INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON MICROCHEMICAL TECHNIQUES AND TRACE ANALYSIS*

General Aspects of Trace Analytical Methods: Part VII
TRACE ANALYSIS OF SEMICONDUCTOR MATERIALS PART B: DISTRIBUTION ANALYSIS

Prepared for publication by

M. GRASSERBAUER[1] YU. A. ZOLOTOV[2] and G. H. MORRISON[3]

[1]Institut für Analytische Chemie, Technische Universität Wien,
Wien, Austria
[2]Vernadskii Institute of Geochemistry and Analytical Chemistry,
Moscow, USSR
[3]Baker Laboratory, Cornell University, Ithaca, NY 14853, USA

In cooperation with

G. STINGEDER (Austria), YU. A. KARPOV (USSR)
and F. A. GIMELFARB (USSR)

General aspects of trace analytical methods: Part VII. Trace analysis of semiconductor materials—Part B: Distribution analysis

The analytical characterization of semiconductors is one of the most challenging tasks of analytical chemistry. Within this field quantitative distribution analysis of trace components, particulary of the dopant elements, is of great importance. For this purpose a variety of complementary techniques are at the disposal of the analytical chemist: electrical and magnetic measurements, infrared and luminescence methods,SIMS, RBS, NAA, CPAA, PIXES and EPMA. In this report the analytical figures of merit of these techniques are critically evaluated. Then the most important method for quantitative distribution analysis, SIMS, is discussed in more detail.

1. INTRODUCTION

Trace elements determine major properties of a semiconductor material (Si, GaAs, InP, etc.) - for example, the growth of epitaxial or oxide layers on silicon, the electrical conductivity of the material used for device production ("intrinsic impurities") and the electrical characteristics of an electronic device ("dopant elements").

The analytical characterization of trace elements must include the determination of:

i)   the bulk level of traces in the materials used for device production (semiconductor materials of different kinds used for specific purpose, e.g.: zonal grown single crystal Si for VLSI-devices or gallium arsenide for laser diodes, chemical vapour deposited polycrystalline silicon for solar cells, epitaxial thin films of gallium arsenide). Bulk analysis is dealt with in part A of the report (1).

ii)   the spatial distribution of the dopant elements in semiconductor devices or "model materials". The x-, y- and z-distribution of the dopant elements determines directly the electrical properties of a device. Distribution analysis must include a separate characterization of the (total) elemental concentrations and the electrically active fractions. This requires the use of techniques for elemental analysis and electrical measurements.

2. DEFINITION OF PROBLEMS

For device modelling or production the (preferably) complete knowledge of the spatial distribution of the dopant elements is sought (2). In practice spatial distribution analysis is limited to z-(depth) distribution analysis because only for this purpose are adequate methods available. Lateral distribution analysis by in-situ techniques such as SIMS is at the present state of development mainly important for studying the homogeneity of large scale (planar) material, for example the distribution of Cr in doped zonar grown gallium arsenide or of implanted dopant elements into silicon.

The main goal of distribution analysis would be to characterize the trace elements in semiconductor devices. Because the structures used in today's technology for silicon devices, are so small $(0,X-10 \ \mu m)$, the feasibility of lateral distribution analysis and direct depth distribution analysis of such samples is very limited (see sect. 4). The existing physical analytical techniques using focused particle beams do seldom exhibit the required lateral resolution.

For this reason mainly large scale samples (dimensions > several mm) are investigated in semiconductor research. With such samples the individual steps of device production are carried out and the physical and chemical behaviour of the dopant elements can be investigated. The accurate

distribution analysis of the dopant elements serves as a basis for
establishing mathematical-physical models which describe the behaviour of
these trace elements as a function of production process parameters
("Process Modelling") (3 - 5). Such models can be used to calculate the
property- determining distribution in the small scale devices (on reduction
of lateral dimensions from mm to μm, depth scale remains constant). This
"transfer of information" permits the optimization of device production, the
study of physical processes in devices and the prediction of electrical
properties of such devices ("Device Modelling").

The major requirements for (depth) distribution analysis in semiconductor
materials are:

i)   the separate determination of electrically active and total elemental
       concentration,
ii)   the possibility of determining   the major dopant elements: B, As, P
       and Sb in silicon and Cr and Si in gallium arsenide,
iii)   a large dynamic range of analysis and high detection power,
       concentration range 10^{14}-5.10^{21} at cm^{-3} [ng/g-%],
iv)   high spatial (depth) resolution: 1-10nm
v)   high accuracy of analytical information [concentration vs. depth]

Only a few analytical techniques fulfill these requirements to a large extent
in the characterization of large scale samples. For device analysis only
in-situ techniques like SIMS or electron probe micro analysis can be used.
Even for large scale samples different methods often have to be combined in
order to obtain technically important information. These techniques, their
figures of merit and limitations, will be discussed in detail here. Finally
a short section will be devoted to basic possibilities and problems in device
analysis. Major emphasis will be put on silicon because it is the most
important semiconductor material.

3. (DEPTH) DISTRIBUTION ANALYSIS IN LARGE SCALE SEMICONDUCTOR MATERIALS

3. 1 DETERMINATION OF THE DISTRIBUTION OF THE ELECTRICALLY ACTIVE FRACTION OF THE DOPANT ELEMENTS

3.1.1 Electrical Measurements

i)   Capacity/Potential (C/V) Measurements (6 - 8) :

       On the surface of a semiconductor the capacity is measured in the
       bias reversed direction as a function of the applied potential. A
       zone up to the depth impoverished with mobile charge carriers is
       introduced. The relation between electrically active dopant
       concentration N(x), capacity C(U) and potential U is described by

$$N(z) = \frac{C^3(U)}{q \cdot \varepsilon_o \cdot \varepsilon_r \cdot A^2} \cdot (\frac{d\,C(U)}{dU})^{-1}$$

