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General Aspects of Trace Analytical Methods: Part VI

TRACE ANALYSIS OF SEMICONDUCTOR MATERIALS PART A: BULK ANALYSIS

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General aspects of trace analytical methods: Part VI. Trace analysis of semiconductor materials—Part A: Bulk analysis

Abstract - The characterization of trace elements in semicon-
ductor materials belongs to the most challenging tasks for
analytical chemistry. This paper gives a critical evaluation
of the most important methods for bulk analysis of silicon,
germanium and gallium arsenide. Decomposition, preconcentra-
tion and determination methods (atomic emission and absorp-
tion spectrometry, spark source mass spectrometry, neutron
activation analysis, electrochemical techniques, gas chroma-
tography - mass spectrometry and others) are discussed mainly
in respect to their information content and figures of merit.

INTRODUCTION

Silicon, germanium, gallium arsenide, indium antimonide, zinc, cadmium and
mercury sulfides, selenides, and tellurides constitute the main semiconductor
materials. With them are classed also the raw materials used in production of
these substances. Analytical chemistry plays a vital role in the development
of semiconductors which are having a great impact on present day science and
technology.

Two main tasks can be distinguished in the analysis of these materials :
(A) determination of bulk concentration of trace elements, and (B) analysis
of surface layers and microsamples and determination of concentration
profiles of elements. The former is essential for semiconductor manufacturing
processes and has become well-established. The role of the latter increases
with the miniaturization of semiconductor devices where the effect of the
surface of a material on its performance properties is important. In addition,
it is necessary to study the chemical forms in which the impurities exist in
the material, and to estimate deviations from stoichiometry. From the
analyst's viewpoint, the estimation of these deviations demands very accurate
determination of sufficiently large concentrations of substances.

GENERAL

High purity substances form the basis of modern semiconductor engineering.
Requirements for higher purity of these materials are constantly increasing.
Depending on the nature of the semiconductor material and its utility, the
effect of impurities on the properties can have variable significance and the
criteria for purity are changed. However, in the majority of cases it is not
possible to estimate theoretically the effect of different impurities on the
properties of a semiconductor device; in a few cases, this can be done only
partially. That is why requirements of "absolute purity" are placed on a
semiconductor material, that is, it should be free of all of the elements.
Such requirements emphasize the need for survey analysis methods which enable
a maximum number of impurities to be determined. In addition, the purity of
semiconductors is checked by electrophysical methods which offer a means of
estimating performance characteristics, (ref. 1,2).

The impurities, from the viewpoint of their analytic specificity, can be
divided into four groups. Gas-forming elements, namely oxygen, carbon,
nitrogen, and hydrogen, are placed in the first group. The concentration of
these elements in practically all of the pure semiconductor substances exceeds
those of other elements, and their determination techniques are complex and
not very sensitive. This is due to the strong effect of the surroundings,
composed principally of the indicated components, on the content of gas-
forming impurities in the substances, especially on the surface, and also
on the blank values. The second group of impurities includes the so-called
"domestic" impurities which, although in sufficiently small amounts, are
rather widely spread in industrial areas, materials of instruments and rea-
gents : iron, silicon, calcium, aluminium, sodium, and others. The third
group contains elements close in chemical properties to the main components

of the material. It is difficult to separate the material from these elements so their concentration is often higher than that of other impurities. All of the remaining impurities constitute group 4 of the elements and are determined as a rule with a much higher sensitivity.

Along with the general requirement of "absolute purity" of semiconductor materials, "special purpose" purity may be specified with respect to allowable levels of individual impurities such gold, boron, and phosphorous in silicon.

DETECTION AND DETERMINATION LIMITS AND ACCURACY

The detection limit and the limit of determination (L_Q) are the most important quantifying parameters that characterize the methods of determining trace elements in semiconducting materials. The former offers a means of qualitative detection of trace element with a given probability. The latter indicates smallest concentration which can be reliably calculated from the data. The detection limit is usually estimated by blank fluctuations. Depending on the required degree of reliability, the standard deviation of the blank is multiplied by a coefficient 2, 3 or 6.

Two techniques are commonly used to determine L_Q. One of the them consists of multiplying the standard deviation of the blank by a coefficient 10. It was noted (ref. 3) that using this coefficient one could neglect other components of the analytical error (instrumental errors, sampling errors, surface contaminations etc.).Such an approach is purely arbitrary. Nevertheless, it is beneficial as it enables the available methods to be compared by a single figure of merit. A summary of information concerning determination of elements is available in (ref. 3), where the values of L_Q are given in μg/mL.

The so-called guaranteed L_Q presents itself as a more reliable parameter. To find its value a sample of the purest material is subjected to a series of analyses. Sample standard deviation is computed from the results obtained and multiplied by a coefficient 2 or 3. The salient feature of this technique is that it involves the use of total standard deviation of analysis which allows for errors at all stages of the determination. The values of L_Q are slightly higher than the actual limit of determination. Such a "safety factor" is justified because in an actual analysis there are always some unaccounted sources of error.

Often a third technique is recommended. A series of samples of the material with known content of determinable elements is taken. The samples are analysed and a relationship is found between relative standard deviation (RSD) and the impurity contents. As the given value of RSD is attained (usually 0.33 or 0.5), L_Q is fixed. Considerable labor is needed to prepare samples with a known wide range of trace element contents. This is the main drawback of this technique.

One distinguishes absolute (expressed in grams) and relative (given in percents) limits of determinations. Often in the analysis of semiconductors one encounters a situation when, using the method with low absolute L_Q, it is not possible to attain such a low relative L_Q due to small amount of the substance being analyzed. In the majority of cases the detection limits and L_Q depend significantly on the total sample composition.

It is essential to confirm the accuracy of determination. Analysis is often performed at the limits of accuracy and precision of the technique; therefore, a slight inaccuracy in the analytical procedure leads to erroneous results. One should pay special attention to the errors of the blank, surface contaminations, impurities that appear in the course of analysis, losses during preconcentration, etc. The main techniques of verifying the accuracy of determination are : round-robin (cyclic analysis), that is, comparison of the results obtained by different techniques and in different laboratories; methods of trace standard addition; preparation and use of synthetic reference samples; variation of sample weight; comparison of analysis results with the properties of the substance; stagewise control of the technique, and others. In checking the accuracy by trace standard addition, use is often made of radioactive and less abundant stable isotopes of the elements being determined. This enables negligible, yet controllable amounts of trace elements to be introduced into a sample without any fear

of contamination. This is done by ion implantation for uniform introduction
of trace amounts of the determinable element into the sample. The likelihood
of erroneous assessment of accuracy tests is the reason why simultaneous use
of several techniques is desirable. However, this is not always achieved. In
recent years the accuracy test has often been performed by round robin
analysis. However it should be carried out with due consideration to surface
impurities of the samples which may have been specially prepared for analysis.
From Table 1 it is evident that preliminary removal of the surface layer in
the analysis by spark source mass spectrometry enables the contents of seve-
ral determinable elements in the uncontaminated bulk to be lowered a factor
of 50 - 100.

DECOMPOSITION OF SAMPLES AND PRECONCENTRATION OF TRACE ELEMENTS

Samples of semiconductor materials are best decomposed in closed reaction
chambers, for instance in analytical autoclaves. The reagents selected for
decomposition should ensure a minimum blank signal. Digestion of the
material being analysed must be done without loss of the determinable ele-
ments. Conditions for subsequent preconcentration of the analyte should be
created. The decomposition conditions for some semiconductor materials and
their parent substances are listed in Tables 2 and 3 (ref. 4).

