

SMC Bulletin

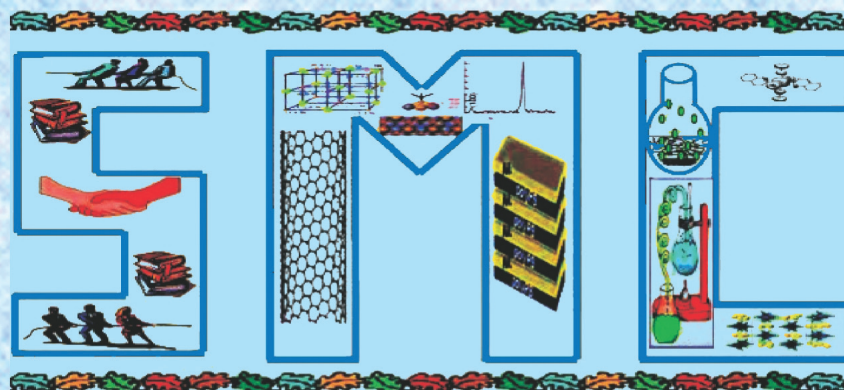
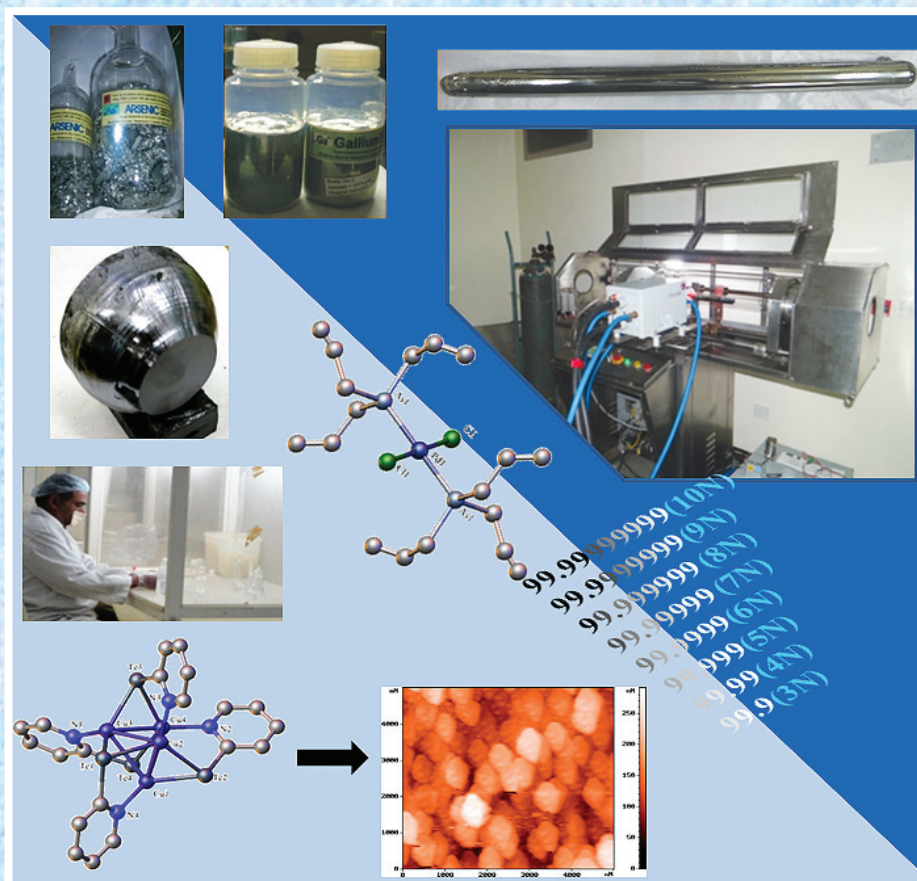
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Volume 6

No. 1

April 2015



SOCIETY FOR MATERIALS CHEMISTRY

Society for Materials Chemistry

Society for Materials Chemistry was mooted in 2007 with following aims and objectives:

- (a) to help the advancement, dissemination and application of the knowledge in the field of materials chemistry,
- (b) to promote active interaction among all material scientists, bodies, institutions and industries interested in achieving the advancement, dissemination and application of the knowledge of materials chemistry,
- (c) to disseminate information in the field of materials chemistry by publication of bulletins, reports, newsletters, journals.
- (d) to provide a common platform to young researchers and active scientists by arranging seminars, lectures, workshops, conferences on current research topics in the area of materials chemistry,
- (e) to provide financial and other assistance to needy deserving researchers for participation to present their work in symposia, conference, etc.
- (f) to provide an incentive by way of cash awards to researchers for best thesis, best paper published in journal/national/international conferences for the advancement of materials chemistry,
- (g) to undertake and execute all other acts as mentioned in the constitution of SMC.

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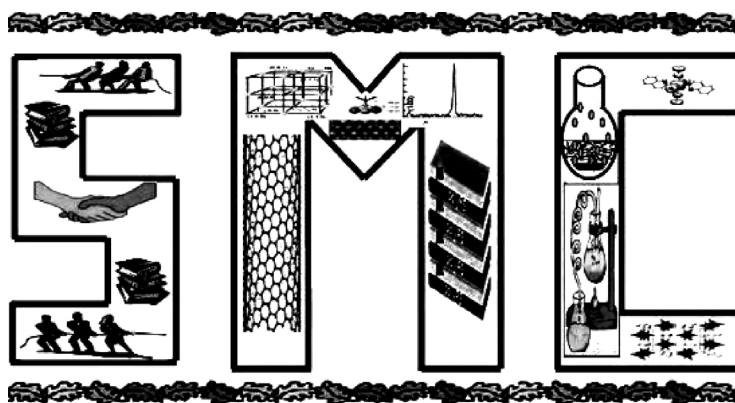
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About the Cover page graphic

The graphic is a collage showing (anticlockwise) general terminology used for indicating purity levels (bottom right); an indigenous zone refining unit extensively used for purification, zone refined germanium (9N) ingot, ultrapure gallium (7N) and arsenic (6N), gallium arsenide single crystal grown from gallium and arsenic; the next image shows special protocols observed for analysis and characterization of high purity materials; high purity organometallic compounds, e.g. $[(\text{CuTepyMe})_4]$ (bottom left) and $[\text{PdCl}_2\{\text{As}(\text{CH}_2\text{CH}=\text{CH}_2)_3\}_2]$ (centre image) used for the preparation of semiconductor materials.

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Guest Editorial



Vimal K. Jain

We are witnessing a major change in our society where high tech devices define our life style. This could be possible due to revolutionary changes in electronic and information technology which could be attributed to rapid progress in materials science. Continuous miniaturization and advancement of electronic devices have thrown new challenges on preparation and processing methods for required materials. Thus the need for high purity materials is inevitable and is dynamically growing with time.

Purity is perceived differently by different communities of scientists. The high purity materials have made a very high impact on technological advancements. Well known examples of applications of high purity materials are nuclear and semiconductor industries. Various materials have now been recognized as strategic materials for advanced technologies provided they are purified to desired levels in terms of either isotopic purity, phase purity or compositional purity.

Trace amounts of impurities significantly affect physical and chemical properties of a material. Compositional characterization of a material is usually referred to purity levels. The material can also be evaluated with respect to the property of interest and phase purity. There are a number of properties, such as optical, mechanical, electrical or magnetic, that are sensitive to the presence of trace amount of impurities in the base matrix.

As the sophistication, complexity and miniaturization of electronic devices is continuously increasing, material requirements are also changing. These changes have not only lead to produce materials with increasing purity, but also resulted in the development of new growth processes which require high purity Organometallic and metallo-organic compounds.

Purity evaluation of high purity materials is a challenging task. In most cases the typical range of ultra-high purity material is 6-7 N, implying a total impurity of the order of 100-1000 ppb in mass. Sophisticated analytical tools can now analyze up to ppb level of impurities. However evaluation of purity greater than 8 N requires special assessment tools.

The activity on high purity materials in India started in the Department of Atomic Energy. The need for high purity materials for strategic technologies was felt in early years, beginning with the preparation and purification of uranium and thorium compounds and the oxides of some transition elements (Nb, Zr, W, Ta). The work on high purity materials for semiconductors was taken up by the Chemistry Division, BARC after publication of Bhabha Committee's report on Electronic Commission of India in 1966. Since then preparation processes for several high purity materials have been developed and have been transferred for commercial production.

Keeping in view the growing demand of high purity materials, this theme based issue of SMC Bulletin on 'High Purity Materials' is timely publication. I am indebted to the Editorial Board of the Bulletin for inviting me to serve as the guest editor of this thematic issue. I would like to put on record my appreciation to all the contributors for agreeing to submit their work to this issue. I sincerely hope that reader will find this issue interesting and useful.

(Vimal K. Jain)
Guest Editor



From the desks of the President and Secretary



Dr. Sisir K Sarkar
President



Dr. P. A. Hassan
Secretary

Dear Fellow members and Readers,

Greetings from the Executive Council of SMC.

You may be aware UNESCO has adopted a resolution declaring 2015 to be the International Year of Light (IYL 2015). The importance of raising global awareness about how light-based technologies can promote sustainable development and provide solutions to global challenges in energy, education, agriculture, health care and security. Presently preparations are in full swing for organizing the third DAE-BRNS National Workshop on Materials Chemistry on Optical Materials, NWMC-2015 (OPT-MAT), during November 20-21, 2015, AERB Auditorium, Anushaktinagar, Mumbai. The focus of the Workshop is on the synthesis and characterization of different types of optical materials and how their properties can be utilized for various applications.

It is with great pleasure we present this thematic issue of the SMC Bulletin on "High Purity Materials", in line with our tradition of publishing articles in frontier areas of materials chemistry. Advancements in materials research and rapid growth of modern technology during the last decades have led to fascinating research towards preparation and characterization of ultra pure materials. High purity materials are extensively used in various applications ranging from consumer electronics, light emitting devices, fluorescent lightings, optics and lenses, solar energy conversion, superconductors, shape memory alloys, nuclear industry etc. The presence of even trace levels of impurities can have remarkable changes in the electronic and optical properties of materials and thus there is a pressing need to develop materials with precise chemical composition. Characterization of these materials has led to significant advancement in the analytical techniques for chemical and isotopic purity evaluation, setting up of ultra clean laboratories etc. The present issue is a blend of articles derived from the expertise and knowledge of both national and international experts. Our aspiration of making the SMC Bulletin truly international has been realized in this issue.

We would like to express our sincere thanks to the Guest Editor, Dr. V. K. Jain, Head, Chemistry Division and Vice President, SMC for sparing his valuable time. We sincerely thank all contributing authors for their keen interest and commitments to bring out this issue in time. Past developments and recent advances in the area of high purity materials such as purification methods, analytical tools, electrical characterization of semiconductor materials, pure metals for nuclear power, materials for radioisotope production, organometallic precursors for high purity semiconductors etc are discussed. We are certain that these articles will provide a deep insight in to this exciting and challenging topic and will serve as a useful resource material for young researchers.

Finally, we wish to express our gratitude to all members of SMC for their continued support and cooperation in the growth of the society.

Dr. Sisir K Sarkar
President

Dr. P. A. Hassan
Secretary

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High Purity Indigenous Materials

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Abstract

The term 'Purity' is relative. It has different meanings for food articles, drugs, pharmaceuticals, primary chemical standards, electronics and nuclear materials. In the beginning of 20th century there were only two categories of pure materials, viz., chemical and medicinal. Presently, there is a host of high purity materials with grades designated as semiconductor, nuclear, lasers, primary standards, ceramics, etc. The demands for ever-increasing purity stem for their use in sophisticated and high performance modern semiconductor and optical devices. This has generated and developed rapidly improved and refined methods for achieving purity of the order of 7N+. Simultaneously, the techniques for more sensitive and selective trace elemental analysis were evolved using in conjunction with lasers and other means of exciting samples. The serious thought to developing indigenous high purity materials came after 'Dr. Bhabha Committee Report' published in 1966, envisaging the requirements of ultra pure materials for the country. BARC with its available technical facilities initiated the task to undertake the ultra purification of materials for use as semiconductors, primary elements for compound semiconductors, dopants, capacitors, solders and for use in the nuclear industry. Classical chemical methods are inadequate to obtain such desired levels of purity and one has to combine several physico-chemical methods such as distillation, liquid/liquid extraction, ion-exchange, iodide, zone refining and solid state electromigration. BARC developed know-how for several ultra-pure materials, viz., Bi, Sb, Sn, Zn, Ag, Au, Pb, As, Ga, In, Zr, Ta, Se, Te, Ti, S, etc. on a laboratory scale and transferred this know-how to NFC, Hyderabad for industrial production. Description of these techniques as applied to various materials is included in this article along with the trace analytical assessment of the ultrapure materials.

1. Introduction

Chemical purity of the order of 99,999 + (5N+) and better is required in the fields of electronics, nuclear energy, aerospace and basic research. The stringent and ever-increasing purity materials' requirements have brought in a variety of improved and refined methods to deal with the demands. For achieving ultra purification, methods such as distillation (vacuum), ion-exchange, liquid/liquid extraction, electrodeposition (electrowinning), iodide, zone refining and solid state electro-migration, are used. At the same time, pervasive demand for assessing higher purity has generated and evolved techniques for more sensitive and selective trace analysis. This has been possible mainly by using in conjunction the advanced lasers and other means of exciting the samples.

The country's requirement of ultrapure materials for electronic industry was envisaged in Electronics Committee Report, Govt. of India, published in 1966. With the available infra-structure facilities within Chemistry Division, Bhabha Atomic Research Centre, (BARC) (earlier known as Atomic Energy Establishments Trombay, AEET) initiated, developed and successfully prepared high purity materials such as Sn, Sb, Bi, As, Se, S, P, Cd, Zn, Ag, In, Pb,

POCl₃ and BBr₃ on laboratory scale. Assemblies fabricated entirely from indigenously available materials and components were used. Upscaling the methods yielded the end products in kilogram quantities. The know-hows generated in the Chemistry Division were transferred to agencies outside, for the regular production of eighteen high purity materials. Assessment of purity (upto 5N+) at each and every stage of the endeavor was carried out by Analytical Chemistry and Spectroscopy Divisions, BARC.

2. Ultra-purification

Through ages, man has known the importance of separating and purifying the valuables from less-valuable in nature's mixtures. By now the art and techniques of separation and purification has assumed a central stage in materials science. Despite this the science and technology of ultra purification received a belated recognition and accorded an independent identity. Methods of ultra purification of materials are an outcome of the struggle that has gone in separation and isolation of marketable quantities of fissionable materials, fission products (isotopes) and materials used in semiconductor industry.

In the beginning of 20th century there were only two purity grades, viz. chemical and medicinal. Presently, we have a host of high purity materials with grades designated as per their specific use, such as semiconductors, nuclear energy, lasers, primary chemical calibration standards (volumetric, spectroscopic), ceramics, dielectrics, magnetics, alloys and intermetallics, composites, nanoparticles, etc.

Till the 16th century man worked with only seven metals, i.e. Ag, Au, Cu, Sn, Fe, Pb and Hg. During the next 3 centuries about a dozen of metals like Sb, Zn, Bi, Cu, Ni, W, Al, etc. were added to the list, which has tripled during the last century. The early slowness in isolation of metals was not due to the lack of knowledge about the some reactive metals but also their scarcity in nature where they bind tightly to their compounds such as oxides, chlorides, etc. Efforts to recover such metals from their ores seemed impossible as these would almost instantly react with air or the container. Perhaps the key development which eventually uncovered their metallic nature was by employing the fused salts electrolysis, developed by Humphry David in 1807, when he obtained globules of K and Na metals. Later, the method was applied to metals such as Ca, Mg, Sr, and Ba. Since then this method has proved very successful for preparing high purity reactive and refractory metals also. Isolation of aluminum from

bauxite was reported in 1886 (by Charles Hall, who applied the method to obtain from a bath of Cryolite, Na₃AlF₆. The attractive physical properties of newly isolated Al at that time made Al costlier than Ag. The earliest work reported on any ultra purification was carried out by Richards about the turn of 19th century, when he could distil silver to fix exact atomic weight for Ag. The method by ion-exchangers to achieve purification was developed by Adams and Leighton Holms in 1935. In fact, the use of ion-exchangers played a significant role in the discovery and identification of actinide elements.

The presence of impurities even as traces, may affect properties, such as physical, optical, magnetic, resistance to oxidation, catalytic, etc. For instant, presence of even 10 ppm of B in Si increases its electrical conductivity by 1000 times, metals such as Cr, W, V, Zr etc. are very ductile when pure, Fe whiskers grown from vapour phase have extra-ordinary tensile strength (1.5x10⁵ kg/cm²) never observed earlier, presence of even 1 ppb (1 part per billion) in SiO₂ (used for fibre optic) results in substantial loss in transmission, 'soft-errors' result in spurious signals due to α-particles emanating from U and Th, present as traces (<20 ppb) in sputters Si and Al employed for fabrication of VLSIC's and the presence of 100 ppb of Ni or Fe drastically mars the electroluminescence efficiency of ZnS phosphor.

Table 1. Trace Contaminations

Percent %	ppm parts per million (1 in 10 ⁶ parts)	ppb parts per billion (1 in 10 ⁹ parts)	ppt parts er trillion (1 in 10 ¹² parts)	Equivalents	Major
10 (10 ¹)					1N
1 (10 ⁰)	10000				2N
0.1(10 ⁻¹)	1000			mg/g; mg/ml; mg/cc; g/l; g/kg	3N
0.01(10 ⁻²)	100				4N
0.001(10 ⁻³)	10	10000			5N
0.0001(10 ⁻⁴)	1	1000		µg/g; µg/ml; µg/ cc; mg/l; mg/kg	6N
0.00001(10 ⁻⁵)	0.1	100			7N
0.000001(10 ⁻⁶)	0.01	10	10000		8N
0.0000001(10 ⁻⁷)	0.001	1	1000	ng/g ;ng/ml; ng/ cc; µg/l; µg/kg	9N
0.00000001(10 ⁻⁸)	0.0001	0.1	100		10N
0.000000001(10 ⁻⁹)	0.00001	0.01	10		11N
0.0000000001(10 ⁻¹⁰)		0.001	1	pg/g;pg/ml; pg/ cc; ng/l; ng/kg	12N

centi 10⁻² parts per hundred
 milli 10⁻³ parts per thousand
 micro 10⁻⁶ parts per million (ppm)

nano 10⁻⁹ parts per billion (ppb)
 pico 10⁻¹² parts per trillion (ppt)
 femto 10⁻¹⁵ parts per quadrillion (ppq)

Interestingly, single crystal of Ni metal, free from chemical and physical imperfections, has catalytic activity 1000 times more than the other faces and single crystal of Cu metal exhibits corrosion behavior 5 times more than other faces. Also presence of every 100 ppm of Hf (opaque material for neutrons) in nuclear grade Zr reduces its neutron transparency by 3%. Even the semiconductor transistor invented and developed by William Schokley, John Bardeen and W.H. Brattain of Bell Telephone Laboratory in 1947, ironically, worked on addition of uniformly distributed dopant of concentration < 0.3 ppm in ultrapure Ge. These instances perhaps suggest having an appropriate definition for a pure material which can be put as, 'that does not contain impurities of such nature and extent as to interfere with its end use'.

This article deals with purification methods employed for achieving high purity for materials. Apart from general descriptive ultra purification, pioneering work carried out within the Department of Atomic Energy for obtaining electronic grade materials is also included.

The presence of trace impurities in a substance may be designated by expressions used for various impurity levels

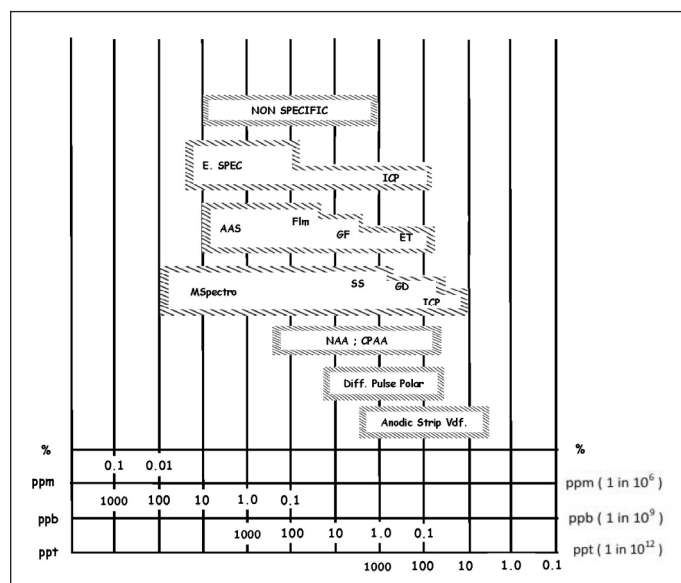


Figure-1. Detection Limits (Generalized)

(Table 1). However, here all the figures are worked out on weight to weight (w/w) basis. For the trace impurities analysis in a substance, it is imperative to have knowledge of degree of purity that is necessary and the acceptable limits of various impurities in the end-use material. A passing reference is made to the modern and advanced analytical techniques employed for trace analysis and their general detection limits are indicated in Figure-1. The important techniques are emission spectroscopy (ES), mass

spectrometry (MS), atomic absorption spectroscopy (AAS), nuclear activation analysis and non-specific method of determining electrical resistance ratio (RR) at room (298K) and liquid helium temperature (4.2K).

3. Ultra-purification methods

Different types of impurities can be categorized into chemical (chemical imperfections) and physical (physical imperfections) impurities. Chemical imperfections are the foreign substances present as interstitials or substitutionals or solid solutions in the base material. Because of their small size the interstitials such as H, N, O and C, are difficult to remove and special efforts are required for their removal to obtain base material in high purity. New concepts and methodologies are evolving and more efficient processes are being developed for producing special high purity materials.

The sources for impurities are of two types, (a) natural and (b) anthropogenic (human ineptness). Natural impurities refer to ones occurring in nature's sources. The second source of impurities are due to human ineptness such as using improper chemicals and gases, contact materials (containers, crucibles, etc.), equipments, environments, storage, etc. Recently the term 'chemically aseptic' is employed for a 'clean room facility' required essentially for both ultrapurification preparation and ultra trace assessment working areas. Extreme care for handling is required to be exercised, is evident from the example given next. In the previous century, one of the most investigated, assessed and thoroughly studied samples was that of 'Lunar Rock' brought back to earth by the astronauts of Apollo 11 mission. The analysis indicated the presence of indium, which in elementary form was used as a gasket material for the sample holder for the lunar rock. Needless to say, that the operations carried out during a scheme to obtain ultra-pure material, the integrity of the samples must be maintained.

There is no royal road to achieve ultrapurification of material. Physico-chemical processes utilize the difference in chemical, physical and electrochemical behaviour of concerned impurities present in the host and refined products. In the periodic table, no element is so unique that no other element will response similarly to a given treatment.

Preparation of ultrapure materials, though seem simple, envisages having a basic knowledge of origin, type and extent of impurities in the starting material (normally a commercial grade) then working out schemes for purifications which may warrant combining or multistaging processes such as distillation, ion-exchange, liq/liq solvent

extraction, electrowinning (electrodeposition), iodide method, zone melting and electromigration in solid state. Figure 2 shows concisely the phases involved during various ultrapurification processes.

4. Distillation

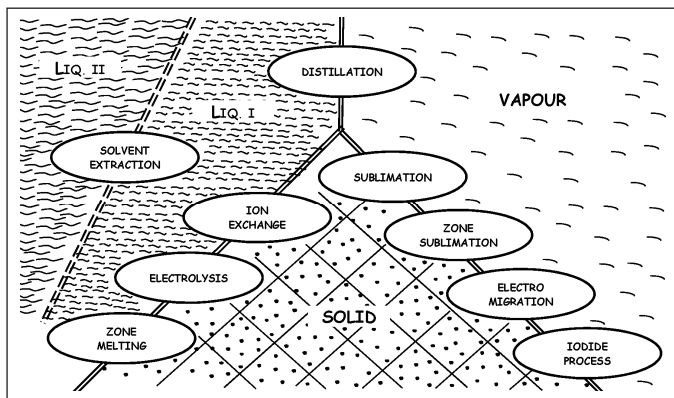


Figure 2. Phase Diagram during various ultrapurification processes

All operations involving evaporation of a substance, carrying away the vapour for condensation and separating the condensate are grouped under the general heading of 'distillation'^{1,2} which constitutes one of the most successful methods employed for ultrapurification. The processes like sublimation, fractionation (rectification), vacuum distillation and sub-boiling (non-ebulliative) all fall in this category. While, generally, rectification, sublimation and sub-boiling are employed to obtain intermediates or compounds, vacuum distillation is a preferred choice for metals and alloys to achieve purity of the order for 5N+. Rectification is useful for purifying intermediates such as GeCl_4 , SiHCl_3 , SbCl_5 , POCl_3 , BBr_3 , etc., while sublimation has proved very effective for compounds like As_2O_3 , SeO_2 , MoO_3 , etc. and sub-boiling for ultra high purity liquids such as acetone, HCl , HNO_3 , H_2SO_4 , H_2O , etc. However, with the advancement in membrane technology several of the rectification processes are being now replaced by membrane separation techniques. Vacuum distillation is applied particularly for metals which have appreciable (workable) vapour pressure at 1000°C. Elements like, As, Zn, Cd, Te, Sb, Bi, Mg, etc. have vapour pressure more than 10^{-3} atmosphere (0.76 torr) at 1000°C and are amenable to distillation at low pressures. A slight increase in temperature brings in a further range of metals that will volatilize and could be purified by vacuum distillation. A survey of vapor pressure (Figure 3), of metals plotted vs. temperature, would guide one and determine whether a metal is sufficiently volatile for distillation. The Figure 3, among other things, also indicates the metals that undergo sublimation. Also vapour pressures of the order 10 - 100

torr lead to successful distillation. The distillation rate, though has a bearings on the rate of evaporation, will depend also on the rate of transfer of vapour from the surface towards the condenser which, in turn, depends on the design parameters of the assembly (still). Till now we were dealing with the case of distillation of a single metal, which never happens. When it is intended to separate an impurity metal from a bulk of alloy (or solid solution) melt, the vapour in equilibrium with the host melt, has a composition of all vapours produced by constituents in the melt. This is governed by Raoult's law to hold for binary system, i.e. activities of the constituents vapour are proportional to their mole fractions in the melt. Purification through vacuum distillation gained prominence on account of availability of a wide variety of vacuum equipments with better operational vacuum, heating devices and more inert and stable refractories at high temperatures. Remember, every melting process is also a contamination step.

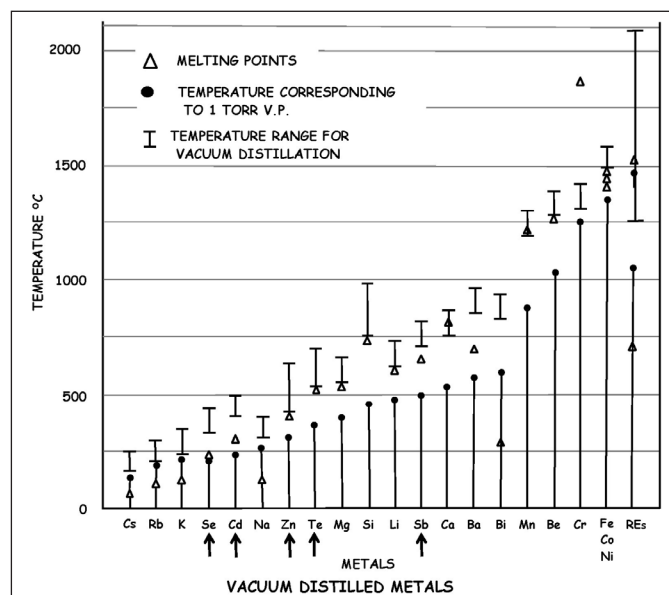


Figure 3. Vapor pressure of metals plotted vs. temperature

Related to vacuum distillation is another technique called pyrovacuum refining², which differs from the former in its application at elevated temperatures for removal of intestinal impurities such as H, O, N and C and other volatiles from reactive and refractory metals. During the application of pyrovacuum refining, the process of sacrificial oxidation may also take place which removes traces of oxygen by producing CO which volatilizes. The process also aids volatilization of low vapour pressure metals and removal of impurities by flotation.

5. Ion Exchange

Ion-exchanger is sparingly soluble organic or inorganic solid with active groups which can exchange for

ions present in a solution. The most commonly used ion-exchangers are organic type made from resins having large cross-linked molecular chains forming three-dimensional lattice which swells in water. Some of the most popular resins are the of styrene (Ph-CH=CH₂) and divinyl benzene [(Ph-CH=CH₂)₂] to which are attached active ionic groups such as sulphonic (-S \bar{O}_3 H⁺) or carboxyl (-C \bar{O} OH⁺) to form a counter ion with a cation or primary (-NH₂), secondary (=NH) or tertiary (\equiv N) amine group to form labile anion, respectively such as -NH₃⁺Cl⁻, =NH₂⁺Cl⁻ and \equiv NH⁺Cl⁻. Several other groups have been incorporated to enhance specificity and selectivity of the resin. Other organic ion-exchangers are made from cellulose or dextran which has applications largely in biochemistry. The exchange properties of ion-exchanger depend on nature and number of functional group, degree of ionization in solution and physical nature of cross-linking.

Separation by Ion-exchanger is brought about due to difference in charge and size of the ions (hydrated) present in solution. Normally ions are loaded on a resin column and then eluted with a dilute solution, called eluant, containing ions with which the resin was initially or originally charged before sorption. During elution the loaded zone having the least affinity for resin comes out first. Efficiency of separation may be enhanced by using eluant with complexing (chelating) properties. For example, an efficient resolution by employing the complexing agent EDTA (ethylene diamine tetra acetic acid) in eluant the separation of RE's is well known. It may be worth noting that during the study on separation of ⁹⁵Am and ⁹⁶Cm by ion-exchange Dowex 50 G.T. Seaborg et. al. encountered innumerable difficulties and tired they assigned names to ⁹⁵Am and ⁹⁶Cm as Pandemonium and Delirium, respectively. Later, separation of other actinide elements ⁹⁷Bk, ⁹⁸Cf, ⁹⁹Es, ¹⁰⁰Fm, ¹⁰¹Md, ¹⁰²No and ¹⁰³Lw also was effected by ion-exchangers. Dowex, Amberlite, Diaso, KU, Kastel, Duolit, etc. are commonly used ion-exchangers.

Zeolites or inorganic ion-exchangers, also known as molecular sieves, are not widely employed for ultrapurification work. Zeolites are hydrated alumino-silicates having Na⁺, K⁺, Mg²⁺, Sr²⁺ and Ba²⁺ cations. However, some of the selective separations may be cited. Their uniqueness stems from the combination of properties, viz. stability at higher temperature, workability at varied pH, withstanding high dose of radiation, higher loading by capacity and better selectivity. They have been successfully used for IonSiv IE-95 for ¹³⁷Cs and ⁹⁰Sr removal from the spillage that happened to occur at 3-Mile Island in 1978 and to contain the recent radio leaks from Fukushima

Dauch Nuclear plant by placing bags of zeolites near the plant and their reduction in the volume of heamodialyser from 100-300 litres to 1-3 litres by the use of zeolite loaded columns.

6. Liquid-liquid extraction

Liquid-liquid solvent extraction³ has been in the industrial separations since 1930 when it was applied as a method for removal of aromatics from kerosene fraction of the petroleum products. The process of liquid / liquid solvent extraction of a substance (to be purified) present in aqueous phase to an immiscible solvent (usually organic) is briefly discussed here. Since organics tend to be soluble in the organic phase, the metal ions or charged species, present in the aqueous phase, are first converted into an uncharged species to facilitate their dissolution into the organic phase. The uncharged species are formed either by ion-pair or by chelation. Formation of a viscous solid phase is prevented by addition of an appropriate diluents or modifiers.

Purification by 1/1 solvent extraction is based on the selective extraction of one or more constituents (species) from base element or impurity from aqueous solution into an organic solvent which is immiscible with water. Purification is possible when the distribution coefficient α , defined as C_{org}/C_{aq} (C_{org} and C_{aq} refer to the concentrations of a component in organic and aqueous phases respectively), has a value greater than unity. In case of two components, if ratio α_1 and α_2 are the distribution co-efficients for component 1 and component 2 respectively, their ration α_1/α_2 , denoted by β , determines the efficacy of separation of both components. The value of β depends on certain experimental factors such as solvent properties, concentration of extractable species in aqueous solution, pH of solution and working temperature. For enhanced extractability the species may be converted into a complexed species (uncharged) by a suitable complexing or chelating agent. In 1/1 solvent extraction mostly esters, ketones, alcohols, amines and hydrocarbons are employed as organic phase. Large scale operations are employed by industry because of the successful development of counter-current transfer and mixer-settlers which facilitate continuous handling of both the liquids and capability of multistaging. A diagrammatic sketch of counter-current 1/1 extraction is shown in Figure 4. Multi-staging with a continuous running operation proved successful and yielded high purity intermediates / compounds of U, Ta, RE's, Cd, Zn, Ga, Pb, Sb, Te, Ni, which on further treatment yielded high purity metals.

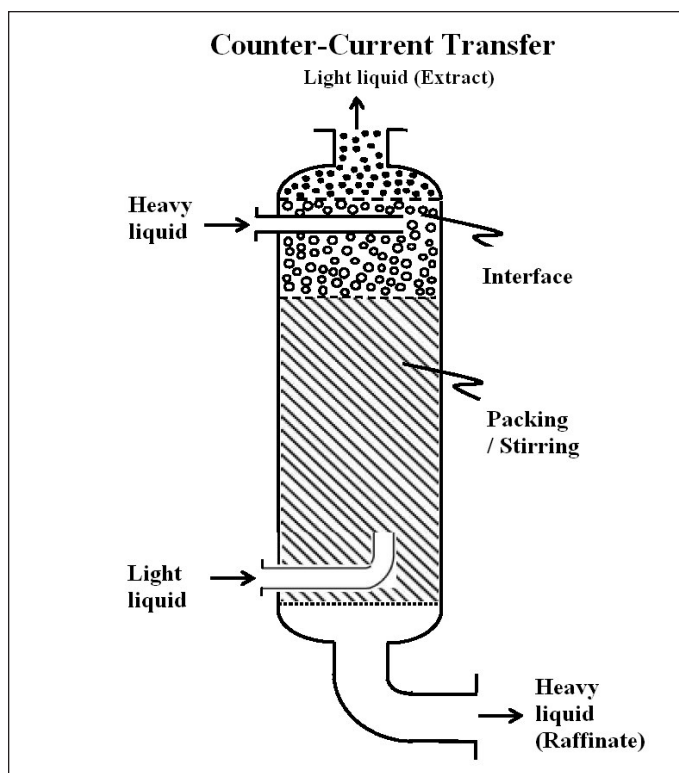


Figure 4. Counter-current l/l extraction

7. Electro-winning (electro-deposition)

The method was discovered by Humphry David in 1807, when he obtained metallic Na and K in the shape of globules by electrolysis from fused caustic soda and caustic potash, respectively. As on today, electrolytically purified metals are obtained by suitably choosing either an electro-winning techniques, i.e. cations in electrolyte are reduced at the cathode or an electro-deposition technique² (also known as electro-refining). In both the cases, however, the highly purified electrolyte is used which may either be aqueous or molten salt / salts solution. Electrodeposition² is carried out either with inactive materials like graphite, Pt, Hg, etc. or with active electrodes shaped out of basic metals as cathode while crude metal acts as an anode. Apart from the cathode potential other working parameters crucial for efficient operation are anode stability, additives for electrolyte, and the temperature of the bath and control of electric current. Although the process is slow, large quantities can be handled by increasing the cell dimensions and converting the operation running on continuous basis. Multistaging of the process is an added benefit for enhancing purity, Ultra high pure metals such as In, Sn, Ga, Cd, Te, Sb, V, Mn, Nb, Ta, Mo, Cr, etc., both on laboratory and commercial scales, have been successfully prepared, by this method.

8. Iodide Method

The iodide method was developed by Van Arkel-de Boer in 1925. It is also known as 'hot filament' method. This method essentially belongs to the methods by which the purification of a metal is brought about by thermal decomposition of chemical vapour^{4, 5} and has been extensively employed to obtain high purity metals such as Ti, Zr, Hf, V and other reactive and refractory metals. The method is based on the reversibility of reaction in a closed vessel, between crude elemental metal and I₂ (in principle any suitable halide can be used) which can be expressed by Eq-1. MI_{2n(g)} formed at temperature T₁ volatilizes to reach the hot filament at higher temperature T₂ and is thermally decomposed into pure metal and the elementary I₂ (Eq-2).