   A = area of contact (Schottky contact = metal on semiconductor)
   q = elementary charge
   ε_r = relative permittivity (dielectric constant)
   ε_o = permittivity of free space
The depth coordinate z is calculated from the measured capacity,
assuming a parallel-plate capacitor

$$z = \frac{\varepsilon_o \cdot \varepsilon_r \cdot A}{C(U)}$$

This procedure has several major limitations. It is not possible
to characterize steep profiles below concentrations of 10^{16} at cm^{-3}
because of insufficient depth resolution. At higher concentrations
(10^{17}-10^{18} at cm^{-3}) and larger depths breakdown can occur owing to
the large potentials that must be applied. Leakage currents and edge
effects may decrease accuracy. The major applications of C/V
measurements are in the concentration 10^{14} to 10^{17} at cm^{-3} at
depths between 100 and 1000 nm.

ii)   Surface   Resistance Measurements

        a) Four-Point Technique   (9, 10)

        The surface resistance is measured with the aid of four point
        electrodes. Depth information is obtained from measurements made
        after repeated etching. The (surface) resistivity vs. thickness of
        etched surface zone can be converted into a concentration vs. depth
        function. Resistivity values are converted into concentrations by
        means of calibration functions. Surface layers are removed by anodic
        oxidation to SiO_2 (thickness determination by ellipsometry) and
        dissolution in hydrofluoric acid.

        The major limitations are that profiles of sufficient accuracy are
        obtained only for steep concentration gradients, the etched films are
        rather thick and the method is very time consuming (about 1 day per
        sample).

        b) Spreading Resistance Measurement (2-Point-Technique)   (11):

        The surface resistance is measured on an angle lapped specimen (1-2°)
        as a function of surface position and converted into a concentration
        vs. depth function. This technique allows the measurement of p/n
        junctions.

        The major limitations are rather low accuray, difficult sample
        preparation, and the necessity of extensive mathematical correction
        procedures.

3.1.2 Magnetic Measurements   (12)

        The sample is brought into a magnetic field oriented normal to the
        surface and the Hall potential is measured. Depth distribution is
        obtained from measurements after repeated chemical etching of the
        surface.

        The most important analytical characteristics of the electrical and
        magnetic techniques are shown in Table 1.

Table 1: Analytical Characteristics for Distribution Analysis of Electrically Active
         Dopant Fraction in Silicon

	C/V measurement	surface resistance measurement		
		4-point technique	2-point technique	magnetic measurement
depth resolution (nm)	$10 - 10^4$	15	10	10
detection limit (at cm^{-3})	2.10^{14}	$10^{17} - 10^{18}$	10^{14}	$10^{17} - 10^{18}$
dynamic range	10^4	5.10^3	10^6	5.10^3
accuracy (% rel.)	5	5 - 10	10	5 - 10

3.1.3   Infrared Spectroscopy and Luminescence Methods

        Distribution of electrically active impurities (as well as some
        electrically inactive impurities in a number of cases) can be
        determined by spectroscopic methods combined with layer-by-layer
        chemical etching. Infrared spectroscopy and luminesence are the
        most important methods.

i)   IR spectroscopy

        In the case of complete ionization of the dopant atoms (of the donor
         D or the acceptor A type) and the absence of compensation the
        concentration of impurities (N_D or N_A) is equal to the concentration
        of the charge-carriers (n), i.e. electrons or holes.
        Concentration and distribution of charge-carriers can be determined
        by measuring spectra of absorption, reflection, Raman dispersion, and

a number of other optical effects. The method of IR reflection in the range of the plasma own frequencies in a semiconductor is the most universal one (13). The method is based on measuring the spectral dependence of the reflection coefficients R (λ). Values of n are evaluated according to the change in spectral location and the form of R (λ) dependence in the range of the plasma minimum. The concentration range accessible depends on the type of the semiconductor. For gallium arsenide it is in the order of $10^{16} - 10^{19}$ cm^{-3}, for instance. The relative standard deviation of the quantitative results (S_r) can be as low as 0,2.

In the case of the simultaneous presence of electrically active impurities of different type (donors and acceptors) their mutual compensation is possible and therefore decrease of n can be observed. In this case analysis can be carried out with Hall effect measurements, which allows a separate determination of N_A or N_D.

Electrically inactive impurities, for instance oxygen and carbon, can also be determined in silicon, germanium, gallium arsenide and other semiconductors by IR absorption. The method based on the resonance absorption of IR radiation at frequencies corresponding to local vibrations of the impurities. The integral areas of the absorption bands and in a number of cases the absorption coefficients at the maxima of peaks are in proportion with the impurities concentration. The concentration range accessible depends mainly not on the type of impurity but on temperature, being for instance for oxygen in silicon $10^{14}-10^{18}$ at cm^{-3} at 4K, and $10^{16}-10^{18}$ at cm^{-3} at 300K. For C relative standard deviations of 0,1 for a concentration of 10^{18} at cm^{-3} can be obtained.

ii)   Luminescence Methods

In semiconductor materials with direct transitions (GaAs, InAs, InSb) luminescence methods can be used to control the distribution of charge carriers both in depth (in combination with the etching methods) and in the lateral direction (with use of focused beams). Electron probes (in case of cathodo-luminescence) or laser beams (photoluminescence) are used to excite the luminescence spectra.

The content of carriers can be determined according to the width of the bordering band of the luminescent spectrum or its spectral location (15). The range of the contents determined essentially depends on temperature. For instance, in gallium arsenide n = $10^{16}-10^{19}$ cm^{-3} at 4 K, $10^{17}-10^{19}$ cm^{-3} at 77 K and $10^{18}-10^{19}$ cm^{-3} at 300 K (S_r=0,2). Within the temperature interval 4-77 K only the non-compensated materials can be analyzed with help of luminescence spectra but at 300 K the analysis of compensated materials is also possible. Inspite of the possibility to determine the concentration of charge carriers, luminescence methods lack selectivity and they can not help in determination of a specific type of impurity.

This method is useful for testing the heterogeneity impurities distribution in the area of microdefects. Thus, in semiconductors with direct transitions cathode luminescence technique can be used to control the distribution of charge carriers in the area of dislocations (for instance, in gallium arsenide doped by tellurium) (16). Excitation and registration in the stroboscopic regime are used to achieve a lateral resolution of 0,1 µm which is shorter than the diffusion length of carriers and the zone of luminescent radiation generation.

