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Elemental Trace Analysis of Surfaces and Interfaces: Goals, Accomplishments and Challenges [and Discussion]

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Elemental trace analysis of surfaces and interfaces: goals, accomplishments and challenges

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This paper describes an analytical approach to quantitative trace element analysis with SIMS and demonstrates the potential and limitations of this method for ultra trace bulk analysis, micro- and nanoanalysis of interface regions and surface analysis of high technology materials. Future challenges for methodological research are presented.

1. Introduction

The development of high technology is to a large extent based on the progress in materials science. Pure and ultrapure materials – often with a narrowly defined trace elemental content – are most important. Since the influence of trace elements on material properties is especially pronounced when enriched at surfaces or at interfaces the analytical characterization of these domains is of greatest significance.

The goals for elemental trace analysis of surfaces and interfaces include to gain qualitative and quantitative information with high spatial resolution and a large detection power. Ideally the distribution of trace elements is characterized in three spatial dimensions (x, y, z) leading to three-dimensional stereometric trace analysis.

The major technique available to achieve such goals is secondary ion mass spectrometry (SIMS) which exhibits the following features (Benninghoven *et al.* 1987; Vickerman *et al.* 1989): all elements can be analysed; surface sensitivity, 90% of signal originate from outermost atomic layer; (destructive) depth profiling, micro- and nanoanalysis (both using three-dimensional characterization); large detection power; large dynamic range.

SIMS, however, has two distinct disadvantages: complexity of the mass spectra, and large chemical matrix effects.

2. Potential of SIMS for quantitative trace analysis

The potential of SIMS for quantitative analysis can be evaluated from the following equation (Wittmaack 1980):

$$I_A^{+(-)} = I_p\, C_A^i\, \alpha_A^{+(-)}\, Y f(\Delta E)\, f(\Delta \Omega)\, T\beta,$$

where $I_A^{+(-)}$ is measured secondary ion intensity (ions s^{-1}), I_p is primary ion current (ions s^{-1}), C_A^i is isotopic concentration of analysed element, ($C_A^i = C_A \eta_A^i$; η_A^i is isotopic abundance), $\alpha_A^{+(-)}$ is ionization yield, Y is total sputter yield (atoms per

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primary particle), $f(\Delta E), f(\Delta \Omega)$ are the fractions of ionized particles that fall in energy and solid angle acceptance window of the mass spectrometer respectively, T is the transmission of the mass spectrometer, and β is the yield of ion detector.

The detection power depends mainly on the ionization yield for different elements, instrumental efficiency and amount of material consumed during analysis and is correlated with the useful yield $U_A^{+(-)}$:

$$U_A^{+(-)} = \alpha_A^{+(-)} f(\Delta E) f(\Delta \Omega)\, T\beta,$$

where $U_A^{+(-)}$ is the number of ions detected per number of atoms sputtered.

Under conditions of sputtering with reactive ions like oxygen or caesium (see below) and use of sector field instruments useful yields in the range from 10^{-2} to 10^{-5} (being mainly determined by the strong variation of $\alpha_A^{\pm}$ for different elements which ranges from 10^{-1} to 10^{-5}) are obtained. Absolute detection limits are therefore between 100 and 10^5 atoms sputtered from the material investigated. This calculation is based on the measurement of one secondary ion. Since detector background is less than 0.1 counts s^{-1}, such a single ion event is statistically significant if it occurs during a counting time of 1 s. For quantitative analysis the limit of determination is valid. To achieve a 10% random error 100 ions must be measured. Relative detection limits depend strongly also on the presence of interfering species in the complex mass spectrum. For many elements and material systems these are in the nanogram per gram range. As far as the potential for quantitative analysis is concerned SIMS exhibits not only a strong variation of the ionization yields for different elements but also a severe matrix effect (influences of up to a factor 100).

This has the consequence that for each particular system to be investigated an analytical strategy for quantitative analysis which is problem oriented and aims at the reduction of random and systematic errors must be established.

3. Strategy for quantitative trace analysis

I present here a strategy for quantitative trace analysis with SIMS. The important steps are discussed together with an exemplary presentation of particular methodological developments to improve analytical results. The point of view is that of an analytical chemist whose task is to gain information about technical materials systems which should be relevant to material properties and of appropriate accuracy.

The basis for quantitative analysis is the use of reactive primary ion species, oxygen (O_2^+, O^-) for electropositive and caesium (Cs^+) for electronegative elements. Reactive ion bombardment increases the secondary ion yield by a factor of 100 to 1000 and introduces a chemical modification of the matrix due to implantation of the primary ions. When the equilibrium between implantation and sputter erosion is reached (only then quantitative analysis is normally possible) which is after sputter removal of the top 5–10 nm of material, a local oxygen or caesium concentration of at least several percent is encountered. Consequently the differences in secondary ion yield of an element in different matrices are reduced. On this basis the analytical strategy for quantitative trace analysis with solid state mass spectrometry consists of three steps: (i) optimization of measurement technique to reduce random and systematic errors; (ii) calibration with reference materials; (iii) assessment of accuracy. These steps are now discussed for SIMS, based on the application of high performance instrumentation (sector field instruments) to technical material systems.

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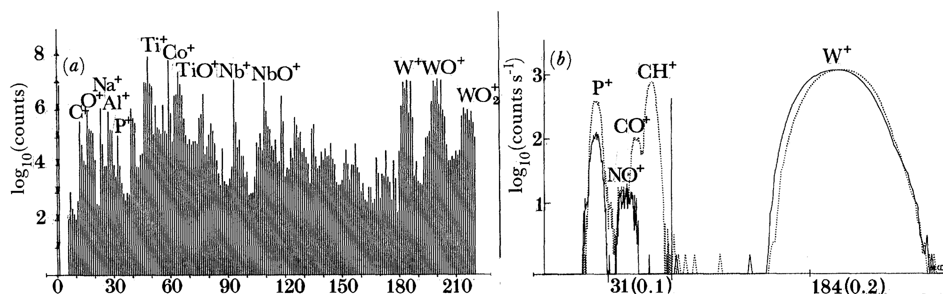

Figure 1. (*a*) Low and (*b*) high mass resolution spectra of a hard metal specimen (88% WC, 6% TiC–TaC–NbC, 6% Co) showing the complexity of secondary ion mass spectra at the trace element level. ...., Presintered material, $-8\ \mu g\ g^{-1}$ phosphorus; ——, sintered metal, $-2\ \mu g\ g^{-1}$ phosphorus; measurement: PI = O_2^+, 5.5 keV, $i_B = 2.5\ \mu A$.

Optimization of measurement technique

Major steps in the optimization of the measurement technique consist in the elimination of spectral interferences, charging and chemical matrix effects. Other optimization steps include reduction of artefacts inherent to ion–target interactions like recoil or cascade mixing effects by variation of primary ion energy or angle, or the selection of appropriate primary current densities and secondary ion optical parameters for sensitive trace analysis in monolayers. For each particular problem these instrumental parameters have to be adjusted to optimal values. With high performance SIMS instrumentation a large potential for variation and optimization of instrumental parameters is available making the technique very versatile also in this respect. Nevertheless, the fundamental problems are associated with interferences, charging and matrix effects.

