. Nuclear methods have also been applied quite profitably for depth profiling of boron in glasses and silicon wafers [12]. Glasses standardize for boron and phosphorus composition and depth would serve as valuable quality control reference materials for analyses by ICP-AES, X-ray fluorescence, and nuclear techniques.

*3. IC Processing Reagents and Chemicals*

In addition to quality control of the device fabrication environment, and the raw materials used in device fabrication, all of the chemicals used in processing devices must be of ultrapure quality. The Semi-Conductor Equipment and Materials Institute has adopted purity specifications and designated analytical procedures for characterizing a broad range of chemicals used in electronics technology (Table 4). For high purity acids, bases such as $NH_3$ and solvents, the induction coupled plasma mass spectrometry method will become the technique of choice. Whether samples of such chemicals certified for trace element content can be generated as reference standards is a continuing unanswered question.

Even more pressing needs exist for the development of suitable methods for characterizing gaseous reagents for electronics. The current state-of-the-art and future prospects for progress in this very challenging analytical area have been discussed previously [13]. More than fifty essential gaseous reagents for electronics have been classified into six groups and methods of analysis reviewed [13]. The most promising

analytical methods existing and on the horizon for such applications are given in Table 5. Due to the existing void of information on the characterization of reactive, toxic, volatile reagents, this topic should be the subject for an important international meeting and workshop.

TABLE 4. PROCESSING REAGENTS AND CHEMICALS

| |
|---|
| Electronic Gases<br>annealing, dopants, implanting, reactive sputtering, insulators |
| Chemical Vapor Deposition Reagents<br>MOCVD, MBE, VPE |
| Lithographic Chemicals |
| Electronic Chemicals<br>acids, bases, solvents |

TABLE 5. ANALYTICAL METHODS FOR ANALYSIS OF GASEOUS ELECTRONIC REAGENTS

| |
|---|
| Helium ionization gas chromatography |
| gas-chromatography |
| GC-Mass Spectrometry |
| FT-Mass Spectrometry |
| Diode Laser IR Absorption Spectrometry |
| FT-IR |
| Metastable Transfer Emission Spectrometry<br>(other chemiluminescence methods) |
| ICP-Mass Spectrometry |
| Gas Sensors |

*4. Other Important Characterization Needs*

There is no discussion here of the needs for high resolution surface, defect, depth profile and interfacial characterization of device structures. Herein lies some of the most challenging characterization problems. Characterization methods for probing these areas hold the key to resolving mysteries about device reliability and functions. An excellent overview of applicable analytical techniques is available [14].

*4.1 Device Processing*

Following the selection of the best raw materials and processing reagents and chemicals suitable for device fabrication, other precautions must be taken to minimize contamination during processing steps. Detecting contamination from diffusion furnaces and other containment vessels has been accomplished by activation analysis [2]. Precautionary wafer processing steps are used to further enhance the probability of preventing mobile impurities from diffusing into the wafer region where the device is grown. Epitaxial layers may be deposited for device fabrication and intrinsic gettering of impurities by oxygen precipitates is exploited [15]. Detailed scrutiny of oxygen precipitation kinetics and considerable focus have been given to the accurate determination of interstitial and precipitated oxygen in silicon. International collaborations on accurate $O_2$ determinations in silicon have been executed using IR, and charge particle activation analysis [16].

*4.2 Device Encapsulation*

Finally after a device has been fabricated successfully by a complex sequence of processes that still appear to be miraculous, it must often be protected from the environment by encapsulation to preclude corrosion or electrostatic damage. Encapsulation materials consisting of room temperature vulcanized (RTV) silicone, epoxies, and ceramics as well as precast hermetic packages for memory devices, require specific characterizations. Considerable attention has been focussed on minimizing soft errors in memory devices by precluding alpha particle emitting impurities from hermetic packages and encapsulating materials [17]. Thus, all components of the ceramic package shown schematically in Fig. 4 must be screened for ppb levels of uranium and thorium. Comparative analyses of commercially available device packages and of plastics for producing molded packages are needed.

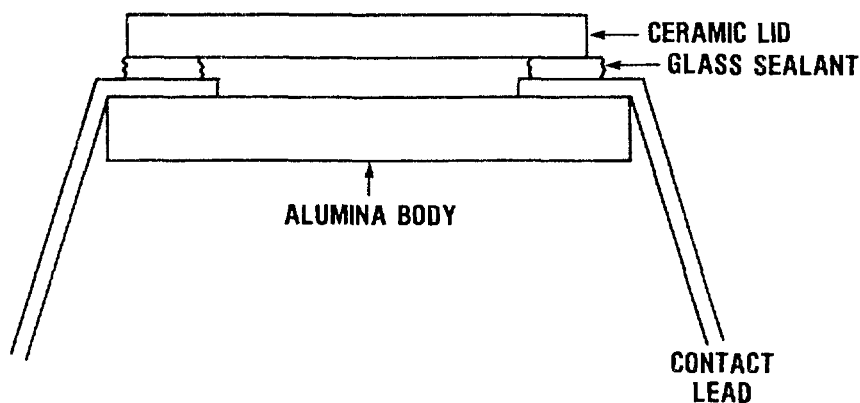


FIG. 4. Schematic of a Ceramic Hermetic Package for Memory Devices.

Molded plastic packages of RTV or epoxy often contain silica or alumina fillers, which can contain significant levels of trace impurities. Among several methods for determining trace uranium, the fission track analysis (FTA) technique is suited uniquely for analyzing semiconductor materials. The high sensitivity (sub-ppb), simultaneous analysis of many samples and microscale imaging of uranium distribution within the package are unique advantages of the method [18]. The author has characterized high purity silica and aluminum for uranium using the FTA method.

Results for analyses of high purity silica prepared by vapor phase flame pyrolysis of $SiCl_4$ and of heavily contaminated aluminum are reported in Tables 6 and 7. Efforts to lower the detection limits of the method further are continuing.

TABLE 6. URANIUM LEVEL IN FUSED SILICA

| Sample | Net Average of Fission Tracks | [U] found, ppb |
|---|---|---|
| 1 | 3.2 ± 0.6 | 8.5 ± 1.6 |
| 2 | 1.7 ± 0.2 | 4.5 ± 0.5 |
| 3 | 1.2 ± 0.3 | 3.2 ± 0.8 |
| 4 | 1.4 ± 0.2 | 4.8 ± 0.7 |
| 5 | 5.2 ± 1.0 | 13.8 ± 2.6 |
| 6 | 10.3 ± 0.8 | 27.4 ± 2.1 |

TABLE 7. FISSION TRACK ANALYSIS OF ALUMINUM

| Sample | Average Number of Tracks per Field | [U] found, ppb |
|---|---|---|
| 1 | 25.4 ± 2.1 | 411 ± 29 |
| 2 | 32.4 ± 1.5 | 525 ± 26 |
| 3 | 14.8 ± 1.8 | 240 ± 29 |
| 4 | 33.7 ± 0.7 | 546 ± 11 |
| 5 | 6.0 ± 0.6 | 113 ± 11 |

### *4.3 Epitaxial Layer Characterizations*

Device structures are now being fabricated in thin (1 to 10 micron) highly crystalline perfect epitaxial layers grown on the surface of silicon wafers. Nondestructive determinations of $10^{12}$ to $10^{14}$ atoms/cm$^3$ of impurities residing in these layers, while the same impurities may be present in the bulk substrate at orders of magnitude higher levels, presents major challenges to the trace characterization scientist. Near resonantly excited laser induced photoluminescence, selective photoluminescence

excitation, and electronic Raman spectroscopies provide the most viable approaches to solving this characterization problem. Quantitation of B and P in silicon has progressed well [19]. Neutron transmutation doping of bulk silicon with P has been used advantageously [20].

Clearly, the status of the analytical chemistry of silicon device technology is sound, but there are enough unsolved problems and newly generated characterization needs to involve analytical chemists in challenging work for many decades.

## REFERENCES


[1] MURGAI, A. ''Impurity incorporation in Czochralski Silicon Grown for VLSI'', Silicon Processing, (GUPTA, D.C., Ed.), ASTM, Philadelphia, PA (1983), 39-49.

[2] SCHMIDT, P. F. and PEARCE, C. W. J. Electrochem. Soc., *128* (1981) 630-642.

[3] SEIBLES, L., personal communications.

[4] THURBER, J. and CARPENTER, B. ''Boron Determination in Silicon by the Nuclear Track Technique'', Anal. Chem. *125* (1978) 654-659.