The pure metal deposited on incandescent filament, heated resistantly, is made from a compatible metal. The released I₂ vapour is recycled, i.e. it diffuses back to react with crude metal further to form fresh metal iodide and the process continues. The recycling capability of I₂ vapour has resulted in very interesting cases. For instant, with the initial charge of just 15 g I₂ high purity Cr metal deposit weighing upto 1 kg, has been successfully obtained in a static set-up. Yet, in another experimental set up run similarly, high purity Zr crystal bar, 15mm diam. and 45mm long was found deposited. Purification during the method takes place because of the following favourable conditions:

- formation of crude metal iodide vapour is manageable at temperature T₁,
- metal iodides are easier to decompose thermally than the corresponding bromides and chlorides.
- impurities in crude metal do not react with I₂ at T₁ and stay behind.
- melting point of metal in question is higher than the dissociation temperature T₂ of the iodide formed.
- iodides of impurities, if formed, at T₁ will not decompose at T₂
- some of the impurities are too volatile at T₂ and do not remain in the hot zone of the filament, and

- vapour pressure of metal at T_2 is low to facilitate its condensation.

The efficacy of the overall success depends on factors such as the type of metal, presence of impurities, their type and extent in crude metal and their tendency to form iodides at T_1 , metal and I_2 charges taken at the start of experiment and last but not the least the geometry of the vessel assembly.

9. Zone Refining

Purification by chemical method of recrystallization is either from a solution or from a melt. Because of the use of a second component, i.e. solvent, in the former, traces of the solvent tend to remain with the recrystallized product. This is not the case with recrystallization from a melt. Recrystallization of melt yields product of better purity. Zone refining⁶⁻¹¹ resembles fractional distillation and gas chromatography as it depends upon the redistribution of an impurity between two phases, liquid and solid in case of zone refining, and between liquid and vapour in both distillation and gas chromatography. Zone refining gained rapid prominence due to the pressing needs of ultra high purity materials for semiconductor industry.

Zone refining, developed by W. G. Pfann at Bell Telephone Laboratories (now Bell Laboratories) in 1957, was first applied for purification of germanium and he was able to reduce the impurities to a level of 1 part in 10^{10} parts of Ge that is 0.1 ppb, a degree of purity almost impossible to obtain by any other known method. Interestingly, it appeared on the scene shortly after the invention of transistor (1948) and revolutionized the entire electronics industry. Nearly 2/3 rd elements in the periodic table, numerous alloys, organic as well as inorganic compounds can be purified by zone refining. Pfann describes the tremendous credibility of zone refining by saying, 'if the two elements Ge and Si, had not been available in the desired purity, the whole development of solid state electronics would have crippled'.

9.1 Theory of Zone Refining

The technique can be best understood by considering a simple equilibrium phase diagram of a binary condensed system, i.e. when the pressure over the system is assumed to be constant (1 atmosphere). Let us consider for example a binary system forming a continuous series of solid solutions – complete miscibility of components in solid state (Figure 5). When a substance B (solute and here impurity) is added to another substance, the melting point M_A of pure A is lowered to a degree governed by the amount of B added. At any composition of A and B above the liquidus curve the mixture exists as a homogenous liquid; in area bound

by liquidus and solidus curves, liquid and solid co-exist, while below the solidus curve a homogenous solid (solid solution) would be present. With substance B (designated as impurity above) added to solvent A (which is in large excess), let us go on the left side of Figure 5. If we start with a homogenous melt C_L in the diagram and allow it to cool gradually till the point X at temperature T, a solid of composition Y will crystallize out of the melt and this has less of B. If now these isolated crystals of composition Y are melted, the corresponding melt composition will be X^1 which on solidification yields crystals of composition Y^1 which is purer than Y. Several repetition of process will yield crystals of pure A. However, the yielded crystals will be fraction of the quantities of A originally taken. Although the refining by recrystallisation from melt has long been understood, it needed Pfann's genius to devise this elegantly simple and powerful technique that too with least handling in between two successive steps of operation.

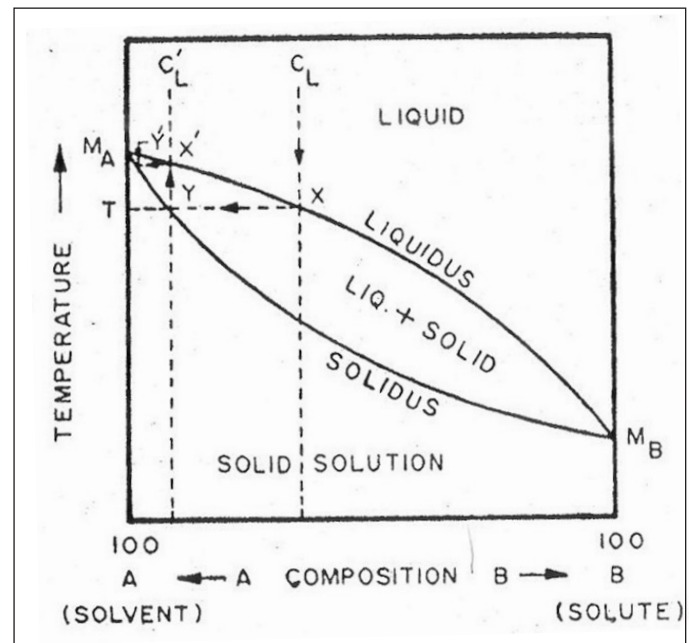


Figure 5. Phase diagram for a binary system forming continuous series of solid solutions

As mentioned earlier, the purification of a substance by zone refining depends on the difference in composition of crystallizing solid and the melt in contact. This difference does exist in majority of systems. The concentration of a solute (impurity) in growing crystal at any point of the phase diagram is obtained from the relation $k_0 = C_s/C_L$, where C_s and C_L being impurity concentrations in solid and the adjoining liquid respectively and k_0 is termed as equilibrium distribution coefficient. Under normal operating conditions of crystallization, equilibrium is not

attainable, hence another effective distribution coefficient, k , is used. The value of k is a critical property of solution – solvent – system and measures the efficacy of refining process. Farther the value of k from unity is, better will be the effective removal of solute on crystallization.

Let us distinguish here a process akin to zone refining known as normal freezing. Basically during zone refining a narrow molten zone is created in a long solid ingot of the charge and moving the molten zone through the ingot so that melting and solidification proceed simultaneously. The operation is repeated unidirectionally to enhance the refining. In case of normal freezing, taking a similar long solid ingot is first melted throughout its length and then allowed to freeze from one end to the other. While during normal freezing there is a presence of a single solid / liquid interface, in zone refining basically there are two solid / liquid interfaces (leaving both ends of the ingot). How distribution of an impurity, with $k < 1$, occurs after single operation of both the techniques i.e. curve A and curve B drawn respectively for normal freezing and zone refining. Figure 6 shows how an impurity with initial uniform concentration C_0 in a substance and k value (< 1) gets profiled along the ingot length L by single operation of these two techniques. For comparison sake, direction of solidification and the rate of freezing interface in both cases are kept identical. The basic difference in both the techniques, which gave a fillip to zone refining, is the cumulative refining brought by repetition (unidirectional

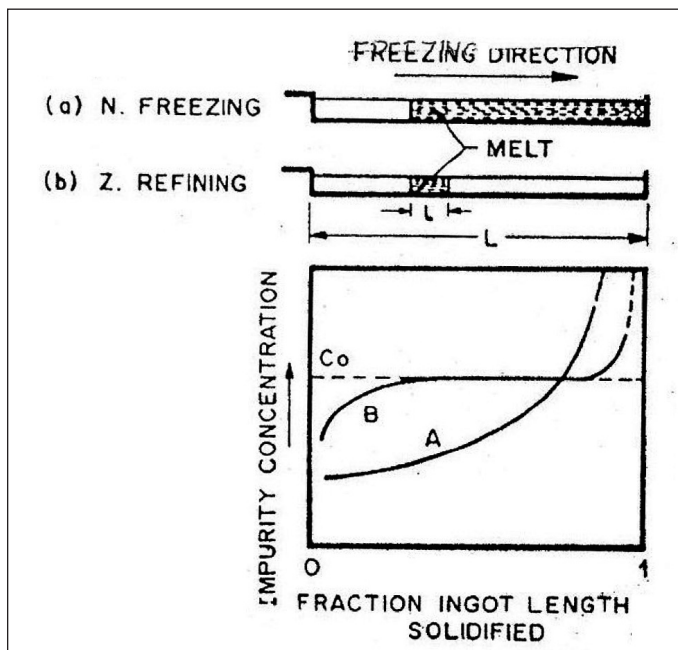


Figure 6. Redistribution of an impurity with an initial concentration C_0 and $k < 1$ along ingot length L after (A) normal freezing and (B) single molten zone (length l) pass.

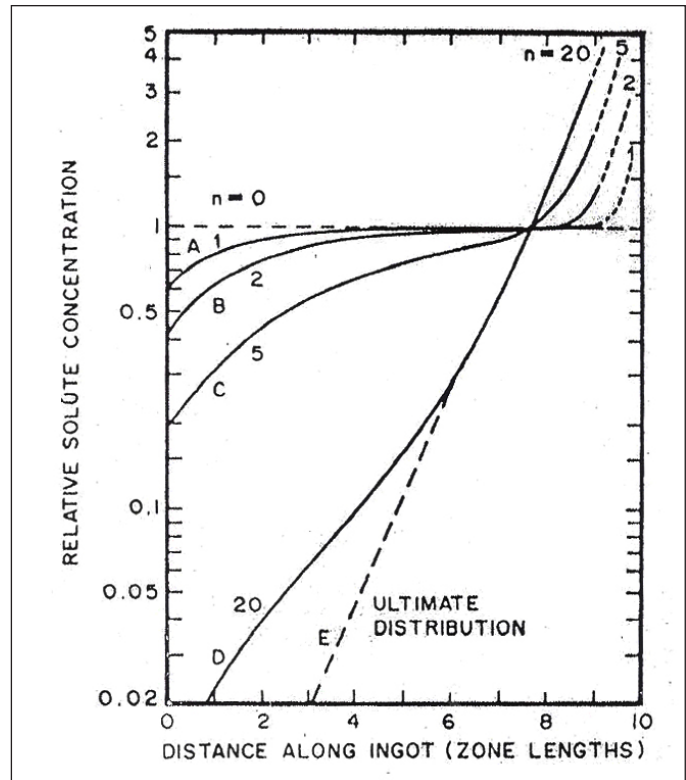


Figure 7. Distribution of solute after 1, 2, 5 and 20 passes of molten zone through an initially uniform ingot 10 zone length long ($k = 0.6$)

passage of molten zone) during zone refining. Figure 7 shows how an impurity segregates and accumulates as the number (n) of molten zone (length l) passes increases for a substance having initial concentration C_0 , $k = 0.6$, ingot length L ($L = 10l$). Curve E represents ultimate distribution of impurity, when a steady state is reached. The forward movement of the solute is balanced by an equal put opposite movement of the solute due to mixing action in the molten zone. The Fig.7 also shows that impurity accumulates at the last frozen end of the ingot of zone refined ingot. However, impurities may move opposite direction when the value of $k > 1$. When $k = 1$, obviously no segregation of impurity takes place.

9.2 Floating (crucible-less) zone refining

No description of zone refining is complete without the mention of vertical mode of the technique called floating zone melting¹²⁻¹⁵ or crucibleless zone refining. The technique was first developed by Keck and Golay for zone refining of elemental silicon because no suitable container material was available for molten silicon. Presently the technique is employed to refine about 75% of silicon commercially. In this technique the rod of silicon charge is held vertically with holders at top and at bottom ends of the rod and a narrow movable molten zone, produced by a suitable heating means such as radio frequency or electron

beam, is held in position by surface tension of the melt only. The intactness or stabilization of the floating zone length L (shown in Figure 8) is a crucial exercise of the operation as it depends on surface tension and the density of the melt. Fig.8 shows the stabilization of the melt length L for silicon and how the value is calculated for a rod of 25mm radius (π_0). The use of floating zone melting was extended for obtaining high purity refractory metals also.

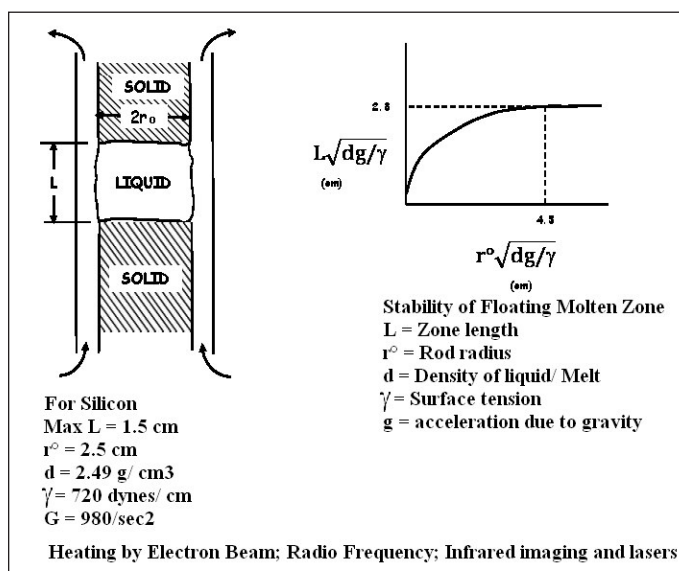


Figure 8. Floating zone melting

Radio frequency (induction) heated specimen to produce a stable floating molten zone may be possible at any pressure of inert gas, reducing or in vacuo. An added advantage of induction melting is increased stirring of the melt due to levitation of the melt. Operations carried out in vacuo have some additional merits such as volatilization and decarbonisation of impurities. Melting of charge for floating zone melting by electron beam (EBFZM) was first demonstrated by Calverley, et. al. which can produce very narrow molten zones is an asset for EBFZR.

Applications, in general, of zone refining are for materials which form stable melts, have manageable vapour pressures at melting points and are crystalline in nature. Electronic grade compounds such as GaP, GaAs, InP, CdTe, CdSe, etc. have been successfully purified by the technique of zone refining.

10. Solid state electro-migration or transport (SSE)

Solid state electromigration² or transport is another technique useful particularly in the removal of interstitial impurities such as H, O, N and C from refractory metals and has met with unprecedented success. It consists of passing direct current (at high current densities) through an ingot of metal at elevated temperatures, thus imparting

motion due to enhanced diffusion at elevated temperatures to the small interstitial atoms. It has a basic difference that the redistribution of impurities is taking place within one phase rather than partitioning between two phases (like zone refining). The apparatus comprises of a vacuum chamber, a mechanism to hold the specimen ingot, provision for high direct current supply and arrangement for adequate cooling of the electrical leads.

11. Purity assessment

Perhaps, the earliest reported trace analysis is that of arsenic by Gulzeit in 1879 when he detected it upto $10^{-5}\%$ (0.1 ppm) in certain pharmaceuticals using Marsh test developed in 1836. With the invention of semiconductor transistors (1947) there was a pervasive need to improve methods for complete and unambiguous analysis of vanishingly low trace levels impurities. Characterisation and assessment of ultra high purity materials have made strides in trace analysis methods employing in conjunction the lasers and other means of exciting samples. The improved and refined techniques have not only better sensitivity and selectivity but can also be carried out with specimen sample with quantity as low as nanogrammes.

Both analytical and spectroscopy techniques play a decisive role for any scheme undertaken for the task of achieving ultra-purity, as it is imperative to carry out the purity assessment of starting materials, intermediates and the final products. It is beneficial to have knowledge of degree of purity and the acceptable limits of various concerned impurities in the final product.

For routine quality control, the emission spectrometric² (ES) method is the key analytical tool. For assuring consistency one resorts to instrumental analysis such as atomic absorption spectrometry (AAS), with refinement as flame AAS (FAAS), graphite furnace AAS (GAAS) and electrothermal AAS (EAAS). Most of the commercially available AAS instruments offer facilities for solid analyte sample which in itself is as an asset for carrying out ultra trace analysis. Essentially, AAS is a one-element method and useful in the measurement of simultaneous detection of multi-elements (60 – 70 elements) and detection limit of 0.01 ppm to 0.1 ppm. Other methods for instrumental analysis are mass spectroscopy (MS) and its refined versions – inductively coupled plasma MS (ICP-MS) and high precision liquid chromatograph MS (HPLC-MS) as well as gas chromatography MS (GS-MS). Others, for ultra trace assessment, are neutron or particle activation analysis (N/PAA), differential pulse polarography and anodic stripping voltametry. Perhaps, the most convenient and rapid method of purity assessment for metals is indirect or non-specific method which envisages the determination

of electrical resistivity^{2,16,17} ratio (RR) measured at room temperature (298 K) and liquid helium temperature (4.2 K). General range of detection limits for various analytical instrumental techniques mentioned here are shown in Figure-1.

Results of purity assessment of a material may be reported either as major constituent (assaying) or as traces (impurities). Table 1 shows the designation as purity of a material in several forms. These figures have been worked out on weight / weight basis. However, there are other units of designating purity in a sample, like ppm (volume/ volume), ppm (weight/ volume) and ppm (atomic). Inter-conversion of one form into another form will appreciably change the value (number). For instance, 100 ppm (atomic) of B present in Si, when converted into ppm on weight/ weight basis will be around 200 ppm (w/w). Ethylene oxide (EO), used for sterilization of spices and for surgical parts, has a maximum permissible upper limit of 5 ppm (v/v) for exposure in the atmosphere, will be equivalent to 8 ppm when calculated on w/w basis.

The significance of having clean room also known as 'chemically aseptic', area, both for ultra purification and trace analysis work would mean taking extreme efforts to keep the sources of contamination away. These sources are shown in Figure-9. While mentioning the human ineptness it may be worthwhile to show Figure-10, which indicates the emission of 0.3µ or larger particles from each person per minute. An instant, which concerns the contamination source by storage, is that of lunar sample which was contaminated with indium because, being soft metal, it was used as a gasket for sealing the sample holder. Lastly, what all matters for successful achieving ultra high purity are shown in a nut-shell in Figure-11.

12. Indigenous work on ultra-purification

The programme to develop ultra-high purity materials in the country was initiated in the year 1966, when a serious thought was given to the preparation of various special materials for applications in the areas of electronics,

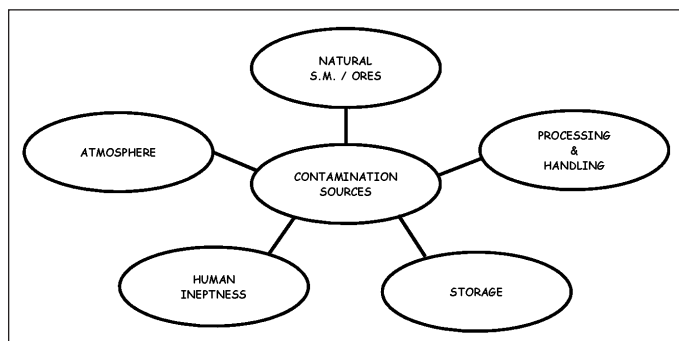


Figure- 9. Contamination Sources

PARTICLES 0.3 MICRON OR LARGER EMITTED FROM EACH PERSON PER MINUTE		
from skin, hair, dandruff, oral and nasal emissions		
	MOTIONLESS, SITTING OR STANDING	1,00,000
	MOTION OF HANDS, FOREARMS, NECK & HEAD	5,00,000
	MOTION OF HANDS, ARMS, TRUNK, NECK, HEAD & LOWER LEGS	10,00,000
	SITTING TO STANDING OR VICE VERSA	25,00,000
	WALKING 3.5 Km/hr	25,00,000
	WALKING 5.5 Km/hr	75,00,000
	WALKING 8.0 Km/hr	100,00,000 (ten million)

Figure-10: Emission of 0.3 micron particles from each person per minute

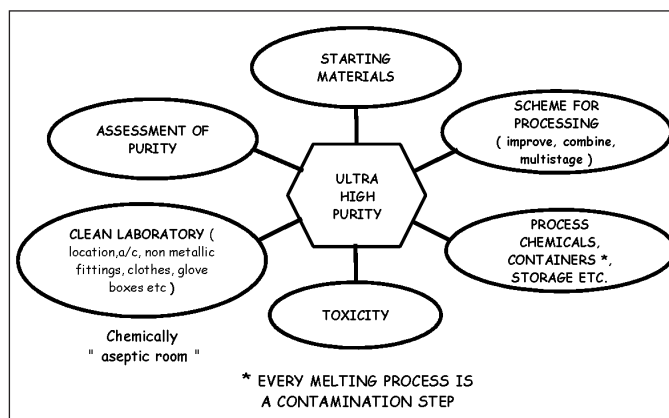


Figure-11. Requirements for achieving high purity

nuclear energy, aerospace, etc. The requirements of these materials was envisaged in the report 'Electronics in India', Government of India, 1966. Chemistry Division, BARC, was among the pioneering laboratories in the country where exploratory, development and production of these special materials on a laboratory scale was taken up. The task included, scrutinizing the availability of starting (crude) materials and fabrication of varied types of assemblies from the indigenously available materials and components.

12.1. Zone Refining

Among the assemblies designed, developed and fabricated for refining materials, the unit for zone refining proved extremely useful and effective^{18, 19, 20}. Figure-

12 shows the first indigenously fabricated horizontal automatic zone refining unit which had a capacity to refine 3 kg of metal per batch. The schematic drawing of movement mechanism of a proto-type horizontal automatic zone refining unit is shown in Figure-13, which was a forerunner for fabrication of several such units for use at NFC Hyderabad (Figure-14). Narrow molten zones moving steadily from one end to the other were produced by split type resistance heaters positioned on a trolley. The speed of moving molten zones could be varied between 20 mm–200mm/hr.

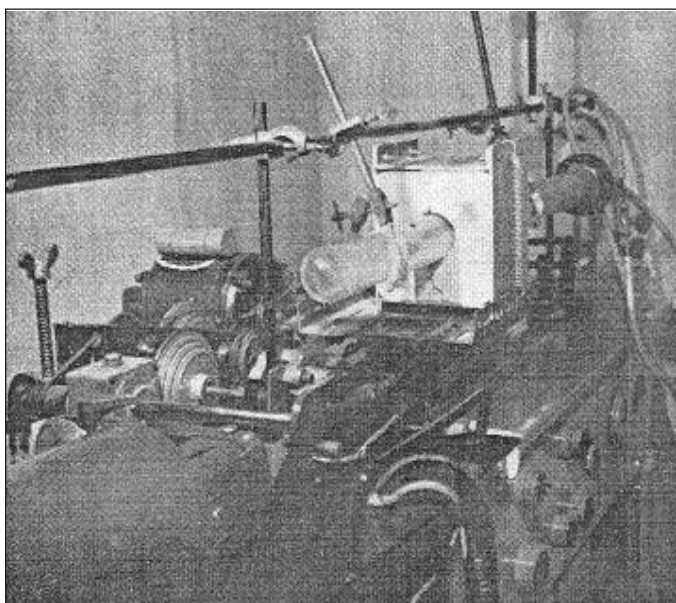


Figure-12. First indigenously fabricated horizontal automatic zone refining unit

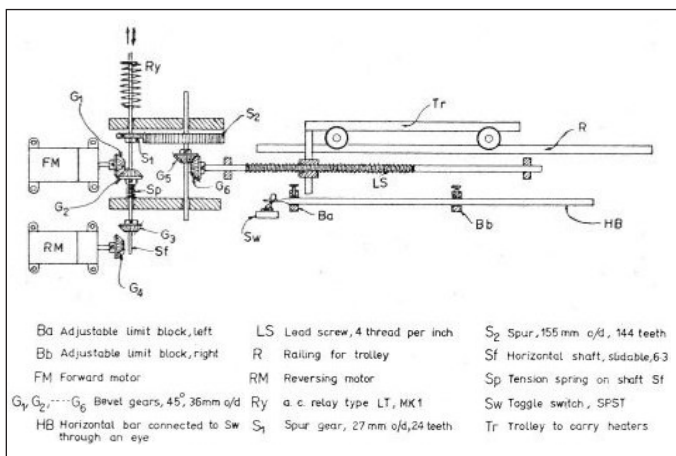


Figure-13. Driving and reversing mechanism for automatic zone melting unit.

The first useful application of the zone refiner was for ultra purification of elementary sulfur²¹ starting with 99.5% commercial grade sulfur, zone refining of pre-distilled

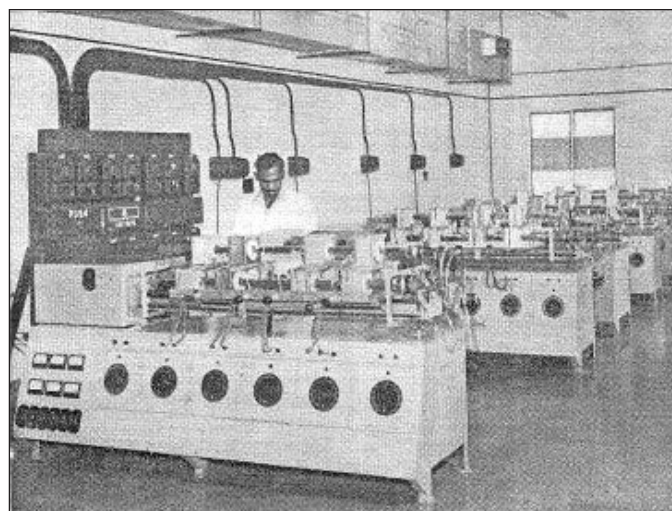


Figure-14. Multiple zone melting units for use at NFC Hyderabad

sulfur, yielded material of 99.99% purity. High purity sulfur was required as target material for preparation of radio-³²P and for synthesizing semiconductor compounds like CdS, PbS, ZnS, La₂O₂S₂, Cd₂O₂S, AgGaS₂ required for basic research.

Apart from successfully employing the zone refiners for the preparation of high purity metals such as Sb, Te, Ga, In, Cd, Zn, Pb, Bi and Se,^{22-27,28,29} the unit was employed also for ultrapurification of organic compounds, such as C-120 dye³⁸ (7-amino-4-methyl coumarin) resulting in enhancement of lasing efficiency and tetraphenyl germane [Ph₄Ge]³⁹ for radiation and photochemical studies.

12.2 Distillation

Work on vacuum distillation³⁰ was started for several metals such as Sb, Te, Cd, Zn, etc. using locally designed and assembled units. Figure-15 shows a typical high temperature distillation still fabricated out of 316 SS pipe welded to a sealable flange of appropriate dimensions. A graphite crucible was placed inside the vessel charged with the metal to be distilled. Another graphite crucible identical to the one used as container, but having a hole, was inverted over the former through collars, and served as a substrate for distillate. Thermocouples were placed for measuring vertical thermal profilers both inside and outside of the vessel. Heating was provided with an external resistance furnace. Pressures of the order of 30 - 300μ were maintained during distillation.

For distillation of sulfur (m.p. 132°C) under nitrogen²¹, an all-glass assembly was employed as shown in Figure-16. A special feature of the glass assembly was the collection of various distilled fractions of S in vertical glass capsules which were sealed for further refining using the automatic zone melter. The zone refined S was found extremely pure

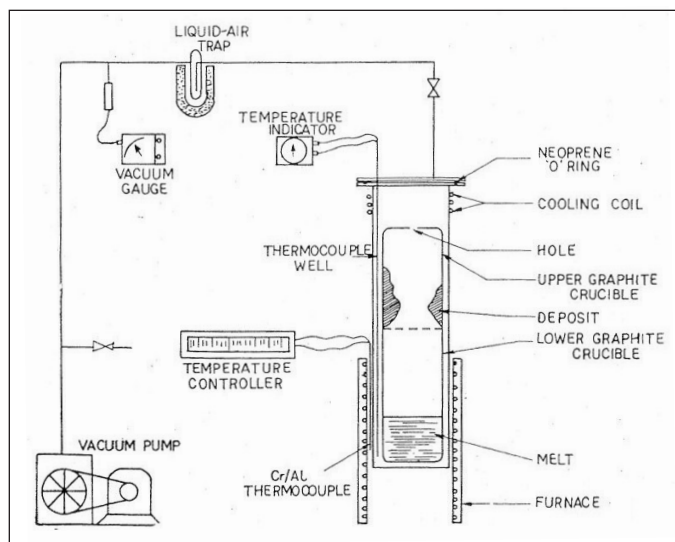


Figure-15. A typical high temperature distillation still

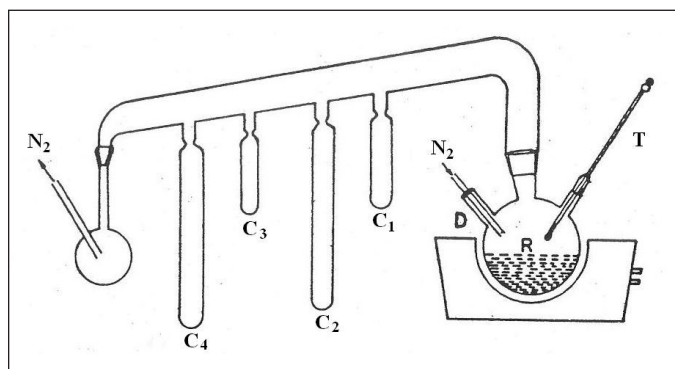


Figure-16. distillation assembly for sulfur purification

below their detection limits of Fe, Al, Ca, Mg, Mn, Cu, Ni, Pb, As, Ag, Te and C as confirmed by preconcentration spectrographic and neutron activation analysis methods

12.3 Electro-refining (electro-deposition / electro-winning)

Work on electro-refining was taken up for Ga, primarily in view of its potential recovery from indigenous Bayer's liquor, a bye-product of aluminum metal industry. The interest in high purity Ga metal is well-known because of its use in the fabrication of III-V semiconductors. In future, the demand of ultra high purity Ga is bound to go up on account of the recent invention of blue LED's, which uses ultrahigh purity, Ga metal for its fabrication. Invention of blue LED by the use of III-V compound semi-conductor, GaN, earned I, Akasaki, A. Armano and S. Nakamura the Nobel Prize in Physics (2014). The invention of the LED has a tremendous impact on modern semiconductor-producing industry because of efficiency and ability to produce bright and energy-saving while light sources.

In BARC recovery of Ga from indigenous Bayer's liquor was done in two steps, (a) the electrolysis of Bayer's liquid employing a Hg cathode to obtain Ga amalgam, and (b) breaking away of Ga from the amalgam to get an aqueous solution of gallium compound, sodium gallate, which was further processed to obtain high purity Ga metal through electrolysis. The know-how generated for this project was transferred to HINDALCO, Bihar to produce 60 kg Ga/annum. Simultaneously, work on preparation of high purity reactive and refractory metals such as V, Nb, Ta and Mo by using fused salts for electro-refining was successfully completed in Metallurgy Division, BARC.

12.4 Ion-Exchange

Work on application of ion-exchange method for efficient separation of individual rare earth oxides was done by the use of a EDTA (ethylene diamine tetra acetic acid) solution as eluant. The starting material mixed rare earth oxides, was received from Indian Rare Earths (IRE), Alwaye. The know-how for the separation method to obtain La, Nd, Pr, Sm was also transferred to IRE, Alwaye in early 1970's.

12.5 Liquid / liquid solvent extraction

The challenging problem to separate, Ta from Nb, starting from tantalum - columbite ore was also taken up by Chemistry Division, BARC. Ta is a useful metal for making of electrolytic capacitors and it has to be pure for its application. A mixer-settler unit for the laboratory scale continuous operation and working on the counter-current principle was exclusively fabricated using high density polythene, HDPE. Because of highly corrosive aqueous (HF-containing) solution nature, compatible material HDPE was chosen for fabrication of the unit. The know-how generated for l/l extraction, for separation of Ta from Nb, was also transferred to NFC, Hyderabad.

12.6 Compound Semiconductors

Synthesis of various II-VI and III-V semiconductor compounds,^{31-37, 40-41} required for diverse applications and basic research, was carried on a laboratory scale. The experience gained during the preparation and handling of high purity materials was helpful in carrying out synthesis of these compounds by direct synthesis from individual elements, often needing working with vapour at high pressures. Synthesis of GaP may be of special interest as the working vapour pressure of P was 36 atmospheres and reaction temperature was of the order of 1500°C. An indigenous autoclave assembly, Figure-17, was designed and fabricated in the divisional workshop, C.D., BARC to carry out successfully synthesis of half a dozen of GaP ingots (50 g each) which were further taken up for single

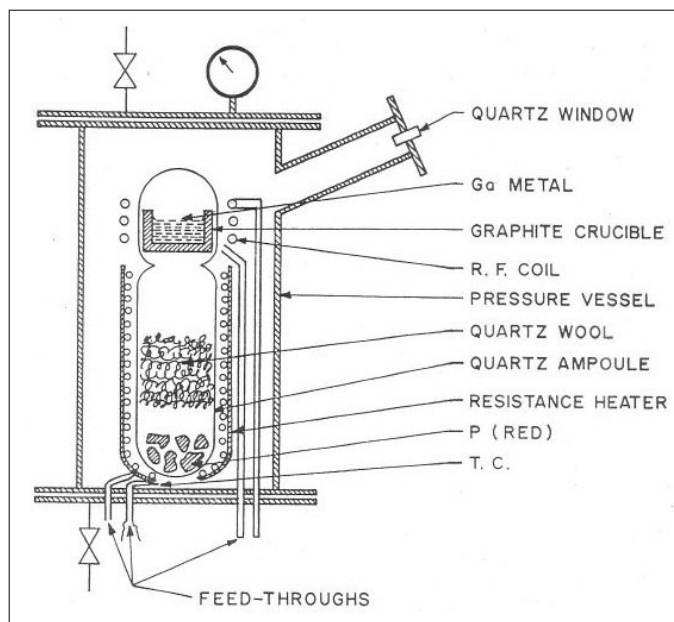


Figure-17. Autoclave assembly for synthesis of GaP

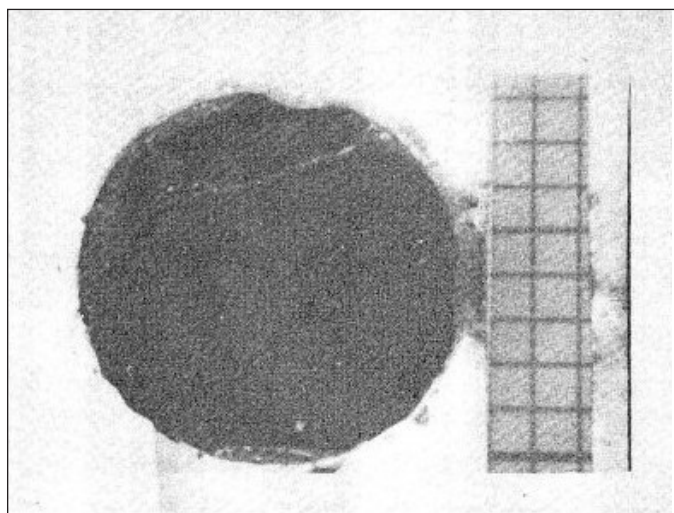


Figure-18. Wafer from GaP single crystal grown indigenously using Bridgman³⁶ technique

crystals growth of GaP by employing encapsulation Bridgman³⁶ technique. Figure-18 shows a wafer cut out of GaP single crystal grown indigenously. Synthesis of other semiconductor compounds were, CdS, CdSe, InP, CdTe, Sb₂As₃, and chalcopyrites AgGaSe₂ and AgGaS₂, required for use in the basic research activities.

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References

1. J. A. Belk, *Vacuum Techniques in Metallurgy*, 1963, Vol-I Pregmon Press, N.Y.210
2. A. J. Singh, *High Temperature Materials & Processes*, 11 (1993) 305.
3. R. K. Iyer and M. Sundaram, *Bull. Ind. Soc. Anal. Scientists*, (1993) 3.
4. C. M. Paul and V. D. Shah, *Proc. INSA-BARC Winter School of Met. & Chem.*, (1975) 461.
5. C. V. Sundaram, S. P. Garg and J. C. Sehra, *Indian Inst. Metals*, (1991) 351.
6. W. G. Pfann, *Zone Melting*, Wiley, New York, 1958.
7. N. L. Parr, *Zone Refining and Allied Techniques*, Newnes London (UK) 1960.
8. M. Zief and W. R. Wilcox, *Fractional Solidification*, Marcel Dekker, N.Y., 1967.
9. W. G. Phann, *Trans. AIME*, 194 (1952) 747.
10. W. G. Pfann, *Zone Refining*, *Sc. American*, (1967) 63-72.
11. E. F. G. Herington, *Zone Melting of Organic Compounds*, Blackwell, Oxford, 1963.
12. P. H. Keck and M. J. E. Goley, *Phys. Rev.*, 89 (1953) 1293.
13. H. C. Theurer, *Trans. AIME*, 206 (1956) 1316.
14. W. Heywang, *Zeit. Forschu.*, 11(1958)291.
15. W. Kaiser, P. H. Keck and C. F. Lange, *Phys. Rev.*, 101(1956) 1264.
16. J. Bressers, R. Creten and G. van Hols'beke, *J. Less Common Metals*, 39 (1975) 7.
17. K. K. Schulze, *J. Metals*, 33 (1983) 33.
18. A. J. Singh, B. S. Mathur, P. Suryanarayana and S. N. Tripathi, *Proc. Symp Non-ferrous Met. Technology*, Jamshedpur, 1968.
19. A. J. Singh, *Indian J. Technol.*, 40 (1973) 465.
20. A. J. Singh, *Chem. Education*, (1987) 10-14.
21. P. Suryanarayana, R. A. Singh and A. J. Singh, *Report BARC / I-363*
22. A. J. Singh, P. Suryanarayana and B. S. Mathur, *Indian J. Tech.*, 5 (1967) 162.
23. J. M. Wermick, K. E. Benson and D. Dorsi, *Trans. AIME*, 209 (1957) 996.
24. R. K. Iyer and T. R. Bhat, *AEET (BARC)*, Report CD/34, 1964.
25. B. S. Mathur and A. J. Singh, *Indian J. Technol.*, 27 (1987) 220.
26. W. A. Tiller and J. W. Rutter, *Can. J. Phys.*, 34 (1956) 96.
27. D. Walton, W. A. Tiller, J. W. Rictter and W. G. Winigard, *Trans. AIME*, 203 (1955) 1023.
28. K. Ya Bergman and N. P. Grundinkina, *Izmeritel Tekh.*, 5 (1961) 23.
29. A. Desalva, P. Gondi, F. A. Levi and F. Zignani, *Met. Ita.*, 55 (1963) 511.
30. T. Kesavadas, A. J. Singh and G. S. Rao, *Intl. Conf. Adv. Chem. Metallurgy*, 47 (1979) 1.
31. S. Govinda Rajan, N. V. Chandra Shekar, G. V. N. Rao, A. J. Singh and R. M. Iyer, *Bull. Mat. Sci.*, 11 (1900)275.