In semiconductors with indirect transitions, specially in silicon, the nature and concentration of hydrogen-like impurities can be determined by luminescence spectra at 4 K (for silicon, they are B,P, Al, Ga, As, etc.)(17). Such determination is possible in the presence of free excitons in crystals which is always realized when the content of impurities is lower than 2.10^{15} at cm^{-3}.The recombination of an exciton connected with the neutral atom of the impurity, gives a characteristic line in the luminescence spectrum, which can also be used to identify the impurity atoms.The concentration of impurities can be determined with help of calibration plots of the ratio of intensities of bound and free exciton lines versus concentration. The range of the contents

determined is in the order of $10^{11} - 10^{15}$ at cm^{-3} [$S_r=0,2$] . The degree of the material compensation does not essentially influence the results of determination by this method.

As far as other optical methods are concerned they can be used for layer-by-layer analysis of semiconductors but only in those cases when procedures for the quantitative determination with sufficiently low S_r are developed. The content of the impurity to be determined in layers removed by chemical etching should exceed the absolute error of determination of the impurity in the material after etching. For instance, impurities on the level of 10^8 at cm^{-3} can be detected   in silicon and germanium by photoelectric spectroscopy (18) , but this method however can not be used yet for the layer-by-layer analysis of semiconductors because of the absence of quantitative procedures.

3. 2 DETERMINATION OF THE ELEMENTAL DISTRIBUTION OF THE DOPANT ELEMENTS

The determination of the elemental dopant concentration is important for the study of all physical and chemical processes for which particles rather than charges are decisive, such as   implantation, diffusion, precipitation and segregation. In such case, besides the distribution of the electrically active fraction (which determines the electrical properties) that of the inactive fraction also has to be known. This is achieved by measuring the total dopant concentration as a function of depth and subtraction of the electrical   profiles. Various techniques for elemental analysis are used.

3.2.1   Survey of Methods

i)   Secondary Ion Mass Spectrometry [SIMS] (19-27)

Analysis is performed by bombardment of the semiconductor surface with positive or negative (primary) ions (O_2^+, Ar^+, Cs^+, O^-, N_2^+) and mass spectrometric measurement of the "secondary" ions generated by the sputtering process. Distribution information is obtained by conversion of the secondary ion intensity vs. time functions into concentrations vs. depth functions with suitable calibration procedures.

All elements can be determined with high detection power. Distinction between different isotopes of an element (e.g. ^{10}B, ^{11}B) is possible. Since the sputtering process causes a subsequent removal of individual atomic layers high depth resolution can in principle   be achieved, although in practice some effects distorting the depth profiles have to be considered.

As it is possible to focus the primary ion beam lateral   distribution analysis and "small area depth profiling" for devices are possible.

Since at the present state of analytical chemistry SIMS offers   most capabilities for distribution analysis of trace elements in   semiconductors major emphasis is placed on this technique.

ii)   Rutherford Backscattering Spectroscopy [RBS] (28)

The surface of a semiconductor is bombarded with a monochromatic high energy ion beam (usually He^+ at 1-5 MeV). The energy distribution of the backscattered ions is measured at a defined angle.

The energy (E) of the ions backscattered at the surface of a   semiconductor is expressed by

$$E = E_o \left\{ \frac{m \cdot \cos \Theta}{m + M} + \left[\left(\frac{m \cdot \cos \Theta}{m + M} \right)^2 + \frac{M - m}{M + m} \right]^{1/2} \right\}^2$$

m = mass of bombarding ions (e.g. He)
M = mass of target atoms (e.g. Si, Sb)
Θ = scattering angle
E_o = initial ion energy

This relationship enables trace elements to be identified.

If the target atoms are not situated at but under the surface the ions lose energy before and after backscattering by interactions of the positive ion charge with the electrons of the matrix atoms. The energy loss ΔE is a function of the electronic stopping power of the matrix atoms and the length of the ion path (x).

The energy distribution of these ions scattered by trace elements represents their depth distribution.

Quantification is based on the principle that the total measured back-scattered intensity is proportional to the number of target atoms. Mathematical unfolding of the signal with the energy loss function of the ions yields the depth distribution of the dopant elements.

Furthermore, a distinction between trace atoms on lattice sites and on interstitial sites is possible if backscattering in random orientation. of the crystal is compared with aligned orientation (e.g <100> for Si). In the latter case only interstitial trace atoms contribute to the backscattered signal for the trace elements. In the case of Sb in silicon these interstitials represent the electrically inactive dopant fraction. This fraction can be determined directly from backscattering measurements in an <100> alignment.

RBS for distribution analysis of trace elements is confined to atoms with an atomic mass larger than the matrix, since only for these sufficient detection power can be achieved. It is mainly used for As and Sb in Si. Other limitations include a loss of spatial resolution with increasing depth due to straggling, and often insufficient detection power (Table 2).

iii) Neutron Activation Analysis [NAA] (11, 29)

This analysis is based on the activation of atoms (in a solid or liquid) by thermal neutrons and measurements of the decay products of the nuclei formed.

Information on distribution can either be obtained from the measurement of the energy loss of emitted particles or through excitation of trace elements in solution after chemical removal of thin layers from the semiconductor surface. The first principle is used for B in silicon. The intensity and energy distribution of α-particles generated by the reaction $^{10}B(n,\gamma)^{7}Li$ are measured. The second principle is used for As, P and Sb in silicon. As is determined in the solution obtained from etching a thin layer from the semiconductor surface (ca. 20-50nm) using the reaction $^{75}As(n,\gamma)^{76}As$. The determination of P is particularly difficult since the γ-radiation of ^{32}P, (generated in the reaction $^{31}P(n,\gamma)^{32}P$ must be measured using a Cherenkov detector. Sb is determined by γ-radiation from the reaction $^{121}Sb(n,\gamma)^{122}Sb$.

NAA is well suited as a reference method for other faster techniques such as SIMS.

iv) Charged Particle Activation Analysis [CPAA] (30)

Positive ions (like $^{2}H^{+}$, $^{3}H^{+}$) at high energy (ca. 5 MeV) are used to excite atomic nuclei of a semiconductor. Energy and intensity of the emitted α-, p-, and γ-radiation are measured. The method is success-fully applied to low atomic number trace elements (e.g. B, N) and it complements RBS in this respect. Distribution information can be obtained in combination with chemical etching (integral measurement of area concentration [at cm^{-2}], etching, differentiation) or through energy analysis of the emitted α-particles e.g. $^{14}N(d,\alpha)^{12}C$.