[5] NASH, D. L., Bell Labs Technical Memoranda, (1984).

[6] KOMETONI, T. Y., Bell Labs Tech. Memo (1986).

[7] DYER, F. F., EMERGY, J. F., NORTHCUTT, K. J. and SCOTT, R. M., J. Radioanal. Chem., 72 (1-2), (1982) 53-67.

[8] CHAKARTI, S. K. and NAGPAVL, K. K., ''Trace Determination of Uranium in Silicon by Fission Track Method'', Nucl. Tracks, *3(1-2)* (1979) 85-88.

[9] YEGNASUBRAMANIAN, S. and MITCHELL, J. W., ''Silicon Nitride Homogeneity and Compositional Analysis by Nuclear Track Counting and 14 MeV NAA'', J. Radioanal. Chem., *110* (1987) 235-243.

[10] KOMETONI, T. Y., unpublished work.

[11] RILEY, J. E., LINDSTROM, R. M., J. Radioanal. Nucl. Chem., *109* (1987) 109-115.

[12] RILEY, J. E., MITCHELL, J. W., DOWNING, R. G., FLEMING, R. F., LINDSTROM, R. M. and VINCENT, D. H., Materials Science Forum, 1984 Vol. *2*, Trans. Tech. Pub. Lld, Switzerland (1984) 123-132.

[13] MITCHELL, J. W., ''Chemical Analysis of Electronic Gases and Volatile Reagents for Device Processing'', Solid State Tech., (March, 1985) 131-137.

[14] BINDELL, J. B., ''Analytical Methods - Semiconductor IC Technology'', VLSI Technology, S. M. Sze ed., McGraw Hill and Co., New York (1988) Chpt. 12.

[15] SEIBLES, L., Applied Spectros, in press.

[16] BULLIS, et al., "Calibration of IR Absorption Measurements of Interstitial Oxygen Concentrations in Silicon", (Proc. 5th Inter. Sym. on Si Mat. Sci. and Tech.), vol. 86-4, (HUFF, H. R., ABE, T. and KOLBESEN, B., Eds.), The Electrochem. Soc., Inc., Pennington, N.J. (1986) 166-180.

[17] MAY, T. C. and WOODS, M. H., "Alpha Particle Induced Soft Errors in Dynamic Memories", *IEEE Trans. Elect. Dev., ED26* (1979) 86-94.

[18] RILEY, J. E., "Determining Trace Uranium in Ceramic Memory Packages Using Fission Track Counting", Semicond. Inter., (May, 1981) p. 109-120.

[19] TAJIMA, M., "Correlation Between Photoluminescence Spectra and Impurity Concentrations in Silicon", Japan *J. Appl. Phys., 16* (1977) 2265-2266.

[20] TAJIMA, M., "Characterization of Neutron-Transmutation Doping in Silicon by the Photoluminescence Technique", *Appl. Phys. Lett., 35* (1979) 242-243.

# TECHNIQUES FOR THE CHARACTERIZATION OF TRACE IMPURITIES IN SILICON

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**Abstract**

Recent advances in microelectronics can be measured by our evolving ability to measure low levels of impurities and dopants in bulk silicon material, thin metal and oxide layer overcoats, and fabricated devices. A variety of techniques are available which rely on probes of electrons, ions, and light to measure ppma-ppba levels of single element and electrically active species in silicon. Each has its strength and weakness with regard to the inevitable compromise between point-to-point x-y spatial resolution, depth resolution, and detectability (signal-to-noise). Modern applied methods include secondary ion mass spectroscopy (SIMS), neutron activation analysis (NAA), photoluminescence spectroscopy (PL), and glow discharge mass spectroscopy (GDMS). Promising new technologies are emerging which are capable of ppta and sub-ppta performance. One example is laser resonance ionization spectroscopy (RIS) which relies on post ionization of sputter liberated neutral particles to achieve both ppta sensitivity and 20A depth profiling. Other breakthroughs have resulted from the synergism of combining separate technologies. Fourier transform photoluminescence (FTPL) and accelerator based mass spectroscopy (SuperSIMS) will be discussed in this context. Some fundamental constraints of sampling and signal-to-noise are also pointed out which impose ultimate limits to our progress in increasing sensitivity to trace elements.

---

## 1. INTRODUCTION

Development of diagnostic techniques for the characterization of trace levels of dopants and impurities in silicon continues to be driven by requirements of the semiconductor industry for smaller feature size and increased material purity. Progressive shrinking of very large scale integrated circuits (VLSI) into the submicron regime, and the emergence of quantum structures on the nanometer scale increase the challenge for materials characterization specialists because inspection of failures typically involves defects which are an order of magnitude smaller than minimum geometry. More recently, designers have turned to the third dimension to fabricate isolation channels and trench capacitors which penetrate up to ten microns into the bulk material. These structures have become increasingly susceptible to atomistic defects which form points for high field strength, charge leakage, material stress, hot electron effects, and active junction degradation.

Traditionally, wet chemical methods requiring dissolution of the sample in a solvent have pressed frontiers for trace element analysis, but these have been ultimately limited by purity of the chemicals, extractions, concentrates and containing vessels required. Other methods employing beams of electrons, photons and particles have attempted to achieve point-to-point spatial resolution while retaining the sensitivity advantage. These avoid chemical contamination, but encounter other limiting barriers.

The intent of this review is to focus on physical methods for the analysis of solids which optimize the compromise between x-y spatial resolution and technique sensitivity. Figure 1 shows how probes of light, electrons, ions and x-rays are evolving to meet this need relative to LSI, VLSI and quantum device technologies. Several breakthroughs are on the horizon which will be discussed relative to analysis technique and the materials issues involved.

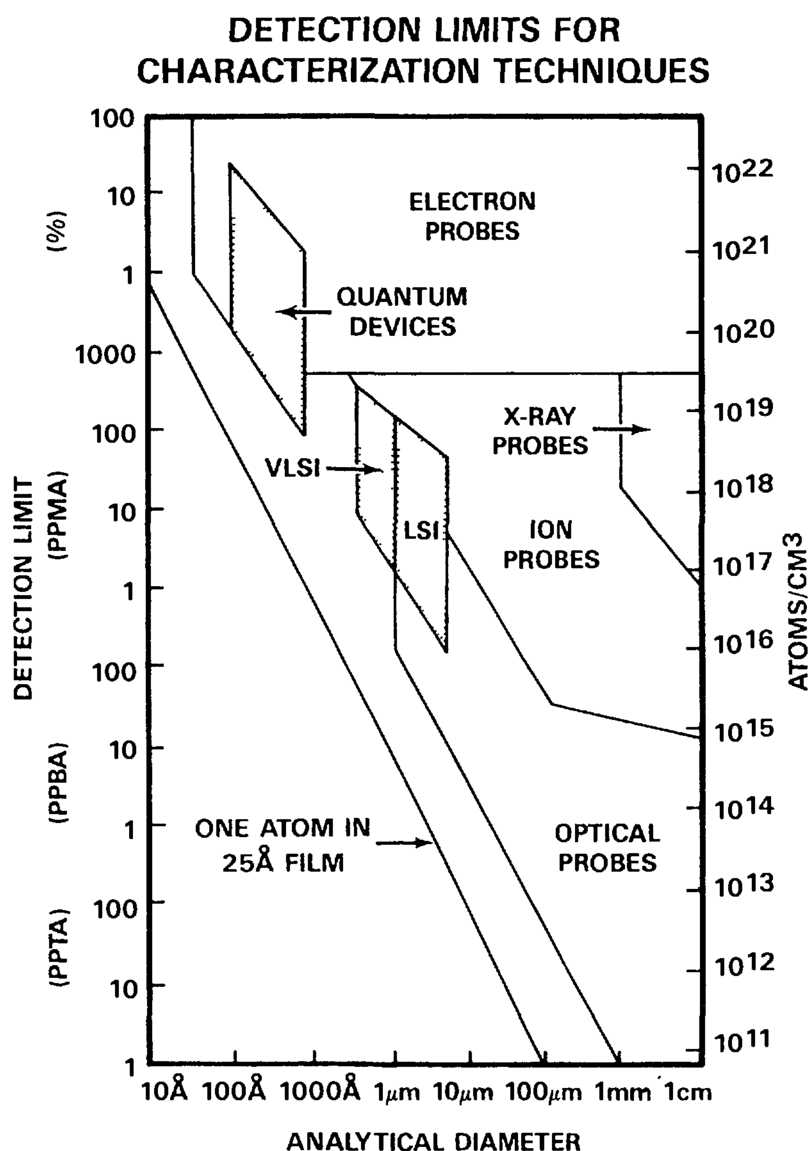



FIGURE 1: Materials characterization techniques offer a choice between detection limit and analyzing spot size. The probing radiation must be selected according to the nature of the problem at hand.