32. S. K. Deb, A. J. Singh and A. P. Roy, *Solid State Physics (India)*, 31C (1988) 358.
33. A. J. Singh and S. K. Deb, *Current Trends in Crystal Growth and Characterization*, Editor, K. Byrappa, (1981) pp 451-457.
34. A. J. Singh, P. Suryanarayana, K. B. Bhat and B.S. Mathur, *Bull. Electrochemistry*, 47 (1979)1.
35. A. J. Singh, *Prec. Indo-German Seminar on Trends and Techniques in Mat. Res.*, (1987) 287.
36. S. Govinda Rajan, N. V. ChandraShekar, G. V. N. Rao, A. J. Singh, and R. M. Iyer, *Bull. Mat. Sci.*, 11(1988) 274.
37. B. S. Mathur, P. Suryanarayana, K. B. Bhat, K. N. Shelar and A. J. Singh, *BARC/I-921* (1987).
38. J. T. Kunjappu, A. J. Singh and R. M. Iyer, *J. Photochem & Photobiology*, 41(1987) 121.
39. H. Mohan and A. J. Singh, *Indian J. Chem.*, 25A (1986) 587.
40. J. N. Roy, S. Basu, D. N. Bose and A. J. Singh, *Indian J. Pure & Appl. Pys.*, 21(1983) 395.



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Analytical Methods for Chemical Characterisation of High Purity Materials

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Abstract

There are a number of high purity materials like arsenic, gallium, tellurium, germanium, silicon, indium, cadmium, etc., which have strategic applications and are required at a very high level of purity. There is no single technique or procedure that can be used for their complete chemical characterisation. Thus chemical characterisation of high purity materials poses an immense challenge as the impurities are present at ultra trace levels of concentration. The analytical procedures to analyse these materials generally involve separation of matrix and/or pre-concentration of impurities using solvent extraction, ion exchange, matrix volatilisation, precipitation and controlled dissolution, etc. The detection is done by highly sensitive instruments, such as Inductively Coupled Plasmas Mass Spectrometer (ICP-MS), Graphite Furnace Atomic Absorption (GFAAS), Total Reflection-XRF. Instruments, like High-Resolution-Glow Discharge Mass Spectrometer (HR-GDMS), used for direct multi elemental analysis at ppb/ ppt levels need suitable standards for quantification. The analysis of high purity materials is a specialised area in analytical chemistry. The analysis becomes very expensive because of sophisticated instruments and operation and maintenance of the clean rooms that are necessary for prevention of contamination.

1. Introduction

High purity materials are required in electronics, space, defence and nuclear energy programs. For example, multi junction solar cells used for space applications, require high purity materials such as Ga, As, In, Si, Ge, etc.¹ Defence industry needs high purity germanium and CdHgTe for night vision equipments.^{2,3} High purity Ag, Au, are used for efficient contacts in integrated circuits, and rare earth elements/oxides are used in, LCD screen, magnets and other hi tech devices. To ascertain the purity of materials, quantification of each of the impurity component present in the sample needs to be carried out. For example, in a 6N (99.9999% or 6 nine) material the total impurity concentration is 1 mg/kg, but the individual analyte species could be in ppb to sub-ppt range. The purity requirement of detector grade material (e.g., germanium) is in the range 10-13N purity, which may not be possible to ascertain by chemical methods but after certain stage physical methods are required.

There is no one single technique or procedure that can be used for complete chemical characterisation of high purity materials. The method of analysis basically depends upon the type of matrix and the nature and the concentration levels of the impurities present. High purity gallium can be analysed using controlled/partial dissolution method,⁴ while 7N tellurium (7 N) is analysed by separating the matrix through precipitation as TeO₂ and

determining impurities that are present in the solution.⁵ Matrix volatilization has been used for determining impurities in high purity germanium⁶, arsenic⁷ and quartz/silica.⁸ The impurities are generally determined by highly sensitive instrument such as Inductively Coupled Plasmas Mass Spectrometer (ICP-MS), or Graphite Furnace Atomic Absorption (GFAAS) or both. These procedures require processing of the sample prior to analysis where chances of contamination are a major problem. Application of clean room technology, though expensive, can minimize contamination and should be used in such analysis. However, direct determination of impurities without dissolution is a desirable method where sample processing is minimal which in turn help in reducing the chances of contamination.

There are instruments such as High-Resolution-Glow Discharge Mass Spectrometer,⁹ where multi elemental analysis up to ppb levels of impurities can be done directly, but this type of analysis cannot be done for all the matrices due to lack of suitable standards.

2. Contamination control for analysis of high purity materials

There are four major sources of contamination, viz. (i) environment, (ii) containers, (iii) reagents, and (iv) analyst himself. Clean rooms for chemical application are designed in such a way that, it is not only dust free but also free from exposed metal surfaces. Figure 1 shows a class

100 clean room with class 10 laminar flow workbenches of Ultra Trace Analysis Laboratory at NCCCM. As can be seen, all surfaces are epoxy coated and only materials which do not corrode such as FRP, glass, etc. are used in inner construction. In rooms there are about 100 particles of the size $\geq 0.5 \mu\text{m}$, called class 100, while on laminar flow clean work benches there are not more than 10 particles of size $\geq 0.5 \mu\text{m}$ (class 10). All sample preparation activities such as sample dissolution, evaporation, extraction etc are carried on laminar flow clean work benches. Air particulate matter is controlled using HEPA filters which have 99.7% efficiency for $0.3 \mu\text{m}$ size particles. Containers used in ultra trace analysis are mostly made from fluoro polymers such as, PTFE, FEP, PFA, instead of glass due to the possibility of leaching of trace impurities (e.g., B, Si, Na) from the surface. Contamination can also come from reagents, therefore only high purity reagents are used for ultra trace analysis. Clean room garments made from lint free materials must be used by the analyst to prevent contamination from dead skin cells, hair and dust particles. All analysts working inside clean room must be trained and follow the protocol for working inside a clean room.



Figure 1. Class 100 clean room with class 10 laminar flow work benches of Ultra Trace Analytical Laboratory at NCCCM

3. Methods for analysis of high purity materials

Selection of methods for analysis of high purity materials is very important. The methods which involve one step matrix separation as well as analyte pre-concentration technique are most suited for analysis of high purity materials. Some representative methods employed for analysis of high purity materials are described below:

3.1 Gallium

For analysis of gallium a method recommended by Jackwerth and Messerschmidt⁹ called partial dissolution is used. In this method, gallium sample (2.0 - 2.5 g) is partially

dissolved in 50 ml mixture of 3 M HCl and 0.15 M HNO₃ and heated to at 95 °C till less than 5 mg gallium is left. The solution is decanted. The residue is dissolved in a mixture of 50 μl HNO₃ and 50 μl HCl and made up to 2 ml with freshly prepared milli Q water. A portion (1 ml) of it is taken for analysis by GFAAS while 0.2 ml of the remaining 1 ml solution is diluted to 10 ml for analysis by ICP-MS. Standard additions' calibration is used for quantification. Advantage of this method is that besides removing gallium, impurities lower in electro chemical series than gallium are pre-concentrated to almost thousand times. LOD obtained is in ng/g range and suitable to analyse 6-7N pure gallium.

3.2 Germanium

High purity germanium sample (~ 10 g) is taken into a pre-cleaned quartz boat in a class 10 clean bench. The boat is transferred to a cleaned PFA screw cap container to the experimental setup (placed in a normal fume hood) and then placed inside the reaction vessel. Chlorine gas is generated *in situ* using manganese dioxide and concentrated HCl in a 1000-mL round bottom flask heated to 75 - 85 °C. Chlorine gas evolved is passed through two consecutive concentrated H₂SO₄ traps along with argon carrier gas and then into a reaction vessel containing the high purity germanium sample (in a quartz boat). The above reaction vessel is maintained at a temperature of $200 \pm 10 \text{ }^\circ\text{C}$ for eight hours. After complete removal of the germanium matrix as germanium chloride, the quartz boat, containing approximately 4 mg residue, is dissolved in 100 μl each of sub-boiled HNO₃ and HCl inside a class 10 clean bench. After separating the matrix, the residue solution containing the trace elements, along with rhodium as internal standard is passed into the ICP-MS after suitable dilution. For some of the elements for which the isotopes with the highest abundance suffered from spectral interferences, alternative isotopes of lower abundance having minimum or no isobaric interferences is chosen. The quantification of the trace elements in the germanium sample is done using external calibrations. About 50 elements can be analysed with LOD in the range of pg/g. Based on these nearly 8N pure germanium can be analysed.

3.3 Arsenious oxide/ Arsenic

Arsenious oxide sample (2-5 g) is taken in a polypropylene (PP) sample container, which is placed inside a larger outer container (PP) containing 50 ml of concentrated HCl, and the outer container is closed. After 24 h, the container is opened in a fume hood, the inner container is taken out with Teflon tongs, and the residual liquid was diluted to the required volume with Milli-Q

Table 1 Summary of analysis of some high purity materials

Matrix	Method	Elements	Purity	Reference
Gallium	Partial dissolution	Ag, Au, Cu, Hg, Ni, Pb, Sn	6N	4
Germanium	Matrix volatilization by chlorine gas	Li, Be, Mg, Al, Pb, Sc, Ti, Cr, V, Mn, Co, Ni, Zn, Cu, Ga, As, Se, Sr, Mo, Ru, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, Ta, Re, Ir, Pt, Au, Hg, Tl, Bi	7-8 N	6
Arsenic oxide/ arsenic	Vapor phase digestion in HCl, aquaregia	Al, V, Cr, Mn, Co, Ni, Zn, Cu, Ga, Sr, Zr, Mo, Cd, In, Ba, Cs, Ce, Gd, Lu, Te, Pb, Bi	5N	7
Antimony	Matrix volatilization	Cr, Mn, Ni, Co, Cu, Mo, Cd, Ba, Pb, Bi	5N	11
Tellurium	Precipitation as tellurium oxide	Al, Ag, Cd, Co, Cr, Cu, In, Mn, Ni, Pb, Zn	7N	5
Quartz/ silicon	Vapor phase digestion in HF	Li, Be, B, Al, Cr, V, Mn, Co, Ni, Zn, Cu, Ga, As, Se, Sr, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, W, Pt, Au, Hg, Tl, Pb, Bi	5N	8

water and analyzed by inductively coupled plasma- atomic emission spectrometer (ICP-AES) using aqueous standards. For analysis of arsenic, aquaregia is used instead of HCl. By this method 5N pure material can be analysed.

3.4 Antimony

The procedure for analysis of antimony involves removal of the matrix as antimony bromide. To antimony sample (200 mg) 3 ml of conc. H_2SO_4 is added, along with 3 ml conc. HCl drop wise under warm conditions till the sample is completely dissolved. Antimony is removed as volatile bromide by three successive additions of HBr of 1 ml each maintaining the temperature at 200 °C. Excess Br_2 is removed by adding 0.5 ml of conc. HNO_3 and evaporating to near dryness. The volatilization is carried out under open conditions in a clean fume hood. On cooling, 0.5 ml of conc. HNO_3 is added to the residue. The solution is made up to 10 ml with water in a volumetric flask analysed by ICP-MS. By this method up to 5N pure antimony can be analysed.¹¹

3.5 Tellurium

Tellurium chunks (1.0-1.2 g) are dissolved in 4 ml (1:1) nitric acid diluted with Millipore water and warmed on an IR lamp in a class 10 clean bench. After 30 minutes the reaction ceases and the supernatant solution is taken in PTFE evaporation disk with eppendorf pipette. The white precipitate is washed 2 times with 2-3 ml cold water and the washing is added to evaporation disk. Excess of nitric acid is removed by heating under an IR lamp in a class 10 clean work bench and the volume is made up to 2 ml. This solution (0.5 ml) is analysed by GFAAS. Remaining solution is diluted 20 times and analyzed by ICP-MS. The limit of detection obtained is 5 to 0.5 ng/g for about 15 elements suitable for analysing 7 N tellurium.

3.6 Quartz/silica

For analysing quartz, a Multi Channel Vapour Phase Digestion (MCVPD) has been developed, where 15-16 samples can be processed at the same time. Quartz samples (0.5 g, size -50 to +100 mesh) is weighed into a PFA vial in a class 1000 clean room. The PFA vials are placed in the grooves (31mm diameter) of the sample rack. Hydrofluoric acid (130 ml, AR grade) is carefully poured into the reagent reservoir through a polypropylene funnel. The vessel is capped and the assembly is placed on a single hole (diameter 180 mm) water bath (90 °C) for digestion. An exposure time of 7 h is required for complete digestion of 15 quartz samples (15 × 0.5 g, six blanks). When the dissolution is complete, the MCVPD assembly is allowed to cool to room temperature. PFA vials is removed from the sample rack and evaporated on a IR hot plate until about 200µl residue remains. The solutions is made upto 10 ml and analysed by ICP-AES/MS. In Table 1 method of analysis of high purity materials are summarised.

4. Conclusion

The method described here only used wet chemical procedures. There are instruments where metals for example, gold, silver and rare earth elements, can be analysed directly in solid form such as HR-Glow Discharge Mass Spectrometer. This technique is also suitable for determination of lighter elements like B, C, O, N, F, Cl, etc. However, lack of suitable standards and the fact that only the surface region (not bulk) of the materials can be analysed, are limitations.

References

1. M. C. Beard, J. M. Luther and A. J. Nozik, *Nature Nanotechnology*, 9 (2014) 951.
2. M. Bochmann, *Organometallics and Catalysis: An Introduction*, Oxford university press, Oxford, 2015.

3. D. J. Ando and M. G. Pellatt, *Fine Chemicals for the Electronics Industry II*, The Royal Society of Chemistry, London, 1991.
4. S. J. Kumar, N. N. Meeravali and J. Arunachalam, *Analytica Chimica Acta*, 371 (1998) 305.
5. M. A. Reddy, N. N. Meeravali and S. J. Kumar, *Atomic Spectroscopy*, 25 (2004) 267.
6. M. A. Reddy, R. Shekhar and S. J. Kumar, *Atomic Spectroscopy*, 34 (2013) 119.
7. S. C. Chaurasia, A. C. Sahayam and R. K. Mishra, *Anal. Chem.*, 74 (2002) 6102.
8. K. Dash, S. M. Dhavile, K. Chandrasekaran and S. C. Chaurasia, *Atomic Spectroscopy*, 24 (2003) 143.
9. W. Vieth and J. C. Huneke, *Anal. Chem.*, 64 (1992) 2958.
10. E. Jackwerth and J. Messerschmidt, *Anal. Chim. Acta*, 87 (1976) 341.
11. M. V. B. Krishna, D. Karunasagar and J. Arunachalam, *F. J. Anal. Chem.*, 363 (1999) 353.



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Pure Metals for Nuclear Power

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Abstract

The data on the level of purity of metals produced by different physical methods in National Science Center "Kharkiv Institute of Physics and Technology" using development and implementation of efficient methods for refining are presented. The characteristics of the main structural materials for some types of new generation reactors and pure metals with need to produce them are presented. It has been shown that the development of nuclear power is largely dependent on the development of promising structural materials for new generation reactors and improving materials for operating nuclear power plants.

1. Introduction

Modern tendencies of development of reactor technologies are aimed to further increase reliable and safe operation of power units and to provide efficiency and competitiveness of nuclear power. This requires an increase in power density, power of units, increasing the duration of campaigns, more efficient fuel burning, including by improving the quality of construction materials.¹⁻³

Further increase in operational reliability of fuel and improvement in techno-economic indicators of fuel cycles are primarily due to an increase in resource characteristics of construction materials and their products. Improvement of structural materials for reactor cores of VVER involves the use of construction zirconium materials with low hafnium content for claddings and spacing grids and guide channels in fuel assemblies with improved physical and mechanical properties.

The progress achieved in the field of nuclear physics, reactor physics and reactor materials in recent years, led to the development of a number of advanced nuclear energy systems.¹ These projects have advantages in economy, security, reliability and non-proliferation of nuclear materials.

Analysis of the working conditions and the main characteristics of advanced nuclear reactors show that the

desire to maximize the efficiency of power installations involves a move to higher operating temperatures, and this, in turn, leads to the development of new structural materials. Materials of new reactors must satisfy the unique requirements dictated by the design of high-temperature systems, which involves consideration of the effects of temperature, radiation, coolant, corrosion, as well as static and dynamic stresses.

New structural materials must be pure. We know that high levels of impurity and gases in steels and alloys significantly reduce their mechanical, corrosion and radiation properties and, therefore, limit their use in operating and designing reactors. Use of high-purity metals as initial components of new structural materials will provide desired properties in the resulting products.⁵ Table 1 shows high purity metals used for producing some of the structural materials required in nuclear power installations. Consideration of these data allows determining metallic elements which are necessary components to produce structural materials which are of interest for nuclear energy of present and future.

2. Methods and technologies for refining of metals

For obtaining pure metals at different stages of refining use various chemical and physico-chemical methods, but

Table 1. Metals used for creating structural materials of nuclear reactors

Metals	Applications	Operating temperature, °C
Zr, Hf, Nb, Fe, Sn	Materials for the reactor cores, absorbing elements of reactor control and safety systems	Up to 350
Fe, Ni, Cr, Mo, Mn, Sc	Steels and alloys of different types (austenitic and ferritic-martensitic steel, nickel-chromium, nickel and other alloys)	Up to 700
V, Cr, Ti	Low activated alloys	
Ni, Mo, Cr	Heat-resistant and corrosion-resistant alloys	Up to 850
Nb, Ta, Mo, W, C	Modern high-temperature alloys, composite materials	Above 700

usually refining process comprises of physical methods – distillation, zone recrystallization, electrotransport and various combinations thereof. These methods are mainly physical processes: evaporation and condensation, crystallization, diffusion and electromigration, etc. The advantages of these methods over the others are the ability to yield high purity material and the final product is obtained in a compact form, including single crystals with a perfect crystal structure.

Various physical methods have been developed based on the nature of an impurity or groups of impurities during the refining of metals by National Science Center “Kharkiv Institute of Physics and Technology” (NSC KIPT). Highly efficient methods of refining metals include:

- methods based on distillation processes, including the condensation of steam on the column with a temperature gradient in a closed volume, heating and distillation of metal one refining cycle and their combination in a certain order;
- melting and zone recrystallization in ultra-high vacuum and controlled (active) environments using electron beam heating;
- zone melting in combination with electrotransport;
- various combinations of the above methods.

Comprehensive refining, based on the use of complementary physico-chemical, physical methods and implementation of controlled environments in wide use of ultra-high vacuum technology, achieves the highest degrees of clearing and obtaining large amount of metal in its purest form. This approach to the problem of especially pure metals developed and widely used in NSC KIPT. Methods of obtaining ultrapure metals are continuously improved in order to increase purification efficiency, productivity and cost reduction.

Further progress in the deep purification of metals connected with the search for the most rational complex schemes of refining, with the prevention of interaction residual gases and construction material with metal of installations used for refining.

The developed methods and technologies for refining of metals found a practical application in the industry for the production of Be, Nb, Ta, Zr, and many alloys with special physical-mechanical properties (heat resistant, refractory, reactor, superconducting, etc.). These technologies are based on the extensive use of vacuum technology and studied regularities of behavior of impurities in metals. Thanks to this research, NSC KIPT became one of the founders of a new direction - vacuum metallurgy.⁷

Electron beam melting (EBM) of metals is performed on an ultra-high vacuum installation. For pumping of installation used two hetero-ion pumps with a pumping speed of 5000 l/s each, and a titanium sublimation pump. Application of such a system of vacuum pumping allows to get an ultimate vacuum in the installation $1.7 \cdot 10^{-6}$ Pa.⁷ In the spectrum of the residual gas in installation were absent heavy hydrocarbons. Refining of metals is carried out in vacuum $(1-5) \cdot 10^{-5}$ Pa. Refining is conducted in the regime: heating \Rightarrow melting \Rightarrow excerpt of metal in molten state \Rightarrow crystallization \Rightarrow pulling ingot. Zone recrystallization with an electron-beam heating is carried out, as a rule, in installations with combined pumping systems.^{7,8} Diffusion pumps are equipped with sorption and condensation traps; sorption, cryogenic and ion-sorption pumps which are used to give “oil-free” ultrahigh vacuum. Electron-beam zone recrystallization is carried out in vacuum $1 \cdot 10^{-6} - 1 \cdot 10^{-5}$ Pa. Choice of pumping system for different methods of refining determined mainly by degree of interaction metals in refining conditions with residual gases of the vacuum environment.

3. Results and discussion

Results of physical methods of refining of some metals which are important components for the production of new alloys for nuclear power are briefly given below.

3.1 Titanium

Titanium sponge TG-90 and titanium, which was received by iodide refining (ITi), is used as starting materials for purification by electron-beam melting (EBM). Titanium ingots with diameter of 150 mm and purity 99.99 wt.% are produced by method EBM. Pure titanium was obtained after EBM of the initial iodide titanium (ITi). Impurity contents in the metal iodide (ITi) after two electron-beam remelting are: Al – $8.0 \cdot 10^{-5}$; P – $1.0 \cdot 10^{-5}$; S – $8.0 \cdot 10^{-5}$; K – $6.0 \cdot 10^{-5}$; Ca – $2.0 \cdot 10^{-4}$; V – $3.0 \cdot 10^{-4}$; Cr – $3.0 \cdot 10^{-4}$; Mn $< 9.0 \cdot 10^{-5}$; Fe – $1.5 \cdot 10^{-3}$; Ni – $5.0 \cdot 10^{-3}$; Cu – $3.0 \cdot 10^{-4}$; Zn – $2.0 \cdot 10^{-4}$; As – $8.0 \cdot 10^{-5}$; Sn $< 8.0 \cdot 10^{-4}$ wt.%.

It should be noted that EBM of titanium favorably affects to the vacuum conditions of the installation due to the good getter abilities of layers of titanium deposited on the chamber walls due to evaporation at EBM.⁹

3.2 Zirconium

Zirconium As a starting material were used zirconium, which was received by iodide refining (IZr), and metal employed by calcium-thermal recovery from zirconium tetrafluoride (CTZ). EBM is a very effective process for refining of zirconium. Impurity contents in CTZ and iodide zirconium (IZr) after electron-beam melting are shown in

Table 2.¹⁰ Experimental results of the zone melting of metals showed the existence of two mechanisms of purification – zone recrystallization and evaporation. Therefore, it is possible to obtain higher purity of zirconium by using the zone melting. The holding of six passes of zone in vacuum $6 \cdot 10^{-6}$ Pa at a speed displacement of zone 1.2 cm/h it is possible to obtain a high-purity zirconium: relative residual resistivity $RRR = R(300K) / R(4.2K) = 250$ and the value of micro-hardness of 590 MPa. Contents of oxygen, nitrogen and carbon equal $2.0 \cdot 10^{-3}$, $1.7 \cdot 10^{-3}$ and $9.0 \cdot 10^{-3}$ wt.%, respectively, the content of metallic impurities is less than 10^{-5} wt.%.

Table 2. The content of impurities in zirconium after EBM

Impurity	The content of impurities 10^3 , wt. %		
	Iodide Zr (IZr)		CTZ after EBM
	Initial	after EBM	
Cu	4	0.1	0.4
Fe	9	0.8	0.5
Al	4	0.8	0.5
Ni	40	0.6	3.5
Mg	0.4	0.3	-
Mn	1.5	0.1	-
Cr	1.3	0.2	0.9
Si	18	4.5	-
Ti	2	0.4	-

3.3 Hafnium

Refining of hafnium is carried out by electron-beam melting. The starting material is hafnium, obtained by calcium-thermal recovery of hafnium tetrafluoride. The experiments of refining of hafnium by EBM showed that an increase in power density of melting not only accelerates the process of refining of hafnium from metal impurities, but also the purification from oxygen due to its removal in a monoxide HfO. This process is known as distillation deoxidation.

Calculations showed that the purification of hafnium from silicon is difficult by EBM, and removal of the more volatile impurities^{9,11} is reduced in a series of Zn > Be > Mn > Cr > Cu > Al > Fe > V > Co > Ni > Si. Hafnium with purity ≥ 99.9 wt.% could be obtained after two successive electron beam melting. Its chemical composition is follows: N₂ – $1.0 \cdot 10^{-3}$; Al – $1.0 \cdot 10^{-3}$; W < $1.0 \cdot 10^{-3}$; Fe – $5.0 \cdot 10^{-3}$; O₂ – $1.0 \cdot 10^{-2}$; Si – $3.5 \cdot 10^{-3}$; Mn < $1.0 \cdot 10^{-4}$; Cu – $2.0 \cdot 10^{-4}$; Ni < $1.0 \cdot 10^{-3}$; Nb < $2.0 \cdot 10^{-3}$; C – $5.0 \cdot 10^{-3}$; F < $1.0 \cdot 10^{-3}$; Cr – $2.0 \cdot 10^{-4}$ wt.%.

3.4 Iron

Refining of the starting materials (sponge of carbonyl iron and rods of Armco iron) is carried out in an electron

beam furnace. Brinell hardness of the initial samples of Armco iron was 830 MPa, after refining – 624 MPa and carbonyl iron – 558 MPa. The impurity contents in iron carbonyl after EBM are shown in Table 3. It is evident that the most difficult impurities to remove in vacuum are Co and Ni. To further reduce the impurity distillation method is adopted. Impurities in iron after distillation (bottom of the distillation column, T ~ 1500 °C) are shown in Table 3. It is possible to obtain metal purity more than 99.98 wt.% by distillation of iron carbonyl remelted by EBM. The purity level of iron is largely determined by the content of nickel and cobalt.⁹

Table 3. Content of impurities in carbonyl iron

Impurity	Content of impurities (10^3 , wt. %)		
	Initial	After EBM	Distillate
Mn	120	2	0.1
Al	20	10	0.3
Cu	150	10	4
Co	17	17	8
Ni	150	100	20
Si	200	50	2
C	50	10	1
O	30	20	2
N	6	3	<1

3.5 Nickel

Double EBM in a high vacuum of initial electrolytic nickel with purity 99.987 wt.%, allowed to obtain metal with purity 99.994 wt.%. The refining resulted in reduction of Fe, Co, P, Al, Mg while the concentration of As, Zn, Se, Cl decreased significantly. Purification of nickel by EBM from metallic and interstitial impurities has been experimentally demonstrated. Electron beam remelting of nickel leads to reduction of interstitial impurities - oxygen, nitrogen, carbon up to 0.0005, 0.00006, and 0.002 wt.%, respectively. Such interstitial impurities content has practically no effect on the properties of nickel. If purity of nickel increases then the hardness decreases, for the initial nickel and after two EBM, HB is 1690 and 800-900 MPa, respectively. High-purity single crystals of nickel with relative residual resistivity $RRR = 1000$ and micro-hardness 950 MPa could be obtained by zone melting. Studies have shown a significant improvement in the quality of metal after refining.¹²

3.6 Copper

Copper refining process was carried out by electron-beam melting and distillation.¹³ The materials used in this process technical copper and oxygen-free copper. Double

Table 4: The content of impurities in the technical vanadium after EBM and ZM

Type of metal	Content of impurities $\cdot 10^4$, wt.%						
	Fe	Cr	Cu	Mo	Si	Mg	Al
Initial	1000	30	5	60	1500	16	200
After EBM in vacuum $5 \cdot 10^{-4}$ Pa	200	<30	2.4	40	1500	5	20
After ZM in vacuum $2 \cdot 10^{-5}$ Pa	17	<30	<1.4	20	1300	<0.5	<10

electron-beam melting of copper gave samples of RRR = 340. Electron beam melting in a high vacuum is effective for refining copper from metal impurities as well as the interstitial impurities. To reduce the impurity content of iron, silicon and nickel, which limit the purity of copper is possible by means of the distillation process. The use of double electron-beam melting followed by distillation of the metal allowed to give purity 99.99 wt.%. Typical analytical data for purified copper are as follows: As < $2.0 \cdot 10^{-5}$; Ag - $4.0 \cdot 10^{-4}$; Sb < $1.0 \cdot 10^{-5}$; Fe - $6.0 \cdot 10^{-4}$; Ni - $2.0 \cdot 10^{-4}$; Pb < $4.0 \cdot 10^{-5}$; Sn < $2.0 \cdot 10^{-5}$; S - $2.0 \cdot 10^{-4}$; P < $1.0 \cdot 10^{-5}$; Zn < $1.0 \cdot 10^{-5}$; Bi < $1.0 \cdot 10^{-4}$; $O_2 \sim 1.0 \cdot 10^{-4}$ wt.%.

3.7 Vanadium

The initial materials used for research: rods of technical vanadium, electrolytic vanadium VEL-1 and vanadium, which was received by iodide refining (IV). Studies have shown that carrying out EBM of electrolytic vanadium reduces the metallic impurities; although almost no reduction in iron, nickel and even silicon was noted.⁹ Carrying out zone melting can effectively remove impurities of aluminum, iron, nickel, copper and chromium. Silicon is slightly removed while impurities of refractory metals (tungsten, molybdenum, tantalum and niobium) accumulated during long recrystallization of vanadium.⁹ Table 4 compares the effectiveness of purification of technical vanadium rods by methods of EBM and zone melting (ZM).

Zone melting of vanadium is carried out at speed of 4 cm/hour. The data in Table 4 show that the ZM is more effective method for purification of vanadium samples than EBM. Silicon content in a technical metal is high, and it is the limiting impurity for zone melting process.

The most pure vanadium was obtained using method of electrotransport on wire samples obtained from metal after double EBM of electrolytic powder vanadium. Studies have shown that interstitial impurities are migrated to the cathode side of the vanadium sample when passing a constant electric current of high density, i.e. effective charge of these impurities is positive. From the numerical calculating of solution of the equation for electrotransport follows that at 1650°C for 200 hours at a current density of approximately $5 \cdot 10^3$ A/sm² electrotransport will

result in a significant reduction in oxygen, nitrogen and carbon. It is experimentally shown that under the above conditions the RRR of vanadium samples after purification by electrotransport increases^{7,9} from 50 up to 1600. The chemical composition of high-purity vanadium with RRR = 1200, which was obtained by electrotransport is as follows (mass spectral method, at.%): Na < $1.0 \cdot 10^{-5}$; K - $1.0 \cdot 10^{-5}$; Ca - $4.0 \cdot 10^{-5}$; Cu - $5.0 \cdot 10^{-5}$; Mg < $1.0 \cdot 10^{-5}$; Zn < $9.0 \cdot 10^{-5}$; Al - $9.0 \cdot 10^{-5}$; Si - $2.0 \cdot 10^{-3}$; Ti - $4.0 \cdot 10^{-5}$; P - $1.0 \cdot 10^{-4}$; As - $3.0 \cdot 10^{-5}$; S < $4.0 \cdot 10^{-5}$; Mn < $1.0 \cdot 10^{-5}$; Fe - $2.0 \cdot 10^{-5}$; Cl - $7.0 \cdot 10^{-5}$; Nb - $4.0 \cdot 10^{-5}$; Cr - $1.0 \cdot 10^{-3}$; F - $1.0 \cdot 10^{-3}$; Ni - $3.0 \cdot 10^{-5}$; Ga - $3.0 \cdot 10^{-5}$; Zr - < $5.0 \cdot 10^{-5}$; Mo - $2.0 \cdot 10^{-5}$; C < $1.0 \cdot 10^{-2}$; N_2 < $1.0 \cdot 10^{-2}$; O_2 < $9.0 \cdot 10^{-3}$.

Analysis results indicates that for a higher degree of purification of vanadium, it is necessary to use combination of different refining methods which would allow to remove impurities such as silicon, refractory metals, carbon, nitrogen, oxygen from vanadium. Vacuum distillation of vanadium, which can reduce silicon content in the metal more than ten times as well as impurities of refractory metals, is worth exploring.

3.8 Scandium

It was previously simulated distillation process. It is shown that the position of the maximum of mass of metal,

Table 5: The chemical composition of initial scandium and metal after three distillations

Impurity	Contents of impurity, wt.%			
	Initial	The number of cycles of distillations		
		1	2	3
Copper	0.01	0.003	0.002	0.0007
Titan	0.02	0.003	0.0015	0.00022
Iron	0.1	0.06	0.01	0.0035
Calcium	0.2	0.0004	-	-
Magnesium	0.02	0.002	-	-
Aluminum	0.01	0.002	0.001	0.0007
Zirconium	0.01	0.006	-	-
Yttrium	0.01	0.0014	-	-
Chrome	-	0.013	0.006	0.004
Wt.% of Sc	99.62	99.92	99.98	99.99

which settled along the distillation column, is determined by the geometry of the crucible and the column, the rate of evaporation, the temperature gradient along the column. Table 5 shows the chemical composition of initial SCM-3 scandium and distilled metal after one, two and three cycles of distillations.¹⁴ Parameters of scandium distillation are as follows: $T_{ev} \sim 1500-1530^{\circ}\text{C}$, $T_{cond} = 1300-1100^{\circ}\text{C}$, the evaporation rate of 2.5 g/hr. After three distillations, scandium purity is 99.99 wt.%.

3.9 Niobium

The initial material for EBM was niobium after calcium-aluminum-thermal recovery. Results of consecutive electron beam melts of niobium are summarized in Table 6. The content of metal impurities after two consecutive remelting of niobium by EBM are as follows: Al - 0.004; Fe - 0.0001; Cr < 0.001; Ni < 0.0004; Si - 0.005; Cu - 0.0006; Ca < 0.003 wt.%.