Preconcentration of trace elements has several advantages (ref. 5-8). The
detection limits can be lowered by increasing the absolute amount of trace
elements in the sample. Isolating trace elements from the matrix favors in-
dependent determination under optimal conditions. Preconcentration of trace
elements permits the use of one series of reference samples. Preconcentra-
tion is almost always necessary when trace elements are inhomogeneously
distributed in the sample.

A disadvantage of preconcentration is possibility of distorting results due
to the loss of trace elements or contamination of the sample during precon-
centration. Quite often, the matrix is separated completely and the trace
elements are gathered on a specially introduced collector. In several cases
the residue of the separated matrix is used as a collector.

A number of specific requirements have to be fulfilled for successful appli-
cation of the techniques involving sample decomposition and preconcentra-
tion (ref. 5). The materials (quartz, graphite, glassy-carbon, PFTE and
some noble metals) of the vessels in which samples are prepared for analysis
should be as inert as possible. The reagents used should be as pure as
possible (H_2O, HF, HCl, HNO_3 and H_2O_2 can be readily purified). The dust
contribution to the blank can be lowered at least by one order of magnitude
by taking special measures aimed at reducing the background dust level at
work places. This applies especially to elements present in large amounts
in the laboratory dust, i.e. Si, Al, Fe, Ca, P, C, and others.

TRACE ELEMENT DETERMINATION TECHNIQUES

Atomic emission and atomic absorption methods with preconcentration of ele-
ments to be determined, spark source mass spectroscopy, neutron activation
analysis (in instrumental and radiochemical modes), and specific methods of
determining gas-forming traces are the main techniques used to determine the
bulk content of trace elements in semiconducting materials. Ultraviolet and
visible spectrophotometry and electrochemical, and other techniques are also
used.

Table 4 contains absolute values of L_Q for various analytical techniques
(ref. 6).

ATOMIC EMISSION SPECTROMETRY

The methods involving preconcentration of trace elements and atomic emission
are placed into the category of combined techniques involving chemical
sample preparation (surface cleaning, decomposition, preconcentration, sepa-
ration, etc.) and final determination by a physical method. In atomic
emission analysis, preconcentration of trace elements is carried out by
different methods i.e. solvent extraction, evaporation and distillation, pre-
cipitation and coprecipitation, electrochemical enrichment,chromatography,
crystallization concentration, and other techniques.

TABLE 1   RESULTS OF MASS SPECTROMETRIC ANALYSIS OF HIGH PURITY ALUMINIUM, $n \cdot 10^{-3}$% at. (obtained in the Institute of Rare Metals, Moscow, USSR)

Element	Content	
	determined without removing the surface layer	determined after the removal of surface layer
Ti	0.03	0.005
Mn	0.01	0.003
Fe	0.02	0.005
Cl	0.5	0.01
Si	8	0.002
Mg	0.4	0.002
O	10	0.06
N	10	0.02
C	10	0.02

TABLE 2   DECOMPOSITION CONDITIONS OF SEMICONDUCTOR MATERIALS FOR SUBSEQUENT ATOMIC EMISSION ANALYSIS

Analysed materials	Determinable trace elements	Reagents	C_1, % mass
As, As_2O_3	Al,Fe,Ca,Mg,Mn,Cu,Ni,Pb, Sb,Cr,Bi	6M HCl+Br_2	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
As, Ga	Al,Bi,Si,Mg,Mn,Cu,Ni,Sb, Ag, Cr	6M HCl+Br_2	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
Ge	Ag,Au,Al,Ba,Bi,Ca,Co,Cr, Cu,Cd,Mg,Mn,Mo,Fe,Ti,Sn, Pb,Sb	HCl+HNO_3	$10^{-5} - 10^{-6}$
GeO_2	Ag,Al,Be,Bi,Cd,In,Ga,Fe, Mg,Mn,Ni,Pb	conc.HCl	$10^{-5} - 10^{-6}$
Ga	Al,Bi,Fe,In,Cd,Co,Si,Mg, Mn,Cu,Ni,Sb,Ag,Cr,Zn	6M HCl+HNO_3	$2 \cdot 10^{-4} - 5 \cdot 10^{-7}$
Ga_2O_3	Al,V,Bi,In,Co,Si,Mg,Mn, Cu,Ni,Ag,Pb,Cr	6M HCl	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
Ga,Ga_2O_3	V,Cr,Mn,Co,Ni,Mo,Cu,Al, Mg,Ca,In,Cd,Pb,Zn,Bi	HCl	$10^{-6} - 10^{-7}$
Si,SiO_2	Mg,Ca,Al,Ti,V,Cr,Mo,Mn, Fe,Co,Ni,Cu,Ag,Cd,Sn,Pb, Sb,Bi	HF+HNO_3	$10^{-4} - 10^{-5}$
In	Al,Bi,Cd,Si,Mg,Cr,Mn,Cu, Ni,Sb,Ag	HBr	$1 \cdot 10^{-4} - 6 \cdot 10^{-8}$
	Ga,Fe,Au,Mo,Te	6M HCl+HNO_3	$2 \cdot 10^{-4} - 3 \cdot 10^{-6}$
InAs	Al,Be,Bi,Cd,Ca,Co,Cu,Mn, Mg,Ni,Pb,Ag,Zn,Cr	HBr+Br_2	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
InSb,GaSb	Ag,Al,Ba,Bi,Ca,Cd,Co,Cr, Cu,Mg,Mn,Ni,Pb,Tl,Zn	HCl+HNO_3 (3:1)+treatment of dry residue with HBr	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
Te	Ag,Al,Bi,Cd,Cu,Ni,Pb,Zn	HBr+Br_2	$10^{-5} - 5 \cdot 10^{-7}$
Sb	Ag,As,Bi,Ca,Co,Cd,Cr,Cu, Mg,Mn,Ni,Pb,Zn	HCl+HNO_3	$1 \cdot 10^{-5} - 5 \cdot 10^{-7}$
B_2O_3	Al,Ag,Cu,Zn,Ni,Sn,Cr,Mn, Mg,Fe,Cd,Ga,Gd,Sb	HF+HNO_3	$2 \cdot 10^{-4} - 5 \cdot 10^{-7}$

TABLE 3   DECOMPOSITION CONDITIONS OF HIGH PURITY SUBSTANCES FOR DETERMINING
          TRACE ELEMENTS BY POLAROGRAPHIC OR PHOTOMETRIC TECHNIQUES

Analysed material	Determined trace elements	Reagents used for decomposition	Method of determination	c_1, % mass
B_2O_3	S	Reduction mixture $HI+HCl+NaH_2PO_2$	Polarographic	5.10^{-6}
	Te	HCl+hydroxylamine hydrochloride $Na_2S_2O_3$+mannitol	Polarographic	5.10^{-6}
	Se	$6M$ HCl+mannitol+ hydroxylamine hydrochloride + NaH_2PO_2	Polarographic	5.10^{-6}
	Sn	$6M$ HCl+mannitol $+H_2O_2$	Polarographic	6.10^{-6}
	As	$HCl+H_2SO_4$ (7:1)+ mannitol	Polarographic	
$GeCl_4$	Se	$6M$ $HCl+NaH_2PO_2$	photometric	1.10^{-5}
$Si, SiHCl_3$		$HCl+HNO_3+KMnO_4$	Extraction photometric	$10^{-4}-10^{-7}$
$SiCl_4$	B, P			
GaSb	As	HNO_3	Extraction photometric	1.10^{-5}