## 2. TECHNIQUES AND MATERIALS ISSUES

### 2.1. Metal Impurities

Characterization for crystal growth seeks the identification of bulk impurities which ultimately degrade electrical performance. In bipolar devices, problems can occur with p-n junction breakdown, hot electron effects, and reduced transistor gain. In MOS circuits, refresh time, operating temperature, and speed-power product are affected [1]. CCD imagers are particularly sensitive to impurities which can be as small as atom clusters which give rise to dark currents and image artifacts.

Trace metals also influence the properties of silicon solar cells by inducing inclusions, precipitates, or polycrystalline structure. Active impurity centers reduce carrier diffusion length and mobility through scattering loss, and are also cause for degraded contacts and peripheral shunt resistance. Efficiency losses up to 60% can occur in the presence of metals such as Ta, Mo, Nb, Zr, W, Ti and V below the ppba (parts-per-billion atomic) level, and with Co, Cr, Mn, Fe, Al, Ni, and Cu near the ppma (parts-per-million atomic) range [2].

Techniques available for ppma-ppba trace analysis in solid materials have been limited, typically relying on neutron activation analysis (NAA), secondary ion mass spectrometry (SIMS), or Fourier transform infrared (FTIR) spectroscopy. These strive for increased sensitivity, but typify other shortcomings such as large analysis volume, lack of point resolution and surface sensitivity, and sample annihilation.

### 2.2. Neutron Activation Analysis

In NAA, the specimen is placed in a thermal neutron flux within the core of a reactor and radioactive nuclei are formed through nuclear reactions on stable isotopes [3,4]. The gamma radiation from their decay is measured and used to identify nuclei with detectability approaching $10^{11}$ atoms/$cm^3$ (2 parts-per-trillion atomic). Although this is achieved at the expense of large specimen volume (typically near 1 $cm^3$), controlled chemical etching offers a means for removing select surface layers of oxide or silicon prior to analysis. The technique is unaffected by all chemical or handling contaminants introduced after irradiation.

NAA is used to monitor the level of electrically conducting impurities such as Au, Na, Cu, As, Co and W in silicon ingots and wafers at select process steps. In Figure 2 for example, Cu introduced through the wall of a hot diffusion furnace quartz liner was recorded over a twenty month period and ultimately brought under control by implementing a double wall configuration. Even at levels below $10^{11}$ atoms/$cm^2$, the increased mobility of Cu in silicon at elevated processing temperatures can result in high concentrations at layered interfaces and surface contact points.

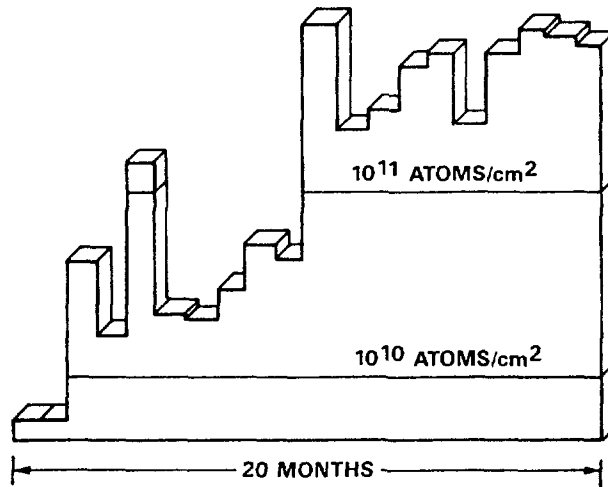



FIGURE 2: Copper introduced through the wall of a hot diffusion furnace quartz liner was monitored in this plot over a 20 month period using neutron activation analysis. A double wall configuration was adopted to resolve the problem.

2.3. Oxygen and Carbon

The approach of entraping metal impurities within the bulk of silicon away from active surface junctions has been exploited as an effective alternative, when purity requirements cannot be met by straightforward impurity reduction. The gettering properties of oxygen precipitates in silicon have been studied for this purpose and there has been considerable development of this technology during the past decade [5].

Czochralski silicon contains oxygen which is introduced during crystal growth from dissolution of the quartz crystal crucible. Typical ingots contain 20 to 40 ppma, with both radial and axial macroscopic variations. At temperatures where

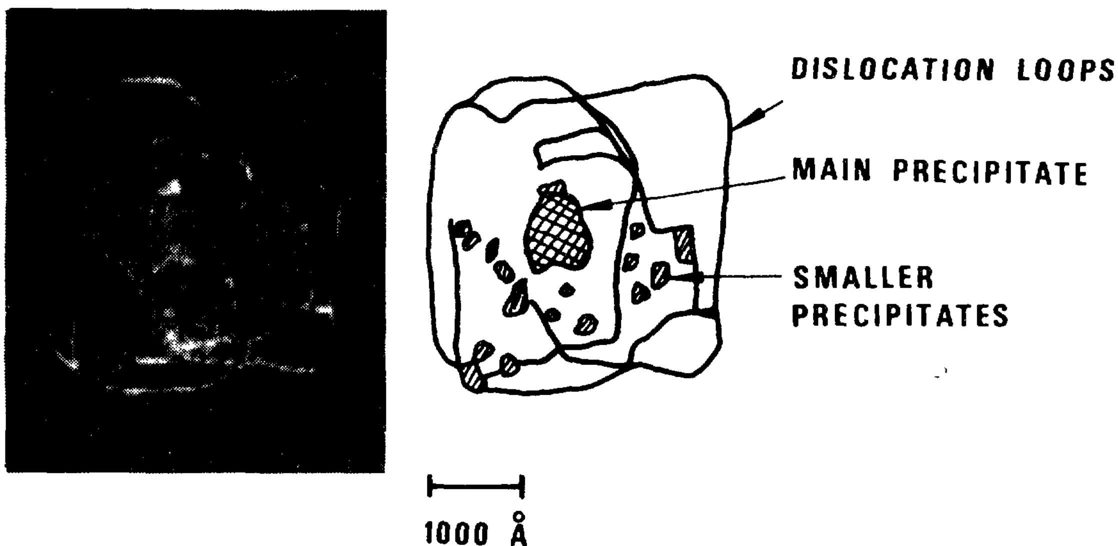



FIGURE 3: Transmission electron microscopy was used to image this oxygen precipitate in silicon. Accompanying punched out dislocation loops can be seen which act as entrapment sites for metal impurities.

device processing occurs, the oxygen concentration is greater than its solubility in silicon, and precipitates form during cooling which cause strains and disruptions in the lattice. The transmission electron micrograph in Figure 3 shows that these can form a highly efficient internal gettering network for entrapment of contaminant atoms and clusters.

Infrared spectroscopy has evolved as the technique of choice for oxygen in silicon, as well as carbon and various dopants (groups IIIA and VA) with ppma precision [6,7]. Spectrometers that employ a Michelson interferometer as the dispersing element realize orders of magnitude advantage in sensitivity because the light otherwise lost in a narrow slit grating can be collected. The resulting diffraction information can be transformed by Fourier analysis to yield the desired spectrum and is the basis for Fourier transform infrared (FTIR) spectroscopy. The high sensitivity for thick samples (0.2-1 cm) and insensitivity to surface contamination are advantages for bulk analysis.

ASTM (American Society for Testing and Materials) procedures have been defined for the measurement of oxygen in polished slabs of silicon by infrared spectroscopy [8]. However, there has been difficulty in achieving agreement between different instruments and instrument vendors, because software based corrections for internal reflections and baseline calibration are not standardized. In addition to ASTM, JEIDA (Japan Electronic Industry Development Association) standards have gained credibility over the years, but are generally difficult to obtain [9]. SIMS methods are now being evaluated for oxygen quantification, but the influence of hydrocarbons from the vacuum environment remains poorly understood, and needs further study.

The influence of carbon on the precipitation behavior of oxygen is now recognized, and its measurement is also dependent on FTIR. A two-phonon silicon lattice band at 610 $cm^{-1}$ overlaps the carbon absorbance and limits sensitivity for carbon to about 0.5 ppma.