Table 6: Results refining of niobium

Material	Contents of impurity 10 ³ , wt. %				RRR	HB, MPa
	C	O	N	H		
Initial	40	210	18	6	-	-
1-t EBM	5	5	3.5	0.5	94	500
2-d EBM	3	4	1.6	<0.5	172	420
3-d EBM	1.4	-	<1	<0.5	450	384

Annealing in active environments (for example, oxygen), and then in an ultra-high vacuum of wire samples of niobium allows to increase the purity of the metal up to RRR = 2500, which corresponds to the content of a basic element of 99.995 wt.%, excluding tantalum.⁹ Material of higher purity could be obtained after the refining of niobium by zone melting method. The content of impurities in ZM metal with RRR = 12000 (according to neutron activation analysis) are as follows: Na - $5.0 \cdot 10^{-5}$; Cs < $1.0 \cdot 10^{-6}$; Cu < $1.0 \cdot 10^{-4}$; Ag < $1.0 \cdot 10^{-4}$; Au < $8.0 \cdot 10^{-9}$; Rb < $1.0 \cdot 10^{-5}$; Zn < $1.0 \cdot 10^{-5}$; Cd < $1.0 \cdot 10^{-5}$; Ga < $2.0 \cdot 10^{-8}$; Se < $2.0 \cdot 10^{-7}$; La < $3.0 \cdot 10^{-6}$; Eu < $5.0 \cdot 10^{-8}$; Lu < $1.0 \cdot 10^{-6}$; Yb < $3.0 \cdot 10^{-6}$; Dy < $3.0 \cdot 10^{-7}$; Th < $1.0 \cdot 10^{-5}$; Hf < $5.0 \cdot 10^{-6}$; As < $8.0 \cdot 10^{-7}$; Sb < $8.0 \cdot 10^{-7}$; Ta - $8.0 \cdot 10^{-5}$; Cr < $2.0 \cdot 10^{-5}$; Te < $1.0 \cdot 10^{-5}$; W - $1.0 \cdot 10^{-5}$; Mn < $5.0 \cdot 10^{-8}$; Fe < $5.0 \cdot 10^{-4}$; Co < $2.0 \cdot 10^{-6}$; Re - $4.0 \cdot 10^{-6}$; Ir < $2.0 \cdot 10^{-7}$; Br < $5.0 \cdot 10^{-8}$; Ar < $5.0 \cdot 10^{-6}$ wt.%.^{7,8}

3.10 Tantalum

Powder and rods of tantalum with purity of 99.8 wt.% was used for purification. Vacuum electron beam melting reduces metallic impurities in tantalum samples and significantly reduces the interstitial impurities ($\times 10^{-4}$ wt.%):

Al - $3 \cdot 10^{-2}$; Si - $3 \cdot 10^{-2}$; Cr < 5; Fe - $5 \cdot 10^{-1}$; Cu < 1; H₂ - $1 \cdot 10^{-6}$; C - $3 \cdot 10^{-2}$; N₂ - $1 \cdot 10^{-1}$; O₂ - $5 \cdot 10^{-5}$. Degassing and evaporation of volatile impurities are the main purification processes of tantalum by electron beam melting. Float-zone melting in an ultra-high vacuum and controlled environment in combination with electrotransport was used to improve purity of tantalum to grow single crystal. Single crystals of tantalum obtained by zone melting in a controlled environment of oxygen had 99,999 wt.%. The impurity contents in the tantalum are as follows: Ag < $7.0 \cdot 10^{-6}$; In < $1.0 \cdot 10^{-5}$; Rh < $1.0 \cdot 10^{-5}$; As < $1.0 \cdot 10^{-5}$; K < $3.0 \cdot 10^{-6}$; Ru < $1.0 \cdot 10^{-4}$; B - $3.0 \cdot 10^{-5}$; Mg < $1.7 \cdot 10^{-6}$; S < $2 \cdot 10^{-6}$; Ba < $2.0 \cdot 10^{-5}$; Mn < $1.0 \cdot 10^{-5}$; Sb < $7.0 \cdot 10^{-5}$; Bi < $5.0 \cdot 10^{-4}$; Mo < $2.0 \cdot 10^{-4}$; Se < $5.0 \cdot 10^{-5}$; Br < $2.0 \cdot 10^{-5}$; Na < $1.0 \cdot 10^{-6}$; Si - $6.6 \cdot 10^{-6}$; C - $4.0 \cdot 10^{-3}$; Nb - $2.4 \cdot 10^{-4}$; Sn < $1.0 \cdot 10^{-4}$; Cl - $2.0 \cdot 10^{-5}$; Ca < $3.0 \cdot 10^{-6}$; Sr < $1.0 \cdot 10^{-4}$; Co < $3.0 \cdot 10^{-5}$; Ni < $4.0 \cdot 10^{-5}$; Th < $6.0 \cdot 10^{-5}$; Cr < $1 \cdot 10^{-5}$; O < $3.0 \cdot 10^{-3}$; Ti < $1.0 \cdot 10^{-5}$; Cs < $1.0 \cdot 10^{-5}$; Os < $7.0 \cdot 10^{-5}$; Tl < $2.0 \cdot 10^{-4}$; Cu < $1.0 \cdot 10^{-5}$; P < $1.0 \cdot 10^{-5}$; V < $9.0 \cdot 10^{-6}$; Fe - $1.2 \cdot 10^{-5}$; Pb < $6.0 \cdot 10^{-5}$; W < $4.0 \cdot 10^{-4}$; Ga < $1.0 \cdot 10^{-5}$; Pd < $5.0 \cdot 10^{-5}$; Zn < $1.0 \cdot 10^{-4}$; Ge < $1.0 \cdot 10^{-5}$; Rb < $2.0 \cdot 10^{-5}$; F < $1.0 \cdot 10^{-6}$; I < $4.0 \cdot 10^{-5}$; Re < $3.0 \cdot 10^{-4}$ wt.%.

Zone refining were gave oriented single crystals of tantalum with diameter 7-10 mm and length 150-180 mm and disorientation elements of substructure <0,01° and micro-hardness 750 MPa.^{9,15}

Table 7: Pure metals for nuclear power[#]

Metal	Method of refining	Impurities, limiting purification	Content of the basic material wt. %	RRR = R(300K)/R(4,2K)
Cu	EBM+D	Si, Ag, Fe, Ni, S	99.998	340
Ni	EBM, ZM	Fe, Co, Si	99.994	1000
Fe	EBM+D	Ni, Si, Co	99.96	230
Ti	EBM	Fe, C	99.99	-
Zr	EBM+ZM	Si, Hf, O, N	99.99	250
Hf	EBM	Si, O, N	99.9	-
V	EBM+ZM+ET	Fe, Ni, Si	99.998	1600
Sc	D	Cr, Fe	99.99	-
Nb	EBM+ZM	W, Ta, C	99.9995	12000
Ta	EBM+ZM	W, Nb, Re, C	99.999	290

[#]EBM - electron beam melting, ZM - zone recrystallization, D - distillation, ET - electrotransport.

The method of purification and purity levels of metals required for the development of materials for nuclear power are summarized in Table 7.

4. Conclusions

Behavior of structural materials in nuclear reactors largely determines the safe and efficient operation of nuclear power plants (NPP). Therefore, further development of nuclear power is largely dependent on the development of advanced structural materials for new generation reactors and improving materials operated nuclear power plants through the use of high-purity metals as starting components and the use of new technologies of their production, which will provide extension of service life, reliability and safety of structural elements of nuclear reactors. Application of pure and high-purity metals as initial materials for components of construction NPP largely determines the further development of nuclear energy:

- Zirconium alloys and high purity hafnium needed to improve fuel assemblies and control rods reactors operating nuclear power plants;
- High purity steel for reactor vessel provides increased service life, reliability and safety of the reactor pressure vessels;
- New high-temperature, corrosion-resistant and radiation-resistant materials of construction - the basis of the elements of a new generation of reactors to ensure their high performance;
- Superconducting materials with a combination of high values of critical parameters of superconductivity, strength, ductility and other physical properties to provide reliable operation systems of fusion reactors.

References

1. *A Technology Roadmap for Generation IV Nuclear Energy Systems, Issued by the US DOE Nuclear Energy Research Advisory Committee and Generation IV International Forum*, GIF-002-00, 2002.
2. S. D. Lavrynenko, M. M. Pylypenko and P. N. V'yugov, *Problems of Atomic Science and Technology*, 4 (2014) 72.
3. V. N. Voyevodin, *Herald of the National Academy of Sciences of Ukraine*, 8 (2014) 25.
4. V. N. Voyevodin and I. M. Neklyudov, *Evolution of the Structure Phase State and Radiation Resistance of Structural Materials*, Naukova dumka: Kiev, 2006.
5. V. M. Azhazha, S. D. Lavrynenko and M. M. Pylypenko, *Problems of Atomic Science and Technology*, 4 (2007) 3.
6. M. M. Pylypenko, *Problems of Atomic Science and Technology*, 1 (2008) 10.
7. G. F. Tikhinsky, G. P. Kovtun and V. M. Azhazha, *Obtaining of Ultrapure Rare Metals*, Metallurgy: Moscow, 1986.
8. V. M. Azhazha, P. N. V'yugov and S. D. Lavrynenko, *Problems of Atomic Science and Technology*, 2 (1974) 18.
9. V. M. Azhazha, P. N. V'yugov, S. D. Lavrynenko and M. M. Pylypenko, *Special Metallurgy: Yesterday, Today and Tomorrow*, Polytechnica: Kiev, 2002.
10. M. M. Pylypenko, *Problems of Atomic Science and Technology*, 2 (2008) 66.
11. V. M. Azhazha, P. N. V'yugov, S. D. Lavrynenko, et. al, *Proc. Int. Conf. "Problems of Zirconium and Hafnium in Nuclear Energy"*, Alushta, Ukraine, 1999.
12. V. M. Azhazha, Yu. P. Bobrov, V. D. Virich, et. al, *Journal of V. N. Karazin Kharkiv National University. Physical Series: "Nuclei, Particles, Fields"*, 2 (2003) 118.
13. V. M. Azhazha, P. N. V'yugov, S. D. Lavrynenko and M. M. Pylypenko, *Problems of Atomic Science and Technology*, 1 (1999) 44.
14. S. D. Lavrynenko, *Proc. Int. Conf. "Radiation Damage and Performance Structural Materials"*, Belgorod, Russia, 1997.
15. V. M. Azhazha, P. N. V'yugov, V. A. Elenskiy, et. al, *Problems of Atomic Science and Technology*, 1(1998) 63.



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High Purity Materials: Purification Methods and Applications

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Abstract

Processing of ultra-high purity (UHP) metals ($\geq 7N$ purity) is a challenging task due to the complexity of several process methodologies, characterization and unique process equipment required which are not readily available. The UHP materials have been produced commercially for use in electronic applications as the demand is increasing rapidly due to more stringent specifications for the usage in high-performance devices. The purification techniques mainly depend on the physical and chemical properties of the base metal and impurities present in the respective host material matrix. The rate of removal of metallic impurities in any material matrix below parts per million (ppm)/parts per billion (ppb) levels can be achieved by conventional purification processes such as zone melting, fractional crystallization, distillation, sublimation, electro-transport, electrorefining, cementation, ion exchange, solvent extraction, etc. A combination of purification processes were adopted based on physical and chemical properties to be exploited for separation of impurities. The purification methods were discussed systematically with experimental experiences and analytical results.

1. Overview

Any material is considered to be pure, if its physical properties determined by the atomic-crystalline structure and intrinsic defect, but not by the dissolved or substitutional impurities.¹ The purity is generally represented in terms of percentage (%), for example 99.9% means 3N (3 Nines) or it contains 0.1% of impurities or 1000 parts per million (ppm) or 1 million parts per billion (ppb). Table 1 represents various purities and respective concentration of impurities in parts per million (ppm) or parts per billion (ppb).

Table 1. Different kinds of purity representation in (%), (ppm) and (ppb).

Purity	(%) Percent Impurity	Impurity content (ppm)	Impurity content (ppb)
99.9 (3N)	0.1	1000	1000000
99.99 (4N)	0.01	100	100000
99.999 (5N)	0.001	10	10000
99.9999 (6N)	0.0001	1	1000
99.99999 (7N)	0.00001	0.1	100
99.999999 (8N)	0.000001	0.01	10

Ultra-high purity (UHP) materials are crucial building blocks for research & development, and production of advanced materials technologies, which generally require optimum properties, performance, quality and efficiency. Typical applications of ultra-high purity materials are in

compound semiconductors like cadmium telluride (CdTe), cadmium zinc telluride (CdZnTe or CZT), gallium arsenide (GaAs), ultrapure germanium (Ge), etc. CZT is very attractive material for radiation detectors. In Monolithic Microwave Integrated Chips (MMICs), the substrate has to be semi-insulating to accommodate necessary conducting lines and passive components. The active components are made in isolated conducting regions of the semiconductor material. For the connections (microstrip lines) and passive components, it is important that the substrate forms a dielectric with low losses. For this purpose GaAs is preferred owing to its higher resistivity in undoped state. For the active components, GaAs is also better than Si because of its higher electron mobility. Ultra-high pure germanium is used for gamma ray and infrared detector applications.²

Although major interest in ultra-high purity (UHP) is generated by advanced technologies (optoelectronics, high vacuum processes, cryogenics, etc), extreme purification is also motivated by theoretical and practical limits of determining the intrinsic physical properties of the pure material.³ The carrier mobility which depends on the scatter mechanisms is a function of crystal perfection and purity.⁴ Important properties of the materials can be enhanced substantially by reducing the concentration of impurities to extremely low levels. Insufficient purity of starting materials, used for synthesis and growth of crystals is responsible for weak device performance⁵. The sustainable development of latest technology basically requires adequate ultra pure materials. Therefore, the high

level purification of materials is emerged as an important phenomenon.

Concentrations of impurities as low as one part in million in the major metal matrix can significantly influence physical properties. Electrical properties are generally influenced by substitutional impurities, homogeneously dissolved in the material, while mechanical properties are strongly dependent on interstitial ones. The influence of minute quantities of impurities on the physical properties of the base metal can be applied for the purpose of indirect purity evaluation, thus providing quantitative comparative methods to accompany direct elemental analysis, which is generally cumbersome due to isotopic interferences.

Refining consists of purifying an impure material and it can be metal, semiconductor, insulator in the form of liquid or solid. It is to be distinguished from other processes such as smelting and calcining in that those two involve a chemical change to the raw material, whereas in refining, the final material is usually identical chemically to the original one, but it is purer when compared to original one. Different types of processes are used for purification including pyrometallurgical and hydrometallurgical techniques.

2. Purification Methods

Techniques of metal refining and purification rely on the differences in physico-chemical properties of the base metal and the impurities. In order to reach the desired ultra-high purity (UHP), a sequence of complementary purification steps is required. These steps fundamentally apply in the form of chemical, electrochemical and physical methods.

General methods of purification are discussed in the following sections. Aqueous precipitation techniques and fire refining are suitable for removing large quantities of different impurities, as applied in commercial hydrometallurgical and pyrometallurgical operations, and under appropriate conditions they can also be applied to fine purification. In order to achieve ultra-high purity, however, further ion-selective methods have to be applied, usually in aqueous media. The metals are generally extracted from the purified solution by electrolysis or hydrogen reduction of the crystallized and dehydrated salt. Remaining traces of impurities can be eliminated by refining through electrolysis or by different physical methods, including vacuum melting, distillation, zone melting, and hydrogen-plasma melting or, in special cases, electrotransport. The result of the procedure may equally depend on the primary (gross) and the secondary (fine) purification steps. The purified metal is annealed in

ultra-high vacuum or hydrogen, and finally brought to a form suitable for the application or the testing procedure in several steps of mechanical shaping and annealing. Concomitant superficial contamination is removed by repeated chemical and electrochemical polishing.

2.1 Pyrometallurgical refining

Difference in the chemical properties of the base metal and the impurity permit a large number of chemical-metallurgical refining techniques. The principal chemical property is reactivity, or affinity toward added agents, such as oxygen, chlorine and sulphur. In the common fire refining process, the reagent added to the molten metal at an appropriate temperature.

2.2 Hydrometallurgical refining

High purity materials are often obtained from aqueous solutions by hydrometallurgical methods, offering the possibility of eliminating a large number of impurities from a variety of base metals. Preliminary purification of the solution is carried out usually by precipitation techniques (example ion exchange or solvent extraction). The base metal of high purity can be extracted from the solution by the following alternative methods.

- Evaporation to dryness, followed by hydrogen reduction of the compound (usually a chloride or iodide of the metal).
- Precipitation of the metal (with NH_4OH as hydroxide, or with organic agents as oxalates, stearates or citrates) and calcinations followed by hydrogen reduction of the oxide.
- Cathodic reduction by direct electrolysis of the purified solution.

The procedure and the applied reagents used for extracting the base metal from the purified solution are selected with due care to avoid contamination. Materials are obtained from solution phase generally in a loose, powdery form, requiring melting to produce bulk material in a compact shape.

3. Purification based on main property

The purification methods based on main property are assembled in Figure 1.

3.1 Zone Melting

Zone refining is one the most important purification techniques. In zone refining, a solid is refined by passing a number of molten zones through it in one direction. The number of such passes depends on segregation coefficients of certain or all impurities present in the host material

matrix. Each zone carries a fraction of the impurities to the end of the solid charge, thereby purifying the remainder. Zone refining was first described by the U.S. scientist “W.G. Pfann” working for Bell laboratories and was first used in the early 1950s to purify germanium for transistors⁶. The purity achieved was less than one part of detectable impurity in 10,000,000,000 parts of germanium. The method was adopted in transistor manufacture around the world. It is now considered to be more elevated and preferable technique to achieve ultra-high pure metals in ppb levels. The materials have tremendous applications in modern developments of electronic industry.

3.1.1 Principle of zone melting

Zone refining is not a technique which resulted from the discovery of new principles. In retrospect one can clearly see that zone refining was a logical extension of the use of the freezing or crystallization process as a means of purification. To use crystallization as a means of purification one takes advantage of a well known physical fact, namely, when a solution starts to freeze the solute is almost always unevenly distributed between the liquid and solid phases⁷.

The relative positions of liquidus and solidus lines in the equilibrium phase diagrams indicate that the solubility of impurities may differ considerably in the molten and the solid metal phases. The portion of impurities rejected by solidifying base metal is pushed along by a solidification

front. The rate of solidification is controlled by proper temperature gradients, impurities can be concentrated in a moving molten zone, which carries them to one end of the metal rod. Impurities whose solubility is higher in the solid phase are partially rejected by the molten zone; therefore, they are concentrated in an opposite sense. The equilibrium partition (or segregation) coefficient is the ratio of the equilibrium concentrations of the impurity in the solid and in the liquid phases (equ. 1).

$$k = \frac{C_i (solid)}{C_i (liquid)} \quad (1)$$

For dilute solutions - as in the case of almost pure metals - the segregation coefficient calculated as the ratio of the intercepts of the initial solidus and liquidus tangents with any horizontal line drawn from the temperature axis^{8,9}.

Due to the slow diffusion transport of the segregated impurities from the boundary layer proceeding the solidification front, the effective value of the partition coefficient¹⁰ at finite rates of solidification set by the travel speed of the molten zone, is lower than the equilibrium k_0 value, where v_s is the rate of solidification, δ is the thickness of the diffusion boundary layer and D is the diffusion coefficient (equ. 2).

$$k_{eff} = \frac{k_0}{k_0 + (1 - k_0) \exp(-v_s \frac{\delta}{D})} \quad (2)$$

The efficiency of this purification method can be enhanced by applying relatively longer specimens, slower rates of zone travel and narrower molten zones at the enhanced purity levels, in which case the technique is considered as zone refining. The relative impurity concentration (C/C_0) along the length of the bar after n passes of the zone is given in equ-3 where x is the distance from the head of the rod of the total length L .¹⁰

$$\frac{C}{C_0} = [1 - (1 - k_{eff}) \exp(-k_{eff} \frac{x}{L})]^n \quad (3)$$

The initial and the actual concentration of the impurity in a section of the rod are c and c_0 , respectively. The effect of various values of the segregation coefficients on the concentration profile of the impurity as a result of one zone

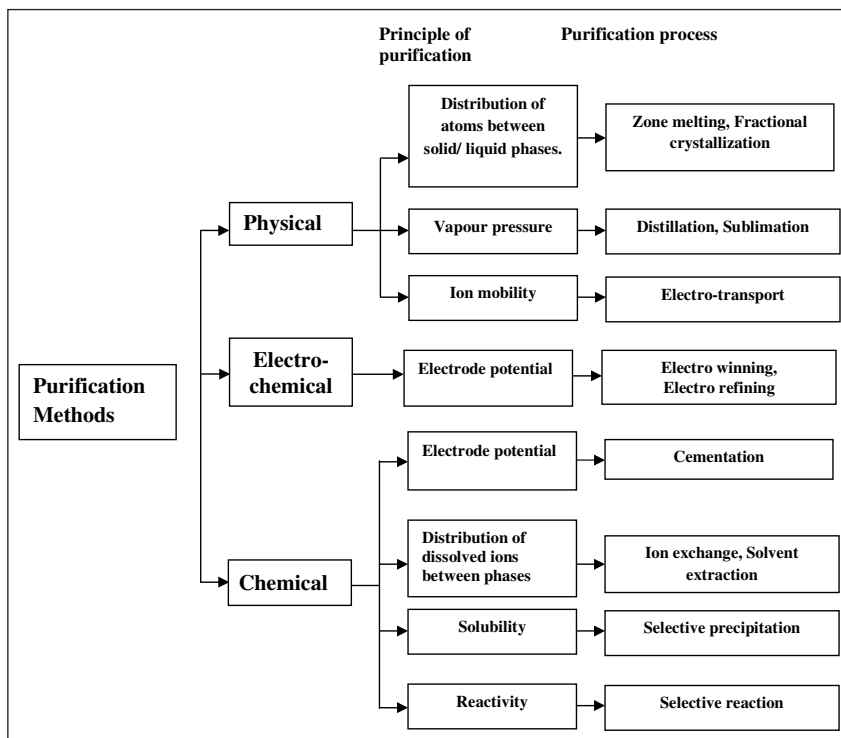


Figure 1. The flow-chart showing purification methods based on main property

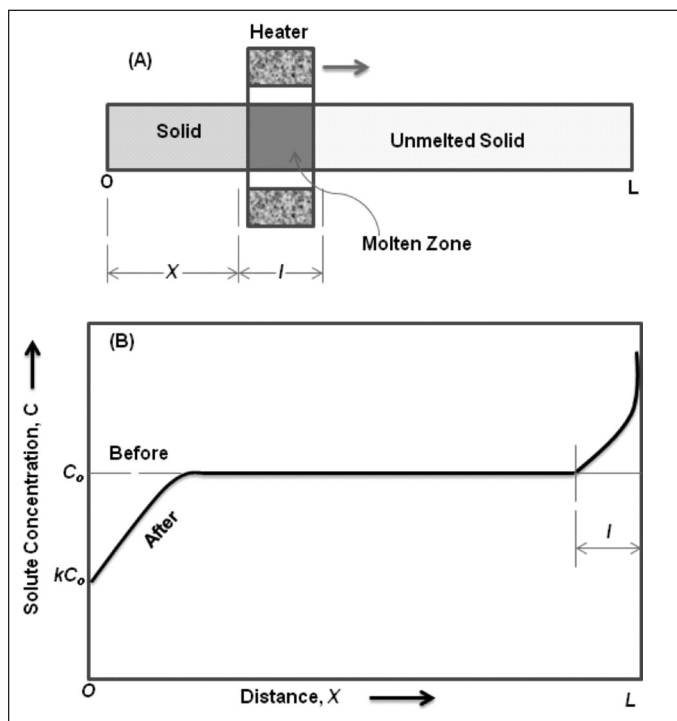


Figure 2. (A) Molten zone of length l traversing a cylindrical ingot of length L ; (B) Approximate concentration of solute after passage of one molten zone through a charge of uniform mean concentration C_0 .

pass at the optimum speed of travel is demonstrated in Figure 2.

As the impurity content of the liquid phase is continuously increasing during the operation, a single pass of the molten zone cannot yield any appreciable degree of purification. High purity can only be achieved by applying sufficiently pre-refined material and multiple (e.g. 15-25) passes of zone. Impurities with effective partition coefficients less than unity ($k_{eff} \approx 1$) move in the direction of zoning, and are concentrated at the end of the rod, while those with partition coefficients higher than unity ($k_{eff} \approx 1$) travel in the opposite direction. However, no segregation can be expected when the value of the partition coefficient does not differ significantly from unity ($k_{eff} \approx 1$). The purifying effect of zone melting is most often combined with that of melting in vacuum or reactive gas. For volatile metals, an inert or reactive gas atmosphere may be required. The metals purified by zone refining are Te, Cd, Ge, Ga, Fe, Mg, Al, Cu, Mo, W, Co, Re, Ti, Zr, Pb, Zn, U, Sn, Bi, Sb, In, Be, Pt and Si¹¹. The purity of the product is highly sensitive to the material of the container- as a source of contaminants-applied in horizontal arrangements. We have listed some of the container materials used for zone refining (and crucibles for distillation) of the specific metals in Table 2.

Table 2. Selection of container materials for zone refining and Crucible materials for vacuum distillation

Crucible	Elements to be distilled
Iron	Cd, Mn, Pb, Zn, Ca, Ba, Sr, Cs
Low Carbon Steel	Mg, Na, Li, K, Sc, Sb, Sn
SS (Ni/Cr)	Mg, Na, Li, K, Ca, Sr, Ba
Ta (Mo)	Rare earths, Cr
Al ₂ O ₃ (MgO)	Cd, Zn, Sn, As, Cu, Co, Fe, Ni, Mn, Se, Te, Ge, Ga, Pb, Tl, Ca, Bi, In, Ag
Quartz	Te, Se, Sb, Bi, As, In, Ca, Tl, Zn, Cd, Sn, Rb, Cs
Beo, ThO ₂	Be, Fe, Cs, K, Na, Li, As, Te
Pyrex	Mg, Pb, Cs, K, Na, Li, As, Te
Graphite	Zn, Cd, Sn, Ag, Au, Ge, Mg, Sr, Hg, Al

The use of a container is avoided by the floating zone melting of vertically arranged specimens. The molten zone is stabilized by the surface tension of the material and the electromagnetic forces of the induction coil. This technique has the added advantage of efficiently stirring the molten zone, which enhances the transport of impurities and results in higher effective segregation coefficients. Zone refining is a slow and expensive technique. Therefore, it is usually applied as the final purification step in the preparation of ultra-high-purity metals, following large-scale purification by less expensive and more generally efficient methods.

3.2 Fractional crystallization

Fractional crystallization is a method of refining substances based on differences in solubility. If a mixture of two or more substances in solution is allowed to crystallize, for example by allowing the temperature of the solution to decrease, the precipitate will contain more of the least soluble substances. The proportion of components in the precipitate will depend on their solubility products. If the solubility products are very similar, a cascade process will be needed to effectuate a complete separation. This technique is often used in chemical engineering to obtain very pure substances, or to recover saleable products from waste solutions.

3.3 Distillation

Sufficient differences in vapour pressure may allow purification techniques involving the preferential volatilization of either the base metal or the impurities. The former technique applies to relatively volatile metals,

characterized by high vapour pressures at convenient temperatures, whereas the latter option may serve the purification of refractory metals. The vapour pressure of some components may reach a significant value even below the melting point, in which case sublimation can be carried out in a simple way. Although distillation requires a relatively sophisticated operation, it offers higher efficiencies¹².

3.4 Sublimation

At a particular temperature and pressure/vacuum, it is possible to separate various metals and compounds from each other by sublimation process. Sublimation is a preferred process for the separation and purification of especial chemical compounds. In this process, the solid compound is heated under vacuum in a sublimation reactor. The solid under consideration sublimes and condenses on water cooled cold coils/fingers as purified compound which is later collected^{13,14}. The residue left over after removal of vacuum and cooling is usually the non-volatile impure component of the compound. Since sublimation is an endothermic process, it is considered energy intensive and used rarely.

3.5 Electro-transport

This process used when extremely high purity of metals is required due to very high costs involved for special applications only. This is a solid state purification process, where in atoms when subjected to an electric field of high magnitude, they migrate at rates depending on the effective charge obtained due to electron collisions¹⁵. Typically current densities in the range of 10^3 - 10^5 A cm⁻² are applied in this process. This calls for smaller cross section of the subject material used. Electron migration process is particularly useful in the removal of interstitial impurities, like, oxygen, nitrogen, carbon and hydrogen since their mobility compared to substitutional impurities is significantly higher.

3.6 Electro-refining

This process is basically an electro deposition process commonly used for purification or refining of impure metals. Typically, impure metal to be purified is taken as an anode with a suitable electrolyte. The pure metal gets deposited on cathode electrode selectively based on the chemistry of the electrochemical bath and the current densities used. Electro-refining is typically used for the separation of heavy metals such as plutonium, caesium, and strontium from uranium matrix in the nuclear industry. The other variation of the electrochemical process of purification is called, the electro-winning. Here, the metals to be separated or purified are taken in liquid form,

dissolved typically using a leaching process (selective dissolution) in acidic or molten salt form. The anode and cathode are typically inert metal bars. When current of required current density is applied across the electrodes, metals selectively get deposited on the inert cathode. Lead, copper, gold, silver, zinc, aluminium, chromium, cobalt, manganese, some rare-earths and almost all alkali metals are produced by electro-winning¹⁶. Electro-extraction process is also useful in the treatment of many industrial wastes for removal of toxic and sometimes valuable metals from them.

3.7 Cementation

This is a process sometimes used for the recovery of metals from leach liquors. It is a typical heterogeneous precipitation process where, the metals of interest are reduced at a solid metallic interface. Copper cementation process is a typical example, where, iron is used to reduce copper ions on an iron surface because of their large difference in electrode potentials. Here iron oxidizes and copper reduces at the solid iron - copper ion leach interface¹⁷.

3.8 Ion exchange and solvent extraction

These processes are typically used for difficult to separate metal systems, like, tantalum-niobium, zirconium-hafnium, nickel-cobalt, etc. These sets of metals typical have similar physical and chemical properties, which make them difficult to separate from each other. The difference in solubility of these species in aqueous and organic media is utilized to bring about separation in this case. Equilibrium distribution coefficient determines the effectiveness of separation for a particular extraction system, defined as a ratio of unit volumes/weights of metals in organic (solid or liquid) phase to aqueous phase (equ-4).

$$D = \frac{OM_C}{AM_C} \quad (4)$$

In solvent extraction process, also called as liquid-liquid extraction process, the aqueous solution containing metal species to be separated is mixed with an organic solvent (e.g., tri butyl phosphate, mono iso butyl ketone, etc.) during which, mass transfer takes place and one of the species transfers to organic phase and when allowed to settle, organic solvent and aqueous solutions separate by their density difference-this brings about physical separation of the metals and thus purification. This process is done industrially in equipment called mixer settlers. In the ion exchange process, the mixed metal aqueous is passed through ion exchange columns, where, depending

on the process conditions, the metals get selectively adsorbed onto the resins in the exchange column which are later separated by desorption treatment, there by bringing about purification/separation.

Figure 3 shows the vapour pressure of metals in periodic table as a function of temperature based on the thermochemical equations. The impurities with higher vapour pressures than that of base metal were expected to be eliminated easily from base metal components. On the other hand, such impurities were not separated due to closer and lower vapour pressures than that of base metal.

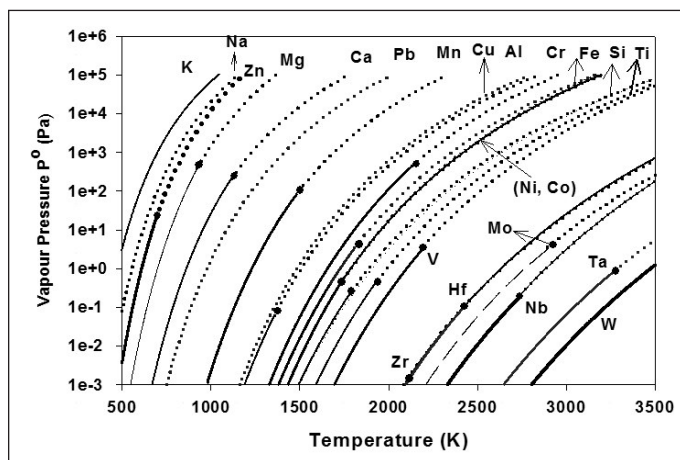


Figure 3. Typical profile of vapour pressure vs. temperature for various elements in periodic table

4. Applications

High purity materials are mainly associated with their applications in microelectronics, space engineering, atomic energy, medicine and basic science research. High purity materials purification by vacuum and solid-liquid interface techniques is usually termed as dry processes. Most radical ways of enhancing the efficiency of materials purification is to employ refinement techniques with different mechanisms of impurity separation. Many of the processes begin with chemical, physico-chemical and end up with dry processes like vacuum distillation (selective vaporization), and zone refining. The final purity is invariably achieved by growing single crystals with perfect lattice structures. Purification methods for some metals with their analysis data carried out in C-MET, Hyderabad are discussed below.

4.1 High purity cadmium

Cadmium is generally associated with several zinc ores and therefore is a by-product of zinc industry. Cadmium is one of the major constituents of II-VI compound semiconductors. The most remarkable characteristics

Table 3. Analysis results of input, filtered and residue cadmium (all in ppm)

Elements	Input	Filtrate	Residue	Detection limits
Hg	<1.0	<1.0	<1.0	<1.0
Cr	<0.1	<0.1	0.2	<0.1
Zn	7	0.5	2	<0.1
Pb	120	230	115	<1.0
Bi	<1.0	<1.0	<1.0	<1.0
Co	<0.1	<0.1	<0.1	<0.1
Ni	3	6	5	<0.1
Fe	1	1	<0.1	<0.1
B	<1.0	<1.0	<1.0	<1.0
Si	<1.0	15	<1.0	<1.0
Mn	<0.1	<0.1	<0.1	<0.1
Mg	3	1	<0.1	<0.1
Cu	100	210	40	<0.1
Ag	<1.0	<1.0	<1.0	<1.0
Al	<1.0	<1.0	<1.0	<1.0
Ca	12	7.5	0.75	<0.1
O	140-150	10-20	NA	<2

NA= Not Analyzed.

of cadmium are its great resistance to corrosion, its low melting-point and excellent electrical conduction. We have developed process technology for the preparation of 6N (99.9999 at.%) cadmium (Cd) starting from 3N (99.9 at.%) purity. This high purity cadmium is one of the major constituents in technologically important compound semiconductors. CdTe and CdZnTe substrates are used for growing epi-layers for Focal Plane Arrays (FPAs), whose major applications are in night vision cameras and thermal imaging devices in the kilometres range, predominantly used by army during night time operations. High purity cadmium possesses a large capture cross section for thermal neutrons and is also used to fabricate moderator rods for nuclear reactors. Purification of cadmium is achieved by vacuum distillation.

As discussed earlier the raw material for cadmium extraction obtained from the zinc residue, due to the partition coefficient of Zn in Cd under melt-vapour condition is 2 and vapour pressure of Zn is very close to that of Cd at 425 °C (which is generally the distillation temperature) indicating that the removal of Zn is very difficult. Initially, the input cadmium was filtered to remove the high density metallic impurities, which are concentrated in the filtrate. In other words, the elements like Cu, Pb and Ni which are more denser than cadmium

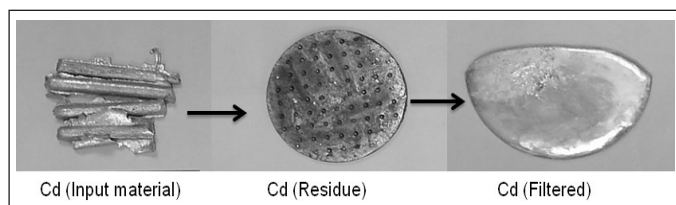


Figure 4. Cadmium metal (filtered) collected after filtration process.

got concentrated in the filtrate, the elements like Zn and Mg which are less denser than cadmium stayed back in the residue and finally filtered cadmium metal is obtained as shown in Figure 4. The residue and filtered cadmium was analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the results are compared with the input material which is given in Table 3. As evident from Table 3 the filtration process minimizes impurities in cadmium (residue) material before subjected to vacuum distillation.

Vacuum distillation results have been studied for most common impurities in cadmium. For vacuum distillation the basic design and fabrication of the vessel is based on the following operational methodology. The mean free path, λ of Cd vapor was estimated to be around 9.1 cm using the Sutherland formula $\lambda \text{ (cm)} = 2.33 \times 10^{-20} \times T / (\xi^2 P)$, where T is soaking temperature (723 °K), ξ is diameter of Cd atom ($2 \times 1.48 \times 10^{-8}$ cm) and P is initial vacuum (2.1×10^{-3} torr). Therefore, this distillation process could be called as ‘viscous’ type (when $\lambda < L$), where L is the distance between the molten metal surface (bottom) and cold collection surface (top). Once the evaporation starts, resulting in decrease of λ to 4×10^{-3} cm and the vapor flow thereon is expected to be turbulent. The vapor pressures, P_v of major impurities at 450 °C were calculated using $\log(P_v) = a-b/T$; where p_v is in microns of Hg, temperature (T) in Kelvin and a, b are constants taken from the data given by Dushman¹⁸. These values of vapour pressures of various impurity elements including Cd are plotted in Figure 5 for comparison. This reveals that the vapour pressure of Zn is very close to that of Cd at 425 °C. It can be anticipated that during distillation most of the low vapour pressure impurities, say lesser than one order of magnitude to that of Cd, would tend to remain in the residue. Three consecutive distillations efficiently eliminated impurities having relatively high vapour pressures such as Zn, Mg, Sb, Bi, Se, As, Pb, Ag. The increase of the distillation temperature from 375 to 450 °C contributed to increase in rate of distillation of Cd without significant changes in the purity. Further increase in temperature caused degradation in the purity of distilled Cd. High volatile impurities such as Cs, Li, K, Na, P and S have lower molal heat of vaporization, since the heat of vaporization, as

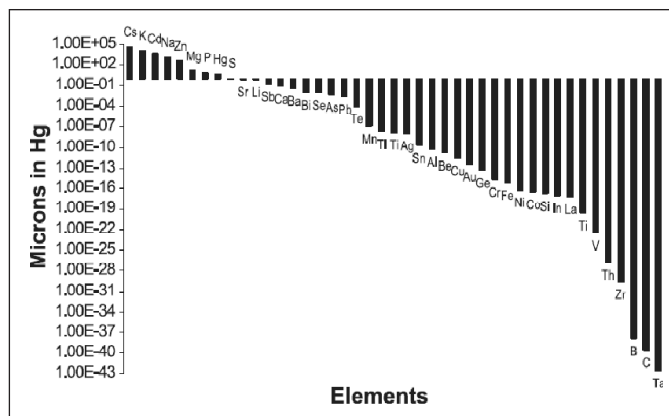


Figure 5. Vapour pressure of impurities at 723 K. (reproduced from ref. 19)

per Trouton’s law, is roughly proportional to the normal boiling point. Therefore, these impurities have been removed by preheating and degassing of cadmium charge and these were not detected in the distillate, as their content fall below the detection limit.