Interferences are severe in every solid state mass spectrometric technique except laser resonance ionization SNMS since always a large variety of species (atoms, clusters, molecules) are generated. Particularly for trace analysis interferences may completely distort the signals. Figure 1 shows the low resolution ($M/\Delta M = 300$) mass spectrum of a hard metal (WC–TiC–TaC–NbC–Co alloy) in which phosphorus should be determined. While there is a pronounced peak at $M = 31$ (P^+) investigation with high mass resolution ($M/\Delta M = 4300$) shows that there are strong interference of the phosphorus peak by molecular species which – if not eliminated – would have caused a significant analytical error.

Interferences occur very often in the trace level domain and must be eliminated by either energy filtering (if the energy distributions of the analytical ion and the interfering species are substantially different) or by high mass resolution measurements, as it is the case for the analysis of phosphorus in silicon, which is an important technical problem. These, however, demand an extremely high reproducibility of cyclic mass switching (reference ions always have to be measured too during a depth profile) or, in other words, the possibility to reset magnetic field values with a precision of 10^{-5} to 10^{-6}. This is very difficult to achieve. Also long magnetic settling times cause a decrease of depth resolution in the profiles.

This problem can be solved by incorporation of peak-centring routines in the computerized measurement cycle of the depth profiles.

By scanning over the phosphorus peak with high mass resolution and continuously registering the secondary ion intensity the centre of gravity of the phosphorus peak

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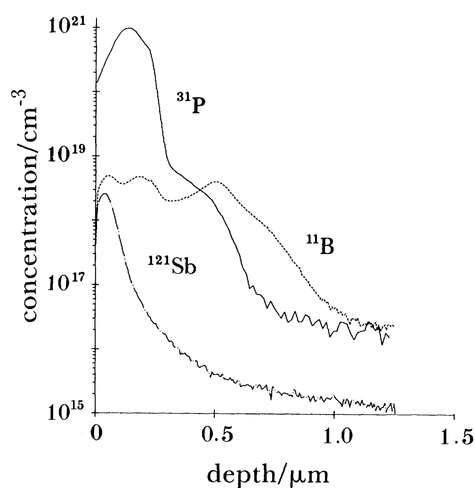

Figure 2. High accuracy depth profiles of boron, antimony and phosphorus in silicon obtained with computer-based peak centring routines. Small effects at 230 nm depth can be clearly observed. Sample preparation: (i) implantation of boron: 200 keV, 2.5×10^{13} atoms cm^{-2}; 600 keV, 9×10^{13} atoms cm^{-2}; 20 keV, 5×10^{13} atoms cm^{-2}; (ii) implantation of phosphorus: 50 keV, 7×10^{15} atoms cm^{-2}. All implantations through 20 nm SiO_2 (etched-off before measurement); (iii) annealing 800 °C, 15 min, N_2. Measurement: PI = Cs^+, E_0 = 14.5 keV; SI: $^{31}P^-$, $^{11}B^{28}Si^{-121}Sb^{28}Si^-$. (From Stingeder *et al.* 1989*a*.)

is determined and this intensity used for evaluation. This measurement technique is the basis for the accurate representation of quantitative profiles (Stingeder 1988).

For multielement depth profiling with high mass resolution a method has been developed which is based on the application of the peak-centring routine on a reference ion and transfer of the magnetic field shift to the analytical masses allowing to reduce the time necessary for adjustment (Stingeder *et al.* 1989*a*). Highly accurate profiles can be obtained even for very high mass differences ($^{31}P^-/^{121}Sb^{28}Si^-$). Figure 2 shows the depth profiles of boron, antimony and phosphorus in a silicon wafer. Due to the high accuracy of these measurement techniques small (but technologically significant) effects can be characterized in the profiles, e.g. the 'kink' in the phosphorus distribution and the local enrichment of boron due the segregation into a defect band (as observed by TEM).

Charge compensation is necessary in the analysis of insulators. The problem is particularly difficult for measurements with high mass resolution and in thin (greater than 100 nm) films of high resistivity (e.g. thermal SiO_2 on Si), since the amount of charging changes during depth profiling. Charging can be up to several hundred volts. Although there are techniques for reduction of charging (Werner *et al.* 1984), e.g. by electron beam bombardment, a complete compensation of the 'local charge' (in the area of extraction of the measured ions) does not seem possible to an extent necessary for measurements in high mass resolution. Charge compensation is particularly critical in this case since the energy window is rather small (e.g. 45–50 eV compared with 130 eV in low mass resolution). Small changes in the local surface charge influence the measured signal strongly.

Therefore it is necessary to develop high precision techniques for charge compensation. For the determination of P in SiO_2/Si this could be achieved with a new method to determine the local amount for charging by measuring the shifts of

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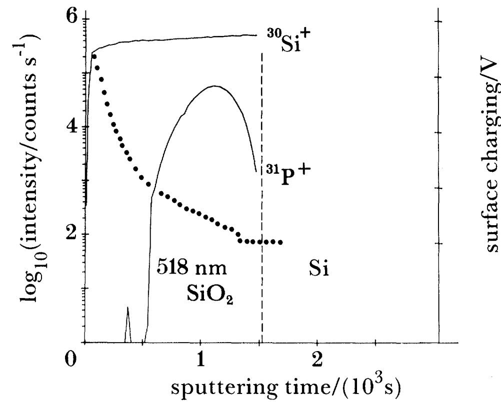

Figure 3. SIMS depth profile of P in SiO_2 measured at high mass resolution ($M/\Delta M = 4300$) applying a computerized charge compensation technique. Implantation: P in 326 nm SiO_2, 150 keV, 1×10^{16} cm^{-2}; covering with 192 nm CVD–SiO_2. PI = O_2^+, $E_0 = 5.5$ keV. (From Stingeder *et al.* 1989*a*.)

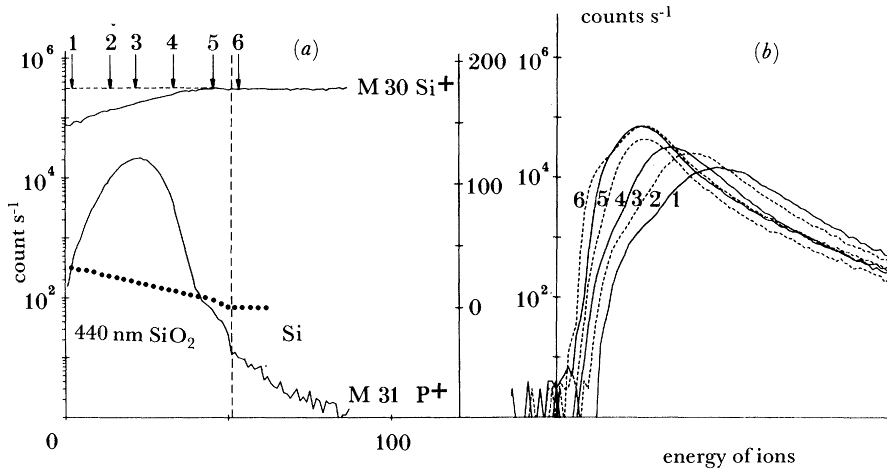

Figure 4. (*a*) SIMS depth profile of P in highly insulating thermal SiO_2 and (*b*) energy distribution of $^{30}Si^+$ at various amounts of charging. Implantation: 150 keV P, 1×10^{16} cm^{-2} into 440 nm SiO_2. PI = O_2^+, $E_0 = 5.5$ keV, partial charge compensation by electron flooding. (From Stingeder *et al.* 1989*a*.)

the energy distribution of a reference ion (Si^+) at the steep flank of its energy distribution curve enabling the adjustment of the sample potential (Stingeder 1988). This measurement is extremely sensitive towards charging. Through computerized cyclic measurements of the energy distribution and adjustment of the sample potential it was possible to get stable profiles of P in SiO_2 even if charges of up to 170 V occurred (figure 3).