Methods for the detection of dopant and impurity species in crystal ingots also apply to single slices, but additional fabrication steps such as sawing, edge grind, polish and back-side damage require that specialized techniques be available for characterizing large and small defects induced by mechanical processes. In many instances, such physical defects can have as much impact on the electrical properties of silicon as metallic impurities themselves. Techniques of x-ray topography and optical spectroscopy and microscopy have been applied to these problems [10].

### 2.4. Interfaces with Metals

Metal contaminants introduced during device fabrication are associated with stainless steel and aluminum parts of sputter etch stations, metal and oxide deposition chambers, ion implanters, and processing gasses of inorganic composition. Intermixing of deposited layers with silicon can also occur. Backside gold is used at elevated temperature for example, to form eutectics with silicon for improved strength and uniformity during chip-to-header bonding. Aluminum interconnects and a variety of metal-silicided contacts (e.g., Ti, Mo, W, Pt) are also prevalent in circuit design.

Secondary ion mass spectroscopy (SIMS) is useful for these problems, because it combines a sensitivity adequate for ppma analysis with depth profiling capability and near micrometer spatial resolution. There are variations in the way it is implemented, but all methods employ an ion beam to sequentially etch the specimen to release charged molecular fragments and atoms. These are collected and analyzed for charge-to-mass ratio. Simple configurations use a beam of argon and a quadrapole spectrometer. In sophisticated instruments, the yield of positive fragments is increased with an $O_2^+$ probe, while negative fragments are optimized with $O^-$ or $Cs^+$. Modern spectrometers couple electrostatic and magnetic analyzers for optimum mass resolution (near 7000M/dM) and sensitivity (sub-ppma for most elements). If a rastering focused ion probe is used to achieve x-y positioning, the instrument is called an ion microprobe, while focusing optics analogous to the light microscope are the basis for the ion microscope.

Implants of boron and phosphorus in silicon are also monitored by SIMS. It is straightforward to achieve $10^{15}$ atoms/$cm^3$ detectability for boron, but the detection of $^{31}P$ is complicated by the presence of $^{30}SiH$ molecules which are of nearly equal mass. This requires that high mass resolution analysis be used at the expense of sensitivity. New approaches are now evolving which address this mass interference problem.

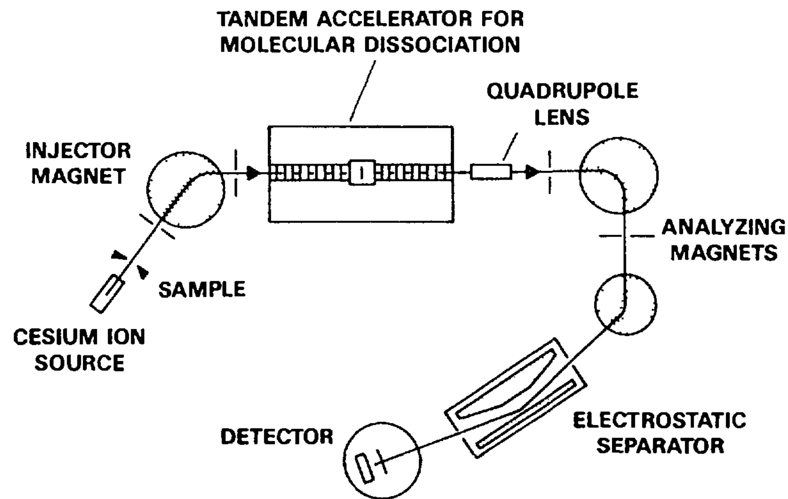
## 3. EVOLVING TECHNIQUES

### 3.1. Accelerator Based Mass Spectroscopy

A promising new technique based on an older technology designed for ultrasensitive radioisotope dating is now being developed [11,12,13,14]. This is an accelerator based mass spectroscopy we call "SuperSIMS," which couples the conventional SIMS machine to a high energy tandem accelerator. Sputtered molecular fragments are accelerated several million electron volts into a stripper gas which dissociates them into constituent atoms. At these energies, post-accelerator single atom detection can be realized using established nuclear particle counters and techniques. Ppba sensitivity has been achieved in preliminary experiments with Super SIMS (Figure 4), and expectations for achieving ppta (parts-per-trillion atomic) are limited only by purity of the ion source.

### 3.2. Laser Assisted Mass Spectroscopy

Another approach for improving SIMS relies on laser ionization of neutral particles generated by the ion beam. It has been designated by a variety of acronyms [15,16,17,18,19,20]. The one adopted here will be NRIS, for nonresonant ionization spectroscopy. Neutral atoms and molecular fragments account for more than 90% of the sputter yield in SIMS, so that it is possible to increase signal strength by post-ionization of these species. Laser light can be used with total efficiency, and sensitivities approaching ppma for impurities in silicon have been realized.



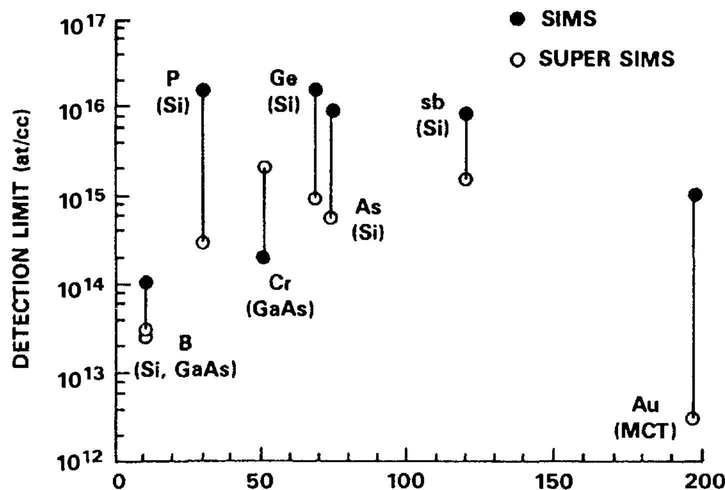
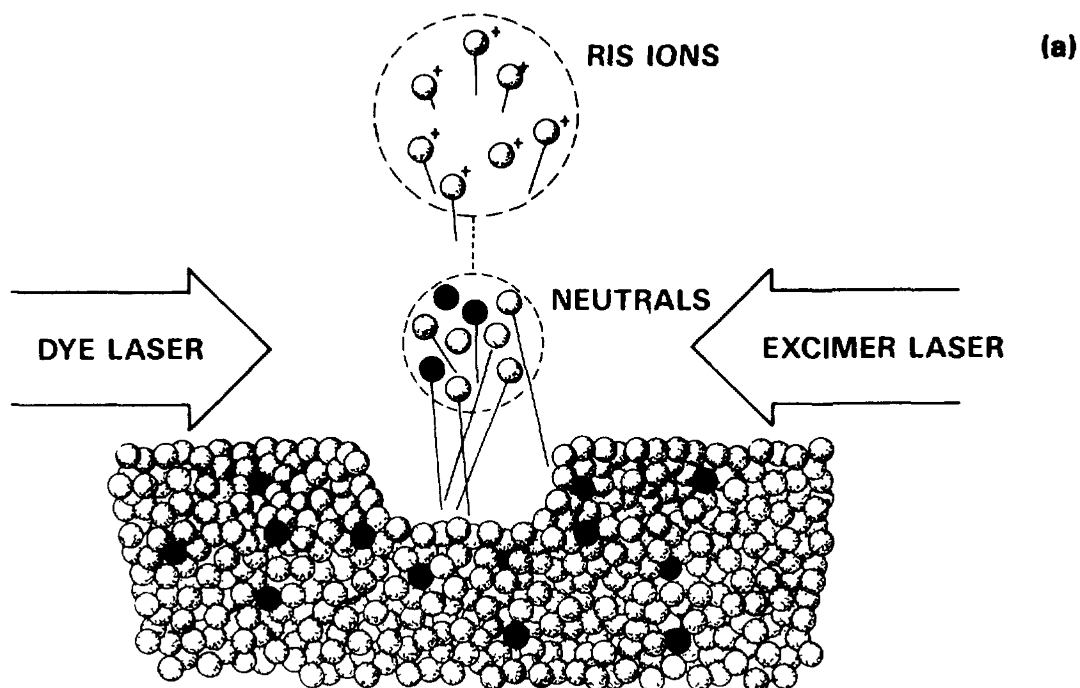




FIGURE 4: Accelerator based mass spectroscopy couples the conventional SIMS machine to a high energy particle accelerator to break apart ambiguous mass fragments. The data demonstrate orders-of-magnitude advantage of the approach.