The residue left at the evaporator contained major

Table 4. ICPOES analysis data of cadmium (reported from ref. 19)

Impurity element in Cd	Initial Starting Cd	Vacuum distilled Cd		
		After 1 st distillation	After 2 nd distillation	After 3 rd distillation
B	0.1	0.07	0.07	0.07
Mg	0.1	0.08	0.08	0.08
Ca	3	1.75	0.97	0.09
Ti	0.1	0.08	0.07	0.07
V	0.1	0.07	0.07	0.07
Mn	0.1	0.08	0.08	0.08
Fe	1.28	0.38	<0.1	<0.1
Ni	41.8	13.83	2.24	<0.1
Cu	47	1.23	0.13	0.09
Zn	1.95	0.58	0.38	0.20
As	3.0	0.9	<0.1	<0.1
Se	0.73	0.52	0.35	<0.1
Ag	39.84	4.7	2.35	0.02
Sn	0.12	<0.1	<0.1	<0.1
Sb	2.0	0.7	0.38	<0.1
Tl	11.7	2.4	0.6	<0.1
Pb	32.68	3.33	1.5	<0.1
Bi	3.9	<0.1	<0.1	<0.1

Al, Si, P, Cr, Co, Hg, Ga, In, Ba, Be, Te < 0.1 ppm each in input and distilled Cd. All values in ppm.

impurities such as Fe, Ni, Cu, Zn, Ag, Sb, and Bi. The impurities such as Zn, Ag and Cu were found to be difficult to separate from cadmium matrix. The presence of 0.2 ppm of Zn was detected even after three successive distillations. This can be attributed to differences in vapour pressures of impurities at distillation temperature 450 °C. The impurities content in the starting material and the vacuum distilled cadmium are given in Table 4. The values in ppm show the compiled average analysis of a large number of samples of around 30 experiments. It is observed that most of the impurities except Zn had gone below the detection limit after third distillation. The table shows gradual reduction of Zn, Cu, Sb, Ag, Ni, Pb and Se impurities on subsequent distillations.

4.1.1 Vacuum distillation of cadmium through oxide layer

Similarly, to the vacuum distillation of cadmium, in a separate experiment, the filtered cadmium was oxidized with a predetermined oxygen flow rate of nearly 40 SCCM for 30 min using mass flow meter (Bromkhost high-tech type E-7600-AAA). The duration of time was selected based on series of distillation experiments with variable oxide formation time. The thickness of the CdO layer was estimated microscopically after taking a transverse section of the top portion of the ingot, polishing the piece and taking the image. The thickness was measured to be around 0.001 mm. The distillation experiment was repeated for various times in the same manner as described above for vacuum distillation of cadmium without oxygen layer. These experimental results of distilled cadmium revealed that the rate of distillation as a function of distillation time decreased exponentially with the increase in oxide concentration on the cadmium melt surface, at least up to 40 min. The weight of input material quantity, oxide layer formation time and rate of distillation (g/h) are shown in Table 5. Based on the behaviour of impurities during cadmium purification, it was expected that the impurities such as Cu, Ag, Au, Pb, S, Bi, Co, Ni, Pt should remain in the evaporator in the form of solution in Cd while Li, Na, Be, Mg, Ca, Zn, Sr, Ba, B, Al, Sc, Ga, Y, In, La, Si, Ti, Ge, Zr, Sn, Hf, V, Nd, Ta, Cr, Mo, W, Mn, Fe should remain in the oxide phase³. This implies that Zn impurity was expected to remain in the oxide phase. Detailed GDMS analytical results of 58 impurity elements from the first and second distillations through oxide phase from is shown in Table 6.

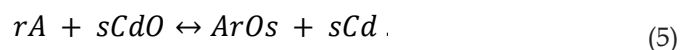
4.1.2 Separation of metallic impurities

Cadmium purification results with and without oxide layer showed substantial reduction of zinc impurity in cadmium distilled with oxide layer. On the other hand,

Table 5. Rate of distillation of cadmium as a function of oxygen flow rate onto Cd melt.

Input Cadmium (g)	Oxygen layer formation Time (min)	Rate of distillation of cadmium (g/h)
845	Without oxide layer	342
847	10	152
885	20	70
880	30	40
860	40	20

without the oxide layer, the Zn in Cd was reduced from 2 ppm to 0.6 ppm after first distillation and then to 0.4 ppm after subsequent second distillation¹⁹. In the present work, Zn in Cd was reduced from 78 to 57 ppb after first distillation in the process where there is no oxide layer and to <4 ppb after first distillation through oxide phase. The basic reaction mechanism was according to equ-5 where 'r' is the number of impurity atoms of 'A' to be separated and 's' the number of CdO molecules or cadmium atoms.



During the process of purification, the most difficult impurity to remove is zinc, because of its distribution coefficient in melt-vapour systems, which is two²⁰. It was also demonstrated that the behaviour of the physico-chemical system used in purification by adding new phases changes the behaviour of several impurities. Hence, in this case by introducing CdO into the system essentially influences the results of purification of impurities with greater affinity to oxygen than cadmium. This class of impurities includes zinc in addition to others²¹. The other impurities like Mg, Al, Fe, Cu, Pb, Ag, Co, Ni, Sb, Bi have also been reduced by nearly two orders. The results tabulated in Table 6 also indicated that the degree of separation of Ni, Cu, Zn, Ag, Sn, Hg and Tl were higher during distillation through oxide layer, when compared to without oxide layer. It was also observed during experimentation that the rate of distillation decreased from 350–400 g/h (without oxide film) to 125–150 g/h (with oxide film). This indicated a mesh like behaviour of oxide layer on the cadmium melt by retaining the metal oxides and allowing the metal to evaporate.

4.1.3 Zone refining of cadmium

As discussed in the above section nearly 5N purity of cadmium by vacuum distillation is achieved while for electronic applications 7N purity is required. Hence, the chunks of the vacuum distilled cadmium were subjected to zone refining. The input material was uniformly melted

Table 6. GD-MS analytical results of vacuum distilled cadmium. Cd-RM is input material, Cd-1 is after 1st vacuum distillation, Cd-2 is 2nd vacuum distillation, Cd-O-1 is 1st vacuum distillation in the presence of oxide layer and Cd-O-2 is 2nd vacuum distillation in the presence of oxide layer (reported from ref. 22)

Impurity	Cd-RM	Cd-1	Cd-2	Cd-O-1	Cd-O-2	Impurity	Cd-RM	Cd-1	Cd-2	Cd-O-1	Cd-O-2
Li	<7	<5	<11	<9	<7	Br	<8	<8	<15	<6	<7
Be	<2	<1	<2	<1	<1	Rb	<0.4	<0.3	<1	<0.4	<0.4
B	<2	5	11	<2	2	Sr	<0.4	<1	<0.2	<0.2	<0.3
C	900	4000	2500	4200	1700	Y	<0.3	<0.2	<0.5	<0.3	<0.3
N	110	2800	640	760	690	Zr	<0.3	<0.3	<0.5	<0.5	<0.3
O	4300	7600	2200	99000	2800	Nb	<0.4	<0.3	<1	<0.4	<0.4
F	<4	<1	<5	<1	<2	Mo	<1	<1	<2	<0.9	<0.9
Na	49	7	97	20	<3	Pd	NA	NA	NA	NA	NA
Mg	<3	<1	<3	<2	<2	Ag	7400	<40	<25	<25	<8
Al	<2	<2	<2	5	<1	Cd	Matrix	Matrix	Matrix	Matrix	Matrix
Si	4	14	45	19	7	In	<20	<45	<45	<120	<25
P	<1	<1	<2	<1	<1	Sn	57	<15	<25	<7	<8
S	87	5	<5	5	<2	Sb	290	<2	<2	<1	<0.9
Cl	5	26	67	44	8	Te	<35	<90	<30	<85	<55
K	<1	<2	<10	<4	<1	I	<20	<15	<130	<75	<75
Ca	<10	<8	<40	<10	<10	Cs	<3	<3	<10	<9	<6
Sc	<0.6	<0.4	<0.9	<0.5	<0.5	Ba	<8	<5	<30	<8	<12
Ti	<0.3	<0.9	<0.5	<0.3	<0.3	La	<3	<65	<15	<25	<20
V	<0.2	<0.2	<0.3	<0.2	<0.2	Ce	<6	<11	<25	<45	<30
Cr	<1	<0.8	<3	<1	<1	Hf	<0.3	<0.3	<0.5	<0.2	<0.3
Mn	<20	<20	<20	<20	<20	Ta	NA	NA	NA	NA	NA
Fe	<15	<15	<15	<15	<15	W	10	15	<1	<0.8	<0.6
Co	1000	<0.3	<0.7	<0.2	<0.2	Pt	<0.6	<0.5	<1	<0.5	<0.6
Ni	27000	10	20	<3	<2	Au	<5	<5	<5	<5	<5
Cu	570000	190	330	33	<2	Hg	110	40	32	<10	<5
Zn	78	57	130	<4	<4	Tl	9800	6	18	67	0.8
Ga	<1	<0.9	<2	<1	<1	Pb	480000	130	110	36	<0.7
Ge	<3	<2	<4	<2	<2	Bi	19	<0.4	<0.7	<0.4	<0.4
As	<10	<10	<10	<10	<10	Th	<0.6	<0.5	<0.9	<0.9	<0.8
Se	<15	<25	<25	<6	<25	U	<0.09	<0.06	<0.1	<0.08	<0.08

NA=Not Analysed

around 450 °C under hydrogen gas flow in a quartz boat of length 560 mm, breadth 33 mm and 20 mm height with 1×5 mm thickness. The cooled cadmium ingot was taken out and momentarily etched using dil. HNO₃ and nanopure water under class 100 laminar air flow wash bench. The ingot was subsequently dried using nitrogen gas before loading into the quartz tube for zone refining. Figure 6 shows the zone refined ingot of 7N purity cadmium. The ICP-OES analysis of zone refined cadmium shows that majority of impurities are less than the detection limits (Table 7). Comparatively, zinc is the most difficult impurity



Figure 6. Zone melted Ingot of cadmium.

element to remove in cadmium matrix by zone refining.

4.2 High purity gallium

Gallium occurs in very low concentrations in the earth crust. It is not present in pure metallic form but is usually extracted as a by-product during processing of aluminium from Bauxite by Bayer process. Initial concentration of the impurities in gallium depends on by which technique it has been extracted. Gallium usually contains many metallic impurities, such as Al, B, Fe, Hg, In, Cd, Zn, Cu, Pb, Co, Ni, etc. The specific targeted impurities, such as Zn, Pb, Fe, Ni, B, Cr, Mn, Cu and Al may tamper the device performance by spoiling the electronic and optical properties. 3N/4N pure gallium obtained by extraction, electro-refining processes has to be further purified to 6N level for its use in growing device quality crystals and multilayered epitaxial structures^{24,25}. The most useful compounds of gallium are gallium arsenide (GaAs) and gallium phosphide (GaP) which is used in the manufacture of electronic devices. GaP is used to fabricate light emitting diodes (LEDs). Since GaAs has the ability to convert electrical energy into optical energy and vice-versa, it is used in the fabrication of optoelectronic devices such as laser diodes, photo diodes, and solar (Photo-voltaic) cells. GaAs-based ICs,

Table 7. ICP-OES analytical data for the trace impurities in cadmium (reported from ref. 23).

Element Starting Material	Middle region after cycle (ppm)				End region after cycle (ppm)				
	1	2	3	4	1	2	3	4	
Ag	9.2	3.5	0.5	<0.1	<0.1	0.76	0.65	<0.1	<0.1
Al	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
B	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<0.1	<0.1	<0.1	<0.1	<0.1	0.93	0.25	<0.1	<0.1
Cr	<0.1	<0.1	<0.1	<0.1	<0.1	0.32	<0.1	<0.1	<0.1
Cu	4.5	<0.1	<0.1	<0.1	<0.1	65.4	31	<0.1	<0.1
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	0.88	<0.1	<0.1	<0.1
Mg	1.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	5.4	<4.5	3.7	2.0	<0.1	42.5	3.61	1.02	<0.1
Pb	14.6	13	12	6	<0.1	167	67.3	<0.1	<0.1
Sb	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<0.1	<0.1	<0.1
Se	<0.1	<0.1	<0.1	<0.1	<0.1	<1.0	<0.1	<0.1	<0.1
Sn	0.2	<0.1	<0.1	<0.1	<0.1	<1.0	<0.1	<0.1	<0.1
Mn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	24.4	21	12.6	2.5	0.62	230	29	11.3	6.42

although developed in the recent years, are primarily used in applications such as satellites, supercomputers, and defence because they can send information about five times faster, withstand more radiation and operate at higher temperatures than that of silicon-based ICs.

4.2.1 Hydro-chemical processing of gallium

Hydro-chemical processing of gallium with acids makes it possible to remove oxide and hydroxide inclusions and metallic impurities. The low-melting metals, including gallium, are capable of absorbing water. This hydro-chemical processing may take care of the metallic impurities especially Na, K, Al, Mg and Zn. In hydro-chemical processing 4N/5N purity raw gallium has been treated with different concentrations (15%, 25% and 30%) of sub boiled hydrochloric (HCl) acid. With different acid concentrations the weight loss observed after hydro-chemical processing is in the range of 0.5–2.0%. The spent acid solutions were made to react with aqueous ammonia at certain pH and converted into gallium hydroxide, which was dried at 100 °C for 2 h followed by calcination at 850 °C for 2 h to make commercial grade gallium oxide. The overall impurity separation (Sc) for each impurity element

by hydro-chemical processing was calculated using $Sc = (C_i - C_f)100/C_i$, where C_i and C_f are concentration of each impurity element in starting and purified gallium, respectively. While calculating the separation coefficient for hydro-chemical processing with different acid concentrations, C_f value has been taken as the lowest value according to its acid concentration. Table 8 depicts the Graphite Furnace -Atomic Absorption Spectroscopy (GF-AAS) analysis of raw gallium and sub-boiled HCl-treated gallium with different acid concentrations. From Table 8, it is obvious that the purification efficiency of the elements Cr, Pb, Fe, Ag and Sb are more than 80% compared to the other impurity elements.

Table 8. GF-AAS analysis of hydrochemically processed gallium (ppm) (reported from ref. 26)

Element	Raw gallium	15% S.B. HCl	25% S.B. HCl	30% S.B. HCl	Purification efficiency
Al	0.082	0.112	0.020	2.800	75.60
Cr	0.104	<0.003	<0.003	<0.003	97.11
Zn	0.140	0.035	<0.03	<0.03	ND
Pb	6.200	0.08	0.045	0.065	99.27
Cu	0.054	0.07	0.08	0.050	7.40
Fe	0.615	<0.02	0.07	0.020	96.74
Mn	<0.01	<0.01	<0.01	<0.01	ND
V	<0.03	<0.03	<0.03	0.600	ND
As	<0.007	<0.007	<0.007	<0.007	ND
B	0.04	0.025	0.035	0.050	37.30
Ag	0.150	0.007	0.021	0.052	95.33
Sb	<0.330	<0.002	<0.002	<0.002	98.66
In	0.062	<0.002	<0.002	<0.002	96.77
Hg	0.800	0.700	1.050	0.650	18.75

ND = Not detected or determined

4.2.2 Vacuum refining of gallium

This process is used to remove residual moisture, dissolved gases and impurities that are more volatile than gallium not only metals (alkali metals, Cd, Zn, Mg and others) but also their compounds. The process will be run in a dynamic vacuum (10^{-5} mbar) in a quartz reactor. Gallium will be taken in a graphite boat, which ensured a large vaporization area. The process temperature and duration will be 900-1000°C and 2 hrs, respectively. After vacuum heat treatment, gallium will be cooled, transferred

to a special container in an inert atmosphere and then analyzed for the impurities. The heat treatment under vacuum will reduce the Cd, As, P, Te, S, Se, Zn, Hg and other low boiling impurities.

4.2.3 Purification of gallium by zone-refining

Research methodology include, creation of narrow and uniform solid-liquid interface, maintenance of proper ultra low temperature conditions through circulation of coolant (+5 to -20°C), optimization of zone travel rate (crystallization rate) during controlled zone-refining (crystallization) of gallium, elemental purity analysis, RRR measurements. Importantly, segregation study pertaining to the impurities (Al, Fe, Cu, Zn, Sn, Pb, In, Bi, Cd) present in the gallium (major) matrix will form one of the major segments of this process step. GF-AAS analysis data of zone refined gallium are given in Table 9.

Table 9. GF-AAS analysis of different fractions of (Zr-1 to Zr-4) zone refined gallium samples which were cut longitudinally in series from one end (reported from ref. 26)

Impurity element*	Zr-1	Zr-2	Zr-3	Zr-4
Fe	100	179	140	675
Pb	20	4300	3900	5200
Cr	25	82	91	187
Mg	40	35	49	58
Ag	5	83	93	109
In	25	33	49	56
Al	49	64	69	92
Hg	60	58	75	72
Cu	<10	32	60	50
Zn	5	41	3900	60
Sb	45	51	69	65
Sn	80	85	100	115

*values are in parts per billion (ppb).

4.2.4 Fractional crystallization of gallium

Fractional crystallization technique is very simple in operation and apparatus and industrially advantageous. Here the starting raw gallium which is in molten stage will be crystallized fractionally by using a coolant condenser. The trace metal impurities whose distribution coefficient is less than unity will start solidifying on the coolant

condenser, leaving the impurities in the molten state gallium. The solidified gallium metal has to be removed before its external walls touch the inner walls of the liquid gallium vessel. As the solidification is slower the purity will be better. We have to optimize the solidification rate, where it depends upon the flow rate and cooling media temperature.

4.3 High Purity Tellurium

Tellurium is sometimes found free in nature. More commonly, it is found combined with metals, such as in the minerals calaverite gold telluride, (AuTe₂) and sylvanite (silver GOLD telluride). Commercially, tellurium is obtained as a by-product of electrolytic copper refining. Tellurium is one of the major constituents of II-VI compound semiconductors. The ultra high purity (UHP) tellurium is required for preparation of the compound semiconductors. The tellurium based semiconductor devices are used in infrared (IR) detectors, solar cells, thermo-electric coolers, etc. These devices are mainly used in strategic electronics such as defence, space, etc. Purification was done by electro-refining, vacuum distillation and zone refining. Majority of impurities are removed by electro-refining and vacuum distillation and analyzed by atomic absorption spectrometry (AAS). The impurities at ppb/ ppt level are removed by zone refining and analyzed by Mass spectrometry such as GDMS.^{27,28}

4.3.1 Vacuum distillation

The raw tellurium (3N pure) was kept in a graphite crucible and distilled at about 525°C under dynamic vacuum. The material deposited over the water cooled stainless steel (SS) fingers was then subjected to ICP-OES analysis. The overall purity of trace impurity elements was more than 99.995% except selenium which is around 115 ppm. The gaseous impurities like oxygen and nitrogen in vacuum distilled tellurium were < 1 ppm. The following represented the block diagram of vacuum distillation setup (Figure 7).

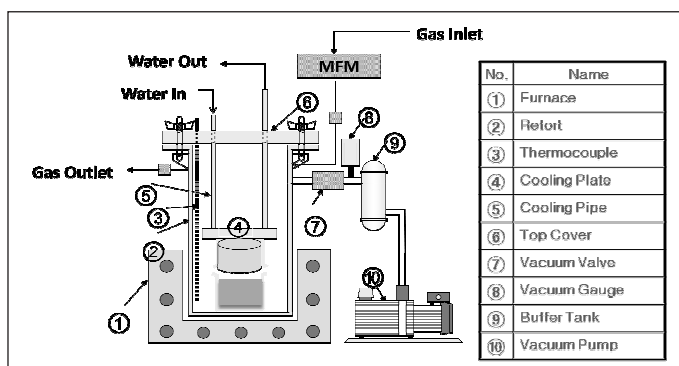


Figure 7. Block diagram of pit furnace, retort, crucible, SS tubes collection of tellurium vacuum distillation system.

The results of the ICP-OES analysis of the starting material, first fraction, the distillate material (middle fraction) and residue are given in Table 11. The values show the compiled average analysis of samples of 5 batches of experiments. The first fraction experiment is carried out at time intervals of 15, 20 and 30 min at 500 °C and found that in case of soaking time of 15 min the material was partially melted, whereas for 30 min soaking time, 50% of the material got evaporated which is not expected in the first fraction experiment. Thus, the soaking time of 20 min was the optimum wherein ~20% of the material got deposited which implies that not much tellurium was evaporated and at the same time high vapour pressure impurities namely, Cd, Zn, Mg and Pb could successfully separate and were found to the extent of 4.5, 2.5, 1.82 and 1.62 ppm, respectively. Thus, the purpose of carrying out “first fraction” experiment is clearly understood; otherwise, these impurities (Cd, Zn, Mg and Pb) with higher concentration would have been observed in the distillate.

Table 10. Analytical data of vacuum distilled tellurium (ppm) (reported from ref. 28).

Element	Raw Material	First Fraction	Distillate Material	Residue
Al	2.5	<1	0.1	60
Cr	1.6	<0.1	<0.1	51.8
Zn	0.7	2.50	0.08	4.9
Cd	1.0	4.5	0.70	<0.1
Pb	54	1.62	<1	1900
Cu	127	<1	<0.1	3450
Bi	1.3	<1	<1	48.5
Co	<0.1	<0.1	<0.1	3.85
Ni	16.5	<0.1	0.31	425
Fe	41.3	<0.1	<1.0	837
Mn	4.9	<0.1	<0.1	72.5
Mg	1.4	1.82	0.67	30
Ca	30	1.0	<0.1	572
Ag	1.75	<0.1	<0.1	410
B	0.3	<0.1	<0.1	6.2
Sb	7.2	<1	<1	210
Si	11.2	<0.1	<1	226

It is seen from the analytical data of the distillate (middle fraction) material that the tellurium contained less content of Fe, Ni, Cu, Sb, Mn, Ca, Al, Cr, Pb, Zn, Bi, Co, Ag, B and Si impurities. On the other hand, the analysis of the residue material shows the enrichment of all the above-mentioned impurities. The impurities Mg and Cd, after removing considerable content in the first fraction, present in the distillate material in the order of 0.67 and 0.70 ppm, respectively, and in order to further reduce the concentration of these impurities, repeated distillations need to be carried out. It is also observed from the results that the concentration of Pb is more in the first fraction when compared to Bi, despite of their comparable vapour pressure which is in the range of $3\text{--}7 \times 10^{-5}$ torr, at 500°C . This is because of higher content of Pb (54 ppm) in the starting material than Bi which is of 1.3 ppm only. Thus the rate of evaporation of impurities, which is a function of mole fraction, is minimum for impurities that have low concentration in the starting material.

4.3.2 Zone refining

The chunks of vacuum distilled tellurium (5N pure except selenium) of nearly 1000 g weight was taken in a thoroughly cleaned and etched quartz (GE214 grade) boat container of dimensions $34 \times 38 \times 560$ mm (ID \times OD \times L) and melted at a temperature, T_m , nearly 13 to 15% more than the melting point of tellurium in a uniform temperature gradient furnace under a constant flow of hydrogen gas (IOLAR I grade). After completely melting, the H_2 gas flow continued till the tellurium bar temperature was cooled down to room temperature (RT) to avoid any possible oxidation. After taking out the tellurium bar, a small portion of tellurium at one end was cut and analysed to check for any added impurities during melting. It was observed from the analysis that the selenium impurity content was 115 ppm and the sum of the amounts of the remaining elemental impurities content indicated the

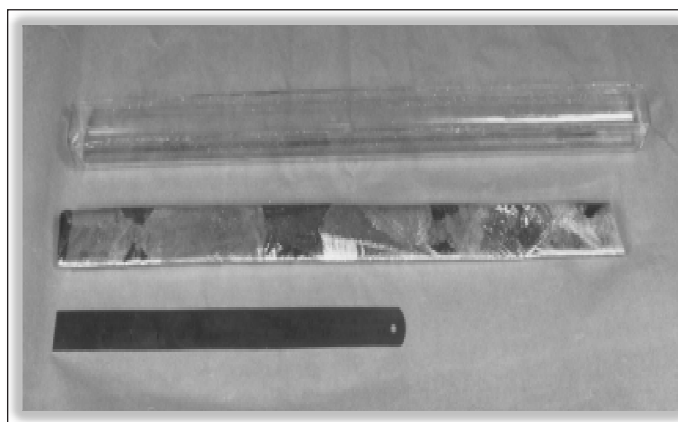


Figure 8. Zone melted Ingot of tellurium

purity of tellurium bar (Figure 8) remaining nearly as 99.999 at. %.

A pre-stage fifteen-pass cycle zone refining experiment with circulation of coolant at $(+5$ to $-8^\circ\text{C})$ on the homogenized sample was carried out in order to sensitize the system parameters and establish suitable experimental conditions and narrow zone(s). In the second stage refining, to further narrow down the liquid region, a twenty-five-pass cycle zone refining experiment with circulation of coolant at a temperature of $+5$ to -15°C is carried out. In this stage, a twenty-five pass zone-levelling experiment on the sample is conducted with coolant temperature at $+5$ to -20°C .

4.3.3 Dendrites

Generally, Dendrites form as the material solidifies in to the melt, leaving molten metal behind that has been reheated from the heat evolved in the solidification process (Figure 9). A liquid when cooled solidifies. Alternatively, it may solidify when the pressure is decreased or increased, depending on the sign of the density change. Once nucleation has occurred, solidification proceeds by the movement of an interface. The process may generate

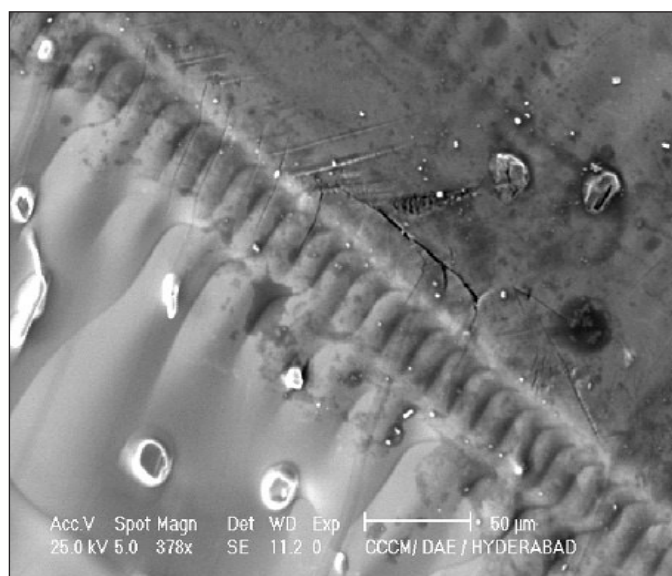


Figure 9. Dendrites formation on zone-refined tellurium during zone refining.

heat if the enthalpy of the solid is less than that of the liquid. Similarly, solute may partition into the liquid, if its solubility in the solid is less than that in the liquid.

4.4 High purity tantalum

Tantalum, always together with chemically similar niobium, occurs in minerals tantalite, columbite and

coltan (a mix of columbite and tantalite). Capacitor grade tantalum powder is used extensively for making tantalum capacitors which are used in computers, cell phones, automobiles and many other electronic applications where utmost reliability is required in terms of life and severe temperature conditions. The other applications of tantalum are in high temperature furnaces, super alloys, structural applications, chemical industries and also in electrolytic bath as electrodes.^{29,30} The major part of tantalum is consumed by capacitor manufacturers which is almost 70% of total demand. The extraction of tantalum from its ore (tantalite ore), its subsequent purification and conversion to tantalum powder consist of a number of process steps. Mostly these steps include crushing and milling of the ore to powder form followed by its dissolution in acid to bring tantalum to solution form. Then the tantalum is required to be separated from the other impurity elements by solvent extraction. The tantalum containing pure solution is then converted to tantalum containing potassium salt where further purification takes place. The salt is then reduced to tantalum powder by sodium reduction process. The reduced tantalum is then washed with combinations of acids and water to get pure tantalum powder. The Ta powder so obtained is dried and subjected to powder processing techniques to get low voltage capacitor grade tantalum powder. For high voltage capacitor grade tantalum powder, the as-reduced tantalum powder is subjected to Electron Beam (EB) melting for its further purification. This is then subjected to hydriding, milling and dehydriding to get high voltage capacitor grade tantalum powder.

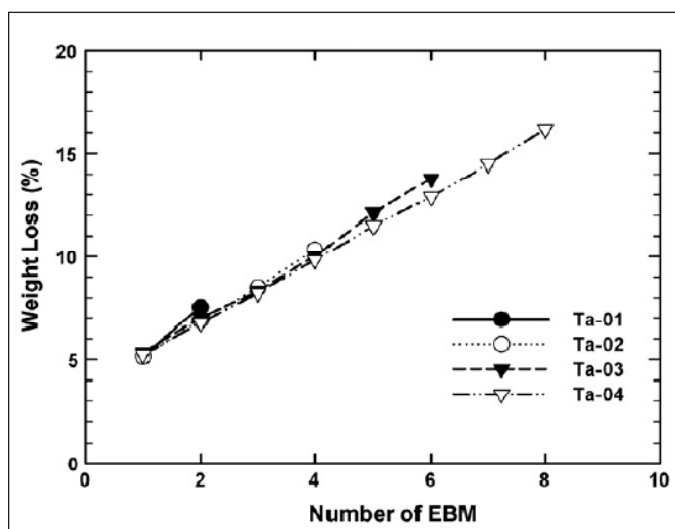


Figure 10. Weight loss of Ta buttons after EB melting vs. number of EB melt cycles. Each sample was given two melts (one melt cycle), one in forward and the other after inverting (reproduced from ref. 31)

4.4.1 Electron Beam Melting

The weight loss of tantalum buttons after EB melting was calculated by weighing material in an electronic weighing balance and the percentage of weight loss of tantalum as a function of melting time was plotted (Figure 10). During the initial melt of tantalum button, the weight loss was as high as 6.8% and in the subsequent melt cycle, it was reduced to nearly 3% due to drastic decrease in the evaporation of residual and metallic impurities. This weight loss during the melt was attributed to vaporization of interstitial impurities caused by increase in temperature and decrease in pressure of the tantalum melt.

The appearance of as-melted tantalum buttons is shown in Figure 11. The tantalum buttons after EB melting were of 55 mm in diameter at the bottom and 60 mm at the top. The Vickers hardness in tantalum was increased with the increase in oxygen concentration and also hardness was affected by the variation in the grain size in the EB-melted Ta button.³² The Vickers hardness, total content of C, N, O and the other metallic impurities in the EB-melted tantalum buttons were plotted against the number of the sample specimens as shown in Figure 10. The behaviour of hardness curve was similar to the rate of removal of gaseous or metallic impurities. In other words, the decrease of total impurities in tantalum has resulted in the decrease of its hardness. Similar behaviour was also observed, where in, the increase in purity of tantalum from 2N to 4N grade, resulted in decrease of hardness.³³

4.5 High purity niobium

Niobium, also known as columbium has a melting point of 2468°C and density of 8.57 gm/cc, which is often found in the “pyrochlore mineral”, the main commercial source for niobium, and “columbite”. It has many properties that make it an excellent candidate for fabricated parts that must be made of a refractory metal. Its high melting point warrants its use at temperatures above the maximum service temperatures of the iron, nickel, and cobalt base metals. It has excellent ductility and fabricability. Pure niobium has a recrystallization temperature range of 982 °C to 1093 °C. Niobium has been used as an alloy for many years. Nb/1%Zr was, and still is, used in nuclear reactors as the tubing for the fuel pellets. As C-103 alloy, it has been used for rocket nozzles and exhaust nozzles for jet engines and rockets. Niobium mill products are used in fabrication of corrosion resistant process equipment including reaction vessels, columns, bayonet heaters, shell and tube heat exchangers, U-tubes, thermowells, spargers, rupture diaphragms, and orifices. Niobium metal powders have found electrolytic capacitor

applications recently as an alternative to tantalum. Capacitor grade niobium powder has been prepared by hydrogen reduction followed by magnesiothermic reduction of the niobium pentoxide.

High purity niobium pentoxide (Nb_2O_5) is an important raw material for a large number of advanced technological applications. High purity niobium pentoxide (>99.99%) is used in the production of lithium niobate single crystals for application in surface acoustic wave devices for TV receivers. 99.9% Nb_2O_5 is used for the production of optical lenses, for ophthalmic, microscopes and video camera lenses, and niobium containing ceramic condensers and actuators. Other than the applications in fine ceramics, niobium pentoxide is the raw material for the production of different purity grades of niobium metal. Technical grade niobium pentoxide is used for the preparation of niobium carbide which is being used in cutting tool industry.

4.6 High purity hafnium

In the production of hafnium and zirconium metals, predominantly used ore is zircon. This is largely because of the ready availability and low cost of zircon as by-product of rutile, monazite and ilmenite mining operations. Hafnium metal content in Indian zircon ore is roughly 2.1 percent and zirconium content varies from 60 to 65%. Therefore, generally Hf to Zr ratio is taken as 1:50. Hafnium production from zircon broadly involves following steps:

- Ore opening and removal of silicates
- Separation of hafnium from zirconium by solvent extraction.
- Extraction of hafnium from the raffinate of zirconium extraction plant.
- Hafnium sponge production

Each of the above steps is enumerated briefly as follows:

Zircon is an inert material and generally not reacted by any mineral acids at normal operating conditions. Commercially it is attacked by fusion. Zircon fusion with caustic soda is generally adopted for opening of ore as the first step in hafnium production. Zircon and caustic soda are taken in a mild steel pot and heated to 6000 °C in a pot furnace. The resultant frit is a mixture of sodium zirconate, sodium hafnate and sodium silicate. Removal of sodium silicate and conversion of sodium zirconate and sodium hafnate into respective hydroxides are achieved by leaching frit with water. Hafnium and zirconium hydroxide mix thus obtained thoroughly washed further and dried to minimize silica in the mix, which is generally

called upgraded ore or washed and dried frit of zirconium and hafnium (WDF). The upgraded ore is subjected to the separation of hafnium and zirconium and get their pure products.

Hafnium and zirconium separation is very difficult by chemical methods because they have great similarity in their chemical properties due to lanthanide contraction effect. Solvent extraction is a simple, economical and effective hydrometallurgical process for separation of hafnium and zirconium. There are several solvent extraction methods employed for separation and manufacture of zirconium and hafnium. TBP-Nitrate method of solvent extraction for hafnium and zirconium separation is more favourable for Indian environment. TBP extracts zirconium in preference to hafnium under certain concentrations of nitric acid. Under any nitric acid conditions hafnium cannot be extracted exclusively by TBP. This is because; the distribution coefficients of both zirconium and hafnium vary directly with nitric acid concentration of the system. The coefficient for zirconium is more than one, while the coefficient for hafnium is less than one. However, the separation factor decreases with increasing acid concentration. Hence, in this methodology, zirconium separated in first step and hafnium with gangue impurities are rejected by zirconium producing industries, through raffinate and intermediate stream, scrub raffinate. Though major portion zirconium extracted in first step, the scrub-raffinate of zirconium extraction process contains zirconium along with hafnium in the proportion hafnium to zirconium 5-7 percent with zirconium ranging from 20 to 40 gram per litre. This scrub raffinate solution is the starting materials for the hafnium plant situated at C-MET, Hyderabad laboratory.

At C-MET, separate solvent extraction circuits are used and the scrub raffinate received as effluent from zirconium industry is subjected to further removal of zirconium to enrich hafnium to 70 to 80 percent using TBP under nitric acid media. Since, hafnium and zirconium separation to get 97-99% hafnium is difficult at low concentrations of hafnium and zirconium in feed material, the hafnium solution from the first circuit of solvent extraction (Hf=70%) is concentrated by precipitation and re-dissolution technique and once again subjected for removal of zirconium to get 95 to 97% hafnium in the a second circuit of solvent extraction systems. In all the aforesaid processes hafnium gets enriched in aqueous raffinate phase along with gangue impurities of zircon hence, a final step of solvent extraction using TBP to purify the hafnium to meet the specification for the use in aero-space industry is carried out at higher concentrations of nitric acid in the third and final circuit of solvent extraction. This process, called as

co-extraction and selective stripping yields 99% hafnium with respect to zirconium in its nitrate solution form.

Pure hafnium nitrate solution obtained from the separation process is converted into its corresponding oxide by precipitation and filtration. The precipitated hydroxide is dried and calcined to get hafnium oxide. Direct reduction of oxide to metal does not give ductile hafnium metal with low oxygen content. Hence, hafnium oxide further chlorinated in the presence of carbon to get hafnium tetra chloride. Reduction of hafnium tetra chloride



Refined Product

Hafnium Sponge

Figure 12. Produced Hafnium Sponge after various refining processes.

is carried out using magnesium by Kroll-Reduction method and hafnium metal sponge obtained from reduction is separated from the reaction product, magnesium chloride by Vacuum distillation. 99% pure hafnium sponge is thus obtained (Figure 12).