For highly accurate measurements of P in SiO_2/Si, however, another effect which is a consequence of charging must be investigated. This is the change of the shape of the energy distribution of the secondary ions due to the distortion of the extraction field and local variations of charging (see figure 4). While the shift can be compensated, the change of the shape cannot. Thus the influence of the varying shape of the energy distribution of the secondary ions on the intensity ratio

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analytical to reference ion (here $^{31}P^+/^{30}Si^+$) must be studied. By varying the initial degree of charging (using an electron gun to compensate charging partially) for different depth profiles it could be shown that the intensity ratio P^+/Si^+ is reproducible within ± 10%. This means that quantitative distribution analysis of P in SiO_2 can be accurate to ± 10% concerning the phosphorus content. These methodological developments enable the quantitative characterization also of other insulating material systems, e.g. glass or ceramics (Schreiner *et al.* 1989).

Elimination of the chemical matrix effect is in principle possible if the matrices investigated can be transferred to a fully oxidized state and sputter coefficient corrections are applied. In the case of quantitative analysis of a dopant element through the system SiO_2/Si a complete oxidation of Si is possible by a chemical saturation of the surface with additional oxygen supply at the sample surface. It was found advantageous to monitor the degree of oxygen saturation when sputtering from SiO_2 into Si to obtain an SiO_2 matrix from the original silicon. A method was developed for this purpose consisting of measuring cluster and molecular ions which react very sensitively to oxygen coverage. It was found that ratio SiO_2^+/Si_2^+ is ten times more sensitive to oxygen coverage than the analytical ion P^+, thus giving a magnification of the effect. This is the basis for a complete compensation of the chemical matrix effect for the analysis of P in SiO_2/Si and allows to measure segregation profiles with an inaccuracy of smaller than ± 30% (figure 5) (Stingeder *et al.* 1989*a*). Generally it should be stressed, however, that profiles are often disturbed at interfaces due to recoil and cascade mixing or oxygen induced segregation (Morgan *et al.* 1988; Traxlmayr *et al.* 1984).

Calibration with reference materials

For quantitative solid state mass spectrometry the use of reference materials (RMS) to determine relative sensitivity factors (RSFS) has been established as a reliable method. However, quite stringent requirements exist for such materials, particularly for SIMS. For this technique the reference materials must in principle have the same matrix as the specimen and the elements to be determined have to be in the same chemical state in RM and specimen. Furthermore the distribution of the trace elements must be known with high spatial resolution in order to be able to evaluate the representativity of signals measured in RMS. Since the secondary ion yield is mainly determined by the element analysed, its bonding and the matrix a linear relation between I_A^+ and C_A can be found for trace element concentrations below 0.1% provided that the element analysed shows a homogeneous dispersion in the matrix (Takadoum *et al.* 1984). This large linear range for calibration greatly enhances the possibilities of SIMS for quantitative analysis.

The critical point is of course the availability of RMS. Thus production of RMS suitable for SIMS is studied on a large scale.

Ion implantation is used routinely for the preparation of monoelement RMS. Fluences are determined from the target current; backscatter or sputter effects can be corrected. RSFS can be obtained with high accuracy from implant reference materials: e.g. ± 5% for B in Si evaluating the integrated profile (Magee 1988). There are very few technical limitations to ion implantation, thus with this method RMS can be produced for most elements and matrices. The major drawback of this method of preparation of RMS is of course that practically only single element RMS are produced.

Chemical doping of substances is in principle a powerful mean to produce multielement RMS. To achieve the same chemical state of the trace elements the

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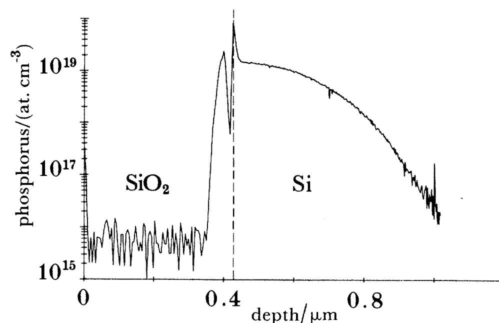

Figure 5. Quantitative SIMS depth profile of P in SiO_2/Si for the determination of the segregation coefficient. Process parameters: 30 nm thermal oxide, implantation: 50 keV P, 5×10^{14} cm^{-2}. Annealing: 1000 °C, 10 min, O_2+3% HCl (60 nm SiO_2); 1000 °C, 10 min, N_2; 400 nm CVD–SiO_2, 900 °C, 260 min, N_2. PI = O_2^+, E_0 = 5.5 keV, oxygen flooding. The actual segregation coefficient m_{Si/SiO_2} = 175. (From Stingeder *et al.* 1989*a*.)

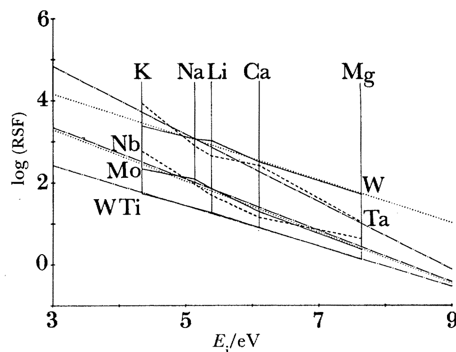

Figure 6. Relative sensitivity factors (RSF) for Li, K, Na, Ca and Mg in various metals determined from implant RMS with SIMS against ionization potential (E_i). Measurement: PI = O_2^+. (From Friedbacher *et al.* 1990.)

reference materials should be produced by the same process as the specimens to be investigated, e.g. for ultra trace analysis of refractory metals used as sputter targets for electrode lines in VLSI devices RMS containing 30 elements in the microgram/gram range could be produced by doping the starting materials of the refractory metals, the corresponding oxides with aqueous solutions of the trace components (Wilhartitz *et al.* 1987). A major drawback of such RMS is their inherent inhomogeneity, thus elaborate measurement and statistical data evaluation techniques which allow to characterize the inhomogeneity of the material have to be used. An estimate of the accuracy of SIMS for multielement ultra trace analysis using such RMS which includes the sampling error yields a typical error factor of 2. This inaccuracy is acceptable since changes in trace element content encompass up to five orders of magnitude.

The preparation of multielement RMS opens up a large area of application of high performance SIMS (HPSIMS), particularly ultra trace analysis of materials used in microelectronics industry (Grasserbauer 1988). The preparation and characterization of such RMS is, however, very expensive and tedious. Thus alternative ways of obtaining quantitative or, at least, semiquantitative results with SIMS should be studied.

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Transferability of RSFS from one matrix to another would lead to a substantial reduction of effort and thus were highly desirable. The main question for SIMS is whether this is possible at all. To study this question RSFS for Li, K, Na, Ca and Mg in Mo, W, Nb, Ta, and WTi10 were determined from measurement of implant specimens (Friedbacher 1990). It was found that the best mathematical description of the dependence of the RSF on elemental properties is obtained by plotting log RSF against E_i (first ionization potential), if the RSFS are defined on number concentrations. A fairly good linear representation is obtained for the different matrices (figure 6). This shows that a scaling factor can be used to determine the RSFS for another matrix if the concentrations of two or three elements are known in the second matrix allowing to determine the position and shape of the regression line. This can greatly facilitate quantitative analysis since often a few elements are present in the material in a concentration accessible with another technique. Similar results have been obtained by Wilson & Novak (1988) for semiconductor matrices.