Through variation of the angle of incidence it is possible to obtain structural information about the structural position of trace elements. The lateral distribution information can in principle be obtained by focussing the primary beam and applying of beam scanning (lateral resolution ca. 1 μm).

v)   Particle Induced X-Ray Spectroscopy [PIXES] (31)

Various positively charged particles such as protons or ions
with energies between 0,1 and 5 MeV are used to excite the X-ray
spectrum of the sample. Because the continuous radiation background
is lower by a factor 10 to 1000 than by EPMA, trace analysis in semi-
conductors is possible. Depth distribution information can be
obtained by combination with chemical etching. An   increase of the
detection power and the surface selectivity is possible by   selective
excitation of trace elements with heavy ions. The use of the technique
is confined to those elements for which X-ray measurement with a high
yield is possible ($Z>14$).

The analytical figures of merit of the techniques described are given
in Table 2.

Table 2: Analytical Characteristics for Elemental Distribution
Analysis of the Major Dopant Elements in Silicon

element	lateral resolution (μm)	depth resolution (nm)	detection limit (at cm^{-3})	dynamic range	accuracy (%rel.)
RBS					
As	$10 - 10^4$	$5 - 100$	$10^{18} - 10^{19}$	10^4	10
Sb	$10 - 10^4$	$5 - 100$	10^{17}	10^4	10
PIXES					
As	$1 - 10^3$	$50 - 500$	10^{19}	$10^4 - 10^5$	4
Sb	$1 - 10^3$	$50 - 500$	2.10^{18}	$10^4 - 10^5$	4
NAA					
B: ^{10}B(n,α)^{7}Li mm-cm	$10 - 50$	10^{14}	10^3	1
As: ^{75}As(n,α)^{76}As mm-cm	$10 - 50$	$10^{16} - 10^{17}$	5.10^4	10
P: ^{31}P(n,γ)^{32}P β- decay mm-cm	$10 - 50$	10^{17}	5.10^4	10
Sb: ^{121}Sb(n,γ)^{122}Sb mm-cm	$10 - 50$	5.10^{15}	10^6	10
SIMS					
B	$(1) - 60$	$(1) - 10$	10^{14}	10^7	$5 - 10$
As	$(1) - 60$	$(1) - 10$	2.10^{16}	10^5	$10 - 20$
P	$(1) - 60$	$(1) - 10$	5.10^{15}	10^6	> 15
Sb	$(1) - 60$	$(1) - 10$	5.10^{16}	10^5	$10 - 20$

vi)   Electron Microprobe   (32,33)

X-ray microanalysis with electron probe excitation (EPXMA) allows to achieve detection limits (C_{min}) of 10^{-2}-10^{-3} % in determination   of impurities in semiconductors. The correct usage of EPXMA for   the control of impurities distribution demands a calculation of C_{min} in each separate case (34).   It can be concluded from the definition of C_{min} that the minimal concentration value which is significantly different from zero with some confidence level P, can be calculated from the following equation:

$$C_{min} = t\ (P,f) S_C$$

where t (P,f) is the Student coefficient and S_C the standard deviation for the concentration of the element to be determined, or:

$$t(P,f)\ \cdot\ S_C/C_{min} = t(P,f)S_{r,c} = 1$$

where $S_{r,c}$ is the relative standard deviation for the reproducibility of the determined element concentration.

When the concentration of the element to be determined in a sample is close to the detection limit, the following equation can be used for the minimal detected analytical signal (I_{min}) (34):

$$I_{min} = \frac{\sqrt{2}\ \cdot\ t(P,f)}{m_\tau\ \cdot\ I_{SRS}}\ \sqrt{\frac{I_B}{I_{SRS}}}$$

Here m is the number of measurements, each made during time period of τ and I_{SRS} is the average value of X-ray intensity on a standard reference sample.

The transition from an analytical signal to the concentration is carried out with help of calibration characteristics:

$$C_{min} = g(C_1,\ C_2\ ...)\ \ I_{min}$$

where $g(C_1,\ C_2,\ ...)$ is a correcting multiplier which takes into account the differences in effects of electron backscattering, absorp-tion and fluorescence between the analyzed and the standard reference sample.

The latter two equations allow to calculate C_{min} for the element determination in any matrix with use of any standard reference sample and to choose optimal conditions for analysis near the detection limit.

Variations of the primary electrons' energy (35) presents one of the perspective ways of non-destructive layer-by-layer control of impurities distribution in semiconducters. To use this method it is necessary to obtain the experimental dependence of the analytical signal on   the energy of the primary electrons I(E) and to recalculate it into   the concentration profile according to the depth of the sample C(z).   The calculation can be carried out by solving the following integral equation:

$$I(E) = R\ \int_0^z C(z)\ \cdot\ \ \rho(z)\ \cdot\ \varphi[C(z),z,E]\ \cdot[f\ C(z),z]\ dz$$

where I is the relative intensity of the chosen X-ray radiation, C is concentration of the element to be determined, R is the constant which depends on a standard reference sample, $\rho(z)$ is the sample density as function of depth, $\varphi[\ C(z),z,E]$ is a function that describes the

distribution of the generated intensity at energy E and $f[C(z),z]$ is a function which describes the absorption of the generated X-ray radiation during emittance from the sample.

Solution of this equation is not stable in the left part since small changes in I(E) may lead to large errors in C(z) determination. Another equation is used for stabilization, its solution being very close to the initial one. When stabilization is introduced the C(z) function is determined by solution of a variation problem on minimal divergence between experimental and calculated values of the function I(E). Values of function are selected either in points of z-even network or as parameters or the C(z) function of a given class. The solution is carried out with a computer. Good agreement between theoretical calculation and experiment can be obtained (35). Experimental finding of a distribution function $\varphi[C(z),z,E]$ is a possible alternative to increase the accuracy of the control of the concentration profile in heterogeneous systems. In this case the acceptance angle of the X-ray radiation emitted from the sample is varied.

In such a way impurities distribution can be controlled in local areas of the submicron layers without destruction of the sample. The lower limit of determination depends on the s_r value achieved in the experiments.