5. Conclusions

The purification techniques mainly depend on the physical and chemical properties of the base metal and impurities present in the respective host material matrix. The rate of removal of metallic impurities in any material matrix below parts per million (ppm)/parts per billion (ppb) levels can be achieved by conventional purification processes such as zone melting, fractional crystallization, distillation, sublimation, electro-transport, electro-refining, cementation, ion exchange, solvent extraction, etc. A combination of purification processes was necessary to exploit the separation of impurities. Calculated leakage of oxygen to form oxide face on to the metallic surface during selective volatilization will result in effective separation of impurities for which the separation coefficient is more than 2. Hydrometallurgical methods, offer the possibility of eliminating a large number of impurities from a variety of base metals like hafnium. Ultra-high purity (UHP) materials are crucial building blocks for research and development, and production of advanced materials technologies, which generally require

optimum properties, performance, quality and efficiency. Decrease of total impurities or increase in purity in tantalum has resulted in the decrease of its hardness. Zone refining for low temperature melting points materials like cadmium, tellurium, gallium, germanium, and electron beam melting for high melting point metals tantalum, niobium, and hafnium are very much useful. There is a large process technology gap between indigenous demand of high purity, ultra high purity materials and compound semiconductors which can result in savings of several billions of dollars continuously for the exchequer and has the potential to create substantial jobs in the country.

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References

1. C. V. Kpoczky, Encyclopedia of materials science and engineering, Pergamon press, Oxford, 3 (1986) 2148.
2. V. A. Lejbov, J. Drapala, J. M. Ivanov and L. Kucher, Transaction of the University of Mining and Metallurgy, Ostrava, 35(1989) 69.
3. T. Kekesi, European integration studies, Miskolc, 1 (2002) 109.
4. L. Kucher, J. Drapala and J. Lunacek, J. Cryst. Growth, 161 (1996) 94.
5. Y. A. Chulzhanov, B. G. Nenashev, S. P. Popov and M. G. Chulzhanova, Chem. Sustainable Development, 8 (2000) 29.
6. W. G. Pfann, J. Metals, 7 (1955) 297.
7. Y. Waswda and M. Isshiki, "Purification process and characterization of ultra-high purity metals" Springer (2001).
8. N. L. Parr, Zone refining and allied techniques, George Newnes, London (1960).
9. T. Lyman, Metals Handbook, American Society of Metals (ASM), Cleveland, Ohio, (1948).
10. W. G. Pfann, Zone Melting, New York, John Wiley and Sons (1958).
11. I. Meszaro and I. Molnar, Magyar Alluminium, 19 (1982) 46.
12. O. Winkler, R. Bakish, Vacuum Metallurgy, Elsevier (Amsterdam, London, New York (1971).
13. R. B. King, Organometallic Syntheses: Transition-Metal Compounds, Academic Press, New York (1965).
14. L. M. Harwood and C. J. Moody, Experimental organic chemistry: Principles and Practice Wiley Blackwell, (1989) 154-155.
15. Z. Horvath, A. Mihalik and K. Sziklavari, Elmeleti Khaszattan, Tankonyvkiado publishing, Budapest (1986).

16. U.S. Congress, Office of Technology Assessment, Copper: Technology and Competitiveness, OTA-E-367, Washington, DC (1988).
17. H. Temur, A.Yartaşı and M. M. Kocakerim, BAÜ Fen Bil. Enst. Dergisi, 8 (2006) 63.
18. S. Dushman nad J. M. Lafferty, Scientific Foundations of Vacuum Technique, 2nd ed., Wiley, New York (1962) p. 806.
19. S.T. Ali, N. R. Munirathnam, C. Sudheer, R. C. Reddy and T. L. Prakash, Materials Letters, 58 (2004)1638.
20. S. V. Kovalevski, V. I. Kosyakov and I. R. Shelpakova, J. Cryst. Growth, 167 (1996) 208.
21. I. R. Shelpakova, V. I. Kosyakov and T. A. Chanisheva, J. Anal. Chem., 48 (1993) 610.
22. N. R. Munirathnam, K. S. Rao and T. L. Prakash, Bull. Mater. Sci., 35 (2002)163.
23. N. R. Munirathnam, D. S. Prasad, Ch. Sudheer, J. V. Rao and T. L. Prakash, Bull. Mater. Soc., 28 (2005) 209.
24. S. A. Kozlov, N. A. Potolokov, A. V. Gusev and V. A. Fedorov, Inorg. Mater., 38 (2002) 1212.
25. S. A. Kozlov, N. A. Potolokov, A. V. Gusev and V. A. Fedorov, Inorg. Mater., 39 (2003) 1267.
26. U. Rambabu, N. R. Munirathnam and T. L. Prakash, Materials Chem. Phys., 112 (2008) 485.
27. N. R. Munirathnam, D. S. Prasad, J. V. Rao and T.L Prakash, Bull. Mater. Sci., 28 (2005) 309.
28. D. S. Prasad, N. R. Munirathnam, T. J. V. Rao and T.L. Prakash, Materials Letters, 59 (2005) 2035.
29. D. S. Wu, C. C. Chan, R. H. Horng, W. C. Lin, S. L. Chiu and Y. Y. Wu, Appl. Surf. Sci., 144-145 (1999) 315.
30. S. Kim and D. J. Duquette, Surf. Coat. Technol., 201 (2006) 2712.
31. G. S. Choi, J. W. Lim, N. R. Munirathnam, I-H. Kim and J-S. Kim, J. Alloys Comp., 469 (2009) 298.
32. T. Izumi, Mater. Japan., 33 (1994) 1.
33. I-H. Kim, J.-I. Lee, G.-S. Choi and J.-S. Kim, Adv. Mater. Res., 26-28 (2007) 1059.



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Development of High Purity Materials - Some Specific Achievements and Practical Aspects in Production and Characterisation

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Abstract

High purity materials are the backbone for sustainable development of semiconductor industry including all other advanced engineering applications. Handling practice of pure materials plays a pivotal role. Electronic materials have introduced strict quality specifications with respect to low level of chemical impurities in ppm, even to ppb level and structural imperfections, as the applications in this field are dependent on the intricate details of the materials. These achievements of high purity have been possible not only by relentless pursuit of process innovations in the field of production but also by enforcing exceptionally high standards of cleanliness and hygiene, and evolving matching techniques for the quality control, materials characterization by enhancing reliability in evaluation. Varieties of high purity materials developed and produced at Special Materials Plant (SMP) are Ga, In, Bi, Au, Ag, Sn, Sb, Cd, Se, Te, POCl_3 , BBr_3 , Te, GPC, NaI, Sb_2O_3 , Ta_2O_5 , Nb_2O_5 , gem grade ZrO_2 , Al coated Zr powder, refractory metals and their alloys such as NbTi, ZrNb, C-103, NbZrC, TaW, NbW, NbZrW, etc. This article covers details of processes developed for production of a variety of high purity materials covering specific achievements and practical aspects in production and characterization.

1. Introduction

It is often said that necessity is the mother of invention and it is true in the case of development of high purity materials. The need and urge to meet certain specific requirements has led to enormous R & D work on various materials. Production of a product may be based on several technologies and each technology can be basis for several products. Application of materials in components is a boundless field and is more attractive as it directly ends up in value added product, more so many times being a monopoly item. A process can be called as technology only when each and every problem of the basic science and engineering details are totally understood and are completely solved, including the economy and also with a clear cut, closed cycle for handling/ disposal of the effluents/ wastes.

As an integral part of advancement in the Indian industry, development of special materials has been realized since the constitution of Homi Bhabha Committee in 1966. Efforts in this direction continued and several panel reports & technical reports were brought out. A departmental programme was initiated in DAE and preliminary works carried out at BARC, Trombay. Realizing the growth and demand of certain items, a facility named Special Materials Plant (SMP) was set up at Nuclear Fuel Complex, Hyderabad, during 1970s. Development and production of large variety of high purity materials was initiated at SMP, mainly to meet the requirement of nuclear industry and also that of electronic

industry and R & D institutes. The materials developed and produced at SMP can be broadly classified into two parts, namely metals/ alloys, and semiconductor/ special materials.

2. Importance of high purity materials

The field of design and construction of nuclear reactors, equipment for space applications or any other advanced modern machinery including processors and sensors has brought in totally new standards and specifications with regard to materials selection, manufacturing and characterization. Among these inputs, 'Materials' is of critical importance, as they involve repetitive and continuous production. High purity materials are the backbone for sustainable development of semiconductor industry including all other sophisticated engineering applications. Electronic materials have introduced strict quality specifications with respect to low level of chemical impurities and structural imperfections as the applications in this field are dependent on the intricate details of the materials. For example, individual impurity tolerances in electronic grade silicon or gallium, are specified in parts per million (total impurity tolerance is only of the order of 1 ppm or less), and it is conventional to speak high purity in terms of 5 nines (5 N, i.e. 99.999% or 10 ppm) or 6 nines (6 N, i.e., 99.9999%) in the case of these materials. However, for scientific purposes instead of expressing the purity in number of nines, exact concentration of impurity level are spelt out in ppm or

ppb as the effect of the impurities is not the same for all the elements and is dependent upon specific applications. For semiconductor applications, the impurities are classified as active or shallow level contaminants. The silicon micro chip that incorporates a vast extent of integrated circuitry is a marvel of miniaturization that has totally transformed the fields of instrumentation and control, communication, computation, entertainment in modern electronics. Smallest feature sizes of the order of one micrometer have been achieved in micro-electronic circuitry. These achievements have been possible not only by relentless pursuit of process innovations (e.g., zone refining, distillation, solvent extraction, ion exchange, electrolytic processes, electron beam refining, crystal growing, chemical vapor deposition, molecular beam epitaxy, ion implantation, etc.) in the field of production of high purity materials but also by enforcing exceptionally high standards of cleanliness and hygiene, and evolving matching techniques for quality control, materials characterization by enhancing reliability in evaluation. The issue in production of high purity materials is not only the right combination of purification process but also material of construction, cleanliness and hygiene of the working environment, handling of materials, expertise of the working personnel and extent of automation.

Varieties of high purity materials developed and produced at Special Materials Plant are Ga, In, Bi, Au, Ag, Sn, Sb, Cd, Se, POCl_3 , BBr_3 , Te, GPC, etc. Among the important products developed, produced and supplied for supporting nuclear industry are supply of tonnage quantity of magnesium granules used in the reduction of uranium fluoride at Uranium Metal Plant, BARC, tonnage quantities of Nb metal and ZrNb master alloy for manufacturing of Zr2.5%Nb coolant tubes, Nb sheets for fabrication of superconducting resonators at RRCAT, antimony trioxide for its use as neutron source at FBTR/PFBR, sodium iodide to ECIL for growing single crystals of scintillation counters, tellurium metal for production of isotopes at BRIT, lead sheets and silver gaskets for use at NPCIL, number of Ta fabricated items for research in radio metallurgy and for use at IRE, fabricated products of refractory metals and their alloys such as NbTi superconducting alloy for high magnetic field applications, NbZrC alloy for high temperature applications. Development works were carried out towards recovery of Mo from scarp generated at uranium plants during sintering operations. The offshoot of technology development has helped in generation of wealth from waste by usage of off grade Zr sponge as micron size powder in detonator industry, conversion of waste ZrOCl_2 into gem grade zirconia.

3. Understanding of high purity materials

3.1 Expression of purity

Describing purity in terms of parts per billion (ppb) even though widely practiced has become less meaningful. It is more relevant to emphasize the impurity content itself and ppm has become established terminology for many materials and for most of the semiconductors/ electronic applications ppb is needed. For applications of materials in semiconductor & nuclear field, the concentration of impurities needs to be controlled at ppm or even at ppb level.

3.2 Structural imperfections

In certain branches of modern technology the structure of a material and imperfections in it, such as vacancies, dislocations and stacking faults play a role comparable to that of chemical impurities in ultra pure materials. 'Imperfection' to any deviation from perfect lattice has its effect. Certain imperfections are known to have harmful effects on electrical, magnetic and mechanical performance of the material. In fact many of the new and unusual qualities may be found if only materials can be made pure enough. RRR grade niobium sheets made at NFC for use in superconducting (SC) radio frequency (RF) cavities at RRCAT Indore is one such application wherein electrical conductivity and magnetic property depend on cumulative concentration of the chemical impurity as well on structural imperfections in addition to the temperature.

3.3 Methods used for characterization

Concentration of chemical impurities in high purity materials at very low level are analyzed by a combination of spectroscopic, i.e. atomic absorption spectroscopy (AAS), AAS with graphite furnace, inductively coupled plasma (ICP), atomic emission spectroscopy (AES), and inert gas fusion with non-dispersive infrared (IGF-ND-IR), activation techniques, mass spectrometry, chromatography (gas/ ion), electro analytical methods, etc. Sensitivity, resolution, precision and availability of certified standards of an analytical method chosen for a specific material are of great importance and need thorough understanding of the matrix and impurities present in it. At NFC analytical methods have been standardized for analysis of all the critical impurities in the high purity materials.

Physical methods like Hall Effect techniques, cyclotron resonance, magneto resistance, magneto thermal oscillators and RRR (residual resistance ratio) tool are useful in characterization of high purity materials. All these methods involve motion of electrons in the crystal lattice. As the lattice becomes more and more perfect, the obstacles to electronic motion become lesser and the electronics

become less random with the result that they are then more sensitive to intricate details of the crystalline fields. By proper calibration, these methods can be used for characterization.

3.4 How to take care of defects

The harmful type of imperfections are structural defects, thermal vibrations and impurities. Structural defects are minimized by using near perfect single crystals, thermal vibrations by performing the experiments/usage at very low temperatures. Chemical impurities are eliminated by removing them bodily by adopting highly selective separation methods.

3.5 Need for clean working place

For handling and processing of high purity materials the concept of clean room with controlled concentration of dust particles is essential. Depending upon the level of purity, i.e. class-1000 or better control is essential. This can be achieved by maintaining laminar flow, use of non-shedding construction materials, providing anti-room, use of HEPA Filters, use of clean room apparels and ultimately by training the operating staff followed by restricting their movements.

4. Reasons for materials not to be in pure form in the nature

Materials get additional stability by virtue of presence of the chemical impurities. This stability is partly due to chemical bonding. Hence materials tend to get contaminated. Thermodynamically addition of impurities to a high purity material reduces the free energy. Statistically, the stability of materials due to the presence of impurities can be explained in terms of configuration entropy, which is the portion of a system's entropy that is related to the position of its constituent particles rather than to their velocity or momentum. It is physically related to the number of ways by arranging all the particles of the system while maintaining some overall set of specified system properties, such as energy. Entropy is also a measure of energy distribution through a system. As energy becomes more dispersed or evenly distributed the possibility that energy being used for mechanical work is decreased i.e entropy is increased. Natural processes (in this case contamination by impurity) always increase towards increase in disorder.

Variation of configuration entropy of materials is equivalent to the variation of the macroscopic entropy of thermodynamic systems, defined as $dS = \delta Q/T$, where δQ is the heat exchanged between the system and the surrounding media, and T is temperature. The configurational entropy

is related to the number of possible configurations by Boltzmann's entropy formula $S = k_B \ln W$ where k_B is the Boltzmann's constant, which is equal to $1.38065 \times 10^{-23} \text{ J/K}$. and W is the number of possible configurations given by $W = N! / (N-n)! n!$ where N is the number of matrix atoms and n is that of impurity. It refers to total number probabilities that a system can be in states n with probabilities. In statistical mechanics, Ludwig Boltzmann expressed entropy that can also be expressed as $S = k \ln P$, where P is the probability or the number of "Complexions", i.e number of possible ways a system can be arranged to yield a specific state. Hence, increase in the probability or "Complexions" by addition of impurity leads to a state of greater stability.

Following Stirling's approximation expressed in logarithmic form ($\ln n! = n \ln n - n$). The change in entropy can be written as $S = k [N \ln N - (N-n) \ln (N-n) - n \ln n]$. This formula gives the stability of a material due to addition of impurity. This means that configurational entropy increases as logarithm of W . For example, one mole of a solid contains 10^{23} atoms. If a small quantity of impurity element gets mixed randomly, it will end up with an extremely large number of distinguishable configurations and an appreciable amount of configurational entropy. Since W can never be less than one, configurational entropy is either zero or positive. It is zero for an absolutely pure material consisting of the same kind of atoms on all its sites or for perfectly ordered solid like an ultra high pure compound with absolutely no impurity at zero K temperature when available as a single crystal. As the temperature increases the atoms begin to vibrate. The average energy per mode is called thermal energy and is equal to kT where T is temperature in Kelvin and K is Boltzmann's constant equal to $1.38 \times 10^{-23} \text{ J K}^{-1}$. For one mole of atoms thermal energy becomes $NkT = RT$ where R is gas constant. Hence, it is practically impossible to have an absolutely pure material without any structural defects in it above zero Kelvin.

5. Need for purification and principle of refining

As naturally available material is always impure, it is necessary to adopt purification processes to remove impurities in it. The purification method to be adopted depends upon the nature of matrix material as well as the nature of the impurity. There is no universal single process that can be adopted for all the materials. In literature, varieties of processes are reported. It is the wisdom of the individual to select a right process for their specific applications. Materials with higher purity have very strong tendency to pickup impurities to remain in lower free energy state. In a refining process, we are generally

concerned with removal of one or more constituents from a material that contains a number of impurities. This can be illustrated by considering a simple case of an impurity B present in a metal A. The partial molar free energy of formation of solution of B in A, can be given by Eq-1.

$$\Delta G_B = RT \ln a_B \quad \text{---- (1)}$$

where a_B is the activity of B in metal A

When we consider purification of the metal, the activity (a_B) of the component B in A, tends to be zero. In such a case, ΔG_B tends to $-\infty$, indicating the formation of solution of B in A is thermodynamically highly favorable. In other words, to remove the impurity B when $a_B \rightarrow 0$ an enormous amount of work will be necessary.

In the process of their extraction, materials invariably pick up impurities present in the various sources, primary or secondary, from which they are extracted. Whether one likes it or not, the presence of foreign elements is an inevitable and unavoidable consequence in the metal extraction process. It must be emphasized that the word impurity can have different meanings in different situations. The presence of an element, A, may be regarded as an impurity in a metal B; the same element A in metal C may not be regarded to the same extent. Its presence may, rather, be desirable instead of an unwanted impurity. Thus, for example, the presence of a minor amount of boron in steel is considered desirable and it is intentionally added to bring about certain improvements in the properties of steel when called for. Its presence, however, in uranium used as nuclear fuel is not tolerated.

6.0 Separation processes adopted for purification

After extraction, raw materials are generally obtained in 96-99% purity. Crude materials cannot be used by industry at this stage because of inferior physical, chemical, and mechanical properties. Their purification is necessary. Three basic refining methods are usually employed, viz. pyro-metallurgical, electrolytic, and chemical. All these methods are based on distinctive properties of the individual elements, such as melting point, density and electro-negativity. Charge to radius ratio of the ions plays important role in effectiveness of the separation. Pure materials are frequently obtained by employing combination of several refining methods. Many specialized and state of the art separation techniques have been developed in the preparation of high purity materials. Generally practiced industrial methods are:

➤ **Liquid-liquid extraction:** Removes an impurity or recovers a desired product by extracting it in a selective organic solvent, whereas impurities of the feed material

are separated in aqueous phase. This can be practiced as cross-current or counter current or co-current fashion. Solvent extraction (SX) generally consists of extraction, scrubbing, stripping, and understanding of hydrodynamics i.e dispersion-coalescence, factors affecting selectivity and extractability play important role in achieving the desired purity. Regeneration of solvent and pre-equilibration of solvent. Selection of the equipment for SX depends upon the application. At NFC slurry extraction units have been developed and practiced in the uranium and zirconium purification streams using tributyl solvent (TBP) to produce hundreds of tonnes of these products per year.

- **Crystallization:** Separates a product from a liquid feed stream, often in extremely pure form, by cooling the feed stream or adding precipitants which lower the solubility of the desired product so that it forms crystals. The pure solid crystals are then separated from the mother liquor by filtration or centrifugation. At NFC, we have produced gem grade zirconia by this process by crystallizing zirconium oxy chloride ($ZrOCl_2 \cdot 8H_2O$).
- **Distillation:** Distillation is a technique of separating and purifying liquids by using a difference in the boiling points. It has a long history, and the origin of distillation can be found in ancient literature. The technique of distillation was improved when condensers were introduced. Separation of liquid mixtures into components is accomplished by fractional distillation. The principle of fractional distillation can be explicable by use of the boiling point-composition diagram. Vacuum distillation, sub-boiling distillation, etc. are modifications of the same. Distillation under vacuum improves the separation factor thereby improving the efficiency of purification. Distillation may be practiced as batch distillation or continuous distillation. It can be simple distillation, fractional distillation, differential distillation, short path distillation, zone distillation, azeotropic distillation, extractive distillation, pressure-swing distillation or multi-effect distillation.
- **Chromatography:** Chromatography is a technique for separating a mixture into its components with the aid of the differences in the physical properties of each component. The device consists in a column in which an appropriate stationary phase (solid or liquid) is packed. The mixture is added to the column from one end and the mixture is moved with the help of appropriate developer (mobile phase). Separation is achieved by the difference of each component in its rate of moving down the column, which is determined by

the strength of adsorption or the partition coefficient between the stationary and mobile phases. Types of chromatography are a) partition chromatography, (b) paper chromatography, (c) gas chromatography and (d) HPLC.

Ion exchange: It is a process in which ions are exchanged between a solution and an insoluble solid, usually a resin. It is a process that allows the separation of ions and polar molecules based on their affinity to the ion exchanger. Impurities can be selectively adsorbed / desorbed leading to purification.

➤ **Liquid ion exchangers:** As the name implies, this process combines the advantages of both solvent extraction as well as ion exchange techniques. The greatest advantage of liquid ion exchanger is that one could regenerate the resin and use it again and again. Therefore the process becomes economical. This is one of the reasons why most of industrial processes for recovery of metals from minerals prefer the use of liquid cation exchanger like LIX 64 N or liquid anionexchangers like Alanine336 or Amberlite.

➤ **Use of organo-metallic compounds:** It is based on selective formation of organo-metallic compounds by certain elements. It is used in purification of metals such as magnesium, calcium, mercury, gallium, rhenium and nickel etc.

➤ **Zone refining or zone melting or floating zone process:** It is a group of similar methods of purifying materials, in which a narrow region of a crystal is melted, and this molten zone is moved along the crystal. The molten zone melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. Extent of separation of impurity depends upon the value 'k' defined as ratio of impurity in the solid to that in the liquid with which it is in equilibrium. If the impurity has higher melting point ($k < 1$) then the solid separating out will contain less impurity than the liquid from which it crystallizes, i.e. the impurity prefers to be retained in the liquid zone. Certain impurities ($k < 1$) concentrate in the melt, and are moved to one end of the ingot. Zone refining was developed by William Gardner Pfann in Bell Labs as a method to prepare high purity materials, mainly semiconductors, for manufacturing transistors. It is a very slow process as near equilibrium is to be achieved for segregation of impurity between liquid & solid. Zone leveling is necessary for obtaining homogeneous high pure material after chopping off of leading and trailing ends.

➤ **Electrolytic methods:** In an electrolytic cell, the impure metal is made anode and a thin strip of pure metal is made cathode. A solution of a suitable salt of the concerned metal is used to fill the electrolytic cell. On passing electricity, the anode undergoes dissolution while the pure metal gets deposited at cathode. Insoluble impurities fall below the anode in the form of anode mud and more active elements remain in solution. During electrolysis process, electrons from the external circuit are captured by ions of the principal metal. Electrolysis can be used to separate metals because the principal metal and the admixtures have different electrochemical potentials. Electrolytic method can be aqueous electrolysis or fused salt electrolysis. At SMP, high pure indium metal is produced by electro refining, antimony by electro-winning and gallium after anodic polarization.

➤ **Refining by chemical transport mechanism:** It involves formation of a volatile compound of metal to be refined by means of a reactive gas (e.g., iodine, carbonyl) followed by its decomposition at higher temperature to yield the pure metal and to generate the reactive gas for recycling. Examples include purification of Zr, Hf, Ti, Th, Nb by iodide process, Ni, Fe by carbonyl process, Al by sub halide process.

➤ **Pyrovacuum processing:** This involves treatment under high vacuum and high temperature. Removal of impurities takes place due to degassing, evaporation, chemical reaction. Prior to electron-beam refining refractory metals are purified by this method. Self resistance sintering furnace is modified form of this, in which, current is directly passed leading to heating and removal of volatile impurity. Operations under vacuum has got an advantage in avoiding reactions with atmospheric oxygen. Vacuum assists in improvement of separation factor leading to better quality pure product and nitrogen present above the hot reactive material. Hence any hot processing of refractory materials has to be carried out under high vacuum conditions.

➤ **Electron beam (EB) refining:** This involves melting under high vacuum and casting in a water cooled copper crucible. Removal of impurities takes place due to degassing, evaporation, distillation and chemical reaction. High purity refractory metals are invariably produced by this method. Residence time of the feeding and in casting pool governs the extent of purification. High level of purification is possible during EB refining as the vacuum above the molten liquid pool is several order higher compared to that of vacuum in

Vacuum Arc Remelting (VAR) or Vacuum Induction Melting (VIM) or any other melting techniques due to continuous retraction of the cast ingot in EB melting process.

Principles in purification during electron beam melting

In electron beam melting by virtue of high vacuum, purification takes place due to distillation of volatile impurities and degassing of gaseous impurities as per the following equations. In distillation relative volatility factor α , is defined as:

$$\alpha = \frac{\gamma_I \rho_I}{\gamma_S \rho_S} \quad \text{--- 2}$$

where γ_I , ρ_I , γ_S , ρ_S denote respectively, the activity coefficient and vapor pressures of the impurity and the base metal.

The degassing is governed by Sievert's law. The dissolution of gases in metal is governed by:

$$\frac{1}{2} A_2(g) = [A]_{\text{metal}} \quad \text{--- 3}$$

where A stands for gas, which may be hydrogen / nitrogen

The main advantage of electron beam purification is effective separation of impurities due to high power density, use of water-cooled crucible, high pumping of gaseous products, continuous removal of impurities and thereby disturbing the equilibria. In addition to this, melting and casting rate can be controlled in a wide range allowing optimum purification. At SMP pure refractory elements like Ta, Nb, Zr and their alloys are being produced regularly.

7. Separation processes practiced at NFC

Many specialized separation techniques are being practiced in our complex in the field of production of high purity materials, e.g. special distillations such as fractional distillation (e.g., POCl_3 , SbCl_3 , GaCl_3 , BBr_3), vacuum distillation (e.g., Te, Cd, In, Pb), sub-boiling distillation (e.g., HNO_3 , H_2SeO_3); electrolytic processes such as electro-refining (e.g., In), electro-winning (e.g., Sb, Te, Sn), anodic-polarization (e.g., Ga); crystallization (e.g., $\text{KAu}(\text{CN})_2$), zone refining (e.g., Bi, Te, Sn, Zn, Cd), pyrovacuum processing (e.g., Ga, Ta), electron beam refining (e.g., Nb, Ta, Ti, Cu) etc.

We are the only one in the country to practice electron beam (EB) purification and produce tonnage quantity of refractory and reactive metals. Operation of electron beam melting furnace requires multidisciplinary skills and highly trained manpower. We have been able to extend the scope of EB melting in preparation of special alloys such

as Nb1%Zr0.1%C required in compact high temperature reactors (CHTR), Nb46%Ti super conducting alloy, C-103 columbium alloy (Nb-10Hf-1Ti) for space applications, etc. We have taken up the task of producing high RRR (residual resistance ratio) grade niobium required for RF resonating cavities of superconducting linear proton accelerator, superconductor magnets used in plasma reactors.

8.0 Technical knowhow developed at SMP, NFC

8.1 Development for magnesium granules

Magnesium metal is used for reduction of uranium fluoride to get uranium metal and same is practiced at UMP, BARC. Magnesium in the form of granules/chips is preferred for the best results in reduction and high recovery of uranium metal during reduction. Technical knowhow for this was developed at SMP based on rotating electrode process (REP) and tonnage quantity of granules were produced and supplied to BARC.

For nearly a decade, REP process was practiced at SMP to produce pure magnesium metal granules. For this, magnesium metal in brick shape was the starting material. Hence the purity of raw material was dictated by the international availability of magnesium to nuclear industry. The Mg granulation section at SMP had designed capacity of 24 MT per year and was achieved to its full capacity. When pure magnesium of required grade was not available, technical know-how for vacuum distillation of magnesium was standardized and adopted. Production of magnesium granules involved casting to 800 mm dia and 600 mm length magnesium cylindrical ingots by casting under argon atmosphere at 800 °C. Pure magnesium ingots (purity >99.5%) were pickled in HCl acid bath, washed and dried. This cast ingot was used as rotating electrodes in granulation process by adopting vacuum arc melting to obtain magnesium granules. Coarse size magnesium granules obtained after REP were ball milled under argon atmosphere, then sieved. Magnesium granules of required size were obtained after separating out into different mesh size fractions with the help of the screen vibrator. After completion of quality control magnesium granules were packed in polythene bags under argon flushing and finally packed in drums.

Due to the inherent pyrophoric nature of magnesium in powder form a lot of safety precautions are essential at each stage of the operation. Maintaining the purity of the metal during various stages of operations required strict control over the process parameters and handling methodology.

During 90's production of magnesium chips produced by CMC operated lathe machine became popular. Its

use for reduction of uranium fluoride technology had totally changed the scenario of magnesium. Chips production is very simple process and has very few steps compared with the REP process. The recoveries and cost of production are drastically low in the new method. It has completely replaced the REP process for production of Mg granules.

8.2 Process for reactor grade Nb metal, RRR grade Nb sheets, Zr-Nb master alloy, ZrHf alloy, TaW alloy, Nb based alloys such as NbTi, NiTi, NbZrC, NbW, NbZrW, etc.

Standardization of process and development of equipment for production of reactor grade (RG) niobium metal and capacitor grade tantalum powder at SMP involved thorough understanding of the intricacies of hydrometallurgical operations. Starting raw material for this process flow sheet has been indigenous columbite tantalite (CT) ore mined by Atomic Minerals Division. Handling of highly corrosive acids, high temperature and high vacuum operations required carefully designed equipment, machinery and training of the manpower. Missing of element, i.e. tungsten in the specifications had lead to wastage of metal produced for years. Extremely high level of hydrolysis of TBP, contamination from the cement used in the liner of alumino-thermic reduction (ATR), dangerous effluents and cost of production have been some of the concerns in the production of special quality niobium metal. Process was developed at SMP in preparation of alloys of Nb, Ta and Zr through EBM and intermediate Hydriding- Dehydriding or extrusion route.

8.2.1 Liquid-liquid solvent extraction as a separation technique for Ta-Nb

Separation from many metals (e.g. Ti, Zr, Sn, Mo, and Fe) is achieved by extraction of the stable niobium and tantalum fluoride complexes with oxygen-containing solvents like TBP. By suitable choice of acid concentrations (HF , H_2SO_4) tantalum is separated from niobium at lower acidities and niobium at higher acidities. Niobium and tantalum are stripped from the organic phase using aqueous solutions.

At SMP, an air lift type mixer settler made out of plastic material having eight stages of extraction and four stages of stripping was designed and fabricated. At lower acidity conditions, tantalum forms H_2TaF_7 , whereas niobium forms H_2NbOF_5 . But at higher acidity conditions, both tantalum & niobium form H_2TaF_7 and H_2NbF_7 . Among these complexes, only H_2TaF_7 is extracted by TBP as a solvated complex, at both lower and higher acidity whereas

niobium is extracted only at higher acidity. This difference in the extractability is made use in the selective extraction of tantalum first while starting with ore and selectively niobium afterwards from the raffinate solution.

8.2.2 Developments in the field of niobium

The most important and striking developments that were carried out in the separation of niobium and tantalum have been with reference to multifold increase in the loading of the metal into the solvent, elimination of scrubbing operation, stripping of loaded solvent using water instead of acidic solution, drastic decrease in the consumption of chemicals, decrease in quantity of effluents, designing and fabrication of airlift type of mixer settler made out of plastic and adoption of pyrohydrolysis for converting hydroxide to oxide. The number of operations and quantity of solutions handled were brought down to improve the overall productivity. Extraction and stripping parameters were suitably adjusted to have saturation loading and efficient stripping. Many process parameters were reworked so as to get high purity niobium oxide. In the stream of tantalum also, process improvements were carried out to produce required quality of tantalum oxide. Nb and Ta metals can be produced from oxide reduction or carbothermic reduction or chloride reduction or electrolytic reduction starting with suitable raw material. Choice of reduction process depends on scale of operation and quality of the product.

Pure niobium oxide is reduced using aluminum metal. Reduction methodology for open alumino thermic reduction (ATR) for a 10kg batch was standardized. Studies were carried out for ATR reduction using water cooled crucible. In situ dealuminisation and controlled sacrificial deoxidation in EB melting furnace helped in bringing down the number of multiple melting. Process parameters were standardized for EB purification of thermanit and hydriding dehydriding route for conversion to chunklets. Methodology for conversion of Nb ingots into RRR grade Nb sheets was worked carefully.

8.2.3 Conversion of niobium to Zr2.5Nb alloy

During 1980's production of Zr2.5Nb coolant tube was carried out by addition of Zr40%Nb master alloy during sponge compacting followed by vacuum arc remelting (VAR). Tonnage quantity of this mater alloy was produced at SMP by electron beam melting (EBM) and supplied to Melt Shop. Process parameters were standardized for EB melting and conversion of master alloy into chunk lets.

Later on, successful experiments were carried out for direct production of Zr2.5Nb alloy by electron beam

melting, but the output from the 60 kW EB melting furnace was not able to match with the requirement of coolant tubes. Based on the studies, direct usage of niobium sheets along with zirconium sponge compact was introduced during VAR melting. The insitu master alloy formation resulted in homogenous ingots. Recently process was standardized for converting EB refined niobium ingots into chunklets and using them in VAR melting. Conversion to chunklets instead of rolling to 0.4mm thick sheets has enhanced process recovery of niobium by more than 50%. This practice of using chunklets is continuing in Melt Shop.

Activities in the preparation of RRR grade niobium sheets for superconductor (SC) resonator applications at RRCAT Indore, and niobium flanges for accelerator programme at BARC required support of several agencies and mechanical, metallurgical, electrical and magnetic multidisciplinary knowledge in achieving of the desired properties. Few Nb sheets made at NFC were sent to Fermi Lab by RRCAT for studying cavity formation and found to be satisfactory.

Development of alloys (not elements) like NbTi superconducting alloy, with alloying element (not elements) having higher vapor pressure was handled by dynamic purging of argon gas into the melt chamber during EB melting. Preparation of NiTi shape memory alloy, and Nb1%Zr0.1%C required careful charge preparation and EB melting.

8.2.4 Development of Nb1Zr0.1C alloy

The alloy was developed by electron beam melting route starting with reactor grade Nb, Zr and spectroscopic graphite powder for use in high temperature applications. Various methods were tried for charge preparation to get homogeneous alloy. Studies were taken up in EB welding, Laser welding and microstructural characterization of the alloy sheets. EB melted alloy ingot was extruded and rolled to thin sheets. Finally it was converted to a loop which was successfully demonstrated at desired temperature. For the first time in the world a loop has been continuously operated at 1000 deg C at BARC.

8.3 Development of antimony trioxide

Process parameters were standardized for production of antimony trioxide starting from commercial grade antimony and its conversion to antimony chloride followed by antimony trioxide. Monel reactor was designed and fabricated in-house for the purpose of chlorination. Provision was made for percolation of tri- and pentachlorides to pass through antimony metal powder for complete conversion into trichloride. Differential

distillation column made of all glass assembly and distillation in 6N HCl media helped in removal of arsenic and other impurities. Conversion to trioxide was achieved by addition of aqueous antimony chloride into ice cold 10N ammonia solution. Electro-winning cell was built for recovery of pure antimony in elemental form from aqueous antimony chloride solution. This was followed by zone refining to obtain high purity metal.

Initially antimony in the form element was supplied for studies related to its use as neutron source. Later on based on the requirement from IGCAR for applications in FBTR, selectively antimony trioxide was prepared by avoiding antimony tetra oxide and pent oxide. After extensive trials, a methodology was worked out for defect free casting of antimony trioxide (99.99% purity) into narrow SS tubes where in capillary effects are dominant. Hundreds of antimony tri oxide cast SS tubes were supplied for use in fast breeder reactors by placing them in beryllium blocks and irradiating in research reactors.