TABLE 4   ABSOLUTE LOWER LIMIT OF CONTENTS (c_1) DETERMINED BY DIFFERENT
          METHODS IN SEMICONDUCTORS

Method	c_1, g		Method	c_1, g	
	for most elements	in certain cases		for most elements	in certain cases
Photometry	10^{-9}	10^{-11}	Same as last item in first column (electro-thermal variant)	10^{-12}	5.10^{-14}
Fluorometry	10^{-10}	10^{-11}			
Kinetic methods	10^{-11}	10^{-13}	Gas chromatography of chelates	10^{-11}	10^{-13}
Inverse voltammetry	5.10^{-11}	10^{-12}	X-ray fluorescence method	10^{-9}	–
Atomic absorption or atomic fluorescence spectrophotometry (flame variant)	10^{-10}	10^{-12}	Activation analysis	10^{-13}	10^{-14}
			Mass spectrometry	10^{-12}	10^{-15}

For analysis of the concentrate, use is made of various sources of light --
arc sources, hollow cathode discharge, inductively coupled plasma, and
lasers (ref. 9,10). The concentrated sample is placed in a carbon electrode
cup followed by a total burn of the sample using a DC arc which provides the
atomic spectra of the respective elements.

Table 5 shows absolute detection limits of trace elements determined by
atomic emission analysis with preliminary chemical treatment using a DC arc
and a hollow cathode. Hollow cathode discharge has a promising future
despite additional difficulties involved in the analysis.

ATOMIC ABSORPTION SPECTROMETRY

Use is made of atomic absorption analysis in those cases where the number of
impurities to be determined in semiconductor materials is not large. An elec-
trothermal variant of this technique ensures very low L_Q. Nevertheless, a

TABLE 5   DETECTION LIMITS OF TRACES, DETERMINED BY ATOMIC EMISSION ANALYSIS USING A DC ARC AND A HOLLOW CATHODE

Trace elements	Detection limits, g		Trace elements	Detection limits, g	
	Arc excitation	Hollow cathode excitation		Arc excitation	Hollow cathode excitation
Ag	2.10^{-10}	1.10^{-13}	Ga	2.10^{-10}	6.10^{-12}
Ãl	–	2.10^{-11}	Ge	8.10^{-10}	–
As	2.10^{-8}	2.10^{-9}	In	4.10^{-10}	1.10^{-11}
Au	1.10^{-9}	2.10^{-11}	Mg	–	3.10^{-12}
B	2.10^{-8}	5.10^{-11}	Mn	2.10^{-10}	4.10^{-12}
Ba	2.10^{-9}	–	Ni	2.10^{-9}	1.10^{-10}
Be	2.10^{-10}	2.10^{-12}	P	–	6.10^{-10}
Bi	6.10^{-10}	2.10^{-11}	Pb	1.10^{-9}	1.10^{-10}
Ca	–	6.10^{-10}	Pt	1.10^{-8}	–
Cd	2.10^{-10}	1.10^{-11}	Sb	4.10^{-9}	1.10^{-10}
Co	1.10^{-9}	5.10^{-11}	Sn	1.10^{-9}	3.10^{-11}
Cr	2.10^{-9}	2.10^{-10}	Te	1.10^{-8}	–
Cu	2.10^{-10}	1.10^{-12}	Tl	1.10^{-9}	4.10^{-11}
Fe	–	4.10^{-12}	Zn	2.10^{-10}	4.10^{-11}

TABLE 6 DETECTION LIMITS OF TRACE ELEMENTS (%) IN SOME SEMICONDUCTOR MATERIALS DETERMINED BY AAS

Trace element	Ga	Sn	In	As
Ag	2.10^{-8} [x]	2.10^{-6}	$(0.8-5).10^{-8}$ [x]	2.10^{-6}
Al	2.10^{-6}	–	$(1-5).10^{-6}$ [x]	9.10^{-6} [x]
As	5.10^{-7}	–	–	–
Ba	2.10^{-6}	6.10^{-5}	2.10^{-6}	–
Bi	2.10^{-7} [x]	–	$(0.7-5).10^{-7}$ [x]	–
Be	5.10^{-8}	3.10^{-7}	5.10^{-8}	–
Ca	4.10^{-5} [x]	2.10^{-5} [x]	$(1-5).10^{-5}$ [x]	3.10^{-4} [x]
Cd	2.10^{-9}	3.10^{-7}	$(1-3).10^{-8}$ [x]	5.10^{-7}
Co	2.10^{-7}	5.10^{-6}	2.10^{-7}	5.10^{-6}
Cr	4.10^{-8} [x]	1.10^{-6}	$(1-3).10^{-7}$ [x]	1.10^{-6}
Cu	1.10^{-7} [x]	$2.5.10^{-6}$	$(0.4-1).10^{-6}$	2.10^{-6}
Eu	1.10^{-6}	–	1.10^{-6}	–
Fe	–	6.10^{-6}	–	9.10^{-6} [x]
In	1.10^{-7}	–	–	–
Hg	–	1.10^{-6}	1.10^{-6}	–
Li	6.10^{-8}	–	6.10^{-8}	2.10^{-6}
Mg	4.10^{-6} [x]	5.10^{-6} [x]	$(6-9).10^{-6}$ [x]	5.10^{-6} [x]
Mn	1.10^{-7} [x]	1.10^{-6}	$(4-9).10^{-7}$ [x]	8.10^{-7}
Ni	4.10^{-6} [x]	7.10^{-6}	$(5-9).10^{-7}$ [x]	7.10^{-6}
Pb	1.10^{-7} [x]	–	$(5-9).10^{-7}$ [x]	4.10^{-6}
Sc	2.10^{-6}	–	2.10^{-6}	–
Sr	2.10^{-7}	5.10^{-6}	2.10^{-7}	6.10^{-6}
Y	3.10^{-6}	1.10^{-5}	3.10^{-6}	–
Yb	4.10^{-8}	2.10^{-6}	4.10^{-8}	–
Zn	9.10^{-6} [x]	–	$(0.8-3).10^{-5}$ [x]	5.10^{-6}

[x]The detection limit is limited by the blank value.

direct atomic absorption analysis of a solid sample is difficult due to com-
plications in preparing an adequate reference sample and the reaction of the
sample with the atomizer material(most often, atomizers are made of graphite).
Besides, it is necessary to account for the mutual interferring effect of
the main and minor components present in the sample. That is why in atomic
absorption analysis the sample of semiconductor is generally dissolved and
chemical preconcentration of trace impurities is carried out. To determine
the elements that form volatile hydrides (As, Sb, Sn, etc.), the trace ele-
ments to be detected are converted into gases by reacting with sodium tetra-
borohydride. This technique enables L_Q of the above mentioned elements to
be lowered to $10^{-7} - 10^{-8}$ % by mass (ref. 11,12).

The detection limits that can be attained in atomic absorption analysis
of some semiconductor materials are tabulated in Table 6.