3.2.2 Quantitative Distribution Analysis with SIMS

i)   Physical principles

Bombardment of a solid state material with high energy (E_O = 5-20 keV) primary ions leads to implantation of these ions into the target material as well as sputtering of target atoms, clusters and molecules because of momentum transfer and the partial ionization of these particles. Structural changes in the surface zone (mainly amorphization in semiconductors) and displacement of target atoms in the solid (recoil and cascade mixing) also occur (36-43).

The implantation depth of the primary ions can be calculated from the nuclear stopping power. The concentration maximum is described by the mean projected range (R_p). In silicon R_p is about 30 nm if the primary particle has an energy of 1 keV per nucleon. This yields values   for 5 keV primary ions of ca. 5 nm for O_2^+, 10 nm for O^- and 1 nm for Cs^+.

The thickness of the zone of structural and chemical changes ("altered layer") is 2 R_p for normal incidence. For an angle of incidence (measured between beam and surface normal) the thickness of the altered layer is 2 R_p . cos α .

Within this surface zone equilibrium is not reached and the measured profiles do not show directly the trace element distribution.

After equilibrium is reached quantitative evaluation of the secondary ion signals is possible.

The emission of target particles and molecules takes place within the top few (3-5) atomic layers. The information depth and inherent depth resolution of SIMS is therefore ca. 1 nm. In practice depth resolution is also determined by surface roughening during the sputtering process, atomic mixing effects and different sputtering rates in heterogeneous structures. For silicon and a typical maximum depth of analysis of 1 μm, the depth resolution is between 1 and 10 nm.

The most probable energy of the emitted particles is 10-20 eV with atomic ions extending up to several 100 eV and molecular or cluster ions to about 100 eV. This difference in energy distribution can often be used for the effective separation of interferences in the mass spectrum ("energy filtering").

ii)   Detection Power

Measurement of the secondary ions from trace elements in semiconductors should be carried out in instruments with high efficiency of ion collection, dispersion and detection systems. Instrumental features like a high extraction potential (several keV), focussing of the secondary ion emission spot into the entrance slit of the mass spectrometer, use of an electrostatic and magnetic mass analyzer with high transmission and of open electron multipliers for ion counting provide the basis for achieving the detection power necessary for ultra trace analysis.

Emission can be described quantitatively by the following equation:

$$I_{S(A)}^{+} = I_p \cdot S \cdot \alpha_A^{+} \cdot c_A \cdot i_{S(A)} \cdot \eta$$

$I_{S(A)}^{+}$ = (positive) secondary ion intensity of the measured isotope of element A (cps)

I_p = primary ion intensity (ion sec^{-1})

S = sputter yield (atoms/primary ion)

α_A^{+} = (positive) ionization probability of the sputtered atoms

η = efficiency of secondary ion measurement (extraction yield, transmission of mass spectrometer, detector efficiency)

The magnitudes for these variables are:

I_p = 1-5 µA = ca. 10^{13} ion sec^{-1}

S = 1

α_A^{+} = 0,1-10^{-5} (depending mainly on E_i (ionization energy) of the analyzed atomic species

$i_{S(A)}$ = 0,01 - 1

$\eta \approx 0,1$

Theoretical detection limits calculated from this formula are in the range between 10 pg g^{-1} and 10µg g^{-1} (44). Since elements with low positive ionization yield (electronegative elements) usually have a high negative ionization yield the theoretical detection limits are of the order 0,01-10 ng g^{-1} when either positive or negative secondary ions are measured.

The practical detection power is lower than the theoretical if interferences between the analytical ion and other ions occur or contamination of the sample during analysis is encountered. In the first case elimination of interferences by energy filtering or high mass resolving power causes a loss of secondary ion intensity of one or two orders of magnitude and consequently a loss of detection power by the same amount.

Contamination from the primay beam (CO, NO, ...) can be eliminated by mass filtering the beam. Contamination from residual gas (p = 10^{-8} mbar) is the main limitation for the detection power for H, O, C and N (typical practical detection limits are 10-50 µg g^{-1}. Metals which are used in ion optical parts of the instrument are sputtered off during analysis (mainly Cr, Fe, Ta) and create a background of 10-100 ng g^{-1}.

Furthermore for distribution analysis the practical detection limit must be seen in relation to depth resolution since enough target material must be sputtered off to allow a statistically valid detection or determination of the trace element (45). The thickness of the layers to be sputtered as a function of analyzed area and trace element

concentration can be calculated from the absolute detection power of
SIMS. For modern instruments it is about 10^{-21} g for B and
10^{-19} g – 10^{-20} g for As, P and Sb in silicon corresponding to about
100 to 10 000 atoms in the volume sputtered during a single measurement.

Table 3 contains as an illustration the interferences encountered in
the analysis for the most important dopant elements in silicon, their
possible elimination, and the resulting practical detection limits for
distribution analysis. For bulk analysis these values would be a
factor of 10 – 50 lower because of the possibility of increased material
consumption and therefore better counting statistics.

A compilation of practical detection limits for trace elements in silicon and
gallium arsenide is contained in Table 4.

iii)   Quantification   (58-67)

Quantification in depth distribution analysis includes a conversion of
the measurement time into depth and secondary intensity into (atomic)
concentrations.

Accurate depth calibration in semiconductor analysis can be achieved
by measurement of each crater with profilometry or interference micros-
copy.   If heterogeneous surface structures are analysed either the
thickness of the various layers (e. g. SiO_2 on Si) has to be determined
by ellipsometry or the different sputtering rates of the layers must be
determined with standard samples. The first technique yields results
of higher accuracy since there are frequent experimental difficulties
in achieving constant sputter rates between standard and sample.

For the conversion of secondary ion intensities into concentrations
external standards can be used to advantage.   Such standards can be
produced for many trace elements by homogeneous doping or implantation
of semiconductor materials. Relative sensitivity factors (trace/matrix
element) are determined and applied for quantification.

In the case of homogeneous doping, reference methods like NAA   or
charged particle activation analysis are used to characterize the bulk
content of the   trace elements in the standard.   For generation of
standards by ion implantation   the distribution (concentration vs.
depth) of the trace elements in the standard can be calculated from
physical parameters (e.g. using LSS theory) (68).

Highly accurate quantitative distribution analysis demands considera-
tion of backscattering and channelling effects in ion implantation(69).
An improvement of existing implantation models is still necessary.