Another major advantage is that the yield of neutrals is not influenced by complex charge states of the parent etched surface. This translates into improved uniformity for sensitivity factors of all elements in the periodic table, and a first order capability to perform the analysis without standards.

Further development of these ideas leads to the resonant ionization spectroscopy (RIS) method. As before, a sputtered cloud of neutral particles is generated, but a dye laser is used of specific wavelength to selectively ionize only the single element of interest. Selective ionization permits species discrimination without the intensity loss of a mass spectrometer, and it is possible to realize as much as three orders of magnitude increase in sensitivity. Significant progress has been made in realizing ppta sensitivity for Fe using RIS, as shown in Figure 5.



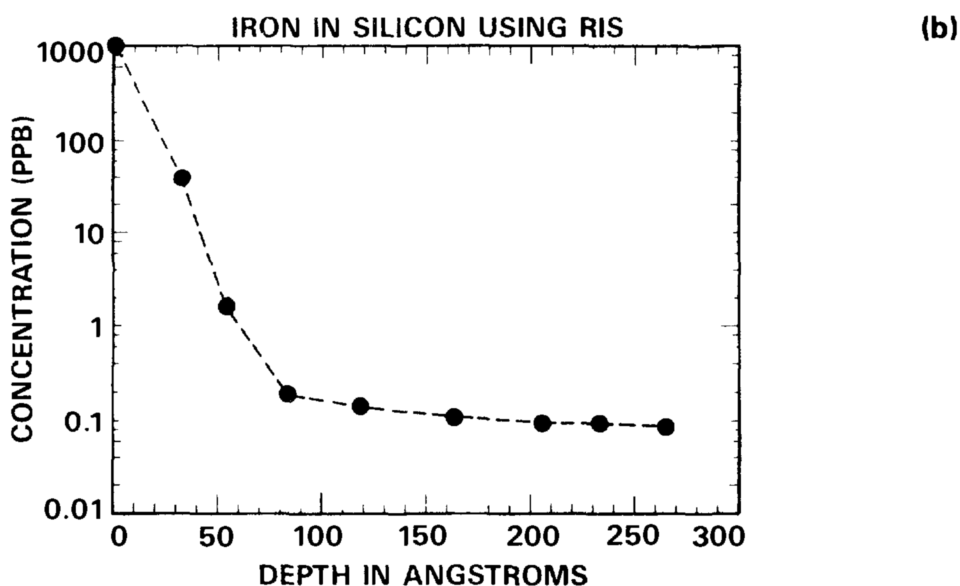




FIGURE 5: The resonance ionization spectroscopy (RIS) technique offers ultrasensitivity by selectively ionizing from a cloud of neutral atoms only those that are of interest. Iron in silicon at the ppta level has been detected.

3.3. Sputtered Neutral Mass Spectrometry

Yet another variant of these methods takes advantage of the fact that a low potential gas glow discharge can be used instead of high energy ion beams to gently remove surface atoms with minimal production of molecular fragments [21,22]. The sample itself forms the cathode for discharge in an inert gas at low potential (0.2 to 1 keV) and pressure ($10^{-1}$ to $10^{-4}$ Torr). Positive gas ions are accelerated towards the sample, liberating neutral species into the glow discharge environment.

Those which are ionized by collisions with gas atoms are extracted through a small slit and accelerated into a high resolution mass spectrometer.

As with NRIS, this method claims uniformity in elemental sensitivity for analysi without standards, and sub-ppba sensitivity is possible in some cases. The limitation is with sample geometry, which must be either flat or a thin pencil of material. In addition, ionization chamber walls can be a source of contamination and must be cleaned for optimum performance.

### 3.4. Photoluminescence Spectroscopy

In photoluminescence spectroscopy (PL), a population inversion of electronic excited states is created by visible laser light stimulation, and emissions resulting from relaxation to the ground state are analyzed. This is fundamentally an electrical characterization technique, because it senses band structure that gives rise to the detected electronic transitions. A review of the method has been given [23] and applications for the determination of dopants in silicon reported [24,25]. When coupled with the sensitivity advantage of the Michelson interferometer, the measurement is incredibly sensitive. Trace levels of P, B and As can be quantitatively measured in silicon in the sub-ppta range (Figure 6). The shortcoming of PL is that a low temperature liquid helium environment is required, and the number of elements amenable for analysis is small.

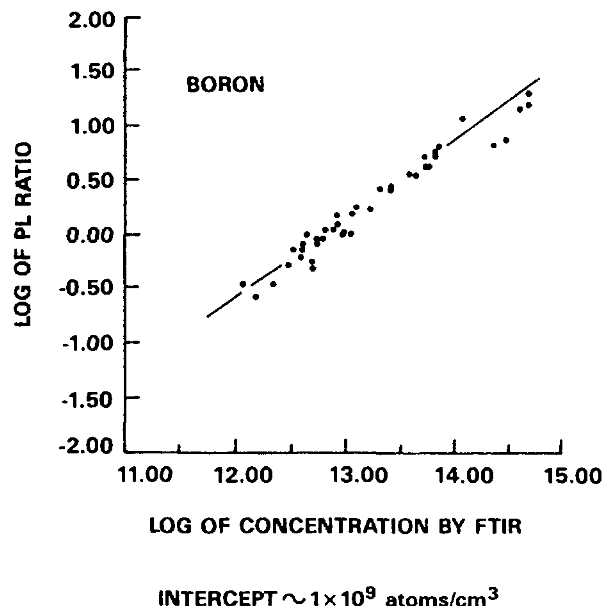



FIGURE 6: The sensitivity of photoluminescence spectroscopy (PL) can be increased by orders-of-magnitude through the use of an interferometer based detector (Fourier transform PL). Standards were unavailable to confirm this predicted limit of $10^9$ atoms/$cm^3$ for boron in silicon.

## 4. PERSPECTIVE

A comparison of the techniques highlighted in this report is given in Table I. Although such details of capability can be appreciated, it is noteworthy in perspective that the frontiers for trace element analysis are truly advancing by orders-of-magnitude. In the absence of standards below a ppba, it is necessary to resort to indirect approaches for quantification, such as extrapolation of data (as in Figure 6) or development of reliable models for physical processes which permit first-order quantification without standards (the laser assisted and sputtered neutral methods).

Nuclear techniques have advantage for fabricating standards, because they are free from chemical matrix complications and have a firmly established statistical basis for quantification. Techniques such as nuclear reaction and charged particle activation analysis, and transmutation doping have potential for furthering our ability to fabricate stable standard materials. Accurate levels for dopants such as B, P, As or Sb in silicon at the ppta level would be of considerable value for calibrating new equipment and establishing unproven methods.

TABLE I: Techniques for the analysis of trace impurities and dopants in silicon must be selected according to the problem at hand. Those which offer a compromise with spatial resolution are compared here.

| Method Acronym | Surface Ability | Matrix Effects | Mass Overlap | Sensitivity Level | Comments |
|---|---|---|---|---|---|
| NAA | 1 μm | no | | ppba-ppta | etch for surface sensitivity |
| GDMS | 20 Å | minimal | minimal | ppma-ppba | flat or needle shaped specimems |
| FTPL | 1 μm | yes | | ppba-ppta | low temperature, limited elements |
| SIMS | 200 Å | yes | yes | ppma | established workhorse tool |
| SuperSIMS | 1000 Å | yes | no | ppba-ppta | accelerator is required |
| NRIS | 20 Å | minimal | yes | ppma-ppba | laser ablation mode available |
| RIS | 20 Å | minimal | no | ppta | limited elements |

### 4.1. Silicon Superlattices

Interest in artificially structured materials is evolving, with emphasis being placed not only on the development of a fundamental understanding of atomic multilayered structures, but also on techniques of fabrication by molecular beam epitaxy (MBE) [26]. With group IV superlattices (i.e., Si and Ge), research is seeking to produce direct bandgap materials with enhanced electron mobilities.

The ability to characterize a single interface for impurities and defects with single atom resolution is becoming important to support this technology.

### 4.2. Single Atom Detection

Techniques already at the forefront of single atom detection and imaging include ion microscopy, high resolution transmission electron microscopy, and scanning tunneling microscopy. These evoke familiar questions about detectability and the fundamental limits we should ultimately encounter.