SPARK SOURCE MASS SPECTROMETRY (SSMS)

Spark source mass spectrometry enables very small amounts (1-1000 ppb) of at
least 60 to 70 elements to be determined, the sample being about 10 mg.
Analysis can be carrierd out without reference samples, using a matrix ele-
ment as an internal standard. The contents of trace elements are determined
to an accuracy of the relative sensitivity coefficients (RSC). There are
sufficient reasons to consider that the RSC of an element is independent of
its concentration and the RSC of different elements differ in most cases by
no more than a factor of 5. The development of SSMS over the past 25-30
years has widened the scope of this technique. Modern instruments have large
mass resolving powers (this enables the detection limits of magnesium,
silicon, and sulfur to be lowered). They are equipped with a device for auto-
matic maintenance of spark gap, and an electrometering spectra registration
system.

The users have proposed a number of modifications which, unfortunately, have
not yet found their way into commercial devices. Here, we would like to
mention additional devices for ion source pumping systems (ref. 13,14),
which enable the layer-by-layer analysis technique to be developed for the
determination of carbon, nitrogen, and oxygen, the detection limit being
$10^{-5} - 10^{-6}$ %. Procedures for layer-by-layer analysis have been published
(ref. 15-17). Computer-aided procedures of processing photoregistered mass
spectra are being developed (ref. 18,19), which significantly reduce analysis
times and slightly raise the reproducibility of results. Reviews of earlier
works on SSMS can be found in (ref. 20, 21); and more recent developments in
(ref. 22,23).

TABLE 7 RESULTS OF SPARK SOURCE MASS SPECTROMETRIC ANALYSIS OF GALLIUM
PHOSPHIDE CRYSTAL, PPM (< CORRESPONDS TO THE DETECTION LIMIT)

Ag < 0.06	Cu < 0.05	La < 0.04	Pt < 0.2	Ti < 0.02
Al < 0.006	Dy < 0.2	Lu < 0.07	Rb < 0.03	Te < 0.1
Au < 0.06	Er < 0.1	Mg < 0.004	Re < 0.1	Tl < 0.09
B < 0.03	Eu < 0.1	Mn < 0.01	Rh < 0.03	
Ba < 0.3	F < 0.002	Mo < 0.1	Ru < 0.1	Tm < 0.05
Bi < 0.06	Fe < 0.03	N < 0.03	S < 0.2	U < 0.2
Br < 0.05	Gd < 0.2	Na < 0.004	Sb < 0.07	V < 0.02
C < 0.2	Ge < 0.1	Nb < 0.3	Sc < 0.04	W < 0.2
Ca < 0.01	Hf < 0.2	Nd < 0.2	Se < 0.05	Y < 0.02
Cd < 0.1	Hg < 0.3	Ni < 0.02	Si < 0.03	Yb < 0.2
Ce < 0.7	Ho < 0.08	O < 0.5	Sm < 0.2	Zn < 0.03
Cl < 0.03	I < 0.04	Os < 0.1	Sn < 0.09	Zr < 0.05
Co < 0.01	In < 0.04	Pb < 0.1	Sr < 0.03	
Cr < 0.01	Ir < 0.09	Pd < 0.1	Ta < 0.1	
Cs < 0.03	K < 0.08	Pr < 0.05	Tb < 0.07	
			Th < 0.2	

SSMS is primarily employed for the survey analysis of semiconductors. An example of such an analysis is given in Table 7 (ref. 24). The results obtained without reference samples should be regarded as approximations and semiquantitative results. These data can have independent significance, but for solving the majority of problems it is advisable to use SSMS in combination with other techniques. Thus, in studying the relationship between concentration of free electrons in gallium arsenide and the alloying elements (tin) content, the RSC for thin was determined in samples containing about 10^{18} at. cm^{-3} tin (ref. 25). An absolute chemical technique was employed to determine these concentrations. Taking advantage of the fact that the RSC is independent of concentration, the samples with concentrations up to 10^{14} at/cm^{-3} were then analysed with an accuracy of $\pm$ 30 %. The survey analysis data have revealed that the effect of all electrically active impurities, excepting tin, can be neglected.

Two problems present themselves in estimating the reliability of mass spectrometric survey analysis data.

1. Any views on RSC variation boundaries are subjective, as well as the expression "in the majority of cases" which appears in the statement of these boundaries. The experiment (see, for example (ref. 26)) reveals that relative sensitivities depend not only on the physico-chemical properties of the trace and matrix elements, but also on the analysis conditions. The correlation obtained by Verlinden et al. (ref. 27) between the melting point of the matrix and the consumption of substance in the analysis indicates with sufficient certainty that a major part of the sample is consumed in the liquid phase. The additions to RSC due to selective evaporation from the liquid phase depend on the operation mode of the spark-gap converter, geometry of the spark gap, dimensions of electrodes, etc. The available values of RSC and the empirical formulas to calculate them can be used only for estimating how experimental data tend to deviate from actual contents of impurities in a sample,but not for quantitative analysis.

2. SSMS analysis results are in general not free from deviations caused by the sample surface impurities and also by the constructing material and the impurities of parts that surround the sample. The procedures involving the use of spark source mass spectrometry for semiconductor materials analysis should include surface cleaning of the sample after it is installed in the ion source and coating of screens with matrix material by preliminary sparking. Nonetheless, the result "less than ..." seems to be more reliable than "equal to ...".

Even with the use of a gap adjustment device it is difficult to ensure sufficiently stable ion currents in the analysis of semiconductors. This prolongs the analysis, worsens reproducibility, and creates additional difficulties in organizing check and blank experiments. Absence of a suitable control significantly lowers the value of determinations made with SSMS.

Further developments of SSMS analysis of semiconductors will probably continue with automation and unification of analysis techniques. As applied to geological samples, preliminary chemical preparation of a sample and the application of the method of standard addition or the isotope dilution method (ref. 28) enable a relative error of determination (5-10 %) to be obtained in a routine analysis; analogous results can apparently be attained in SSMS analysis of semiconductors. Possibly, mixing of a sample with graphite powder is not the best variant of the technique when used in the analysis of semiconductor materials. However, encouraging results have now been obtained by probe analysis (ref. 29). In a sufficiently intense and stable ion current the concentrates can be analysed by "frozen drop" (ref. 30) or "thin layer" methods (ref. 31,32).

In the last few years much interest has been shown in other ion sources, particularly in laser sources, for mass spectrometric analysis of high purity substances. Ensuring almost similar detection limits as SSMS, laser mass spectrometry offers, apparently, a means of attaining better accuracy of results in the absence of reference samples (ref. 33,34).

          NEUTRON ACTIVATION ANALYSIS (NAA)

With the advent of gamma and X-ray radiation semiconductor detectors the possibilities of neutron activation analysis of semiconductors, without

TABLE 8   NECESSARY PURIFICATION FACTORS $(F)^x$ WHICH ACCOUNT FOR PURIFICATION OF DETERMINABLE ELEMENTS FROM THOSE INTERFERING WITH NAA OF SEMICONDUCTOR MATERIALS (m = 1 g, FLUX 2.10^{13} n/cm^2 sec, t_{irrad} = 24 h, t_{cool} = 10 h)