A possibility of quantification exists if the trace elements to be
analyzed had been brought into the semiconductor by ion implantation
(as it usually is done in modern technology). In this case the
implantation dose Ω_T (which is known from measurement of the current
of implanted ions and time of implantation and which can be corrected
for backscattering effects) can be used to determine the proportiona-
lity factor (k) between secondary ion intensity and concentration
according to equation:

$$\Omega_T = k \cdot \int_0^\infty \frac{I_A}{I_M} \cdot d_z$$

I_A, I_M = secondary ion intensity of analyte element (A) and matrix
       element (B), and z = depth (nm).

In the course of the development of quantification procedures for
specific problems other techniques with different (independent)
systematic errors must be combined with SIMS. For B, As and P in Si,
NAA may serve as a suitable reference method. For Sb in Si, RBS is
advantageous. Electrical measurements can be used at low dopant
concentrations ($\leq 10^{19}$ at cm^{-3}) where all the dopant atoms are in an
electrically active state.

Table 3: Interferences and Practical Detection Limits for
Distribution Analysis of Dopant Elements in Silicon

Isotope	PI	Interfering Ion	ΔM [A.M.U]	$\dfrac{M}{\Delta M}$	Detection Limit (at/cm³)		
					energy filtering	high mass resolution	instrumental limitations
$^{10}B^+$	O_2^+	$^{30}Si^{+++}$	0,0202	490	–	10^{14}	x)
$^{11}B^+$	O_2^+	$^{10}B^1H^+$	0,0115	960	–	10^{14}	x)
$^{31}P^+$	O_2^+	$^{30}Si^1H^+$	0,0078	3960	–	5.10^{15}	x)
$^{75}As^+$	O_2^+	$^{29}Si^{30}Si^{16}O^+$	0,0235	3200	2.10^{16}	2.10^{16}	x)
$^{121}Sb^+$	O_2^+	$^{28}Si^{29}Si^{16}O_4^+$	0,0293	4130	5.10^{16}	–	x)
$^{123}Sb^+$	O_2^+	$^{29}Si^{30}Si^{16}O_4^+$	0,0257	4780	5.10^{16}	–	x)

x) Possibility of memory effect of extraction lens

Table 4: Detection Limits for Distribution Analysis of Trace Elements in
Si and GaAs (from E. Zinner) (36).

MATRIX: Si					MATRIX: GaAs				
ELEMENT	DETECTED SPECIES	ION BEAM	DETECTION LIMIT (ATOMS/CM³)	REFER-ENCE	ELEMENT	DETECTED SPECIES	ION BEAM	DETECTION LIMIT (ATOMS/CM³)	REFER-ENCE
H	H^-	Cs^+	$5 . 10^{17}$	46	O	O^-	Cs^+	$5 . 10^{17}$	51
C	C^-	Cs^+	$8 · 10^{17}$	47	Si	Si^+	O_2^+	$3 . 10^{15}$	52
N	SiN^-	Cs^+	10^{17}	47	S	S^-	Cs^+	10^{15}	53
O	O^-	Cs^+	$6 . 10^{18}$	47	Cr	Cr^+	O_2^+	$5 . 10^{13}$	54
B	B^+	O_2^+	10^{14}	48	Mn	Mn^+	O_2^+	$4 . 10^{13}$	55
					Fe	Fe^+	O_2^+	$5 . 10^{14}$	56
P	P^-	Cs^+	$5 . 10^{15}$	49	Zn	Zn^+	O_2^+	10^{16}	57
P	P^+	O_2^+	$5 . 10^{15}$	21	Se	Se^-	Cs^+	$3 . 10^{13}$	53
As	$AsSi^-$	Cs^+	$3 . 10^{15}$	50	Te	Te^-	Cs^+	$2 . 10^{13}$	52
As	As^+	O_2^+	$2 . 10^{16}$	21					

The accuracy of the concentration scale in distribution analysis with SIMS for the most important dopant elements in (single crystal) Si was found to be between 5 and 20 % as indicated in table 2. These values have been obtained by comparison with other methods and refer to a concentration level of about 10^{20} -10^{21} at cm^{-3}.

The accuracy of depth calibration depends on sputtering depth and is in order of 5 - 10 % of this depth for single crystals. In poly - crystalline material selective sputtering at the grain boundaries occurs which decreases depth resolution. The amount of such sputtering depends on grain size.

This figures of merit show that SIMS can deal successfully with most problems of distribution analysis. The method has established itself as the major technique for this purpose during this decade.

iv)   Analysis of Heterogeneous Semiconductor Structures

Generally quantification of trace elements in heterogeneous thin film structures must take into account the different sputtering yields and chemical matrix effects.

In most cases, a separate standard with identical matrix has to be used for each layer in order to obtain accurate results. Multiple standards have been generated by implanting an analyte through a layered sample (e.g. Cr into Si_3N_4 on gallium arsenide)(70). This approach is limited, however, by the uncertain depth distribution of implants through layered structures. A different approach to the quan- titative analysis of heterogeneous thin layers has resulted from a recent investigation of superlattices composed of group III and V compound semiconductors. Matrix effects were found to vary linearly with sample composition (71). These matrix effects have subsequently been calibrated and used to correct major and trace element distribu- tions through heterogeneous multilayer structures including matrix gradients and interfaces (71, 72). Another approach which may prove successful is the combined use of several analytical techniques , e. g. quantification of Mn and Na profiles measured with SIMS in electro- luminescent thin film structures could be done by using X-ray fluoresence for the determination of Mn and chemical etching plus flame atomic emission spectrometry for Na in 250 nm ZnS films (73).

For thin layer structures combinations which consist of elements of high oxygen affinity elimination of the chemical matrix effect may be possible by saturation of the "altered layer" with oxygen during ana- lysis (21,74). This is achieved by primary oxygen bombardment and maintaining a rather high oxygen pressure (ca. 10^{-5} mbar) at the surface of the material by an oxygen jet ("oxygen leak"). In the system SiO_2/ Si the chemical matrix effect is completely eliminated which is expressed by the fact that in SiO_2 and Si the same secondary ion signal is obtained. This is of particular importance for studies of Si since these samples usually contain SiO_2-layers from production (thickness 10-500 nm). Optimization of the oxygen partial pressure can be performed by monitoring molecular (SiO_2^+) and cluster ions (Si_2^+). At optimum pressure the ratio SiO_2^+/Si_2^+ is a maximum (21).