The assumption that the number of atoms detected is large and the probability for single atom detection small is the basis for Poisson statistics which describe the majority of analytical techniques in use today. For single atom detection, the conditions are reversed. When the probe radius, depth of analysis, or contaminant level is reduced, the volume of analysis ultimately includes only several species atoms of interest. In the extreme, the volume contains no species atoms at all. The analyst is now confronted with a severe sampling problem in selecting which atoms are appropriate for the analysis. The more general binomial distribution can be used to describe this circumstance, and some results of its application are summarized in Table II.

The point quantified by this treatment is that single atom detection cannot be considered independently of the sampling problem. In its application, one must ultimately rely on the measurement of p, the probability for detection of a single atom, and this is subject to the constraints of recognized measurement theory [27].

TABLE II: Ultra-trace element analysis must inevitably contend with a severe sampling problem. The situation can be described using the binomial distribution.

$$S/N = \sqrt{Np/(1-p)}$$

| Statistics | N Determined By: | S/N Determined By: |
|---|---|---|
| Poisson Distribution (N large) | $\rho \pi r_0^2 z_0$ | $r_0 \sqrt{z_0}$ |
| Binomial Distribution (N small) | $\Sigma \delta_i(r_i<r_0) \delta_i(z_i<z_0)$ | $\sqrt{p/(1-p)}$ |

| | |
|---|---|
| S/N | signal-to-noise |
| N | number of atoms in detectable volume |
| p | probability of detecting a single atom |
| $r_0$ | probe radius |
| $z_0$ | probe depth |
| $\rho$ | atom density |
| $\delta_i(x<y)$ | = 1 when x<y, otherwise = 0 |

One is lead to the realization that new technique development will continue to be governed by the compromise between analysis spot size and limits of detection. As with macroscopic methods, the the analyst must continue to weigh the strengths and weaknesses of each method relative to the problem at hand.

## REFERENCES


[1] KEENAN, J.A., LARRABEE, G.B., "Characterization of silicon materials for VLSI", VLSI Electronics: Microstructure Science, Vol. 2 (EINSPRUCH, N., Ed.), Academic Press, New York, NY (1983) 1-72.

[2] DAVIS, J. R. et al., Impurities in silicon solar cells, Trans. IEEE Elect. Dev. ED-27 (1980) 677-87.

[3] LINDSTROM, R. M., "Activation analysis of electronics materials", Microelectronics Processing: Inorganic Materials Characterization, (ACS Symp. Washington, 1986), Series 295 (CASPER, L.A., Ed.), American Chemical Society, Washington D.C. (1986), 294-307.

[4] KEENAN, J. A., GNADE, B. E., WHITE, J. B., Instrumental neutron activation analysis of processed silicon, J. Electrochem. Soc. 132 (1985) 2232-36.

[5] HUFF, H.R., SCHAAKE, H.F., ROBINSON, S.C., BABER, S.C., WONG, D., Some observations on oxygen precipitation/gettering in device processed Czochralski silicon, J. Electrochem. Soc. 130 (1983) 1551-55.

[6] PAJOT, B., Characterization of oxygen in silicon by infrared absorption, Analysis 5 (1977) 32-42.

[7] STALLHOFER, P., Huber, D., Oxygen and carbon measurements on silicon slices by the IR methods, Solid State Tech., Aug (1983) 233-37.

[8] ASTM Book of Standards, Procedures F121, F123, Part 43, American Society for Testing and Materials, Philadelphia, 1982.

[9] IIZUKA, T., et al., Determination of conversion factor for infrared measurement of oxygen in silicon, J. Electrochem. Soc. 132 (1985) 1707-13.

[10] SHAFFNER, T. J., "A review of modern characterization methods for semiconductor materials", Scanning Electron Microscopy/1986/I (JOHARI, O., Ed.), SEM Inc., Chicago, IL (1986) 11-24.

[11] ANTHONY, J. M., DONAHUE, D. J., Accelerator mass spectrometry solutions to semiconductor problems, Nuc. Instrum. Methods (1987) in press.

[12] ANTHONY, J.M., DONAHUE, D.J., JULL, A.J.T., Super SIMS for ultrasensitive impurity analysis, Mat. Res. Soc. Symp. Proc. 69 (1986) 311-16.

[13] ANTHONY, J.M., DONAHUE, D.J., JULL, A.J.T., ZABEL, T.H., Detection of semiconductor dopants using accelerator mass spectrometry, Nuc. Instrum. Methods, B10/11 (1985) 498-500.

[14] ANTHONY, J. M., THOMAS, J., Accelerator based mass spectrometry of semiconductor materials, Nuc. Instrum. Methods 218 (1983) 463-67.

[15] BECKER, C. H., GILLEN, K. T., Surface analysis of contaminated GaAs: comparison of new laser-based techniques with SIMS, J. Vac. Sci. Technol. A, 3(3) (1985) 1347-49.

[16] HURST, G. S., PAYNE, M. G., KRAMER, S. D., YOUNG, J. P., Resonance ionization spectroscopy and one-atom detection, Rev. Modern Phys. 51 (1979) 767-819.
[17] PELLIN, M. J., YOUNG, C. E., CALAWAY, W. F., GRUEN, D. M., Trace surface analysis: 30 ppb analysis with removal of less than a monolayer. Fe and Ti impurities in the first atomic layer of Si wafers, Nuc. Instrum. Methods B13 (1986) 653-57.
[18] WINOGRAD, N., BAXTER, J. P., KIMOCK, F. M., Multiphoton resonance ionization of sputtered neutrals: a novel approach to materials characterization, Chem. Phys. Lett. 88 (1982) 581-84.
[19] BEKOV, G.I., LETOKHOV, V.S., Laser atomic photoionization spectral analysis of element traces, Appl. Phys. B30 (1983) 161-76.
[20] PARKS, J. E., SPAAR, M. T., MOORE, L. J., "Direct solids analysis sputter-initiated resonance ionization spectroscopy (SRIS)", (Proc. Symp. on Accuracy in Trace Analysis - Accomplishments, Goals, Challenges, Gaithersburg, 1987), U.S. Department of Commerce, National Bureau Standards, Gaithersburg, MD (1987).
[21] SANDERSON, N.E., CHARALAMBOUS, P., HALL, D.J., BROWN, R., "Quantitative aspects of glow discharge mass spectrometry," (Proc. Symp. on Accuracy in Trace Analysis - Accomplishments, Goals, Challenges, Gaithersburg, 1987), U.S. Department of Commerce, National Bureau Standards, Gaithersburg, MD (1987).
[22] MULLER, K. H., OECHSNER, H., "Trace analysis in solids by secondary neutral mass spectrometry SNMS," (Proc. Symp. on Accuracy in Trace Analysis - Accomplishments, Goals, Challenges, Gaithersburg, 1987), U.S. Department of Commerce, National Bureau Standards, Gaithersburg, MD (1987).
[23] SMITH, K.K., Photoluminescence of semiconductor materials, Thin Solid Films 84 (1981) 171-82.
[24] TAJIMA, M., Determination of boron and phosphorus concentration in silicon by photoluminescence analysis, Appl. Phys. Lett. 32 (1978) 719-21.
[25] DUNCAN, W. M., CHANG, P.-H., MAO, B.-Y., CHEN, C.-E., Photoluminescence and microstructural properties of high-temperature annealed buried oxide silicon-on-insulator, Appl. Phys. Lett. 51 (1987) 773-75.
[26] Report on Artificially Structured Materials, National Academy Press, Washington, D.C., Chapter V (1985) 85-109.
[27] CURRIE, L. A., Limits for qualitative detection and quantitative determination, Anal. Chem. 40 (1968) 586-93.

# ANALYTICAL STANDARDS AND SILICON ANALYSIS

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**Abstract**

The quality of silicon and other electronic materials needs to be carefully controlled by appropirated method of chemical analysis. Sufficiently sensitive analytical techniques as well as suitable certified reference materials are, however, lacking to the analytical community. It is argued that semiconductor grade polycrystalline silicon can be a useful standard material because of its high purity.

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The demands for higher yields of more densely integrated circuits place stringent demands on the quality of currently available silicon and other electronic materials, and equally severe demands upon technical methods used to characterize these materials. There is a shortage of laboratory methods of chemical analysis with elemental sensitivity at the ng/g level and with demonstrated accuracy. Even fewer are suitable for routine use in industrial quality control.