Analysed material	F of ratio nuclei formed from the matrix by (n,γ) reactions	F of daughter radio nuclei	F of radio nuclei formed by first order reaction	F of radio nuclei formed by second order reaction
Si	^{31}Si, 10^6	–	–	^{32}P, 10^6
Ga	^{72}Ga, 10^{11}	–	^{69}Zn, 10^5	^{71}Ge, 10^4
Ge	^{75}Ge, 10^9	^{77}As, 10^7	^{69}Zn, 10^4	^{72}Ga, 10^3
	–	–	^{72}Ga, 10^5	^{76}As, 10^4
As	^{76}As, 10^{10}	–	^{72}Ga, 10^5	–
	–	–	^{75}Ge, 10^5	–
Se	^{75}Se, 10^7	^{83}Br, 10^8	^{77}Ge, 10^6	^{76}As, 10^2
	–	–	^{76}As, 10^5	^{82}Br, 10^4
Cd	^{115}Cd, 10^7	^{117}In, 10^9	^{111m}Pd, 10^3	^{116m}In, 10^4
	–	^{115m}I, 10^9	^{112}Ag, 10^4	–
Te	^{123m}Te, 10^8	^{131}I, 10^8	^{128}Sb, 10^3	^{128}I, 10^4
Sb	^{122}Sb, 10^{10}	–	^{123}Sn, 10^2	^{123}Te, 10^2
Hg	^{197}Hg, 10^{10}	–	^{197}Pt, 10^3	^{198}Au, 10^5
	–	–	^{199}Au, 10^3	–

^{x} $F = A_o/A_m$, where A_o is the interfering radionuclide activity stored during irradation of 1 g sample under indicated conditions, A_m is the maximal permissible interfering activity, 10 pulses/sec.

radiochemical separation of elements, have dramatically increased. In a number of cases it is possible to determine at least 35-40 elements by instrumental NAA techniques.

Among the materials which are of interest in semiconductor technology, only silicon can be analysed by instrumental NAA with high sensitivity. Instrumental analysis of germanium, gallium and arsenic involves prolonged holding (50-100 days) of the sample after irradiation, and resulting in a 10-100 fold increase in the detection limits. To obtain low detection limits it is necessary to isolate the matrix and all radioactive nuclei which are formed from matrix elements by nuclear transformations (radioactive decay, consecutive and parallel interfering nuclear reactions of the first and second order). These are the elements located in the periodic table in the neighborhood of the matrix elements. Table 8 contains necessary purification factors (F) accounting for purification of determinable elements from those interferring with NAA of semiconductor materials. From these data it is evident that the values of F appear to be greater by several orders of magnitude than the purification factors that account for the removal of interferring matrix elements, the latter factors being necessary in atomic emission, atomic absorption, and other techniques of analysis. Also it is essential to separate those trace elements whose isotopic activities exceed by 3-4 times those of other radioactive nuclei. For LQ to be minimum in neutron activation analysis, the activity of interferring radioactive nuclei must not exceed 10 pulses/sec.

The studies dedicated to neutron activation analysis of semiconductor materials are reviewed in Table 9.

TABLE 9

NEUTRON ACTIVATION METHODS OF ANALYSING SEMICONDUCTING MATERIALS AND THEIR PARENT COMPONENTS

Sample weight g	Irradiation conditions		Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
	time, h	flux, $n/cm^2 s$				
1	2	3	4		5	6
			Silicon			
0.1	10	1.10^{13}	In, P	10^{-5}	Nondestructive determination	/35/
			Cu, Ga, Sb	10^{-6}		
			As, Au	10^{-7}		
0.5	20	1.10^{13}	K,	10^{-5}	Nondestructive determination	/36/
			Cu, Na, Sb	10^{-6}		
			Au, Ir	10^{-7}		
1	20-100	1.10^{13}	Fe	10^{-5}	Nondestructive determination	/37/
			Zn	5.10^{-6}		
			Cr, Mo	5.10^{-7}		
			Na, Cu, Co, Ta, Ga	5.10^{-8}		
			As, Sb	2.10^{-9}		
			Sc, Au	7.10^{-10}		
1	50	1.10^{13}	21 elements are determined with detection limits	$10^{-5}-10^{-7}$	Impurities are separated by a combination of precipitation, distillation,	/38/
1	100	1.10^{13}	P	10^{-6}	chromatography, and	/39/
			As, Ga	10^{-7}	extraction techniques	
1	100	4.10^{13}	38 elements are determined with detection limits	$10^{-5}-10^{-8}$	Nondestructive determination of impurities with optimiza-	/40/
1	20	2.10^{13}	Fe, Sr, Rb, Zr, Gd, Tb		tion of spectro-	/41/
			Dy, Ho, Tm, Te, Nd, Sn	10^{-5}	metric measurements	
			K, Zn, Se, Mo, Ru	10^{-6}	and the cooling time	
			Pd, Ag, Ce, Yb, Lu, Cu,			
			Pt, Cr, Co, As, Cd, Sb,			
			Cs	10^{-7}		
			Sm, Eu, Hf, Ta, W	10^{-8}		
			Na, Mn, Ga, La, Re, Ir			
			Au, Sc,	$10^{-9}-10^{-10}$		
0.5	20	2.10^{13}	S, Br	10^{-6}	Determinable impurities are extraction separated	/42/
			P, Cl, I	10^{-8}		
			Germanium			
0.3	6x24	10^{12}	In, Ni	10^{-5}	Determinable elements are separated by precipitation methods	/43/
			Cu, Sb	10^{-6}		
			As	10^{-7}		
0.5	13x24	10^{14}	Ag, Cr, Se, Zn, In, Ta	10^{-6}	Nondestructive determination after holding for 100 days	/44/
			Co, Hf, Sb, Sc	10^{-7}		
			Ir	10^{-8}		
0.5	20-100	$n.10^{13}$	Ni	$n.10^{-5}$	Large part of germanium is separated by distillation; the remaining impurities are extraction chromatographically separated	/45/
			Cr, Co, Zr	$n.10^{-7}$		
			Mn, Cu	$n.10^{-9}$		

TABLE 9 (continued)

Sample weight g	Irradiation conditions		Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
	time, h	flux, n/cm^2 s				
1	2	3	4		5	6
1.5	100	$n.10^{13}$	22 elements are determined with detection limits	$10^{-4}-10^{-6}$	Nondestructive determination after holding for 130 days	/46/
0.1	20	$n.10^{13}$	S,Br	$n.10^{-6}$	Determinable impurities are extraction separated	/47/
			Cl,I,P	$n.10^{-8}$		
0.2	20	$n.10^{13}$	Fe,Sr,Ce,Te,Rb	10^{-5}	The maxtrix and the products formed from it are separated from determinable impurities in an extraction chromatographic column with CCl_4 as stationary phase. Aqueous phase 9M HCl+0.03M KI	/48/
			K,Zn,Se,Mo,Ru,Ag			
			Cs,Hf,Cr	10^{-6}		
			Co,Mn,Sb,Eu,W	10^{-7}		
			Na,Sc,La,Re,Ir	10^{-8}		
			Gallium			
0.1	40	5.10^{12}	Te,Sn,Fe,Pt,Ni	10^{-5}	Determinable elements are isolated by a combination of extraction and chromatography techniques	/49/
			Zn,Cr,In,Co,Ta,			
			Se,Hg	10^{-6}		
			Sb,Au	10^{-7}		
0.1	10	10^{13}	Sn	10^{-5}	Gallium is separated by extraction. Impurities are separated individually by ion-exchange chromatography	/50/
			Co,Te	10^{-6}		
			As,Zn,In,Cu	10^{-7}		
0.1	20	10^{13}	Cr,Dy,Tb,Zr,Gd,Nd		Gallium is separated from impurities in an extraction chromatographic column containing chlorex (2,2'-dichlorodiethyl ether)as stationary phase (9M HCl)	/51/
			Pd	10^{-5}		
			K,Ag,Cd,Ce,Eu,Ho,			
			Lu,Mn	10^{-6}		
			Mo,Rb,Ru,Se,Tm,Yb,			
			Zn	10^{-7}		
			As,Co,Cs,Hf,La,Sm,			
			Ta	10^{-8}		
			Na,Sc,Re,Ir	10^{-9}		
			Gallium arsenide			
0.2	20	8.10^{12}	Se	10^{-4}	Individual impurities, in radiochemical pure form, are separated by precipitation	/52/
			Sb,Te	10^{-6}		
			Cu	10^{-7}		
			Au	10^{-8}		
0.5	100	6.10^{12}	Fe,Se,Te,Sn,Ni	10^{-4}	Determinable impurities are separated by precipitation,distillation, and ion-exchange methods after cooling the samples for 5 days	/53/
			Ta,In,Zn,Ag,Cr,Hg	10^{-5}		
			Sb,Sc,Co	10^{-6}		
			Ir,Au	10^{-7}		
0.5	20-100	2.10^{13}	Ni	10^{-6}	Isolation of determinable impurities from the matrix and their segregation into groups are effected in extraction chromatographic columns	/54/
			Mn,Cu,Co,Cr,Zn	10^{-8}		