In structures containing insulating layers charging has to be compen- sated during analysis. Goldcoating of the samples and bombardment with negative primary ions usually eliminates charging to an extent which allows stable secondary ion emission to be obtained. If higher sputtering rates are required which can only be obtained with positive primary ions (due to a larger yield of generation of positive ions in the source) the positive charge can largely be compensated by bombard- ment of the sample surface with electrons during analysis. For highly accurate profiles it is necessary to compensate the remaining charge by continuous adjustment of the sample potential (automatically through a computer subroutine) during analysis. The adjustment is monitored through the measurement of the intensity of molecular secondary ions whose energy distribution has a very steep slope and are therefore very sensitive to sample charging (21). With this technique stable and accurate depth profiles can be obtained even for combinations of several conductive and insulating layers and for large depths (more than 30 μm).

Analysis of heterogeneous multilayer structures may be subject to several artefacts which cause special difficulties in the interpretation of the profiles at interfaces. The major problems arise from recoil and cascade mixing, preferential sputtering at interfaces if the sputtering rates of the 2 matrices are widely different and from ion-induced diffusion (for very mobile small atoms).

Through systematic studies these effects can largely be controlled. In order to obtain a large dynamic range in the profiles crater effects have to be eliminated strictly by analysing only a very small centre area of the crater. For multilayer structures a ratio of at least 10:1 between crater length and the diameter of the analyzed area is usually necessary.

At the present state of analytical techniques SIMS provides by far the largest potential for distribution analysis of heterogeneous structures. One of the problems remaining is the quantification of profiles at interfaces.Investigations to solve these problems are presently under way   (71,72).

4. DISTRIBUTION ANALYSIS IN DEVICES

For device characterization, electrical testing techniques are usually applied. In addition it is often of interest to study the distribution of trace elements directly in electronic devices. Due to the required lateral resolution only focussed particle beams can be used. SIMS offers the largest potential.

The applicability of SIMS is mainly determined by the lateral dimensions of the devices. In electronic technology also devices with larger structural dimensions (> 10 µm) are important -e.g. for electroluminescent displays or gallium arsenide laser diodes. In such cases SIMS can be used with techniques of analysis as for large scale samples. Practically identical figures   of merit are obtained.

In silicon technology integration has progressed to dimensions from several µm to less than 1 µm.

In principle it is possible at the present state of development to obtain depth profiles from analytical sites as small as 1,4 µm in diameter. Even in such cases for boron a detection limit of 10^{16} at cm^{-3} can be achieved. For the other dopant elements As, P and Sb this figure is in the order of 10^{18} at cm^{-3}.

Other problems arise from the fact that the substrate is usually covered by several insulating layers which have to be removed by chemical etching or sputtering before the dopant elements can be measured.

In-situ device analysis is still in an initial stage and has to be developed further. Possibly the use of ion beams focussed to some tenths of a µm will bring a significant progress (liquid metal ion sources) (75).

REFERENCES

1) M. Grasserbauer, Yu.A. Zolotov, G.H. Morrison:
            Evaluation of Methods for the Determination of Trace
            Elements VII. Trace Analysis of Semiconductor Materials.
            Part A: Bulk Analysis.
            Pure Appl.Chem., in Press

2) I. Brodie, J.J. Muray:
            The Physics of Microfabrication,
            Plenum Press, New York 1982

3) D.A. Antoniadis, S.E. Hansen, R.W. Dutton:
            A Program for Process Modelling and Simulation.
            In: Integrated Circuits Laboratory. Standford Electronics
            Laboratories, Technical Report No. 5019-2 (1978)

4) R. Tielert,   IEEE Trans Electron. Dev. ED-27 (1980), 1497

5) E. Guerrero: Thesis, Technical University Vienna 1984

6) C.D. Sharpe, P. Lilley, C.R. Elliot, T. Ambridge:
                     Electronic Letters 15/20 (1979), 622

7) J. Hilibrand, R.D. Gold, RCA Rev. 21 (1960), 245

8) G.O. Thomas, D. Kahn, R.C. Manz:
                     J. Electrochem. Soc. 109, (1962), 1055

9) F.H. Smits: Bell Syst. Tech. J. 37, (1958),711

10) E. Guerrero: Anodische Oxidation von Silizium Einkristallen,
                     Diplomarbeit, Tech. Univ. Wien (1978)

11) H. Ryssel, I. Ruge:
                     Ionenimplantation, Teuber, Stuttgart (1978)

12) L.J. Van der Pauw:
                     Philips Res. Repts. 13, (1958), 1

13) Yu. I. Ukhanov: Optical Properties of Semiconductors,
                     Nauka Publ. House, Moscow, 1977

14) M.A. Il'in, V.Ya. Kovarskii, A.F. Orlov:
                     Zavodsk. Laborat. 50, 24 (1984)

15) J.T. Pankova: Optical Processes in Semiconductors,
                     Prentice Hall, New Jersey, 1971

16) A.I. Berner, F.A. Gimelfarb:
                     Zh. Anal. Khim. 37, 1767 (1982)

17) A.S. Kaminskii, L.I. Kolesnik, B.M. Leiferov, Ya. E. Pokrovskii:
                     Zh. Prikl. Spectroscopii 36, 745 (1982)

18) I.P. Alimarin (ed):
                     Modern Methods for Analysis of Microsamples and Thin Films
                     Nauka Publ. House, Moscow, 1977

19) A. Benninghoven et al. (eds.):
                     SIMS II, Proceedings of the Stanford Conference 1979,
                     Springer Berlin 1979

20) A. Benninghoven et al. (eds.):
                     SIMS III, Proceedings of the Budapest Conference 1981,
                     Springer Berlin 1982

21) G. Stingeder :   Quantitative Dopant Analysis in the Layer System
                     SiO_2/Si , to be published

22) J.A. McHugh: Secondary Ion Mass Spectrometry, in Methods of Surface
                     Analysis (A.W. Czanderna, E.), Elsevier,
                     Amsterdam 1975

23) H.W. Werner: Vaccum 24, 493 (1974)