Assessment of precision and accuracy

The prerequisite for high accuracy in trace analysis with SIMS is a low random error. Basically the contributions to the random error are counting statistics and reproducibility of measurement (containing instrumental variations, etc.). Since the error introduced by counting statistics is negligible – except near the detection limit – due to the high ion intensities encountered the reproducibility of measurement determines the random error.

A measure for the random error is the reproducibility of the RSF. For HPSIMS the relative standard deviation of RSFS is very low, even at trace levels. For the measurement of oxygen in silicon with caesium primary ions with a concentration of 10^{18} cm^{-3} a relative standard deviation of 7.4% has been obtained when all RSFS measured during a five month period were evaluated. Considering the difficult measurement problem this value can be regarded as excellent. It could, however, still be improved by measuring the secondary ions in the energy range 70 to 170 eV instead of those typically analysed between 0 and 100 eV. The relative standard deviation of RSFS during this five month period is only 3.5%. This improvement is attributed to a reduced effect of surface chemistry on the secondary ion yield in the high energy range (Stingeder *et al.* 1989*a*).

While SIMS exhibits very low values for random errors (in thoroughly optimized measurement procedures) it is much more pronounced to systematic errors. The key to accurate quantitative analysis is, as emphasized already, the reduction and preferably elimination as well as the assessment of systematic errors.

Assessment of systematic errors has to combine the variation of measurement parameters and the use of different calibration methods and analytical techniques. The most important variations of the measurement parameters concern primary ion species and surface chemistry (through primary ion implantation and chemical saturation) to study matrix effects, primary ion energy for detection of energy-dependent artefacts, like profile distortion by recoil implantation, and primary beam density to check for contamination effects from the residual gas or (re)sputtering from instrumental parts.

It must be considered as a great advantage of SIMS that many parameters can be varied and thus various influences on the signal can be detected. Different calibration techniques – e.g. the comparison of RSFS determined from external standards with those received from internal calibration from the fluence of implanted trace elements

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Table 1. *Analytical figures of merit for depth profiling of dopant elements in silicon with* SIMS *(from Grasserbauer & Stingeder 1989)*

dopant	primary ion species	secondary ions	detection limit (10^{14} cm^{-3})	detection limit (p.p.b.a.)	inaccuracy (%)
B	O_2^+	$^{11}B^+$	1	2	±5–10
P	Cs^+	$^{31}P^-$	10	20	±20
As	Cs^+	$^{75}As^{28}Si^-$	1	2	±10
Sb	Cs^+	$^{121}Sb^{28}Si^-$	0.4	1	±20
		$^{123}Sb^{28}Si^-$	3	5	±5–10

– allow to give a first estimate of the accuracy and should always be applied. For the previously mentioned determination of oxygen in silicon in the microgram/gram range implant and homogeneously doped RMS are used. Agreement between the differently determined RSFS is better than 10%, differences being obviously caused by the analytical error of the oxygen determination of the reference materials (ASTM Standards 1986).

The application of different analytical techniques each exhibiting a different principle of signal generation and consequently different sources for systematic errors is the most important, but equally the most difficult task, in the assessment of accuracy.

Such a combination of methods is available for the quantitative determination of oxygen in silicon (Stingeder *et al.* 1989*a*): for bulk analysis IR spectroscopy (determining only interstitial oxygen). Inert gas fusion analysis (IGFA), charged particle and photon activation analysis (CPAA, PAA) and SIMS for bulk and distribution analysis. Correlation of results obtained with the various techniques allow to state that the inaccuracy of SIMS is lower than ±10% rel in the concentration range of $0.5–10 \times 10^{17}$ cm^{-3}.

In general, the evaluation of the accuracy of solid state mass spectrometry, particularly SIMS, is severely limited by the lack of reference techniques and reference materials. There is an intrinsic connection between the two problems; without suitable reference techniques it is impossible to characterize reference materials to the desired degree of accuracy. The situation is particularly problematic with RMS for distribution analysis of trace elements, which leads companies to even market (so-called) RMS without analytical characterization. Even for rather simple problems like the characterization of the distribution of dopant elements in silicon or gallium arsenide severe problems exist. While detection limits can be determined with a high degree of reliability (see table 1 for silicon) the accuracy can only be really determined for boron for which an excellent reference method (neutron depth profiling) (Simons *et al.* 1988; Ehrstein *et al.* 1984) exists. There one arrives at a best value of 5% for the concentration scale of SIMS profiles in the higher concentration range. For all other dopant elements a combination of AA (with chemical etching), Rutherford backscattering spectrometry (RBS) spreading resistance or C/V (capacitance/voltage) measurements has to be applied (Grasserbauer 1988). Since these methods may exhibit substantial systematic errors inaccuracies of SIMS can presently be only estimated to the values listed in table 1. Substantial efforts are made to

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characterize RMs in a kind of an iterative procedure with a detailed study of systematic errors encountered with the various techniques used for calibration.

Combination of different techniques with a different information content plays a most significant role in the assessment of accuracy, because it allows not only a more extensive characterization of a material but also enables the detection of sources for systematic errors, e.g. if a trace element is present as a precipitate exhibiting a different ionization yield than in atomic dispersion in the matrix (Stingeder & Pongratz 1989).

An alternative strategy for quantitative analysis

Since secondary ion intensities are strongly dependent on surface chemistry and elaborate calibration procedures have to be applied alternative ways to get to a specific quantitative information, namely the stoichiometry of a precipitate or phase, should be investigated.

The method of direct phase or compound identification is based on the evaluation of cluster ion intensities in the secondary ion mass spectrum which represent at least to some extent the original next-neighbour relationship although ion beam mixing randomizes the structure in the solid and primary ion implantation changes the chemical composition (Werner 1974). Negative cluster ions are rather suited for direct compound evaluation (Yu 1981). An objective selection of those features in the spectra which show the most significant intensity differences could be performed by the application of pattern recognition techniques. Figure 7 shows the graphical representation of the pattern distances in three-dimensional space (which means a strong reduction in selectivity compared with the originally eight-dimensional characterization of the spectral features) for manganese borides. It is evident that the different compounds can be identified directly by evaluation of the cluster ion intensities (Wilhartitz & Grasserbauer 1986). On the basis of these results phase identification could be demonstrated in technical materials like cemented carbides (Virag *et al.* 1988).

4. Potential and limitations of SIMS for material characterization

The major potential of SIMS for materials science lies – as far as elemental analysis is concerned – in the following areas (Grasserbauer 1988*a*, *b*): ultra trace bulk analysis (lateral), micro and nano distribution analysis, surface analysis by depth profiling, three-dimensional distribution analysis through SI image acquisition and processing.

In the following typical applications of SIMS are described to show its potential and limitations in an exemplary manner. For each problem methodological developments as described in paragraph 3 have been performed.

4.1. *Ultra trace bulk analysis*

Bulk analysis of trace elements is often directly connected with problems of surface and interface characterization – particularly if the trace elements to be characterized in the bulk material diffuse into interface regions after processing and influence the material properties there. This is the case for metals from which electrode lines of microelectronic devices are produced by sputtering. Due to the extreme purity demands from VLSI technology these sputter targets have to be characterized for alkali elements and U and Th down to concentrations of 1 ng g^{-1}.