TABLE 9 (continued)

Sample weight g	Irradiation conditions		Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
	time, h	flux, n/cm^2 s				
1	2	3	4		5	6
1	20	1.10^{13}	Co,Sb,Zn,Ni,Se,Cr	10^{-6}	Substoichiometric	/55/
			Sc,Ta,Hg,Ir	10^{-7}	isolation of impurities is carried out	
0.1	200	2.10^{13}	Te	10^{-4}	After holding for 20	/56/
			Fe,Ta,Zn,Ag,Zr,In	10^{-5}	days arsenic is distilled	
			Sn,Co,Cr	10^{-6}	off and the impurities	
			Sc,In	10^{-7}	are determined gamma spectrometrically	
0.1	10	2.10^{13}	Te	10^{-4}	Arsenic is distilled	/57/
			Ni,Cr,Zr,Ba,Sr	10^{-5}	off as bromide;gallium	
			Mn,Cs,Ta,Cd,Ag,		is extraction separated	
			Zn,In,Pd,K	10^{-6}	using chlorex^x;impuri-	
			Co,Cu,W,Hf,Sc	10^{-7}	ties are segregated into	
			Na,Eu,Au,Ir	10^{-8}	groups convenient for scintillation gamma spectrometry,employing subsequent extraction technique	

Arsenic

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
0.2	20	8.10^{12}	Te,Zn	10^{-6}	Impurities are isolated	/52/
			Cu,	10^{-7}	by classical precipitation techniques	
0.1	10	2.10^{13}	Fe	10^{-5}	Impurities are extrac-	/58/
			Ga,Sb,Au	10^{-8}	tion isolated with chlorex^x	

Selenium

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
0.1	10	1.10^{13}	Ca	10^{-5}	Impurities are iso-	/59/
			Te,Ni	10^{-6}	lated by precipita-	
			Ag,Cd,Co,Cr,Ga,In	10^{-7}	tion and ion-exchange chromatography methods	
0.1	100	1.10^{13}	Ni,Te,Tl	10^{-7}	In 7 days after irradia-	/60/
			Co	10^{-8}	tion the impurities are isolated by distillation, extraction,and precipitation	
0.1	70	1.10^{13}	Fe	10^{-5}	From impurities,sele-	/61/
			K,W,Zn	10^{-6}	nium is isolated by	
			Ag,Cr,Cu,Ga,Na,Sc	10^{-7}	distillation and the	
			Au,Cd,Co	10^{-8}	gamma-spectrum of the residue is measured	
0.1	10	1.10^{13}	K,Te,Sn,Pt	10^{-5}	Subsequent extractions	/62/
			Cd,Zn,Pd	10^{-6}	are employed to isolate	
			Ag,W,Re,In,Sb,As,		determinable elements	
			Ga	10^{-7}	into groups convenient	
			Ir,Au	10^{-8}	for scintillation spectrometry	

Cadmium

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
1	180	4.10^{13}	Au	10^{-9}	Electrodeposition before irradiation	/63/
1.5	20 min	8.10^{13}	In	10^{-8}	Substoichiometric extraction is employed to isolate In as diethyldithiocarbamate	/64/

TABLE 9 (continued)

Sample weight g	Irradiation conditions		Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
	time, h	flux, n/cm^2 s				
1	2	3	4		5	6
1	20	$5 \cdot 10^{12}$	Cu,Mn,Co	10^{-7}	Impurities are separated by a combination of precipitation, ion-exchange, and substoichiometric extraction techniques	/65/
			Au	10^{-8}		

Tellurium

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
0.01	0.5	$2 \cdot 10^{13}$	Sb	10^{-7}	Nondestructive determination	/66/
1	100	$7 \cdot 10^{12}$	Ni,Ca	10^{-5}	After separating the matrix by repeated precipitation the impurities are isolated using distillation, precipitation, and chromatography techniques	/59/
			Ag,Cd,Co,Cr,Ga,In	10^{-6}		
			As,Au,Sb,Cu	10^{-7}		
0.5	40	$2 \cdot 10^{13}$	Fe,Gd	10^{-5}	Au and Pd are extracted with organic sulfides, and then the matrix is extracted from 1M HCl+0.5M KI with monothiobenzoic acid	/67/
			Ag,Ce,Cr,Dy,Ho,Lu, Mo,Sr,Pd,Ru,Zn,Tb, Tm,Yb	10^{-6}		
			Co,Cs,K,La,Mn,Rb, Ta,W	10^{-7}		
			Au,Eu,Hf,Ir,Na,Re, Sc,Sm	10^{-8}		

Antimony

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
0.2	20-200	$1 \cdot 10^{13}$	Ni	10^{-5}	Separation of matrix and isolation of impurities are effected by extraction chromatographic technique	/68/
			Cr,Zn,Co	10^{-7}		
			Mn,Cu	10^{-8}		
0.2	20	$1 \cdot 10^{13}$	Zn,Ag,Hg	10^{-7}	Separation of matrix and isolation of impurities are effected with subsequent extractions with isopropyl ether,tridodecyl amine, thionyltrifluoroacetate, and TBP	/69/
			Sc,Co,Th	10^{-8}		
0.1	20	$1 \cdot 10^{13}$	Sn,Te	10^{-6}	Extraction with chlorex[x] and chromatographic separation	/70/
			Zn,Cu,Co,As,In	10^{-7}		
0.5	20	$1 \cdot 10^{13}$	Cr,Dy,Gd,Nd,Pd, Tb,Zr	10^{-5}	Matrix is separated in extraction chromatographic column containing chlorex[x] as stationary phase (aqueous phase 9M HCl)	/51/
			K,Mn,Se,Zn,Mo,Ru, Rb,Ag,Ce,Ho,Lu,Tm, Yb	10^{-6}		
			Co,As,Cs,Cd,Eu,Hf, La,Sm,Ta	10^{-7}		
			Na,Sc,Re,Ir	10^{-8}-10^{-9}		

Mercury

Sample weight g	time, h	flux, n/cm^2 s	Determined impurities and detection limits, % mass		Brief characteristics of the method used	Reference
0.5	20	$1 \cdot 10^{13}$	Fe,Se,Rb,Tb,Dy,Ho, Tm,Yb	10^{-5}	Matrix is extracted from 0.03M HNO_3+KI with dioctylsulfide	
			K,Zn,Sr,Mo,Ru,Ag, Ce,Nd,Lu	10^{-6}		
			Mn,Cr,Co,Cd,Hf,Ta	10^{-7}		
			Na,Sm,Ga,La,Eu,W Re,Ir	10^{-8}-10^{-9}		

[x] 2,2'-Dichlorodiethyl ether.