*Utility of Standard Materials*

It has been repeatedly demonstrated that improvements in analytical science are facilitated if there exists a standard material, such as a Certified Reference Material [1], which is suitable for testing a new procedure and for which the "true" value of the property is known with a high degree of certainty. To obtain a correct value may require highly skilled analysts using specialized apparatus and methods too time consuming or too expensive for use in a quality control laboratory. Not all standard materials need be exhaustively characterized, however. To test for precision and not accuracy, the test material needs only to be homogeneous. Two analysts determining a property of identical portions of a standard material can decide whether they agree even if the true value of the property is unknown. Furthermore, two analysts measuring two different standard materials can decide whether an observed disagreement is one of scale (calibration) or of level (blank).

An illuminating method of assessing the intercomparability of analyses in different laboratories is a blind interlaboratory test, in which the participants analyze identical samples of unknown materials and report their results to a central coordinator [2]. Almost invariably the observed between-laboratory precision is much worse than the participants have expected. In cases where the true composition is known, the accuracy is often poor as well. An interlaboratory comparison of this sort is a dramatic way of pointing up inconsistencies, but it does not of itself point to solutions. Only if the discovery of discrepancies leads to better analytical procedures, generally through iterative intercomparisons, will the state of the analytical art be improved.

No standard silicon material is readily available to the analytical community, and indeed few reference materials of any inorganic matrix are available with a well-known content of impurities at trace (µg/g) or ultratrace (ng/g) levels. Ensuring homogeneity is often a problem at low concentration since in silicon, as in igneous rocks, many trace constituents are concentrated in the last portion of solid to freeze from the melt. Moreover, surface contamination during the production, subdivision, and packaging of high-purity materials is always likely. Most samples of silicon and quartz analyzed in our group have shown great differences in trace element content before and after a non-etching surface cleaning.

No standard semiconductor material is now available to the analytical community. Possibly this implies that there is no need for one. Some arguments for this view are:

1. Semiconductor grade polycrystalline, Czochralski, and float zoned silicon are commodities: materials of commerce with well-defined properties.

2. At the current state of knowledge, it is only necessary in a production environment to know that the current batch of material is as good as the last batch that made good devices. Simple go/no-go or ratio tests are sufficient to decide this question; no absolute standard of concentration or resistivity is needed.

3. The existence of a common standard sample will encourage interlaboratory comparisons which will reveal the adequacy of quality assurance procedures and other sensitive information to competitors.

4. It would be difficult to certify the concentrations of trace impurities in so pure a material as semiconductor silicon if the criteria applied to the certification of NBS Standard Reference Materials are required, namely independent determinations by at least two different analytical techniques.

None of these objections will withstand scrutiny. They are met as follows:

1. The view of silicon materials as commodities is valid only if the properties of silicon do not change from year to year. But as industrial process equipment is modified continually toward more automation and larger throughput, the quality of the resulting materials have in fact improved.

2. Again, the electronics industry is dynamic. The understanding and hence the improvement of production processes and device performance is most efficient if the engineering is founded upon a detailed understanding of the physics and chemistry.

3. Round robin analyses designed to show intercomparability should be conducted blind, so that only the organizer of the intercomparison is able to identify the individual participants. National and international voluntary standards organizations such as the American Society for Testing and Materials and the Association of Official Analytical Chemists [2] often play this role.

4. Finally, for some purposes a homogeneous standard material whose composition is not accurately known can be nearly as useful as a certified reference material. At least one NBS Standard Reference Material fits this description: SRM 4990 Oxalic Acid, which is sold with no information on its composition except that the radiocarbon assay of any subsample from any bottle of SRM 4990 will be identical to any other. Another prominent example is the suite of U. S. Geological Survey standard rocks, the composition of which was only approximately known at the time of issue. It is principally the repeated analysis of these materials over a period of years by a majority of workers in the field, during which a consensus has emerged as to their composition, that has made trace element measurements reliably intercomparable among geochemical laboratories today.

*Producing a Silicon Standard Material*

Suppose we desire a hundred 100-gram units of material; this requires 10 kg of silicon plus another 10 kg to allow for losses during preparation. This is the mass of a 150-mm crystal 50 cm long. A silicon standard material that is homogeneous over such a large volume will not be easy to prepare, particularly if it is intended to be representative of a single-crystal substrate upon which devices are fabricated. The Czochralski crystal growing procedure is also a refining process, so that the concentration of trace impurities in the crystal increases as the melt is consumed, and hence large longitudinal concentration gradients are to be expected. At thermodynamic equilibrium the distribution of solute between melt and solid is described approximately by

$$C_S/C_O = k_\infty(1-X)^{(k_\infty-1)} \qquad [3]$$

where

$C_S$ = concentration in the solid
$C_O$ = initial concentration in the melt
$X$ = fraction of the melt solidified
$k_\infty$ = segregation coefficient.

As a result, the concentrations of some elements in the crystal vary greatly as crystallization proceeds. If we begin with a concentration $C_0$ in the melt of 1 ppm, then the concentration in the solid increases with the fraction solidified as follows:

| Element | $k_\infty$ [3] | Concentration in solid (ppm) for 1 ppm in initial melt, for increasing fraction solidified | | | | |
|---|---|---|---|---|---|---|
| | | 1% | 10% | 50% | 90% | 99% |
| B | 0.80 | 0.80 | 0.82 | 0.92 | 1.27 | 2.01 |
| As | 0.30 | 0.30 | 0.32 | 0.49 | 1.50 | 7.53 |
| Al | 0.0020 | 0.0020 | 0.0022 | 0.0040 | 0.020 | 0.20 |
| Fe | $8.0x10^{-6}$ | $8.1x10^{-6}$ | $8.9x10^{-6}$ | $1.6x10^{-5}$ | $8.0x10^{-5}$ | $8.0x10^{-4}$ |

Most of the transition and refractory metals, those which have the greatest effect on device performance, have segregation coefficients far from unity. Thus the concentrations of these elements in the solid are both small and strongly variable across a crystal.

A useful standard material would be semiconductor grade polycrystalline silicon, the feed material for growing single crystals. Polysilicon is macroscopically more uniform than a large Czochralski crystal even though microscopically most impurities are segregated to the grain boundaries. This material is already highly pure, with most impurities present only at nanograms per gram or lower concentrations. It is at this stage of manufacturing that silicon is characterized in industry [4], both because the polycrystalline ingot is most representative of the crystal and, practically, because the concentrations of many elements in polysilicon are high enough to measure. For many analytical techniques, it would be desirable to have available two standard materials: polysilicon and slices (with low surface/volume ratio compared to a powder) of highly pure float zoned material for use in determining the analytical blank.

The ideal physical form of an analytical sample for many chemical analysis techniques is a moderately fine powder or chips, although many methods are designed to work with wafers. Forming chips from a large Czochralski crystal must be done by crushing, during which silicon is likely to abrade the grinding surfaces and become contaminated. Although brittle, silicon is harder than quartz or hardened tool steel, so alumina crushers would be necessary. Other methods of producing a fairly homogeneous solid material have been proposed, such as casting liquid silicon into small-diameter quartz tubes and quickly quenching, or by spraying droplets of silicon into liquid argon. These rapid cooling methods bear investigation, but since the processes take place far from equilibrium, inhomogenous entrainment of blebs of melt into the crystallites is possible. Whatever the mode of production of standard materials, close collaboration will be required between the designers of the standard and the operators of the silicon foundry.

*References*


1. URIANO, G.A., GRAVATT, C.C., CRC Crit. Revs. Anal. Chem. **6** (1977), 361.

2. BOYER, K.W., HORWITZ, W., ALBERT, R., Anal. Chem. **157** (1985), 454.

3. WOLF, S., TAUBER, R.N., *Silicon Processing for the VLSI Era, v. 1: Process Technology*; Lattice Press, Sunset Beach, Calif, 1986.

4. KEENAN, J.A., LARRABEE, G.B., in EINSPRUCH, N.G., LARRABEE, G.B., eds. *VLSI Electronics Microstructure Science, vol.6: Materials and Process Characterization*; Academic Press, New York, 1983, pp. 1-72.

# SUMMARY OF PRESENTATIONS AND DISCUSSIONS WITH SPECIAL REFERENCE TO THE NEED OF INTERCOMPARISON AND REFERENCE MATERIALS IN ANALYTICAL CHEMISTRY RELATED TO SILICON ELECTRONICS

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## Oxygen and carbon in silicon

The role of oxygen as an agent for gettering metallic impurities in silicon is well known, has been extensively studied, and is prominent in the literature. The need for reliable standards has reached a critical level over the past decade, as the semiconductor industry has developed and become more dependent on a small number of material vendors.