Bulk analysis with SIMS under optimized conditions offers detection limits which

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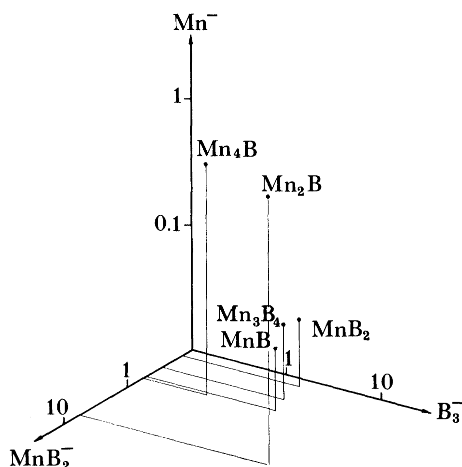

Figure 7. Phase identification by evaluation of cluster ion intensities of secondary ion mass spectra with pattern recognition methods: three-dimensional representation of pattern distances for Mn–borides showing a clear separation of the spectral features of the individual compounds. Circles represent the statistical errors. SIMS measurement: PI = Cs^+, SI = negative. (From Wilhartitz & Grasserbauer 1986.)

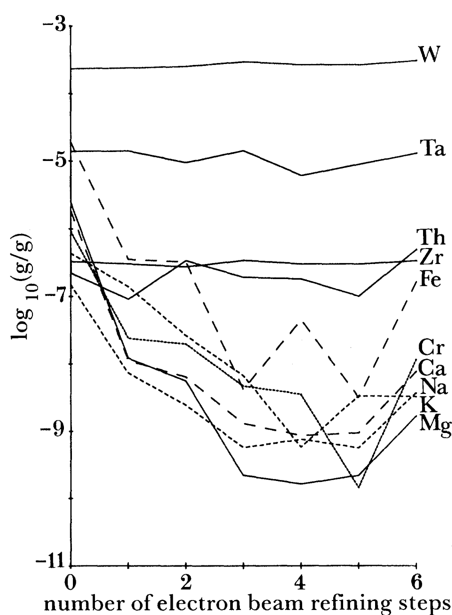

Figure 8. Ultra trace analysis with SIMS: content of technologically significant trace elements in molybdenum after repeated purification steps by electron beam melting. (From Virag *et al.* 1988.)

are about 1 pg g^{-1} for alkali elements and roughly 1 ng g^{-1} for U, Th (Virag *et al.* 1988). The inaccuracy of the analytical result is mainly limited by the inhomogeneity of the materials investigated. Typical error factors of 2 are encountered which is tolerable in this concentration range. Thirty elements can be determined simultaneously with the automatic measurement routines available. Figure 8 shows an example of applications: the change of the trace element content in molybdenum

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after repeated electron beam melting (Virag *et al.* 1988). It can be seen that alkali elements can be reduced in their content to the required levels by three repetitive electron beam melting steps. The thorium level cannot, however, be decreased due to its high boiling point (4000 °C). Thus alternative methods for purification have to be developed. SIMS complements other techniques for ultra trace bulk analysis, like glow discharge mass spectrometry (GDMS), AA or chemical enrichment combined with ET–AAS, ICP–OES, or ICP–MS (Ortner *et al.* 1987). Its advantages are the low detection limits, the small danger of contamination and the additional information about the distribution of the trace elements in the material. Its major disadvantages are the need for multielement reference materials and the low material consumption in analysis (typically a few micrograms often causing representativity problems).

4.2. *Micro and nano distribution analysis*

Micro and nano distribution analysis is obtained by recording ion micrographs or step scan profiles with a finely focused ion beam. These techniques are particularly valuable for the characterization of trace elements at interfaces in heterogeneous materials, e.g. composites. Trace elements can influence the mechanical properties strongly if enriched at the interface. Often the question is posed for the mechanism of the influence of the trace elements which demands for an analytical characterization with high spatial (lateral) resolution and high detection power. Unfortunately these two analytical figures of merit have an inverse relation with each other: an increase in spatial resolution decreases the detection power due to the smaller number of atoms sputtered. Ways have to be sought which allow to generate analytical ions with a maximum useful yield.

In some cases this can be done by applying a chemical surface modification of the material during analysis: e.g. for distribution analysis of trace amounts of phosphorus in a two-phase W–NiFe alloy a molecular ion PO_3^- can be generated by using primary oxygen ions in combination with oxygen flooding of the sample surface which is nearly 1000 times more intense than the atomic ion P^- (Wilhartitz *et al.* 1984). Using a lateral resolution (diameter of analytical area in each point of the step scan profile) of *ca.* 2 μm only about 10^9 atoms are sputtered in each location. Generation of PO_3^- yields a useful yield for the determination of phosphorus of about 10^{-3}. Consequently a detection limit of roughly 1 $\mu g\, g^{-1}$ can be achieved for a microanalytical area of 2 μm in diameter. With this technique it was then possible to study the segregation of phosphorus to the grain boundaries between W and NiFe (binder phase). Figure 9 shows these lateral distribution profiles for a material showing embrittlement. It is evident that there is a strong segregation of phosphorus to the grain boundaries causing this effect. It must be noted that information about the phosphorus species present cannot be obtained by SIMS. TEM, however, allowed us to determine that phosphorus is enriched at the grain boundary as nanoprecipitates of NiP_2 with a typical diameter of 5 nm (Zies *et al.* 1987). This also shows that quantitation of the SIMS signals in the binder phase yields only an average content which is not representative for the nanodomains.

At the present state of development the practical lateral resolution of SIMS is limited to about 100 nm although 20 nm primary ion beam diameters have been applied (Levi-Setti *et al.* 1987). For such high resolution analysis only the very sensitive elements yield signals for the trace level. Post-ionization of neutrals – e.g. by photons – may be a feasible way to increase the useful yield in nanoanalysis (Reuter 1989).

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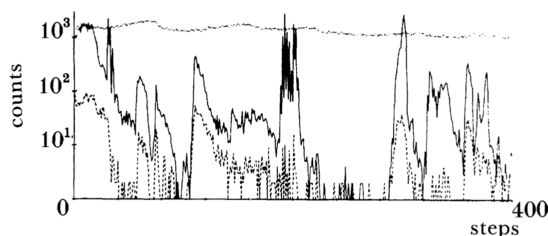

Figure 9. Microdistribution analysis of phosphorus in W–NiFe alloy. Step scan profiles of P measured as PO_3^- (——) and matrix elements measured as WO_2^- (.....) and FeO_2^- ( ). Sample sintered at 1540 °C. Slow cooling (*ca.* 14 h down to 500 °C) causes segregation of phosphorus to the grain boundaries PI = O_2^+, E_0 = 5.5 keV; oxygen flooding. (From Wilhartitz *et al.* 1984.)

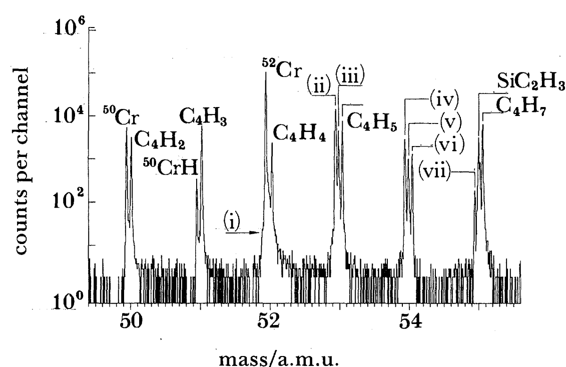

Figure 10. Trace element analysis in monolayers: analysis of surface contaminants on a silicon wafer with TOF–SIMS: spectrum of chromium isotopes and interfering hydrocarbon species of a wafer contaminated by 10^{14} Cr atoms cm^{-2}. Sample consumption: 10% of a monolayer removed from an area of 50 μm in diameter. PI = Ar^+, E_0 = 11 keV. (From Niehuis *et al.* 1989.)