ELECTROCHEMICAL TECHNIQUES

Stripping voltametry proves to be quite effective for the determination of one or a small number of trace elements in semiconductors. This technique is successfully employed to determine sulfur, selenium, tellurium, and several other important impurities. High sensitivity and simple instrumentation are the advantages of this method. Lowering of L_Q encourages concentration of determinable elements on electrodes, keeps track of mutual effects of elements in concentrates, and promotes the use of modern electric devices (ref. 71-73).

PHOTOMETRIC AND LUMINESCENCE METHODS

These techniques are employed to determine those impurities which do not go into the group concentrate during atomic emission analysis with chemical pretreatment, or the impurities are determined by this method with inadequate sensitivity. They are also used in studying the behaviour of individual trace elements in the course of industrial purification of materials (ref. 74,75).

Often the nonmetal impurities, such as phosphorous and arsenic, are determined by photometric techniques involving the formation of reduced heteropolyacids. The "amplication" technique, that is the determination of phosphorous and arsenic from molybdenum associated with it in a heteropolycomplex (P(As):Mo-1:12), involves a decrease of about one order in the limit of determination (L_Q).

Photometric and luminescence methods ensure sufficiently low detection limits for the determination of the common impurity elements (iron, aluminum, etc.). Accuracy of the results of analysis carried out without standard reference samples is an added advantage of these methods. This is because, in the indicated instances, conditions can be created for individual chemical preparation of a sample for analysis with minimum number of operations and reagents.

GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

The frequency of the use of process gaseous atmospheres -- silicon tetrachloride, germanium tetrachloride, silane, trichlorosilane, arsine, phosphine, etc. -- in the manufacture of semiconductor materials has increased in the last few years. Gases can be readily refined and are less contaminated during the production process. Gas chromatography, mass spectrometry, and GCMS are applied for the determination of organic and inorganic impurities in process gases of the semiconductors industry (ref. 76).

In some cases these methods are employed also to determine the impurities that are separated in the gaseous phase from solid samples (ref. 77).

METHODS OF DETERMINING GAS-FORMING IMPURITIES

An essential aspect of the analysis of semiconductor materials is the influence of gas-forming impurities (oxygen, hydrogen, nitrogen, and carbon) which arise from the environment and which contribute to the surface contamination as well as the magnitude of the blank. The detection and removal of surface contaminants are therefore of paramount importance in the determination of low levels of the gas forming impurities. To accomplish this use is made of a combination of analytical techniques. Nuclear and high-temperature vacuum extraction methods appear to be the most promising.

The main advantage of nuclear methods is that surface contamination can be completely eliminated by their removal after irradiation of the sample. The gases absorbed from the atmosphere are non-radioactive and therefore do not affect the analysis results. Nuclear methods used to determine gas-forming impurities in semiconductors take advantage of differences in both the type of radiation employed and the monitored nuclear reaction products (ref. 78-81).

Fast neutrons used for rapid determination of oxygen and nitrogen, the lower limits of determination being 10^{-4} - 10^{-5} % mass, have found wide application in analytical practice. Deuterons can be employed to determine up to

TABLE 10 CHARACTERISTICS OF NUCLEAR TECHNIQUES FOR DETERMINING
          GAS-FORMING IMPURITIES

Element determined	Material analysed	Irradiating particle (energy)	Method of determination	c_1, % mass
oxygen	Al, Si	^{3}He (10 MeV)	instrumental	10^{-6}-10^{-7}
carbon	Al, Si, SiC, GaAs, InSb	^{3}He (10 MeV)	radiochemical isolation	10^{-6}-10^{-7}
nitrogen	Al, Si	protons (6.5-10 MeV)	instrumental	10^{-6}-10^{-7}
	Al, Si, SiC, GaP	protons (6.5-10 MeV)	radiochemical isolation	10^{-6}-10^{-7}

10^{-4} - 10^{-6} % oxygen and carbon. Nitrogen with L_Q of 10^{-8} % by mass can be determined using protons while ^{3}He ions are utilized for the determination of up 10^{-7} % oxygen and carbon. Bremsstrahlung of linear accelerators or microtrons (with an energy of 25-30 MeV) are employed for the determination of oxygen, carbon, and nitrogen (L_Q = 10^{-5} - 10^{-6} %). Procedures involving the use of ^{3}He and proton ion activation have been developed and are applied to the determination of oxygen, carbon, and nitrogen; more than 30 different materials can be analyzed by proton activation techniques (Table 10). To eliminate any probable influence of other sample constituents on the analysis results, a universal technique has been developed for the separation and purification of analytical isotopes. This method involves the distillation of volatile compounds bearing these isotopes. With some modification in the distilled gas purification system, this technique can be applied to all of the materials listed in Table 10 (ref. 81).

Vacuum extraction is a traditional method of determining gases in metals. In the last few years it is being replaced by extraction in a current of inert gas. This is due instrumentation improvements. However, vacuum extraction offers certain advantages in the analysis of high-purity substances, particularly semiconductors (small blank deviations, high rate of extraction, and the possibility of using a very sensitive mass spectrometer).

Carbon is usually determined by burning a sample in a current of oxygen. When used to analyse semiconductors, this technique has serious limitations associated with surface contamination of the sample and large blank deviations caused by carbon in ceramic crucibles and in oxygen. A new variant of vacuum extraction -- oxidative melting in vacuum -- is therefore applied for the determination of carbon (L_Q = n.10^{-6} % mass) (ref. 82).

Significant difficulties are encountered in performing reduction vacuum-melting in graphite crucibles for the determination of nitrogen. This may be attributed to the formation of a graphite-rich film on the melt surface. To obviate the harmful effect of graphite, use may be made of "neutral" vacuum melting, in which nitrogen is extracted from a melt in the absence of appreciable amounts of oxygen and carbon (ref. 82).

A high-purity graphite crucible was employed for the determination of oxygen but reduction of surface contaminations with oxygen was a major difficulty. With this in mind, methane was allowed to react directly at high temperature with surface oxides in the charging device prior to analysis (ref. 83). For this, the surface had to be cleaned of oxygen and protected against repeated contamination with residual gases of the vacuum system. Cleaning can be effected in deep vacuum, a labor intensive process which demands sophisticated equipment. This is why cleaning and graphite coating of the surface were carried out simultaneously by thermal decomposition of methane. The attained value of L_Q was 1.10^{-5} % mass.

TRACE ANALYSIS OF ESSENTIAL SEMICONDUCTOR MATERIALS

The first problem of semiconductor material analysis is the determination of these trace impurity and dopant elements which have the most influence to the properties of the material. Such elements for the most important semiconductor materials are listed in the Table 11.