8.4 Technical knowhow for micron size zirconium metal powder

During production of reactor grade zirconium sponge some quantity of semi reactor grade (SRG) sponge is generated. Recycling of this back to the chlorination is a lengthy and uneconomical process; hence R & D was carried out to convert of SRG sponge into micron size zirconium metal powder which is used in detonators. Tonnage quantity of zirconium metal powder was produced and supplied to ordinance factory in the country. This process involved hydriding/ dehydriding followed by grinding and sieving but required utmost care in handling of highly pyrophoric zirconium metal powder.

8.5 Development of electronic grade high purity materials

Process development were carried out for production of bismuth, boron tribromide, gallium, cadmium, indium, lead, phosphorous oxychloride, tellurium, selenium, tin, zinc, cubic zirconia, copper and their compounds to meet the requirement of DAE and other R&D units in the country. Production of these items required designing and fabrication of specialized equipments. The important process equipment developed are vacuum distillation unit, sub boiling unit, zone refining unit, fractional distillation unit, electro winning, electro refining, anodic polarization, chlorinators, pelletizing unit, solvent extraction unit. A 15 kW EB melting furnace was designed and fabricated by Technical Physics Division, BARC during seventies and used at SMP for more than a decade in melting of tantalum.

8.5.1 Development of chemical processes for precious metals

Processing of precious metals, like gold and silver, to produce high purity materials and their compounds required handling of hazardous and toxic chemicals and strict material accounting. Process equipment was designed in-house for production of high purity gold, silver, gold potassium cyanide etc., Handling and disposal of cyanide solution required elaborative procedures and training.

8.5.2 Technical knowhow for production of high purity selenium pellets

The production process for electronic grade selenium involved oxidation of crude selenium in nitric acid to obtain selenium dioxide, which is dispersed in sulphuric acid and distilled in quartz distillers by sub boiling distillation to get pure selenious acid. The reduction of selenious acid below 10°C using SO₂ results in selenium in elemental form. After drying, vacuum molding and pelletizing below 10°C gives selenium pellets of 99.999% purity. The main difficulties associated with this process are handling of NO₂ fumes generated during dissolution, sulfur dioxide used for precipitation and very low concentration of selenium (<10 ppb) permitted in effluents.

8.5.3 Preparation of potassium tantalum fluoride, tantalum metal powder and tantalum anodes

This process involved a series of hydrometallurgical and pyro-metallurgical operations. The unit operations for this are ore crushing, ore dissolution, feed preparation, solvent extraction, hydroxide precipitation, conversion to PTF (K₂TaF₇), recrystallizing, sodium reduction, leaching, degassing, compacting, remelting, hydriding, milling, dehydriding, agglomeration, powder evaluation by pressing compacting, degassing, sintering, electron beam melting, etc. Pure tantalum oxide is converted to PTF and reduced to tantalum powder for use in tantalum capacitors.

9. Conclusion

Process technology, equipment building and testing methodology developed over the years in the field of preparation of pure materials have been due to contributions of many scientists and engineers in the department. These activities have lead to several indigenous developments and self reliance in the field of materials. The off shoot of the R & D in DAE have been useful in many other high tech applications in the country. SMP/NFC has also made contributions to this field of high purity materials and supplied verities of items to various units

of DAE. Quality of the high purity products produced and supplied to various DAE units & other institutions and the feedback from them has been satisfactory. However scale of operation, cost of production, support for continuing the activities need to be addressed separately. Purity of materials achieved (like five nines) and the quality of product produced are testimony for the works carried out by many scientists and engineers over the years.

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References

1. K. V. Mirji, P. Balakrishna, Chintamani and C. Ganguly, *Production, Scientific-Technical information, Analytical and Educational Methods Journal*, 5 (2001) 23.
2. B. Vishwanadh, K. Vaibhav, S. K. Jha, K. V. Mirji, I. Samajdar, D. Srivastava, R. Tewari, N. Saibaba and G. K. Dey, *J. Nuclear Materials*, (2012).
3. C. K. Gupta and A. K. Suri, *'Extractive Metallurgy of Niobium'*, CRC Press, Inc. (1993)
4. K. V. Mirji and S. M. Rao, *CHEMCON-92* (1992).
5. T. S. Krishnan and S. Choudhary, *Transactions of PMAI*, 3 (1976) 56.
6. N. S. K. Prasad, T. N. Ranganathan and M. S. Sastri, *BARC technical Report* (1966).
7. M. Shankar, K. V. Mirji, M. Chandrashekar, R. G. Baligdad, V. V. Satyaprasad, A. A. Gokhale and B. Prakash, *DMRL technical report, DRDO-DMRL-ERG-050* (2013).
8. P. Alex, J. K. Kumhar, R. C. Hubli, J. K. Chakravartty, K. V. Mirji and N. Saibaba, *BARC Technical report - No BARC/2014/01/008* (2014)
9. G. J. C. Carpenter, *The Metallurgical Society of CIM* (1978) 75.
10. G. R. Kamat and C. K. Gupta, *Metallurgical Transactions*, 2 (1971) 2871.
11. K. V. Mirji, C. Parthasarthy and B. Gopalan, *ISAS XIII National Symposium* (1998).
12. D. Banerjee, B. C. Maji, S. K. Das, K. V. Mirji, S. V. Thakare & M. Krishnan, *NUCAR* (2015).
13. P. Balakrishna, B. N. Murthy, D. C. K. Reddy, K. V. Mirji & S. C. Jain, *29th P/M Conf*, (2003).
14. K. V. Mirji and B. K. Kumar, in *SABTA-2000* (2000)
15. K. V. Mirji, V. K. G. Kutty and Chintamani, *POWMAT-99* (1999).
16. K. V. Mirji, et. al., *National Metallurgists Day- '99, IIT-Kanpur* (1999).
17. S. Nisimura and Isokushima, *Transactions of the Japan Institute of Metals*, 5 (1964) 40.

18. S. M. Rao, P. B. Ojha, M. Rajashri, K. V. Mirji & R. Kalidas, SETC-04 (2004) .
19. B. P. Badgujar, B. Vishwanadh, C. S. Viswanadham, R. Tewari, G. K. Dey, M. Ali, A. C. Bagchi, T. K. Sha & K. V. Mirji, 2nd International Conference on Advances in Nuclear Materials, AMM-'11 (2011)
20. B. Viswanadadh, K. V. Mirji, S. K. Jha, R. Tewari and G. K. Dey, 2nd International Conference on Advances in Nuclear Materials, AMM-'11 (2011) .
21. I. G. Sharma and T. K. Mukherjee, ICCM-1991, Bombay - (1991)
22. K. V. Mirji and Chintamani, Mini Indo-Russian Seminar at DMRL, Hyderabad (1999) .
23. F. Habashi, 'Handbook of Extractive Metallurgy', Vol. III (1997) p. 1403.
24. C. C. Vojcik, J. J. Stephens and L. Ahmad, The Minerals and Material Society, (1991).



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Electrical Measurements as a Tool for Semiconductor Material Characterization

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Abstract

The problem of detecting trace contamination of semiconductor materials with the required sensitivity has been studied for a long time, and various techniques for detecting contamination both at the wafer surface and in the silicon volume are widely used. The methods based on electrical properties measurements are may be the most sensitive of them, however some problems arise under their application, in particular: an identification of impurity type, revealing electrically inactive defects, measurement of total impurity concentration etc. Possible ways for a solution of problems mentioned are discussed and illustrated by the experimental results.

1. Introduction

With decreasing dimensions and increasing complexity of highly integrated circuits the tolerable concentrations of detrimental impurities have to shrink considerably. In particular, a contamination due to transition metals with their high diffusivity is critical for all silicon technology processes. The concentration of such impurities in silicon for microelectronics applications should be extremely low and as a rule is too low to be detected by the direct analytical methods. Therefore, a question arises about the methods allowing measurements of such ultra low concentrations.¹ Total reflection X-ray fluorescence (TXRF) method can be used to measure the metal concentration at the surface with a high sensitivity but to analyze the bulk contamination by this method the special techniques should be developed to transfer impurity atoms to the surface or to getter them from bulk to a thin surface layer. An effective application of secondary ion mass spectroscopy (SIMS) also needs some preliminary gettering procedure to gather impurities to the surface or into a thin surface layer (e.g., into poly-Si layer) to increase the impurity concentration. On the other hand electrical properties of pure semiconductor materials are very sensitive to a minor impurity concentration, therefore electrical measurements in such materials can reveal impurities in the concentration as low as 10^9 - 10^{10}cm^{-3} .¹⁻³ However, some problems should be solved for identification of a particular impurity and a quantitative measurement of its concentration. First of all it should be taken into account that an impurity atom in a common case can occupy interstitial or substitutional positions in the crystal lattice. Besides, it can form complexes with other impurities and/or intrinsic point defects and can also precipitate. An impurity atom in all these states has different electrical properties or can be even electrically inactive. Thus, to measure the total impurity concentration by electrical methods first of all it is necessary to transfer it in electrically active state. To identify the impurity type

from such measurements, it is necessary for any particular impurity to obtain by complementary investigations the parameters of all related electrically active centers. If the spectroscopic methods are used, the energy levels of centers should be known. If lifetime or diffusion length measurements are used, some specific properties of defect such as its annealing temperature, behaviour under illumination, parameter dependence on excitation level and so on can be used.

In the present paper a few examples illustrating these problems and their possible solutions are presented. In the case of iron in Si, they are practically solved, while for copper the problems seem to be more complex and are not solved totally yet.

2. Measurement methods

The most powerful electrical methods for estimation of extremely low impurity concentration are those based on the excess carrier lifetime and diffusion length measurements and the methods based on the capacitance transient after trap filling and their subsequent relaxation to the equilibrium charge state, such as the deep-level transient spectroscopy (DLTS). Lifetime τ is one of very few parameters giving information about the low defect densities in semiconductor materials consistent with recent microelectronics demands. The excess carrier diffusion length $L = (D \cdot \tau)^{1/2}$, where D is the diffusivity and in pure materials it is practically independent of defect density. Therefore lifetime and diffusion length measurements give very similar information concerning the Si contamination. Measurements of these parameters allow detecting defect densities as low as 10^{10}cm^{-3} at room temperature. However, these methods estimate an integral effect of all defects and the identification of defect type needs additional information, which should be obtained by complementary measurements. The other approach to the defect identification is based on an

application of so called lifetime spectroscopy methods.^{4,5} These methods use measurements of lifetime injection or temperature dependences to identify the defect type. Valuable information about the defect type can be obtained from the annealing experiments, if the thermal stability of defects under study is known. Besides, it should be taken into account that the measured lifetime or diffusion length value is some weighted average depending on properties of the semiconductor material on the surface and interface recombination, dopant distribution material, excitation level and so on. If the concentration of some particular defect should be measured, other contributions to lifetime should be lower or at least comparable. In high purity materials the surface effect cannot be neglected under lifetime measurements,⁶ therefore the measured values are always some "apparent" values consisting of bulk and surface components.² To suppress the surface recombination component the samples under study should be passivated by the corresponding layer deposition, by the special chemical treatment or by immersing them in solutions decreasing the surface recombination velocity.⁶⁻¹⁰

The main techniques for the lifetime and diffusion length measurements have been discussed many times (see for example¹¹). Lifetime methods are mainly based on the detection of excess carrier density decay by different methods although the stationary methods are also used, while the diffusion length measurements are mainly based on the study of collected current dependence on the distance of excitation point to the collector. Nowadays, the methods based on microwave absorption or reflection^{5,12-15} are rather popular for the lifetime measurements because they allow to carry out contactless measurements and could provide the spatially resolved regime. It should be noted that the spatially resolved measurements need as a rule a rather high injection level that could be a problem under defect density determination. Very low excitation level can be achieved, for example, by an application of the Elymat (electrolyte-semiconductor-junction) method for diffusion length measurements.^{1,7,8}

Deep-level transient spectroscopy (DLTS) is a powerful and versatile technique for investigating deep-level defects, which allows estimating the concentration, energy levels and capture cross-sections of defects. This method was proposed in¹⁶ and up to now several modifications of this method were developed¹⁷. The basic principles of this method was discussed in.¹⁸ In the DLTS method, the semiconductor device or junction under reverse bias is periodically pulsed with a forward or zero bias and the resulting transient such as capacitance, voltage or current, is monitored at different temperatures. From these

recorded transients at different temperatures, a spectrum can be generated with peaks, each one being associated with particular deep level. The heights of the peaks are proportional to the defect concentrations and their temperature dependence allows obtaining the activation energy of defect. The values of activation energy and capture cross-section allow identifying the defect under study. This method allows to measure deep level centers in the concentration $N_t \sim (10^{-6}-10^{-5}) \cdot N_d$, where N_d is the dopant concentration. Thus, in Si with a dopant concentration of 10^{15}cm^{-3} deep level defects with the concentration of $10^9-10^{10} \text{cm}^{-3}$ can be revealed. As an example demonstrating the high DLTS sensitivity, the DLTS spectra of interstitial Fe (Fe_i) measured in two Si samples with the different Fe concentration are presented in Figure 1. In the low doped Si used for radiation detectors the detection limit can be few orders of magnitude lower.

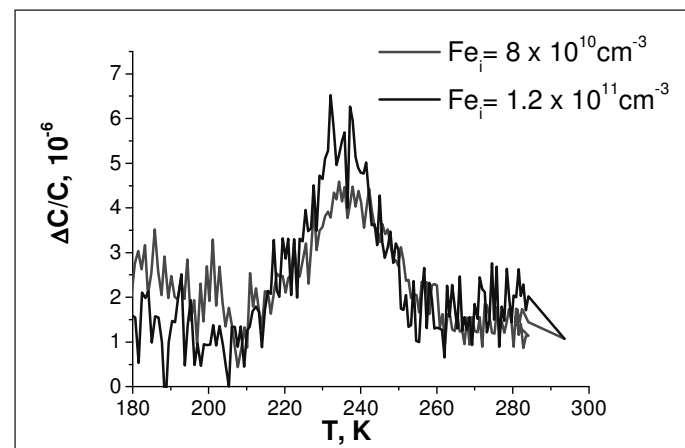


Figure 1. DLTS peaks of Fe_i in two samples with different iron concentration

The methods discussed above allow to measure extremely low defect density in the large enough regions. However in many cases the defect distribution is strongly inhomogeneous. The depth distribution of defects can be measured by DLTS. For a study of lateral distribution the well-known ability of extended defects in Si rather effectively getter point defect can be used.³ As a result of such gettering, clouds with a high defect density can be formed near dislocations and grain boundaries. The number of defects in such clouds can be estimated for example by the Electron Beam Induced Current (EBIC) method.¹⁹ Such estimations show that EBIC could reveal dislocations with the average linear defect density about 10^7cm^{-1} ^{20,21} and the two-dimensional defects such as grain boundaries with the sheet defect density of 10^{10}cm^{-2} .^{20,22} Taking into account that the size of excitation volume under the EBIC investigations is of a few micron, this means that a minimal number of centers, which can be revealed in

such measurements in the analyzed volume, may be as low as 100 - 1000.

The measurements of iron and copper concentrations in Si by the electrical methods will be discussed below in more details. The possibility of electrically inactive defect study by these methods will be also demonstrated.

3. Measurements of iron concentration in Si

Iron is the most detrimental impurity in Si technology since it is a main constituent of the technological equipment and a common contaminant in chemicals.²³ Therefore, many investigations have been devoted to the properties of iron in Si and to the development of technological processes in order to suppress its effect on electrical properties of devices.^{23,24} These investigations provide a good base for determination of iron concentration in Si by electrical measurements. It is well known that if the wafer contaminated with iron is slowly cooled after high temperature annealing about all iron atoms precipitate and could not be revealed by the electrical methods. Thus, to obtain iron concentration in Si by DLTS or lifetime measurements, first of all, it is necessary to transform it to electrically active state. It could be done, for example, by quenching the sample under study from temperature, at which iron solubility limit is higher than its total concentration. The higher is iron content, the higher temperature should be used for iron activation. After quenching iron atoms present in Si mainly at the interstitial positions and in p-Si they easily form pairs with boron even at room temperature. The duration of this process depends on boron concentration and could vary from a few hours to a few days. In both states iron is electrically active and can be revealed by DLTS (Figure 2). The FeB pairs are unstable under illumination or annealing at 200-250°C and both procedures return iron to the interstitial position. This process is reversible and can be repeated many times. If heating to 200-250°C is used for FeB dissociation, after quenching from this temperature Fe_i is revealed by DLTS and a storage at room temperature leads to the FeB pairs formation (Figure 2). As seen in Fig. 2, the heights of Fe_i and FeB related peaks are equal that means that all iron atoms can be transformed between these states by the procedure used. As noted above, the sensitivity of DLTS measurements depends on the doping level of sample under study. Nevertheless, in Si doped with boron to the concentration of about 10¹⁵cm⁻³ iron concentrations as low as 10¹⁰-10¹¹cm⁻³ can be measured by DLTS (Figure 1).

To determine iron concentration from lifetime (or diffusion length) measurements it is necessary to separate iron effect from that of other recombination centers and

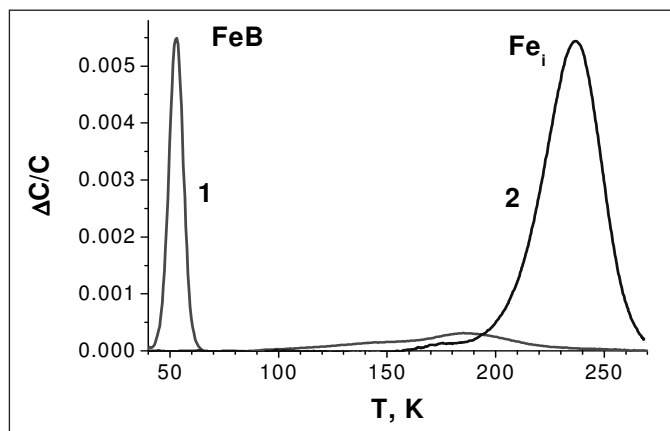


Figure 2. DLTS spectra of Fe related defects after storage at room temperature (1) and after quenching from 220°C (2)

to know the conversion factor between the lifetime value and iron concentration. The well-known procedure for this consists of lifetime measurements with Fe at the interstitial position Fe_i and in FeB pairs. Then the iron concentration could be calculated using the expression^{25,26}

$$[\text{Fe}] = K \left[\frac{1}{\tau_{\text{Fe}_i}} - \frac{1}{\tau_{\text{FeB}}} \right]$$

where **K** is the conversion factor. The problem is that the **K** value is a constant at the low excitation level only and in a common case it depends on the excitation level used under measurements, that is on the relation $\Delta p/p_0$, where Δp and p_0 are the excess and equilibrium carrier concentrations, respectively, and on p_0 value.²⁷ The lifetime dependences on $\Delta p/p_0$ calculated for iron concentration of 10¹²cm⁻³ with iron in the FeB and Fe_i states are presented in Figure 3. These dependences were calculated using the modified Shockley-Read-Hall dependences expressions,²⁸ energy levels of FeB and Fe_i²⁴ and the electron and hole

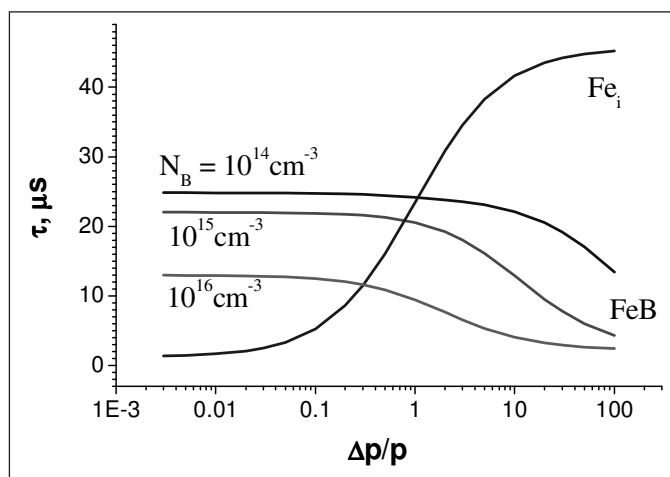


Figure 3. Lifetime dependences on the excitation level calculated for Fe_i and FeB

capture cross-sections for all charge states of defects, which were obtained in.^{27,29}

It should be noted that the dependences $\tau(\Delta p/p_0)$ presented in Figure 3 can be considered as a base for so called injection-dependent lifetime spectroscopy.^{4,5} In this method the measurements of lifetime dependence on the injection level and/or temperature was used for iron identification and measurements of its concentration.³⁰

4. Measurements of copper concentration in Si

Recent introduction of copper interconnects in ultralarge scale integration technology has increased the need for sensitive and reliable detection tools for copper contamination in silicon wafers. Copper is considered as one of the most dangerous impurities in silicon device fabrication. It has the highest solubility and diffusivity among the transition metals^{23,31} and can be easily introduced into the silicon wafers during heat treatment. In comparison to iron, copper detection is much more challenging, partly because copper does not form stable defects in the bulk but tends to outdiffuse to the wafer surfaces even at room temperature. Cu in Si can present in the form of interstitial or substitutional atoms, small agglomerates or complexes and precipitates. Usually only a small fraction of the respective copper solubility is electrically active and forms several deep energy levels. Though numerous studies of electrical properties of copper-related centers have been published, the position of energy levels, introduced by copper-related defects, is still controversial.²³ Besides copper at the substitutional position, complexes with a number of Cu atoms up to four³² and copper-hydrogen complexes introduce the energy levels in the gap and can be revealed by DLTS.^{33,34} However, as noted above, only a small fraction of copper atoms remains in electrically active state. Therefore, the problem of development of reliable procedure for the measurements of total copper concentration in Si by the DLTS is not solved up to now.

Recombination lifetime methods offer an alternative for detecting Cu contamination in Si. However, the copper impact on the recombination lifetime is weaker compared to, for example, iron. In *n*-Si, the Cu concentration has to exceed 10^{12} cm^{-3} to affect the recombination lifetime, and in *p*-Si the copper effect on the lifetime is even weaker.³⁵ Under an optical excitation the diffusion length in Cu contaminated *p*-Si was found to decrease essentially similar to iron contaminated Si.³⁵ It was assumed that the lifetime decrease under excitation was determined by Cu precipitation and a dependence of this process on oxygen precipitate

density, which serve as nucleation sites for copper precipitation, was revealed.³⁶

Thus, it should be stated that at present the electrical methods are not suitable for quantitative detection of trace Cu contamination. To develop suitable methods more experimental studies should be carried out.

5. Revealing electrically inactive defects

A question arises about applicability of high sensitive electrical methods to reveal electrically inactive defects. Of course, such defects cannot be studied directly by such methods. But they can be "activated" by an interaction with other defects. Some examples of such measurements will be presented below.

The most striking from such examples is an application of gold or platinum diffusion for such purposes. The both impurities in defect-free Si diffuse very quickly over interstitial sites but their solubility limit in this state is very small. Therefore the equilibrium concentration of interstitial gold or platinum is reached very quickly and then these atoms are transformed into electrically active substitutional sites via the kick-out mechanism.³⁷ Therefore, the concentration of substitutional gold (platinum) is very sensitive to the concentration and distribution of traps for self-interstitials and to vacancy-related centers, which can directly trap interstitial gold (platinum). If the defects under study play a role of traps for interstitial gold, the gold concentration will be equal to the density of these defects. Thus, the measurements of gold (platinum) concentration by the DLTS allow to reveal such traps even if they are electrically inactive and to measure their concentration and spatial distribution. The gold (platinum) diffusion experiments can be used as a rather sensitive tool for the defect characterization, when the substitutional gold concentration was measured by the DLTS technique.³⁸⁻⁴¹ Examples of such measurements are presented in Figures 4 and 5.

It is known that co-doping of Si with nitrogen suppress the grown-in void formation⁴² that was explained by nitrogen-vacancy complexes formation.⁴³⁻⁴⁵ The optimization of such suppression needs a tool for nitrogen-vacancy complexes monitoring. In floating zone Si such vacancy-related centers can be revealed using gold diffusion and the DLTS study of substitutional gold distribution. The results of such measurements are shown in Figure 4 for two Si wafers with different radial distributions of vacancy-related defects.

High temperature rapid thermal annealing (RTA) of Si wafers leads to quenching vacancy-related centers in the bulk of wafer and to a formation of depleted region near the

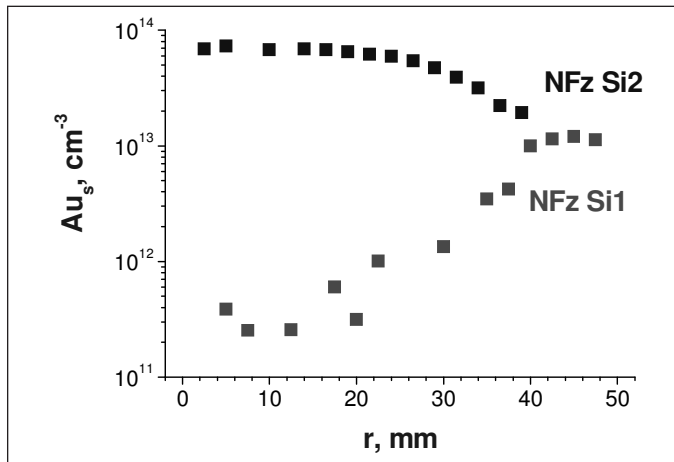


Figure 4. Au concentration as a function of a distance from the wafer center for two floating zone Si wafers

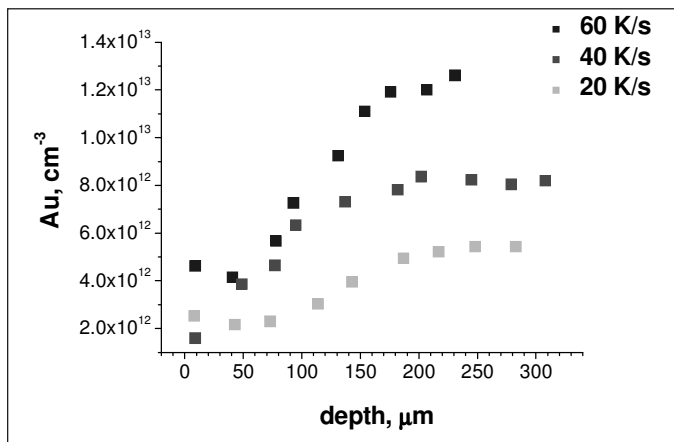


Figure 5. Depth distribution of Au diffused at 730°C for 3 h in Si samples after RTA at 1230°C for 10 s and subsequent cooling with a rate of 20, 40 and 60 K/s

surface due to vacancy outdiffusion.⁴⁶ Such vacancy-related centers distribution can be used to control the distribution of oxygen precipitates playing a role of intrinsic getters for undesirable contamination.⁴⁶ To optimize the vacancy-related defects profile the methods for its measurements should be developed. The problem is that these defects are electrically inactive and their concentration is rather low. It was found that the gold diffusion study is a suitable tool for this purpose.⁴¹ The corresponding depth profiles of substitutional gold measured by the DLTS are presented in Figure 5. Under this study RTA was carried out at 1230°C for 10 s and then the samples were cooled with different rates. Gold diffusion was made at 730°C for 3 hours. It is seen that indeed vacancy-related centers concentration can be measured and their depth distribution can be reconstructed using the gold diffusion. It is seen that the depth profile of defects depend essentially on cooling rates that allows to control it rather easily.

In both examples the vacancy-related centers are electrically inactive and their concentration is too low to be detected by any direct method. However, the application of gold diffusion allows not only to measure the concentration of these defects even when it is lower than 10^{12}cm^{-3} but also to reconstruct their spatial distribution.

Hydrogen in Si is known to passivate electrically active defects in many semiconductor materials. However, sometimes its interaction with other defects can “activate” them or change their electrical properties. As an example of such hydrogen effect in p-type Si due to its interaction with FeB pairs is discussed here. As seen in Figure 2, the DLTS peak corresponding to FeB pairs is observed at temperatures lower than liquid nitrogen temperature. Therefore, if iron exists in the form FeB pairs, it cannot be revealed in Si without cooling down to liquid helium temperatures. However, interaction with hydrogen, introduced under wet chemical etching leads to a partial dissociation of FeB pairs and appearance of interstitial Fe in the near surface layer with the DLTS peak at essentially higher temperature.^{47,48} The Fe_i depth profile measured by the DLTS after wet chemical etching is shown in Figure 6. Other example of hydrogen-related defect “activation” was presented in,⁴⁹ where electrically active defects are formed due to hydrogen interaction with electrically inactive defect introduced in Si by high energy electron irradiation.

6. Summary

Thus, the application of DLTS and lifetime measurements to reveal extremely low impurity concentrations in Si is

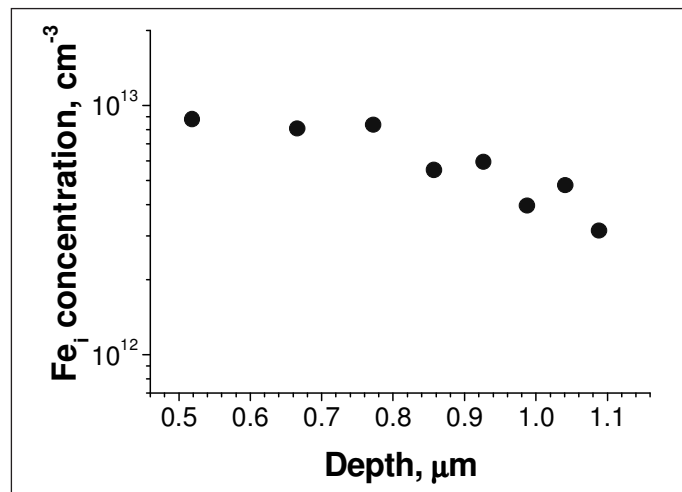
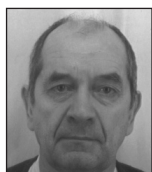


Figure 6. Depth profile of Fe_i after wet chemical etching

discussed. The problems arising under identification of defects are illustrated by measurements of iron and copper concentrations. A possibility to study electrically inactive defects by these methods is also demonstrated.

References

1. M. L. Polignano, D. Codegoni, S. Grasso, I. Mica, G. Borionetti and A. Nutsch, *Phys. Status Solidi A*, 212 (2015) 495.
2. D.K. Schroder, *IEEE Trans. Electron Dev.*, 44 (1997) 160.
3. E.B. Yakimov, *Bull. Mater. Sci.*, 28 (2005) 367.
4. W. Warta, *Phys. Stat. Sol. (a)*, 203 (2006) 732.
5. S. Rein, *Lifetime Spectroscopy*, Springer-Verlag: Berlin, 2005.
6. O. Palais, J. Gervais, E. Yakimov and S. Martinuzzi, *Eur. Phys. J. AP*, 10 (2000) 157.
7. J. Wittmann, W. Bergholz and H. Hoffmann, *J. Electrochem. Soc.*, 146 (1999) 313.
8. M. Rommel, A.J. Bauer and H. Ryssel, *J. Electrochem. Soc.*, 155 (2008) H117.
9. B. Chhabra, S. Bowden, R.L. Opila and C.B. Honsberg, *Appl. Phys. Lett.*, 96 (2010) 063502.
10. N.E. Grant, K.R. McIntosh and J.T. Tan, *ECS J. Solid State Sci. Technol.*, 1 (2012) P55.
11. D.K. Schroder, *Semiconductor Material and Device Characterization*, Wiley: New York, 1990, ch. 8.
12. H. A. Atwater, *J. Appl. Phys.*, 31 (1960) 938.
13. M. Kunst and G. Beck, *J. Appl. Phys.*, 60 (1986) 3558.
14. A. Sanders and M. Kunst, *Solid State Electronics*, 34 (1991) 1007.
15. J. Schmidt and A.G. Aberle, *J. Appl. Phys.*, 81 (1997) 6186.
16. D. V. Lang, *J. Appl. Phys.*, 45 (1974) 3023.
17. P. Kolev and M. J. Deen, *Advances in Imaging & Electron Physics*, Academic Press: New York, 109 (1999) 1.
18. G.L. Miller, D. V. Lang and L. C. Kimerling, *Ann. Rev. Mater. Sci.*, 7 (1977) 377.
19. E.B. Yakimov, *J. Phys.: Condens. Matter.*, 14 (2002) 13069.
20. O.V. Feklisova, E.B. Yakimov and N. Yarykin, *Physica B*, 340-342 (2003) 1005.
21. O. V. Feklisova, B. Pichaud and E. B. Yakimov, *Phys. Stat. Sol. (a)*, 202 (2005) 896.
22. O.V. Feklisova and E.B. Yakimov, *Phys. Stat. Sol. (c)*, 4 (2007) 3105.
23. K Graff, *Metal Impurities in Silicon -Device Fabrication*, Springer-Verlag: Berlin, 2000.
24. A.A. Istratov, H. Hieslmair and E.R. Weber, *Appl. Phys. A*, 69 (1999) 13.
25. J. Lagowski, P. Edelman, M. Dexter and W. Henley, *Semicond. Sci. Technol.*, 7 (1992) A185.
26. G. Zoth and W. Bergholz, *J. Appl. Phys.*, 67 (1990) 6764.
27. M. Rommel, G. Zoth, M. Ulrich and H. Ryssel, *Solid State Phenom.*, Trans. Tech. Public.: Switzerland, 82-84 (2002) 373.
28. S. C. Choo, *Phys. Rev. B*, 1 (1970) 687.
29. O. Palais, E. Yakimov and S. Martinuzzi, *Mater. Sci. Engineer. B*, 91-92 (2002) 216.
30. D.H. Macdonald, L.J. Geerligs and A. Azzizi, *J. Appl. Phys.*, 95 (2004) 1022.
31. A.A. Istratov and E.R. Weber, *J. Electrochem. Soc.*, 149 (2002) G21.
32. N. Yarykin, J. Weber, *Semiconductors*, 47 (2013) 275.
33. N. Yarykin and J. Weber, *Phys. Rev. B*, 88 (2013) 085205.
34. N. Yarykin and J. Weber, *Appl. Phys. Lett.*, 105 (2014) 012109.
35. W.B. Henley, D.A. Ramappa and L. Jastrezbski, *Appl. Phys. Lett.*, 74 (1999) 278.
36. H. Väinölä, E. Saarnilehto, M. Yli-Koski, A. Haarahiltunen, J. Sinkkonen, G. Berenyi and T. Pavelka, *Appl. Phys. Lett.*, 87 (2005) 032109.
37. W. Frank, U. Gösele, H. Mehrer, A. Seeger, in: *Diffusion in Crystalline Solids*, Academic Press Inc.: Orlando, 1984, p. 64.
38. E. Yakimov and I. Perichaud, *Appl. Phys. Lett.*, 67 (1995) 2054.
39. M. Jacob, P. Pichler, H. Ryssel and R. Falster, *J. Appl. Phys.*, 82 (1997) 182.
40. A. L. Parakhonsky, E. B. Yakimov and D. Yang, *J. Appl. Phys.*, 90 (2001) 3642.
41. O.V. Feklisova and E. B. Yakimov, *Physica B: Cond. Matter.*, 404 (2009) 4681.
42. [42] A. Ikari, K. Nakai Y. Tachikawa et al., *Solid State Phenom.*, Trans. Tech. Public.: Switzerland, 69-70 (1999) 161.
43. W. von Ammon, R. Holzl, J. Virbulis, E. Dornberger, R. Schmolke and D. Graf, *Solid State Phenom.*, Trans. Tech. Publications, Switzerland, 82-84 (2002) 17.
44. V. V. Voronkov and R. Falster, *Mater. Sci. Eng. B*, 114-115 (2004) 130.
45. V. V. Voronkov and R. Falster, *J. Crystal Growth*, 273 (2005) 412.
46. V. V. Voronkov and R. Falster, *Mater. Sci. Semicond. Proces.*, 5 (2003) 387.
47. O. V. Feklisova, A. L. Parakhonsky, E. B. Yakimov and J. Weber, *Mater. Sci. Engineer. B*, 71 (2007) 268.
48. C. K. Tang, L. Vines, B. G. Svensson and E. V. Monakhov, *Appl. Phys. Lett.*, 99 (2011) 052106.
49. N. Yarykin, O. V. Feklisova and J. Weber, *Phys. Rev. B*, 69 (2004) 045201.



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Utility of High Purity Materials as Targets for Production of Radioisotopes Intended for Medical Use

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Abstract

Diagnostic and therapeutic applications of radioisotopes in human healthcare have grown in leaps and bounds during the recent past mainly due to the availability of a good spectrum of promising radioisotopes. High radionuclidic and chemical purity (of the order of >99.9%) are absolutely essential quality parameters for any radionuclide to be used in patient care. While the presence of radionuclide contaminants leads to unwanted radiation dose burden to the patients, presence of chemical impurities causes serious problem in the formulation of radiolabeled agents, particularly when peptides, antibodies are used as the targeting ligands. In this respect, purity of target materials to be used for production of radionuclides play a decisive role. The objective of the present article is to elaborate importance of the purity of the target material on the radiopharmaceutical formulation and their subsequent clinical utilization.