4.3. *Surface analysis*

In surface analysis the composition of a material is characterized with maximum spatial resolution perpendicular to the surface. To obtain this information depth profiling techniques must be applied. Different optimized techniques are used, depending on the spatial domain to be characterized: quasi-static depth profiling with sputter rates of less than one atomic layer per second allow the characterization of extremely thin surface layers. Dynamic depth profiling enables us to characterize the depth distribution of trace elements up to micrometres. Special problems arise in the characterization of interfaces due to artefacts generated by the primary ion bombardment.

4.3.1. *Quasi-static surface analysis*

Quasi-static SIMS can be applied for trace element analysis. Trace elements analysis in the nanometre-depth domain is of particular significance in the production of silicon wafers. The trace elements originate mainly from surface preparation (cutting, polishing, cleaning, etc.) procedures and may influence the growth of the thermal oxide or be a source for detrimental metallic contamination in a VLSI chip.

The basic problem of trace analysis in such thin surface layers is the low amount of material available for analysis.

For sector field instruments optimized 'quasi-static' measurement techniques had

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to be developed for the different elements to achieve the optimum between (high) detection power and (low) sample consumption per data point (Stingeder *et al.* 1988), since the amount of material available in analysis is very low: in one atomic layer only 10^{15} atoms (*ca.* 10^{-8} g) are present per cm^2. At a typical analytical area of 10^{-4} cm^2 only 10^{11} atoms are removed. This means for a relative detection limit of 1 μg g^{-1} only 10^5 analyte atoms are sputtered. Only high efficiency measurement techniques with a useful yield of the order of 10^{-1}–10^{-4} provide a sufficient detection power. These figures of merit must be achieved at a high mass resolution power to separate the analytical ions from the interfering hydrocarbon species which are present on the surface of every wafer.

For HPSIMS sector field instruments the practical detection limits for a sample consumption of *ca.* 10^{10} atoms is about 1 μg g^{-1} for aluminium (which serves as a tracer element for contamination). This corresponds to an absolute detection power of 5×10^{-19} g, or *ca.* 10^4 aluminium atoms, and to a surface coverage of *ca.* 10^9 atoms cm^{-2}.

Other elements which must be measured at a higher mass resolution like Fe are about a factor 100 less sensitive. An increase in detection power can be achieved by using SIMS techniques based on high resolution time-of-flight (TOF) mass spectrometers (Niehuis *et al.* 1989). Figure 10 shows as an example the spectrum of the surface of a silicon wafer contaminated by 10^{14} Cr atoms cm^{-2}. The various chromium isotopes can be separated from the interfering hydrocarbon species at a nominal mass resolution of *ca.* 3000. Due to the high transmission of this TOF spectrometer (*ca.* 20%) which is independent on mass resolution large signals can be obtained with extremely small sample consumptions. In the example shown in figure 10 only 10% of a monolayer had been removed from an area of 50 μm in diameter. In general the minimum detectable surface coverage is in the range of 10^8–10^9 atoms cm^{-2}.

Laser resonance ionization SNMS can still lower the detection limits due to the possibility of selective and highly efficient ionization of contaminant atoms by a multiphoton absorption process. This technique is particularly useful for elements which have a low ionization yield and which exhibit strong interferences, like Fe. By this technique a detection limit for Fe of about 2 ng g^{-1} with a material consumption of about one monolayer can be obtained (Pellin *et al.* 1987). This corresponds in absolute amounts to *ca.* 40 iron atoms sputtered during measurement of one data point or a minimum detectable surface coverage of 10^6 atoms cm^{-2}.

Systematic investigations of the surface contamination of wafers – performed mainly with SIMS – have shown that these trace elements are concentrated in the native oxide and that their content depends strongly on the type of cleaning procedure (Stingeder *et al.* 1988).

4.3.2. *Dynamic surface analysis*

The major goal of dynamic surface analysis is quantitative distribution analysis with a high analytical accuracy. This means in the first instance consideration of the matrix and selective sputter effects, then combination of various analytical techniques to study and reduce systematic errors and to increase the information content of the analysis. Different problems and consequently analytical procedures occur for (laterally) homogeneous (like semiconductors) or heterogeneous materials (like most metals).

1. Homogeneous matrices: silicon semiconductors. In the study of semiconductors

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one of the major areas of interest is the characterization of the distribution of the dopant elements within surface layers of typically less than 1 μm (Grasserbauer 1989).

The major requirements to be fulfilled are large dynamic range of analysis and high detection power (concentration range *ca.* 10^{14}–5×10^{21} atoms cm^{-3} (ng g^{-1} %)); large spatial (depth) resolution (a few nanometres); high accuracy of analytical information (concentration against depth).

The basis for highly accurate quantitative analysis is the application of the analytical strategy described in paragraph 3.

With optimized analytical conditions detection limits for distribution analysis are obtained which are in the range between 10^{14} and 3×10^{15} cm^{-3} (table 1). The analytical accuracy is sufficient for the characterization of the redistribution of dopant elements taking place during the various production steps for microelectronic devices (Grasserbauer & Stingeder 1989).

It must be emphasized, however, that these processes are studied not in devices but in non-structured model specimens, since the required figures of merit cannot be achieved at sub-micrometre lateral resolution as would be required for todays highly integrated devices (e.g. the 4 Mbyte DRAM). The highly accurate depth profiles, obtained from specimens subjected to the various technological steps (e.g. oxidation, implantation, annealing), allow physical models to be set up which enable the calculation of the distribution (x, y, z) of dopants in actual devices (Plummer 1984; Pötzl 1988). To achieve a sufficient accuracy of the models and a substantial range of applicability 'small effects' also have to be characterized. For these (as shown in figure 2) the ultimate accuracy of SIMS in concentration and depth scale is required. The values achievable for the concentration scale are contained in table 1. Depth calibration is made by crater depth measurements using largely stylus techniques. An accuracy of several nanometres can be obtained. Figure 11 shows as an example for high accuracy depth distribution analysis the profiles of Sb in silicon after 500 min annealing in N_2 respectively O_2. Annealing in oxygen atmosphere reduces the broadening of the initial profile due to the fact that vacancies (through which Sb atoms diffuse) are annihilated by combining with interstitials which are generated in the oxidation process of the silicon wafer ('oxidation retarded diffusion').

The evaluation of these and other profiles allowed to establish a quantitative model for the diffusion of antimony in silicon (Guerrero *et al.* 1986).

It must be emphasized that SIMS is one of the most important analytical tools in semiconductor research (Grasserbauer 1988; Grasserbauer & Stingeder 1989). To achieve a maximum information about dopant elements this technique is frequently combined with electrical surface resistance measurements, RBS and TEM (Werner 1988).

2. Other materials. SIMS is the major technique for depth profiling of trace elements and is applied to many different material systems: dopant elements in III–V and II–VI semiconductors (Boudewijn *et al.* 1986); impurities in thin layer systems (Wilhartitz *et al.* 1987); corrosion processes of metals (Degreve *et al.* 1988); ion exchange phenomena in glass (Schreiner *et al.* 1989); influence of trace elements on quality of coatings (ceramic, diamond, etc.) (Wilhartitz *et al.* 1986); surface modification of materials by chemical reactions, ion implantation, etc. (Stingeder *et al.* 1984).