TABLE 11 ELECTRICAL BEHAVIOUR OF ELEMENTS IN SEMICONDUCTORS

Semiconductor	Neutral impurities	Donors	Acceptors	Deep levels created impurities	Amphoteric impurities
Silicon	H,N,C,Ge,Sn,Pb, inert gases	P,As,Sb, Li	B,Al,Ga, In	Cu,Au,Zn Mn,Fe,S	-
Germanium	H,N,C,Ge,Sn,Pb, inert gases	P,As,Sb, Li	B,Al,Ga, In	Cu,Ag,Au, Zn,Cd,Mn, Ni,Fe,S, Se,Te	-
Gallium phosphide	H,N,B,Al,In,As, Sb	Si,Te,Sn, S,Se,Ge	Be,Mg,Zn, Cd,C,Cu	O,Co,Fe, Cr,Mn	Si,Sn, (up to 10^{18} cm^{-3} - donor)
Gallium arsenide	H,N,B,Al,In,P, Sb	Si,Te,Sn, S,Se,Ge	Zn,Cd,Be, Li	Cr,Fe,V, O,Ni,Mn, Ag,Au	Si,Ge, Mg (up to 10^{18} cm^{-3})- donor
Indium phosphide	H,N,B,Al,As,Sb, Ga	Sn,Ge, Te,S,Se	Zn,Cd, Be,Cu,Mg	Cr,Fe,V O,Ni,Mn, Ag,Au	-
Indium arsenide	H,N,B,Al,P,Sb, Ga	Cu,Si,Ge, Sn,S,Se, Te	Mg,Zn, Cd	Cr,Fe,V, O,Ni,Mn Ag,Au	-
Indium antimonide	H,N,B,Al,P,As, Ga	Li,Sn,S, Se,Te	Cu,Mg, Zn,Cd, Si,Ge Mn	Cr,Fe,V, O,Ni,Mn, Ag,Au	-

SILICON is a widely used and most important semiconductor material. It is available in different grades (doped and undoped), and more attention is probably paid to the analytical control of silicon than to that of other semiconductor materials.

Silicon is a very suitable material for neutron activation analysis (ref. 36,38,40,84,85). It has a small activation cross-section; enabling the instrumental activation analysis of silicon to be performed for 40-45 impurities (with L_Q varying from 10^{-5} - to 10^{-10} % mass). Oxygen and carbon in silicon can be determined by the instrumental variant of the ^3He particle activation method ($L_Q = 10^{-7}$ % mass) (ref. 80,81). An atomic emission analysis method involving preconcentration of trace elements by distilling off the matrix as volatile silicon tetrafluoride, has been developed for the analysis of silicon. Semiconducting grade silicon is an ultra pure material and it is usually not possible to detect impurities, except gas-forming, some "domestic" (in particular iron), and dopant components, even by very sensitive methods. Ultratrace determination of boron has great significance in silicon analysis. This is achieved by atomic emission analysis ($L_Q = 10^{-7} - 10^{-8}$ % mass) (ref. 86).

GERMANIUM is also a high purity material and the sensitivity of available methods is inadequate for detecting impurities. Since it is activated more strongly than silicon, radiochemical separation of impurities is necessary for its NAA analysis (ref. 87). A special problem in the analysis of germanium is the determination of oxygen which has a decisive effect on the properties of the germanium used in nuclear radiation detectors. Oxygen in germanium is determined by charged-particle activation (ref. 80, 81).

GALLIUM ARSENIDE is so strongly activating that its activation analysis is practically impossible. Nevertheless, analysis procedures have been developed. Spark source mass spectrometry is the most universal method of analysis of gallium arsenide (as well as of other semiconductor compounds of the type $A^{III}B^V$ (ref. 88), it enables the total impurity composition (including oxygen and carbon) to be determined with $L_Q = 10^{-5} - 10^{-7}$ % mass. The sensitivity of atomic emission and atomic absorption techniques is usually sufficient for the analysis of raw and parent materials only.

The development level of the analytical chemistry of $A^{II}B^{VI}$ type <u>compounds</u> and <u>multicomponent solid semiconducting solutions</u> and their parent products lags behind the analytical chemistry of silicon, germanium, and $A^{III}B^{V}$ type compounds. These materials are volatile, often toxic, and have large neutron activation cross-sections. Their impurities are determined mainly by atomic emission spectrometry with preliminary chemical treatment (ref. 89,90). The values of L_Q attained for 10-15 impurities vary between 10^{-5} - 10^{-7} %. Practically no procedure has been developed for the determination of gaseous impurities in these materials, this problem is still awaiting solution.

The task of determining impurities in semiconducting materials is solved by complex utilization of the afore mentioned techniques.

FUTURE TRENDS

The development of the bulk trace analysis of semiconductor materials can be predicted in the following directions.

The task of ensuring sterile conditions for work with high purity substances will attain special significance. New specialized "clean" laboratories will be set up to minimize environmental contamination of the sample. It is expected that special equipment and non-contaminating sampling techniques will be developed. Much research work will have to be done to reduce contamination during sample preparation. These researches will most likely involve constructing high temperature analytical autoclaves, the use of modern materials for laboratory ware (high purity glass-carbon, ceramic materials, PTFE) careful refining of reagents and lowering their consumable mass, and developing non-contaminating techniques of sample handling.

In the preconcentration of trace elements an allowance must be made for the role of gas phase methods permitting minimum contamination. The conversion of determinable elements into gaseous halides, hydrides, oxides, and using modern determination techniques will enable the limit of determination of nonmetals and several metal impurities to be improved significantly. The role of highly sensitive methods of analysing process gaseous-atmospheres and determining unknown components that are extracted in the gas phase will grow. There is a good scope of work in the field GCMS. SSMS techniques will be improved by developing noncontaminating methods of preconcentration of trace impurities. Of great interest is the preconcentration effected directly in an ion source without the use of organic reagents.

In the activation analysis of semiconductor materials, use will be made of more powerful neutron sources, that is of nuclear reactors with fluxes 10^{14} - 10^{15} n.cm^{-2}s^{-1} compared the fluxes $(1-2) \cdot 10^{13}$ n.cm^{-2}s^{-1} often used at present. The application of new reactors will make possible the determination of several impurities by the existing separation techniques; the detection limits will be lower by 1-1.5 orders of magnitude than those attained now. In addition, charged particles and new nuclear reactions will find extensive application.

Atomic emission analysis techniques have much promise in the analysis of semiconductor materials. Maximum gain is expected in improving the spectral excitation techniques especially the increasing possibilities of hollow-discharge cathode and plasma sources.

The development of determination techniques for gas-forming elements will be directed at finding a procedure of analysing highly volatile and strongly activating materials, and also towards creating highly effective and readily available methods for the study of removal and surface contaminations.

Significant progress in the analysis of semiconductors is expected from laser spectrometry. Improvements in traditional (spectrophotometric and electrochemical) methods of analysing pure substances will be followed by the appearance of new analytical techniques. Research will continue for the development of new methods of analysis of semiconductor materials; these methods will be based on specific properties of the materials.

Estimates of the concentration of several impurities can be made from the concentration levels of other impurities, provided they are related. All types of analytical studies will be intimately concerned with the use of computers using information retrieval systems and spectral banks. The role of computers should also be extended to the construction of calibration

charts, keeping the analysis process parameters stable, and taking account of the effect of foreign elements on analysis results, etc.

Thus, the use of analytical methods in the study of semiconductor materials will increase. It is planned to create and develop a complex of the latest techniques involving the application of sophisticated electronic devices and a large number of device physical phenomena. It might be well to point out that the new techniques will have good quantifying parameters, but will still be complex, time consuming, and expensive. Therefore, the methods of analysing semiconductor materials will probably be limited to research work and the development of production processes, and will not be applied to routine quality control of semiconductors. For the latter purpose, recourse should be made to the measurement of service properties of the materials.

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