Typically, oxygen in the 10-40 ppma range is required with precision and accuracy near 0.1 ppma. Fourier transform infrared (FTIR) has evolved as the technique of choice for making the measurement, but reaches its limits of detectability at the low end of this range. An even more serious problem exists for p-type silicon, because it becomes opaque in the infrared at high doping levels (above ≥ 1 ohm-cm).

There has been considerable controversy and confusion about appropriate standards and units for the measurement of oxygen in silicon. The Japan Electronic Industry Develpment Association (JEIDA) standards from Japan have gained high credibility over the years, but have traditionally been difficult to obtain.

Less is understood about the role of carbon in silicon, but it is known that it can alter the level of oxygen precipitation as well as influence morphology of the precipitate itself. Concentrations as low as $10^{16}$ atoms/$cm^3$ can be significant.

Measurement of oxygen by FTIR is complicated by a spectral overlap arising from the silicon matrix, and as above, is restricted to n-type and lightly p-type doped silicon. The lack of a reliable standard for carbon in silicon and an improved technique for its characterization present stumbling blocks for advancements in understanding the role of carbon and for the development of new methods of analysis.

Techniques of nuclear reaction analysis offer a decided advantage for quantitative accuracy, but also reach detectability limits within the range of interest for oxygen and carbon. The precision of these methods is believed to be inferior to FTIR, and availability of a reactor or accelerator facility for fast turnaround time in the analysis is often a problem. Research on the limitations of such methods with the specific aim of lowering detectability limits, improving accuracy and precision, and somehow facilitating availability at reasonable cost to users in the scientific community is needed.

Scanning Lang x-ray topography has been evaluated as an alternative method for the characterization of oxygen in silicon, but itself must be based on reliable standards. This technique requires a prescribed and carefully executed recipe of thermal heat treatments to insure that oxygen will precipitate in a controlled and reproducible fashion. Microscopic strains accompanying each precipitate can be easily detected by the Lang method, which can directly image uniformity of the precipitates across a silicon wafer and can be calibrated for quantitative oxygen level.

Application of the Lang method requires replication of a complicated and poorly understood sequence of thermal anneals, and has received serious acceptance only for qualitative uniformity applications. However, it remains one of the few techniques available for characterizing heavily p-doped material. Crystal growers have attempted calibrations for p-silicon by growing both p- and n-type crystals in the same Czochralski puller under an identical growth schedule. FTIR data for carbon and oxygen is taken from the n-type boule, and is applied in blind faith as a reference for the p-type crystal.

It is recognized that carbon plays an important role in the precipitation and consequent gettering capability of oxygen. Implementation and and advancement of this science would be greatly enhanced by reliable carbon standards, also at the ppm level.

Metallic impurities in silicon

Oxygen precipitation technology in its entirety is based on the premise that it is impossible in the real world to eliminate all metallic impurities in silicon. Precipitation gettering is a patch to the problem, in that it can remove electrically conducting atoms and clusters from the surface where charge leakage and short circuit can cause device failure. A more desirable, and perhaps unachievable, goal would be to eliminate sources of metal contaminants alltogether throughout all process steps.

Neutron activation analysis has evolved as a powerful method for determining low levels of Cu, Au, Na and other species detrimental to VLSI device performance. Levels of copper as low as $10^{14}$ atoms/$cm^3$ for example, can concentrate at interface or active junction regions when its mobility in silicon is increased during high temperature (≥ 1000 C) process anneals. The technique is less useful for other metals, such as iron. Standards for individual elements in silicon would provide a quantitative basis for controlling contamination and for developing new methods of analysis.

Dopants in silicon

Dopant species at the sub-ppma level also need to be characterized. Conventional approaches often rely on electrical (spreading resistance, DLTS) or optical (FTIR, photoluminescence) methods, where data is subject to misinterpretation caused by compensation from unknown impurities or crystal defects.

Other materials

Silicon is only one of hundreds of materials used in the electronics industry. Standards are needed for the characterization of all of them. Clearly the creation of certified reference materials of all of them is impractical, but some of the more important interconnection and encapsulant materials need to be addressed. For example, a need is perceived for a standard high-purity aluminum, characterized for U, Th, and alkali metals. A series of aluminum materials is being prepared for distribution by the BCR, but it will not be certified for U and Th. NBS offers two high-purity aluminum SRMs (C1257 and 44f) that may also be suitable. The IAEA could make an important contribution by coordinating the determination of these elements in the same materials.

Reference materials and problems in preparing them

A few standard materials are available. The American Society for Testing and Materials (ASTM) has produced round-robin specimens that have been widely distributed, but unfortunately the material is no longer availabe after the intercomparison is finished. NBS has made two series of Standard Reference Materials, certified for resistivity and for spreading resistance, but for neither is the physical property correlated with chemical composition.

In connection with a fundamental redetermination of the value of Avogadro's constant, two high-purity silica materials are being produced at the Central Bureau for Nuclear Measurements (CBNM). Since the experiment requires a silicon single crystal of extraordinary purity and crystallographic perfection, valuable synergies may result by cooperation between semiconductor silicon characterization laboratories and such projects as this.

Availability of reliable standards at the ppma level, and ultimately the ppba-ppta level, for P, B, As and Sb would not only firmly establish capability for these techniques, but also favorably influence the development of crystal growth and microcircuit fabrication technologies. Nuclear based methods need to be applied for fabricating dopant standards, because they have clear advantage for avoiding chemical and electrical complications.

Thought needs to be given to the technical issues involved in fabricating such standards. A homogeneous silicon standard material will not be easy to prepare, particularly if it is to represent the single-crystal substrate upon which devices are fabricated. At least several hundred analytical samples need to be prepared for a standard to be useful; this requires a homogeneous lot of a few tens of kilograms. Since the Czochralski crystal growing procedure is also a refining process, the concentration of trace impurities in the melt and hence in the crystal increases as the melt is consumed.

Polycrystalline substrates offer advantage for uniformity, but are likely to deterioriate in time as impurities work their way into grain boundary regions at the surface and into the interior of the specimen. Uniformity in single crystal silicon may be harder to achieve, but stability should be better.

It has been argued that there is no need for standard materials in the semiconductor industry. Commercial silicon in several grades has well defined properties, and production testing is adequately done by comparison with

working standards in each laboratory. However, comparisons among laboratories or between techniques can be made only if a common material is analyzed by both. For some purposes a standard material which is known or can be shown to be homogeneous but whose composition is not accurately known can be as useful as a Certified Reference Material. Round-robin studies of uncertified material can reveal calibration biases or blank problems.

Conclusions:

The following conclusions are expressed in terms of value to the electronics community, not of demand per se. Assessing the quantitative need for standards of silicon and other materials is outside the competence of the attendees. A formal market survey might be performed by advertising in several of the journals addressed to the semiconductor industry.

It would be desirable to have available a standard silicon, characterized for composition. There are many technical questions regarding the actual production of this material that cannot be answered by the participants in this meeting. These include how to produce a relatively homogeneous quantity of silicon, and what physical form (wafers, crushed pieces, or powder) is both most useful and easiest to produce without contamination. The production of such a material must be done and the characterization should be done in collaboration with silicon producers and with such national and international organizations as Semiconductor Equipment and Materials Institute (SEMI), ASTM, and Deutsche Industrie Norm (DIN).

Probably two silicon standards are most useful at this time. One should contain impurity elements at measurable levels, for use as a common substance in interlaboratory comparisons of analytical methods for elemental analysis. There are no readily available, widely distributed standards certified for content of the major dopants: B, P, As, and Sb. Several present controversies could be put to rest if there were standard materials certified at any concentration level. Since the segregation coefficients are near unity, the attainable degree of homogeneity of these dopants throughout a production lot of standards should be good. In view of the low concentrations and steep concentration gradients of transition metals in single-crystal material, the best choice of material may be semiconductor grade polycrystalline silicon.

In addition, the ready availability of a very pure silicon, probably produced by float zoning, for use as an analytical blank would be of use in the development of new methods of silicon characterization and the validation of present-day methods.

There is a need for standard materials for the calibration of oxygen in high purity silicon at the low ppm level. Standards presently exist, the JEIDA from Japan having gained the most credibility during the past decade. Availability of these standards has been restricted, and as the need for calibration between vendors of silicon materials increases, their value has increased.

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