For these tasks SIMS is frequently combined with EPMA, SEM, XPS, AES, TEM and other techniques.

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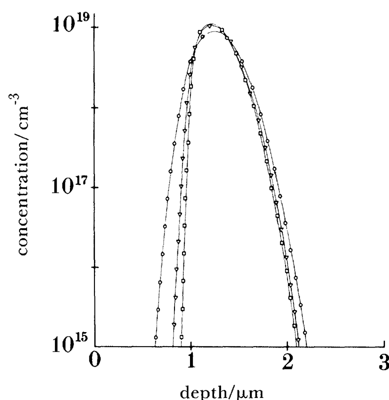

Figure 11. Quantitative depth profiling with SIMS. Study of the oxidation-retarded diffusion (ORD) of Sb in silicon. Measured (○, ▽, □) and calculated (curves) antimony profiles. Squares indicate the 'initial' profile before the final annealing step. The final annealing step at 1000 °C lasted for 500 min. The results for the inert diffusion (under the Si_3N_4/SiO_2 mask) are shown by circles. Triangles indicate the results for the oxidized domain of the sample. Implantation of ^{123}Sb at 80 keV; dose: 4.3×10^{14} cm^{-2}; annealing at 1150 °C for 30 min in N_2 to heal implantation defects; 1.2 μm epi-silicon layer on wafer; annealing in O_2 at 1000 °C with half of waver protected by Si_3N_4 (inert annealing profiles). Oxide and nitride removed before analysis. PI = O_2^+, E_0 = 5.5 keV; SI = Sb^+. (From Guerrero *et al.* 1986.)

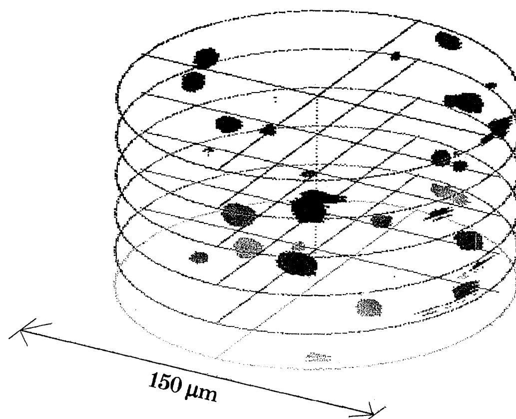

Figure 12. Three-dimensional distribution analysis with SIMS: 3D image of the silicon oxide precipitates in a silicon wafer. Diameter of analysed area = 150 μm; depth = 2.4 μm. PI = Cs^+, E_0 = 14.5 keV, SI = O^-.

It must be stressed that the more complicated the structure of a system is the more necessary it becomes to use additional complementary techniques for materials characterization. Analytical figures of merit obtainable with SIMS depend largely on the specific problem. Representative values are given in the references cited.

4.4. *Three-dimensional (3D) distribution analysis*

Three-dimensional characterization is an inherent feature of SIMS due to the sequential removal of atomic layers during depth profiling. The lateral distribution information can either be obtained with a finely focused ion beam rastering across a specified area on the sample or by exploiting the stigmatic imaging properties of an

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ion microscope. In the latter case the secondary ion image is recorded with either a position sensitive resistive anode encoder or a CCD-camera. In any case a large number of sequentially taken ion micrographs are stored and processed using various mathematical routines (e.g. for smoothing, filtering, background subtraction, quantitation, colour encoding (Rüdenauer & Steiger 1988). The 3D distribution of secondary ion signals is displayed in various modes, e.g. as cross sections, or in transparent cylinders. Figure 12 shows as an example the distribution of silicon oxide precipitates in a silicon wafer. The micrograph represents the intensity distribution of the secondary ion O^- (from SiO_2) corrected for background noise. Looking at the spatial dimensions (diameter 150 μm, depth only 2.4 μm) one inherent problem of SIMS in 3D analysis becomes evident: if the precipitates are smaller than the lateral resolution of the imaging system (or the beam diameter when the scanning technique is applied) the precipitates appear larger than they actually are. For spheric precipitates the diameter can be obtained from the depth profile. In the case of the SiO_2 precipitates a diameter of about 100 nm was found; thus they appear grossly enlarged in their lateral dimension. Lateral resolution in 3D analysis is typically limited to 0.1–1 μm for intensity reasons and computer storage capacity. For a 3D analysis as shown in figure 11 about 100 Mbyte of data were collected and processed. This number demonstrates also the huge increase in potential information compared with a normal (laterally non-resolved) depth profile which contains about 100 kbyte of data.

In principle a semiquantitative evaluation of these representations is possible with RSFs, but the situation is much more complicated than for other typical SIMS results since the trace elements are locally enriched (thus sputter yields and ionization probability change compared with the matrix) and the sputter induced artefacts can be substantial.

One of the other most important areas of application of 3D analysis will be the stereometric characterization of inclusions or precipitates combining chemical and positional information. This will lead to greatly enhanced possibilities for a property relevant characterization of materials (particularly metals) and microelectronic devices.

5. Future challenges

Although SIMS is now an established technique for trace element analysis, particularly for surface and interface characterization, many problems from materials science still need to be treated. SIMS also provides exciting frontier areas in methodological research. Some of the likely developments are models describing signal generation in a quantitative manner; quantitative analysis of delta-layers; data collection for S, $\alpha_A^{+(-)}$, $U_A^{+(-)}$; reference materials for bulk surface and interface analysis; high transmission instruments for nanoanalysis and monolayer characterization; post-ionization of neutral species with photons, electron gas or electron beams (SNMS); integration of more elaborate mathematical procedures for data evaluation (e.g. factor analysis, fuzzy theory); expert system for technical analysis; 'molecular' analysis by evaluation of cluster ions (this area is of greatest significance for 'organic' surface analysis (see A. J. Paul and J. C. Vickerman, this symposium)).

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References

ASTM 1986 Method F 121-83 Annual Book of ASTM Standards, vol. 10.05, 242. Philadelphia: ASTM.

Benninghoven, A. & Rüdenauer, F. & Werner, H. W. 1987 *Secondary ion mass spectrometry*. New York: Wiley.

Boudewijn, P. R., Leys, M. R. & Roozeboom, F. 1986 *Surf. Interface Anal.* **9**, 303.

Degreve, F., Thorne, N. A. & Lang, J. M. 1988 *J. Mater. Sci.* **23**, 4181.

Ehrstein, J. R., Downing, R. G., Stallard, B. R., Simons, D. S. & Fleming, R. F. 1986 ASTM Special Technical Testing Publ. **850**, 409. Philadelphia.

Friedbacher, G., Virag, A. & Grasserbauer, M. 1990 *Analyt. Chem.* (In the press.)

Grasserbauer, M. 1988 Surface and interface analysis for the development of microelectronic devices. In *Reviews on analytical chemistry* (ed. E. Roth). Paris: Les Editions de Physique.

Grasserbauer, M. 1988*a* *Pure appl. Chem.* **60**, 437.

Grasserbauer, M. 1988*b* *Microchem. J.* **38**, 24.

Grasserbauer, M. 1989 *Thin Solid Films* **181**, 17.

Grasserbauer, M. & Stingeder, G. 1989 *Vacuum* **39**, 1077.

Guerrero, E., Jüngling, W., Pötzl, H., Gösele, U., Mader, L., Grasserbauer, M. & Stingeder, G. 1986 *J. electrochem. Soc.* **133**, 2181.