24) E. Zinner: Scanning 3, 57 (1980)

25) G.H. Morrison, G. Slodzian:
                     Anal. Chem. 47, 932 A (1975)

26) V.I. Nefedov, V.T. Cherepin:
                     Physical Methods for Investigation of Surface of Solids,
                     Nauka Publ. House, Moscow, 1983

27) F.A. Gimelfarb, S.L. Shvartzman:
                     Modern Methods for Composition Materials Control,
                     Metallurgia Publ. House, Moscow 1979

28) W.K. Chu, J.M. Mayer, M.A. Nicolet:
                     Back Scattering Spectrometry,
                     Academic Press, New York 1978

29) F. Jahnel et al.:
                   Nucl. Instr. Meth. 182/183, 233 (1981)

30) J.R. Bird: Nucl. Instrum. Meth. 168, 85 (1980)

31) H. W. Werner, R. P. H. Garten:
                   Rep. Progr. Phys. 47, 221 (1984)

32) I.I.B. Borovskii, F.F.Vodovatow, A.A. Zhukov, V.T. Cherepin:
                   Localization Methods for Analysis of Materials,
                   Metallurgia Publ. House, Moscow 1973

33) S.G. Konnikov, A.F. Sidorov:
                   Electron Microprobe Techniques for Investigation of
                   Semiconductor Materials and Devices,
                   Energia Publ. House, Moscow 1978

34) A.I. Berner, F. A. Gimelfarb, T.A. Ukhorskaya:
                   Zh. Anal. Khim. 37, 338 (1982)

35) E.P. Bochkarev, A.I. Berner, F.A. Gimelfarb, M.G. Milvidskii:
                   Poverchnost! Fizika, Khimiya, Mekhanika, No.2,
                   115 (1982)

36) E. Zinner: J. Electrochem. Soc. 130, 199 C (1983)

37) C.W. Magee, R.E. Honig, C.A. Evans:
                   in ref 20, p. 172

38) S. Hofmann: in ref. 20, p. 176

39) W.O. Hofer, U. Littmark:
                   in ref. 20, p. 201

40) V.R. Deline, W. Katz, C.A. Evans, P. Williams:
                   Appl. Phys. Lett. 33, (1978), 832

41) S. Hofmann, J.M. Sanz:
                   Fres. Z. Anal. Chem. 314, 215 (1983)

42) H.W. Werner: Surf. Interface Anal. 2/2 (1980), 56

43) H. Oechsner: Fres. Z. Anal. Chem. 314, 211 (1983)

44) M. Grasserbauer, G. Stingeder, M. Pimminger:
                   Fres. Z. Anal. Chem. 315, 575 (1983)

45) R.V. Criegen, T. Hillmer, I. Weitzel:
                   Fres. Z. Anal. Chem. 314, 293 (1983)

46) C.W. Magee, C.P. Wu:
                   Nucl. Instr. Meth. 149, 529 (1978)

47) C.W. Magee, J.C. Bean, G. Foti, J.M. Poate:
                   Thin Solid Films 81, 1 (1981)

48) T.W. Sigmon: Ref. 20. p. 80

49) C.W. Magee: J. Electrochem. Soc. 126, 660 (1979)

50) P. Williams, C.A. Evans:
                   Appl. Phys. Lett. 30, 559 (1977)

51) P.N. Favenne et al.:
                   Appl. Phys. Lett. 38, 271 (1981)

52) R.G. Wilson, V.R. Deline:
                   Appl. Phys. Lett. 37, 793 (1980)

53) R.G. Wilson, D.M. Jamba:
                   Appl. Phys. Lett. 39, 715 (1981)

54) A.M. Huber et al.:
                    Inst. Phys. Conf. Ser. No. 56 , 579 (1980)

55) A.M. Huber et al.:
                    J. Microsc. Spectrosc. Electron. 4, 493 (1979)

56) A.M. Huber et al.:
                    ref. 19, p. 91

57) J.B. Clegg: Surf. Interface Anal. 2, 91 (1980)

58) J.A. McHugh: In Secondary Ion Mass Spectrometry,
                    NBS Sp 427, (K.F.J. Heinrich, D.E. Newbury eds.)
                    Washington 1975

59) A.E. Morgan, H.W. Werner:
                    Mikrochim. Acta 1978 II,31

60) G.H. Morrison: in ref. 20, p. 244

61) F.G. Rüdenauer, W. Steiger, R. Portenschlag:
                    Mikrochim. Acta, Suppl. 5, 421 (1974)

62) H.W. Werner: Acta Electronica 19, 1, 53 (1976)

63) D.E. Newbury: Scanning 3, 10 (1980)

64) D.E. Newbury, K.F.J. Heinrich:
                    Mikrochim. Acta Suppl. 8, 3,(1979)

65) C.A. Andersen, J.R. Hinthorne:
                    Anal. Chem. 45, 1421 (1973)

66) A. Havette, G. Slodzian:
                    in ref. 20, p. 288

67) A. Lodding: Mikrochim. Acta Suppl. 10, 21 (1983)

68) J. Linhard, M. Scharff, H.E. Schiott:
                    Kgl. Danske Vidsens Kab. Selskab.,
                    Mat.- Fys. Medd. 33, Mo. 14 (1963)

69) W.H. Gries: Int. J. Mass Spectr. Ion Phys. 30, 113 (1979)

70) U. Traxlmayer, W. Fallmann, G. Stingeder, M. Grasserbauer, L. Palmetshofer:
                    In-Depth Profiles of Cr in Si_3N_4-Layers on GaAs with SIMS,
                    Proc. Sem. Surface Physics, Obertraun 1983
                    Technical University Vienna 1983

71) A.A. Galuska, G.H. Morrison:
                    Anal. Chem. 55, 2051 (1983)

72) A.A. Galuska, G.H. Morrison:
                    Anal. Chem. 56, 74 (1984)

73) L. Ninistoe, H. Antson, L. Hiltmen, M. Leskelä, M. Tammenaa, G. Stingeder,
            M. Grasserbauer:
                    Mikrochim. Acta, in Press

74) B. Blanchard, H. Hilleret, J.B. Quoirin:
                    J. Radioanal. Chem. 12, 85 (1972)

75) F.G. Rüdenauer et al.:
                    in ref. 20, p. 43