Levi-Setti, R., Chabala, J. M. & Wong, Y. L. 1987 *Scanning Microsc. Suppl.* **1**, 13.

Magee, C. W. 1988 *J. Res. natnl. Bur. Stand. (U.S.)* **93**, 390.

Morgan, A. E. & Maillot, Ph. 1988 *Secondary ion mass spectrometry VI* (ed. A. Benninghoven, A. M. Huber & H. W. Werner), p. 709. Chichester: Wiley.

Niehuis, E., Heller, T., Jürgens, U. & Benninghoven, A. 1989 *J. Vac. Sci. Technol.* A **7**, 1823.

Ortner, H. M., Plödorn, W., Friedbacher, G., Grasserbauer, M., Krivan, V., Virag, A., Wilhartitz, P. & Wünsch, G. 1987 *Microchim. Acta* **I**, 233.

Pellin, M., Young, C. E., Callaway, W. F., Burnett, J. W., Jorgensen, B., Schweitzer, E. L. & Gruen, D. M. 1987 *Nucl. Instrum. Meth. Phys. Rev.* B **18**, 446.

Plummer, J. D. 1984 Computer aided design of integrated circuit fabrication processes for VLSI devices. Rep. no. TR DXG 501-84, Stanford University.

Pötzl, H. W. 1988 *Siemens Forsch.u.Entwickl.Ber.* **17**, 308.

Reuter, W. 1989 *Trends Analyt. Chem.* **8**, 203.

Rüdenauer, F. G. & Steiger, W. 1988 *Proc. SIMS VI Conference, Versailles 1987*, p. 361. Chichester: Wiley.

Schreiner, M., Piplits, K., March, P., Stingeder, G., Paul, F. & Grasserbauer, M. 1989 *Z. analyt. Chem.* **333**, 386.

Simons, D. S., Chi, P., Downing, R. G., Ehrstein, J. R. & Knudsen, J. F. 1988 *Secondary ion mass spectrometry VI* (ed. A. Benninghoven, A. M. Huber & H. W. Werner), p. 433. Chichester: Wiley.

Stingeder, G. 1988 *Analyt. Chem.* **60**, 1524.

Stingeder, G., Wilhartitz, P., Schreiner, M. & Grasserbauer, M. 1984 *Z. analyt. Chem.* **319**, 787.

Stingeder, G., Gara, S., Pahlke, S., Schwenk, H., Guerrero, E. & Grasserbauer, M. 1989*a* *Z. analyt. Chem.* **333**, 576.

Stingeder, G., Grundner, M. & Grasserbauer, M. 1988 *Surf. Interface Anal.* **11**, 407.

Stingeder, G., Piplits, K., Gara, S., Grasserbauer, M., Budil, M. & Pötzl, H. 1989*b* *Analyt. Chem.* **61**, 412.

Stingeder, G., Pongratz, P., Kuhnert, W. & Brabec, T. 1989*c* *Z. analyt. Chem.* **333**, 191.

Takadoum, J., Pivin, J. C., Pons-Corbeau, J., Berneron, R. & Charbonnier, J. C. 1984 *Surf. Interface Anal.* **6**, 274.

Traxlmayr, U., Stingeder, G., Fallmann, W. & Grasserbauer, M. 1984 *Z. analyt. Chem.* **319**, 855.

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Vickerman, J., Brown, A. & Reed, N. M. (eds) 1989 *Secondary ion mass spectrometry – principles and applications*. Oxford: Clarendon Press.

Virag, A., Friedbacher, G., Grasserbauer, M., Ortner, H. M. & Wilhartitz, P. 1988 *J. Mater. Res.* **3**, 964.

Virag, A., Friedbacher, G., Grasserbauer, M., Schubert, W. D., Fryc, M. & Lux, B. 1988 *Microchim. Acta* **III**, 57.

Werner, H. W. 1974 *Vacuum* **24**, 439.

Werner, H. W. 1988 Diagnostic techniques for micro-electronic materials, processes and devices. *Proc. NATO Adv. Study Institute, Microelectronic Materials and Processes* (ed. R. A. Levi). Amsterdam: Niijhoff.

Werner, H. W. & Warmoltz, N. 1984 *J. Vac. Sci. Technol.* A **2**, 726.

Wilhartitz, P. & Grasserbauer, M. 1986 *Microchim. Acta* **II**, 313.

Wilhartitz, P., Grasserbauer, M., Altena, H. & Lux, B. 1986 *Surf. Interface Anal.* **8**, 159.

Wilhartitz, P., Grasserbauer, M., Danninger, H. & Lux, B. 1984 *Z. analyt. Chem.* **319**, 831.

Wilhartitz, P., Grasserbauer, M., Hiesböck, H. G. & Bartl, C. 1987 *Surf. Interface Anal.* **10**, 267.

Wilhartitz, P., Virag, A., Friedbacher, G., Grasserbauer, M. & Ortner, H. M. 1987 *Z. analyt. Chem.* **329**, 228.

Wilson, R. G. & Novak, S. W. 1988 *Secondary ion mass spectrometry VI* (ed. A. Benninghoven, A. M. Huber & H. W. Werner), p. 57. Chichester: Wiley.

Wittmaack, A. 1980 *Nucl. Instrum. Meth.* **168**, 343.

Yu, M. L. 1981 *Phys. Rev.* B **24**, 5625.

Zies, G., Wetzig, K., Wilhartitz, P. & Grasserbauer, M. 1987 *Z. analyt. Chem.* **326**, 218.

Discussion

D. Littlejohn (*University of Strathclyde, U.K.*). Does the analysis of neutral species vaporized from a sample result in lower interferences (i.e. compared with sims)? If so, and if there are advantages in detection power and speed of analysis, will the analysis of neutrals replace sims in some (or all) applications?

M. Grasserbauer. The analysis of neutral species has the principal advantage that sputtering and ionization are decoupled resulting in a substantially smaller influence of surface chemistry on secondary ion generation than in sims. Matrix effects are still occurring in the analysis of neutral species originating from differences in sputter yield between specimen and reference material or in ionization yield. For a detailed discussion see Reuter (1989). Advantages in detection power over sims have mainly been reported for resonant-photon-positionization, which is, however, a single-element-determination method, and thus lacks the multielement capability of sims. Also in some cases gdms has a higher detection power. But this technique is only suited for bulk analysis.

In general one must state that each of the snms techniques has its specific advantages and disadvantages, as sims. Due to its inherent features sims is a most versatile and widely applicable tool, particularly when high performance instrumentation is used. Thus it will never be replaced by snms completely.

M. J. Pellin (*ANL, U.S.A.*). Dr Grasserbauer's stigmatic imaging was extremely impressive. How would he compare astigmatic and stigmatic imaging?

M. Grasserbauer. Stigmatic imaging has the multiplex-advantage, all pixels within the imaged field are acquired simultaneously. This leads to substantially shorter

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image registration times; a stigmatic ion microscopic image of an area of 100×100 µm and 1 µm resolution is obtained during 1–10 s, while an astigmatic image of the same area and resolution needs 10000 sequential pixels obtained by scanning the finely focused primary ion beam across the sample surface thus would typically take in the order of 1000 s.

The strength of astigmatic imaging is that lateral resolution is determined by the primary ion beam diameter, not the lens aberrations of the mass spectrometer. While the lateral resolution of stigmatic imaging is limited to about 500–1000 nm, astigmatic imaging achieves a resolution of typically 100 nm, in special cases even 20 nm. High resolution is achieved, however, on the expense of detection power, thus in practice stigmatic imaging is much more widely used.

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