1 Introduction

Diagnostic and therapeutic radiopharmaceuticals are radiolabeled molecules comprising of target-specific molecular carrier linked to suitable radionuclide designed either to image or to deliver therapeutic doses of ionizing radiation to specific disease sites. Last two decades have witnessed rapid development in the field of both diagnostic and therapeutic radiopharmaceuticals using a variety of radionuclides. Availability of radionuclides with attractive decay characteristics in suitable radiochemical form have contributed to the accelerated growth of nuclear medicine. Very high level of radionuclide purity and chemical purity (both >99.9 %) are essential requirements for the radioisotopes to be suitable for radiopharmaceutical preparations that are administered to human patients. While the presence of radionuclide contaminants leads to unwanted radiation dose burden to the patients, presence of chemical impurities causes serious problem in the formulation of radiolabeled agents, particularly when peptides, antibodies are used as the targeting ligands. In this respect, purity of target materials to be used for production of radionuclides play a decisive role.

Artificial transmutation of an element by thermal neutrons in a research reactor or by charged particles in a particle accelerator is the main route of production of radioisotopes. Selection of stable nuclides, i.e. target materials, both natural and enriched in isotopic composition of desired element having high purity in terms of chemical and isotopic are important requirements for production of radioisotopes suitable for nuclear medicine applications. Neutron flux/beam current, cross-section, isotopic abundance and time of irradiation, etc. are the other considerations for obtaining radionuclides in good yield and with high specific activity.^{1,2} Radionuclide

and radiochemical purity of the radiopharmaceutical products are directly derived from the purity of the initial radiochemical used for their preparation. Chemical and isotopic impurities from target result in co-production of undesirable radionuclides that affect the effective utilization of radionuclide of interest in medical domain.

Undoubtedly, high purity materials as targets form is essential for production of radioisotopes intended for medical use. Isotope Production and Applications Division, BARC is in the forefront of radioisotope production and supply, catering to the demands for radioisotope applications in the country. Tera-Becquerel quantities of the radioisotopes such as, ⁹⁹Mo, ¹³¹I, ¹⁷⁷Lu, ¹⁵³Sm, ³²P, ⁵¹Cr, etc. are routinely produced and supplied to a large number of users. In the following sections we describe various aspects pertaining to the requirements of the purities of target chemicals for radioisotope production and its implications on radiopharmaceutical preparations.

2. Radionuclide production for medical applications

Radioisotopes are produced by thermal neutron activation of target materials in suitable chemical form in Dhruva research reactor, Trombay. Target chemicals are neutron irradiated from few hours to several days and months at neutron flux in the range of 1×10^{13} n.cm⁻².s⁻¹ to 1.8×10^{14} n.cm⁻².s⁻¹. Table 1 summarizes medically useful radionuclides produced in Dhruva research reactor along with target chemicals, nuclear reactions involved in their production and probable impurities co-produced from competing reactions arising from trace impurities in the target chemical. In the case of ⁹⁹Mo and ¹³¹I, radionuclidic impurities are also formed by competing nuclear reactions involving the naturally occurring isotopes other than

Table-1. Target chemicals used in Radioisotope Production

Target used	Radio isotope	Activation cross section (b)	Natural abundance (%)	Nuclear reaction	Radionuclidic impurities
MoO ₃ ⁹⁸ Mo-24.4%	⁹⁹ Mo	0.13	⁹² Mo (14.8), ¹⁰⁰ Mo (9.6)	⁹⁸ Mo(n,γ) ⁹⁹ Mo → ^{β⁻} ^{99m} Tc	^{93m} Mo, ⁹³ Mo, ¹⁰¹ Mo, ¹⁰¹ Tc, ⁹⁹ Tc, ¹⁸⁶⁺¹⁸⁸ Re
TeO ₂ ¹³⁰ Te-34.5%	¹³¹ I	0.2	¹²⁶ Te (18.8), ¹²⁸ Te (31.7)	¹³⁰ Te(n,γ) ¹³¹ Te → ^{β⁻} ¹³¹ I	¹²⁹ I, ⁷⁵ Se, ¹²⁵ Sb, ¹⁹⁸ Au, ¹⁹⁷⁺²⁰³ Hg
Lu ₂ O ₃ ¹⁷⁶ Lu-2.59%	¹⁷⁷ Lu	2100	¹⁷⁵ Lu-97.41%	¹⁷⁶ Lu(n,γ) ¹⁷⁷ Lu	^{177m} Lu, Radiolanthanides
Sm ₂ O ₃ ¹⁵² Sm-26.7%	¹⁵³ Sm	206	¹⁴⁴ Sm (3.1), ¹⁵⁴ Sm (22.7)	¹⁵² Sm(n,γ) ¹⁵³ Sm	¹⁴⁵ Sm, ¹⁵¹ Sm, ⁵⁵ Sm, ¹⁵⁴⁺¹⁵⁵ Eu, Radiolanthanides
P Elemental ³¹ P-100%	³² P	0.172	³³ S (0.75), ³⁴ S (4.21)	³² P(n,γ) ³² P	⁷⁶ As, ¹²² Sb, ¹²⁴ Sb,
Cr metal ⁵⁰ Cr-4.35%	⁵¹ Cr	15.9	⁵² Cr (83.9), ⁵³ Cr (9.5)	⁵⁰ Cr(n,γ) ⁵¹ Cr	⁵⁵ Cr, ⁵⁹ Fe, ⁶⁰ Co, ⁹⁹ Mo

the one leads to the desired radioisotope. On the other hand, in the case of ³²P, ¹⁵³Sm, ¹⁷⁷Lu and ⁵¹Cr where the corresponding target nuclide is mononuclidic (100% I.E.) or very high isotopic enrichment is utilized, the competing reactions may arise only from the trace impurities present in the chemical. For example, in the case of Sm and Lu adjacent rare earth impurities if present in the target will produce undesired radiolanthanide impurities which will adversely affect the effective utilization of useful ¹⁵³Sm and ¹⁷⁷Lu. Although in trace amounts, presence of undesirable impurities in target can lead to flux depression due to its higher capture cross section for thermal neutron thereby affecting yield and specific activity of the radionuclide of interest thereby imposing serious problem in the formulation of radiolabeled agents, particularly when peptides, antibodies are used as the targeting ligands.

3. Impact of target purity on quality of major radioisotopes produced in India

3.1 Molybdenum-99

Molybdenum-99 is the parent radionuclide for ^{99m}Tc ($T_{1/2} = 6.02$ h and $E_{\gamma} = 140$ keV), considered as the workhorse of nuclear medicine procedures. It is estimated to be used in about 30 million medical diagnoses annually throughout the world. Considering the diagnostic value provided by ^{99m}Tc based imaging agents, it is expected that ^{99m}Tc will continue its central role in diagnostic nuclear medicine into the future.³ Availability of ^{99m}Tc for preparation of diagnostic agents is ensured in the form of ⁹⁹Mo/^{99m}Tc generator system from which ^{99m}Tc is separated under aseptic conditions. ⁹⁹Mo for this purpose is produced by thermal neutron activation of natural MoO₃ target and 900 GBq (~25 Ci) of ⁹⁹Mo is supplied weekly from our laboratory for nuclear medicine applications. The oxide target used has

a number of molybdenum isotopes with varying isotopic abundance. The irradiated target is chemically processed and supplied as ⁹⁹Mo-sodium molybdate to facilitate preparation of ⁹⁹Mo/^{99m}Tc generators. The specific activity of ⁹⁹Mo obtained is about 20-25 GBq (550-800 mCi)/g of Mo. During irradiation of natural MoO₃ target, other Mo radioisotopes co-produced are unavoidable unless MoO₃ target enriched in ⁹⁸Mo is used. Additionally, radionuclidic

Table 2. Radionuclidic impurities in ⁹⁹Mo due to chemical impurities in target materials obtained from four different commercial suppliers

Radionuclide	Supplier I	Supplier II	Supplier III	Supplier IV
⁹⁹ Mo	343 mCi	335 mCi	482 mCi	347 mCi
¹²⁴ Sb	1.36 μCi	-	-	1.6 μCi
¹³⁴ Cs	0.96 μCi	-	-	1.7 μCi
⁵¹ Cr	3.29 μCi	3.1 μCi	-	6.6 μCi
⁵⁹ Fe	0.42 μCi	0.4 μCi	0.05 μCi	0.2 μCi
⁶⁰ Co	0.31 μCi	1 μCi	0.05 μCi	0.3 μCi
⁹⁵ Nb	0.46 μCi	0.5 μCi	0.83 μCi	1.1 μCi
⁴⁶ Sc	0.02 μCi	0.04 μCi	0.02 μCi	-
¹⁸⁸ W	-	2.6 μCi	0.09 μCi	-
^{110m} Ag	-	0.04 μCi	-	-
⁶⁵ Zn	-	-	0.1 μCi	0.04 μCi
¹⁵² Eu	-	-	0.44 μCi	-
¹⁵⁴ Eu	-	-	0.07 μCi	-
¹⁸² Ta	-	-	5.17 μCi	-
²⁰³ Hg	-	-	0.08 μCi	0.12 μCi
RN Purity ⁹⁹Mo	99.99%	99.99%	99.99%	99.99%

impurities can result from the activation of trace impurity elements present in the target chemical. Chromium and tungsten are most common elemental impurities present in molybdenum target. However, presence of other impurities such as Fe, Co, Cs, and Sb contributing to their respective radioisotopes has also been observed in MoO₃ target (Table 2). The radioactivity due to activation of these elements is negligible in ⁹⁹Mo, but is of serious concern if present in a radiopharmaceutical formulation. Technetium-99m is separated from ⁹⁹Mo using ⁹⁹Mo/^{99m}Tc generator either by solvent extraction technique or from a column generator for radiopharmaceutical applications. However, radionuclidic and chemical impurities of ⁹⁹Mo which are carried forward to radiochemically separated ^{99m}Tc is of great concern necessitating stringent pharmacopoeia specifications of the product. Presence of same group element tungsten impurity in Mo target chemical leads to the production of ¹⁸⁶Re and ¹⁸⁸Re radioisotopes on neutron activation of ¹⁸⁴W and ¹⁸⁶W isotopes, respectively. Both technetium and rhenium exhibit similar chemistry and rhenium if formed would co-exist in all ^{99m}Tc products causing radiation burden to patients during diagnostic studies in additions to chemical interference during ligand labeling. The choice of Mo target and its purity therefore has bearing on the purity of final radioisotope and its subsequent use.

3.2 Iodine-131

¹³¹I-NaI is extensively used in the diagnosis and treatment of thyroid disorders including thyroid cancer. About 1.6 TBq (45 Ci) ¹³¹I is produced weekly by neutron irradiation of tellurium oxide and radiochemically processed employing dry distillation technique to obtain ¹³¹I-NaI.⁴ Tellurium has eight isotopes with different isotopic abundance. ¹³¹I is produced by neutron activation of ¹³⁰Te isotope (abundance: 34.08%). Stable ¹²⁷I and long lived ¹²⁹I (T_{1/2} 1.57×10⁷ years) isotopes form as a result of activation of other Te isotopes ¹²⁶Te (18.84%) and ¹²⁸Te (31.74%). Presence of iodine impurity in Te target reduces the specific activity of ¹³¹I produced, which is undesirable for labeling of antibody for its use in radioimmunotherapy. Presence of impurity elements such as selenium and antimony often leads to co-production of their long-lived radionuclides, ⁷⁵Se (T_{1/2} = 119.78 d) and ¹²⁵Sb (T_{1/2} = 2.79y), which accumulate in the radioactive waste generated during the radiochemical processing result in post handling and waste management problems. Hg, Au and Ag impurities if present interferes with distillation of ¹³¹I during radiochemical processing, resulting in low recoveries of ¹³¹I produced.

3.3 Phosphorus-32

Radiopharmaceutical treatment of metastatic bone pain is an effective modality that provides palliation of pain to multiple areas of the skeleton simultaneously without the

significant soft-tissue toxicity. Phosphorus-32 in the form of sodium orthophosphate was the first systemic radionuclide to be used for the treatment of bone metastases which continues till date as a cheaper alternative to the much advocated phosphonate based radiopharmaceuticals. Production of ³²P following the ³¹P(n,γ)³²P route is straight forward, offers the scope of using inexpensive mononuclidic natural elemental phosphorus (³¹P) target material and needs a very simple chemical treatment after neutron irradiation⁵. For production of ³²P following (n,γ) route, about 0.35 g of red phosphorus was accurately weighed, taken in an aluminum container, encapsulated by cold-press welding and irradiated in Dhruva reactor of our institution at a thermal neutron flux of 7.5×10¹³ n.cm⁻².s⁻¹ for 60 days. Phosphorus-32 availed from direct radiative neutron capture route shows the presence of ⁷⁶As (T_{1/2} 1.097d), ¹²²Sb (T_{1/2} 2.7 d) and ¹²⁴Sb (T_{1/2} 60.2 d).⁵ Their origin is due to the trace elemental chemical impurities in the target chemical and their total contribution was 0.034% of the total ³²P radioactivity formed rendering the product 99.966% pure. Higher amounts of impurity in the product will result in product purity less than 99.9% that are not acceptable for nuclear medicine applications.

3.4 Samarium-153

Samarium-153 is used in the formulation of ¹⁵³Sm-labeled EDTMP, the most widely used radiopharmaceutical for palliative treatment of bone pain in metastatic bone cancer patients. It has been successfully deployed in various nuclear medicine centres across the country for almost two decades. ¹⁵³Sm is produced by irradiation of enriched Sm₂O₃ target (I.E 99.8% in ¹⁵²Sm) in a reactor.⁶ Natural Sm₂O₃ consists of stable isotopes of samarium forming ¹⁴⁵Sm (T_{1/2} 340d), ¹⁵¹Sm (T_{1/2} 90y) and ¹⁵³Sm (T_{1/2} 22.3 min) radioisotopes during production of medically useful ¹⁵³Sm. Radioactive decay of ¹⁵³Sm and ¹⁵⁵Sm eventually leads to the formation of long-lived ¹⁵⁴Eu and ¹⁵⁵Eu radionuclidic impurities thus necessitating use of high purity enriched target chemical.⁶ Other rare earth impurities in the target may contribute to formation of radiolanthanides from La to Lu that are cumbersome for real time in-process radiochemical separation post irradiation. Additionally, these chemicals or radionuclidic impurities compete for EDTMP during chemical reaction thereby affecting the yield of desired ¹⁵³Sm labeled EDTMP.

3.5 Lutetium-177

Lutetium-177 is relatively new in the field of targeted radionuclide therapy and this therapeutic radionuclide has emerged as a promising candidate due to its favorable radionuclidic characteristics. In addition, it is relatively easily produced in large quantity as per the requirement and also in high specific activity. Targeted radionuclide therapy with ¹⁷⁷Lu-DOTA-TATE has shown excellent

response and a significantly high overall survival of patients suffering from neuroendocrine tumors (NETs). Lutetium oxide target, which is >85% isotopically enriched in ^{176}Lu , is used for the production of ^{177}Lu following (n, γ) route.⁷ It is essential to have specific activity of >740 GBq (20 Ci) ^{177}Lu /mg Lu for the radiochemical to be suitable for target radionuclide therapy (PRRT). Presence of trace impurities can seriously hamper the specific activity (by flux depression during neutron irradiation) of ^{177}Lu . Some of the lanthanides have very large capture cross section for thermal neutron viz., ^{168}Yb -2300b, ^{174}Yb -69.4b, ^{173}Yb -17.1b, ^{171}Yb -48.6b, ^{167}Er -659b, ^{164}Dy -1040b, ^{157}Gd - 2.54×10^5 b, ^{155}Gd -60900b, ^{151}Eu -5900b, etc. It is essential to ensure that the target chemical Lu_2O_3 is of high purity and not containing any of these stable elements of lanthanide group. Presence of these adjacent lanthanides also affects the yield or radiolabeling of a radiopharmaceutical product by competing with the ligand during chemical reaction.

4. Summary and Conclusion

Use of high purity target materials is essential for production of radioisotopes to be subsequently used for the preparation of radiopharmaceuticals matching pharmacopeia requirements for human administration. Formation of the radionuclidic impurities are observed while from the chemical impurities present in target chemicals, natural or isotopically enriched, depending upon the type of impurity, their isotopic abundance, thermal neutron activation cross section and half life of the radionuclidic contaminant. The best way to minimize their formation is to use target material as pure as possible. However, this is practicable upto a certain limit. Radionuclidic impurities can also be minimized or completely eliminated by proper choice of irradiation parameters and post irradiation cooling

of the target to allow the decay of short-lived radionuclidic impurity. Several chemical impurities present in target material often may not lead to formation of radionuclidic contaminant, but can seriously affect the yield and quality if radiopharmaceutical preparation and in some cases may render them unfit for human administration.

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References

1. M. Neves, A. Kling and R.M. Lambrecht, *Appl. Radia. Isot.*, 57 (2002) 657.
2. IAEA-TECDOC-1340, IAEA, 2003.
3. A. Dash, F. F. (Russ) Knapp Jr. and M.R.A. Pillai, *Nucl. Med. Biol.*, 40 (2013) 167.
4. R. N. Ambade, S. N. Shinde, M. S. A. Khan, S. P. Lohar, K. V. Vimalnath, P. V. Joshi, S. Chakraborty, M. R. A. Pillai and A. Dash, *J. Radioanal. Nucl. Chem.*, 303 (2015) 451.
5. K.V. Vimalnath, P. Shetty, S. Chakraborty, T. Das, V. Chirayil, H. D. Sarma, K. C. Jagadeesan and P. V. Joshi, *Cancer Biother. Radiopharm.*, 28 (2013) 423.
6. N. Ramamoorthy, P. Saraswathy, M. K. Das, K. S. Mehra and M. Ananthkrishnan, *Nuclear Medicine Commun.*, 23 (2002) 83.
7. S. Chakraborty, K. V. Vimalnath, S. P. Lohar, P. Shetty and A. Dash, *J. Radioanal. Nucl. Chem.*, 302 (2014) 233.



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Monogermane $^{72}\text{GeH}_4$ with High Chemical and Isotopic Purity

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Abstract

Ultrapurification of monogermane $^{72}\text{GeH}_4$ with the content of the main isotope 99.953 at % was carried out by the method of low-temperature rectification. The nature and content of molecular impurities in monogermane samples were determined by the method of chromato-mass-spectrometry. By the results of analysis the content of each of 50 impurities, referring to the classes of volatile inorganic hydrides, hydrocarbons, chlorine- and fluoro-hydrocarbons, alcohols, ethers, alkyl- and chloro-germanes, in the rectificate does not exceed 1×10^{-5} mol. %. The mostly high content (mol. %) is of carbon dioxide (3×10^{-5}), of di- and trigermane (10^{-2} – 10^{-4}).

1. Introduction

High-purity germanium is used in semiconductor engineering (diodes, triodes, transistors), infrared optics (night vision instruments, guidance systems, investigation and ground mapping from satellites), and in fiber-optic systems.

Natural germanium consists of five stable isotopes ^{70}Ge , ^{72}Ge , ^{73}Ge , ^{74}Ge , and ^{76}Ge (Table 1)¹. Up to the present time the traditional technique for production of the samples of highly enriched germanium comprised the separation of germanium isotopes by centrifugation using GeF_4 as a working gas, conversion of GeF_4 into GeO_2 with its subsequent reduction up to elementary form. Using this scheme the single crystals of ^{70}Ge (96.3%) and ^{74}Ge (96.8%) were grown for doping with impurities by the method of neutron-irradiation doping². 26 kgs of ^{76}Ge with 85% enrichment were produced at RRC Kurchatov Institute for fabrication of detector used to register neutrinoless double β -decay³. The team of V.I. Ozhogin^{4,5} of this Institute produced the perfect crystals of ^{70}Ge with 99.99% enrichment and their heat conductivity was measured.

Table 1. Isotopic composition (at. %) of natural germanium, $^{72}\text{GeH}_4$ and extracted ^{72}Ge .

Isotope	Substance		
	$^{\text{nat}}\text{Ge}$	$^{72}\text{GeH}_4$	^{72}Ge
^{70}Ge	20.84	0.005±0.001	0.00009±0.00002
^{72}Ge	27.54	99.953±0.008	99.98439±0.00091
^{73}Ge	7.73	0.018±0.003	0.01191±0.00073
^{74}Ge	36.28	0.023±0.006	0.00356±0.00030
^{76}Ge	7.61	0.002±0.001	0.00005±0.00001

However, a complicated scheme of chemical conversions $\text{GeF}_4 \rightarrow \text{Ge}$ can be the reason for contamination by isotopic and chemical impurities. Thus, the degree of isotopic and chemical purity of germanium samples, produced by this scheme, was insufficient for reliable and more complete definition of the isotopic effects in physical and physico-chemical properties of these monoisotopes.

That is why the process of separation of germanium isotopes by centrifugal method was proposed and realized⁶ using monogermane as a working substance. Up to this moment the monoisotopic monogermanes $^M\text{GeH}_4$ were not available and for this reason their properties as individual chemical compounds were not determined. The applied interest to monoisotopic monogermanes is due to the possibility to produce a corresponding high-purity isotope in the form of a simple substance as a result of their decomposition. The hydride method is used for fabrication of the purest samples of elemental semiconductors (Si, Ge, Te)⁷. The physico-chemical fundamentals were developed as well as the methods for production and analysis of special purity germanium hydride and of the extracted elemental germanium⁸. A description is given to the use of the efficient rectification method for ultrapurification of germane with natural isotopic composition⁹.

$^{76}\text{GeH}_4$, $^{74}\text{GeH}_4$, $^{73}\text{GeH}_4$ and $^{72}\text{GeH}_4$ monogermanes were extracted by centrifugal method at Electrochemical Plant, Zelenogorsk City, from the hydride with natural isotopic composition produced by the reaction of germanium tetrachloride with sodium borane and purified by rectification. Previously^{10,11} we have produced high-purity monogermanes $^{76}\text{GeH}_4$ (88.14%), $^{74}\text{GeH}_4$ (99.9377%) and $^{73}\text{GeH}_4$ (99.8942%). It was found that the process of isotopic enrichment of germane by

Table 2. Content (mol. %) of impurities in different samples of $^{72}\text{GeH}_4$ by the data of chromat-mass spectrometry method.

Impurity	Initial	Rectificate	Light fraction	Heavy fraction
SiH_4	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$	$(1.0 \pm 0.2) \times 10^{-5}$	$<1 \times 10^{-6}$
PH_3	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$	$<1 \times 10^{-6}$
AsH_3	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
H_2S	$<3 \times 10^{-6}$	$<3 \times 10^{-6}$	$<3 \times 10^{-6}$	$<3 \times 10^{-6}$
hydrocarbons C_1 - C_2	$<1 \times 10^{-5}$	$<8 \times 10^{-6}$	$(3.6 \pm 0.6) \times 10^{-5}$	$<8 \times 10^{-6}$
hydrocarbons C_3 - C_9	$(7 \pm 2) \times 10^{-5}$	$<2 \times 10^{-6}$	$(1.6 \pm 0.3) \times 10^{-5}$	$(1.6 \pm 0.3) \times 10^{-3}$
chlorine-, fluoro-hydrocarbons (*)	$(6 \pm 2) \times 10^{-6}$	$<4 \times 10^{-6}$	$<4 \times 10^{-6}$	$(6 \pm 2) \times 10^{-4}$
alcohols, ethers	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
alkyl germanes (**)	$(2 \pm 1) \times 10^{-6}$	$<1 \times 10^{-5}$	$<1 \times 10^{-5}$	$(8 \pm 2) \times 10^{-5}$
chlorogermanes	$(7 \pm 2) \times 10^{-4}$	$<1 \times 10^{-5}$	$<1 \times 10^{-5}$	$(3 \pm 1) \times 10^{-2}$
polygermanes	$(1.6 \pm 0.6) \times 10^{-4}$	$(5 \pm 2) \times 10^{-2}$	$(2.2 \pm 0.7) \times 10^{-2}$	$(8 \pm 2) \times 10^{-3}$
CS_2	$(1.1 \pm 0.2) \times 10^{-4}$	$<4 \times 10^{-7}$	$(1.8 \pm 0.4) \times 10^{-6}$	$(7.3 \pm 0.7) \times 10^{-3}$
COS	-	$<4 \times 10^{-6}$	$<4 \times 10^{-6}$	$(1.1 \pm 0.3) \times 10^{-4}$
CO	$<6 \times 10^{-5}$	$<6 \times 10^{-5}$	$(2.2 \pm 0.2) \times 10^{-4}$	$<6 \times 10^{-5}$
CO_2	$(1.0 \pm 0.1) \times 10^{-4}$	$(3.1 \pm 0.3) \times 10^{-5}$	$(2.8 \pm 0.3) \times 10^{-3}$	$(7.6 \pm 0.8) \times 10^{-4}$
$(\text{CH}_3)_2\text{SiF}_2$	$(1.9 \pm 0.8) \times 10^{-6}$	$<3 \times 10^{-7}$	$<3 \times 10^{-7}$	$(1.4 \pm 0.5) \times 10^{-4}$

(*) Chlorine-, fluorine-derivatives of hydrocarbons: CHCl_y , CH_2Cl_y , C_2HCl_y , C_2Cl_y , $\text{C}_2\text{H}_5\text{Cl}$, $1,2\text{-C}_2\text{H}_4\text{Cl}_y$, $1,1,2\text{-C}_2\text{H}_3\text{Cl}_y$, $1,1,2\text{-C}_2\text{F}_3\text{Cl}_y$;

(**) Alkyl germanes: CH_3GeH_y , $\text{C}_2\text{H}_5\text{GeH}_y$, $\text{C}_2\text{H}_5\text{Ge}_2\text{H}_5$.

centrifugal method can be the reason for appearance of special features in the impurity composition of germane. The high-resolution IR-spectra of $^{76}\text{GeH}_4$ (88.14%)¹² monogermane were investigated.

The goal of this work was to produce monoisotopic $^{72}\text{GeH}_4$ with the content of the main isotope of 99.953 % at. and of the impurities of chemical compounds not more than 10^{-5} mol. %. The investigation included ultrapurification, determination of composition and content of impurities.

2. Experimental

Isotopically enriched monogermane $^{72}\text{GeH}_4$ contains a number of impurities (Table 2) requiring its purification from molecular higher- and lower-boiling impurities with respect to monogermane.

Ultrapurification of monogermane $^{72}\text{GeH}_4$ was conducted by periodic rectification at temperature of -85°C and pressure of 1.5 abs. atm. in stainless steel fractionating column with the middle feed tank. The rectifying sections with height of 40 and 70 cm and cross-section area of 2 cm^2 were filled with spiral prismatic packing from nichrome wire $2.5 \times 2.5 \times 0.2\text{ mm}$. The mass of substance loaded into

column was 300 g. To preclude isotopic dilution the column was flushed out from the traces of monogermane of other isotopic composition by specially developed technique. Extraction of fractions, enriched with lower-boiling (light fraction) and higher-boiling (heavy fraction) impurities was carried out simultaneously from top and bottom of the column in discrete mode. Ethane ($\alpha = 1.21 \pm 0.03$) is the mostly hard-to-remove impurity in monogermane. At the end of purification the target product (rectificate) was unloaded from the middle feeding tank. The yield of rectificate was 75%.

Determination of the isotopic composition of monogermane was carried out by the method of mass spectrometry with inductively coupled plasma (ICP-MS) and the results are given in Table 1. The composition and content of molecular impurities in monogermane samples were determined by the method of chromat-mass spectrometry (CMS) by the developed technique¹³. Sampling for analysis was conducted from the gas phase. The results of analysis of the initial and purified samples of $^{72}\text{GeH}_4$ as well as of light and heavy fractions are given in Table 2.

3. Results and discussion

As is seen from Table 2, the content of the impurities of chlorogermanes, polygermanes, CO₂ and CS₂ in the initial isotopically enriched germane ⁷²GeH₄ is at the level of 10⁻⁴ mol. %. It is of interest that the impurity of carbon sulfur was determined not detected previously in germane of natural isotopic composition. The appearance of the impurity of ¹²C³²S₂ in isotopically enriched ⁷²GeH₄ is, probably, connected with concentration of this compound of isobaric nature with the basis during centrifugal enrichment. Rectification efficiently decreases the content of the registered molecular impurities. In the purified monoisotopic ⁷²GeH₄ the content of the impurity of carbon dioxide is at the level of 3×10⁻⁵, of other 50 registered impurities it does not exceed 1×10⁻⁵ with mostly high content of homologue of germane (digermane - 10⁻², trigermane - 10⁻⁴ mol. %). High content of polygermanes is possibly due to their formation from monogermane during heating in the flash still of fractionating column. Monosilane, C₁-C₂ hydrocarbons and carbon monoxide are present in the concentrate of lower-boiling impurities. C₃-C₉ hydrocarbons, chloro- and fluoro-derivatives of hydrocarbons, alkyl germanes, chloro-germanes, carbon sulfide, carbon sulfoxide and silicon dimethyl fluoride are concentrated as the higher-boiling impurities. The direct determination of other chemical elements in the produced high-purity germane was not carried out. Their content is known by the data of mass spectrometric analysis of polycrystalline ⁷²Ge isolated from monogermane: the concentration of each of 68 controlled elements was less than 5×10⁻⁵ mass %.

4. Conclusion

It is for the first time that the sample of ⁷²GeH₄ monogermane with the content of the main isotope 99.953±0.008 at. % was produced by the method of low-temperature rectification. The produced hydride was characterized by the content of impurities connected with different chemical classes: hydrocarbons, chlorine- and fluorine-derivatives of hydrocarbons, alcohols and ethers, alkyl and chlorine germanes, polygermanes, the hydrides of phosphorus, arsenic, sulfur and silicon. The content

of each of 50 impurities in the purified ⁷²GeH₄ does not exceed 1×10⁻⁵ mol. %. Polycrystalline monoisotopic ⁷²Ge was extracted from high-purity monogermane by thermal decomposition in flow-through reactor from quartz glass. There was no isotopic dilution in the process of purification by rectification within the limits of 10⁻² at. %.

5. Acknowledgement

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References

1. *Isotopes: properties, production, application*. In 2 volumes / Editor V.Yu. Baranov. Moscow: FIZMATLIT. 2 (2005) 728 [in Russian]
2. K. Itoh, W. I. Hansen, E.E. Haller, et. al., *J. Mater. Res.*, 8 (1998) 1341.
3. A. A. Vasenko, Yu. N. Vereshchagin, I. V. Kirpichnikov, et al. Moscow, *PTE.*, 2 (1989) 56 [in Russian].
4. A. P. Zhernov *Fizika tverdogo tela.*, 41 (1999) 1185 [in Russian].
5. M. Asen-Palmer, K. Bartkowski, E. Gmelin, et. al., *Phys. Rev. B.*, 56 (1997) 9431.
6. D. G. Aref'ev, S. A. Vasin, S. G. Dolgov, et al., *Perspektivnye Materialy*, 8 (2010) 19 [in Russian].
7. G. G. Devyatykh and A. D. Zorin, [*Volatile inorganic hydrides of special purity*]. Moscow: Nauka, (1974) 206 [in Russian].
8. G. G. Devyatykh, A.V. Gusev and V. M. Vorotyntsev, *Vysokochistye Veshchestva*, 1 (1998) 5 [in Russian].
9. G. G. Devyatykh, A. D. Zorin and V. V. Balabanov, *Trudy Vses. Konf. «Metody polucheniya i analiza veshchestv osoboi chistoty»*. Gorky, 1968. Moscow: Nauka. (1970) 42 [in Russian].
10. S. A. Adamchik, A. D. Bulanov, P. G. Sennikov, et al., *Inorganic Materials*, 47 (2011) 694.
11. S. A. Adamchik, A. D. Bulanov, M. F. Churbanov, et al., *Doklady Chemistry*, 458 (2014) 185.
12. O. N. Ulenikov, O. V. Gromova, E. S. Bekhtereva, et. al., *J. Quant. Spec.*, 144 (2014) 11.
13. V. A. Krylov, O. Yu. Chernova, S. M. Kireev, et al., *Perspektivnye Materialy*, 6 (2008) 227 [in Russian].

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Preparation of High Purity Organometallic Compounds for Semiconductor Applications

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Abstract

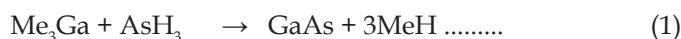
Research and development on preparation of some high purity materials with reference to their utility in semiconductor industry carried out in Chemistry Division, BARC is presented. Metal organic chemical vapour deposition (MOCVD) has emerged as a versatile growth process for deposition of a wide variety of inorganic semiconductors for micro-electronics. Success of this process relies on availability of suitable molecular precursors of desired purity. Thus synthetic methodologies and purification processes for Groups III and V organometallic precursors have been developed. Another approach for delicate and complex structures is the use of single source molecular precursors in the CVD process. Wide variety of single source molecular precursors for metal chalcogenides have been designed and developed, and their utility in the deposition of metal chalcogenide thin films has been demonstrated.

1. Introduction

High purity materials constitute a relatively new and dynamically growing area of materials science and can be traced back to 1950s when the role of semiconductors in electronics industry was realized. As the industry grew so the demand and level of purity increased dramatically. Chemistry Division BARC has been involved with the development of a variety of high purity materials and has responded to the needs and requirements of the time.

Impurities in a material markedly influence its physical / chemical / electrical / magnetic/ optical properties which in turn significantly affect the device performance.¹ Heavy metal impurities in silicon based devices not only decrease the signal-to-noise (S/N) ratio, but also significantly decrease the production yield of VLSI (very large scale integration) devices. For instance the yield of 10² scale integration of silicon based devices varies from 0, 0.37, 0.99, 0.9999% on increasing the purity of silicon² from 7N, 9N, 10N to 11N.

Traditionally single crystals (e.g., Si, Ge, GaAs, etc) are grown by Czochralski, Bridgman or by float zone method. Growing demand of exotic materials in the electronic industry has led to the development of new growth processes such as MOCVD (metal organic chemical vapour deposition), MOVPE (metal organic vapour phase epitaxy), etc. The first successful demonstration of deposition of GaAs using MOCVD by Manasevit³ in 1968 (eq.1) has led to the development of numerous organometallic precursors. At BARC we have synthesized both known as well as new organometallic compounds and have also developed their purification processes.⁴



The stoichiometry requirement, particularly for delicate semiconductor materials, poses severe challenges for deposition of binary/ternary/quaternary materials. For the preparation of such materials a user-friendly approach is desirable. An easily adoptable and versatile strategy is the use of single source molecular precursors. At BARC several molecular precursors for I-VI, II-VI, III-VI, IV-VI, and V-VI materials have been developed⁵⁻⁷ and their role in deposition of metal chalcogenide thin films has been demonstrated. Some of these aspects are briefly described herein.

2. Organometallic Precursors for III-V Materials

Several group III (Ga and In)/ V (As or Sb) organometallic precursors have been designed and developed for deposition of III-V compound semiconductors by MOCVD. Both conventional and new precursor molecules have been synthesized and their purification methods have also been developed.

Crude organometallic compounds typically contain various impurities. The origin is associated with the impurities in the startup materials, reaction byproducts, residual solvents or any combination of these. To be useful in MOCVD process, organometallic compound should be free from such impurities as they can cause adverse effects on the electrical/optical properties of the semiconductor.⁸ Such impurities are often difficult to remove from the desired organometallic compounds. Conventional distillation procedure is usually ineffective in removing trace-level of impurities. Multiple distillations may give desired purity of the organometallic compounds but at the cost of considerable reduction in yield of the compound. Thus we have adopted adduct purification method for

Groups III and V organometallic compounds which helped in accomplishing consistently high level of purity.

2.1 Organogallium compounds

Trialkylgallium compounds, R_3Ga ($R = Me, Et, Pr, Bu$) have been successfully used as molecular precursors for the preparation of gallium based semiconductor materials such as gallium nitride (GaN), gallium arsenide (GaAs), etc. These compounds are highly air and moisture sensitive pyrophoric liquids. They are readily converted into hydroxy derivatives $[R_2Ga(OH)]_n$ in the presence of air/moisture.⁹

Trimethylgallium (TMG) is the most commonly employed precursor. It was first synthesized by Dennis and Pantode¹⁰ in 1932. Since then several synthetic methods have been developed and many of them are primarily transmetallation reactions.⁴ These methods often suffer from the presence of trace metal impurities thus limiting their utility in MOCVD process. A reaction between homogeneous phase of Mg_5Ga_2 alloy with methyl iodide, used for large scale production of TMG, has been developed (eq.2).¹¹ TMG is distilled from the reaction mixture as an ether adduct, $Me_3Ga.OEt_2$ (b.p. 98-99 °C / 760 mm). Although the latter can be used in various chemical reactions without further purification¹², the ether free, high purity TMG is readily obtained by coordinating with a high boiling ether (e.g., diphenyl ether) or other non-volatile coordinating reagents. The latter on pyrolysis in a glove-box afford pure TMG (b.p. 56 °C / 760 mm) which is suitable for MOCVD process (Figure 1).

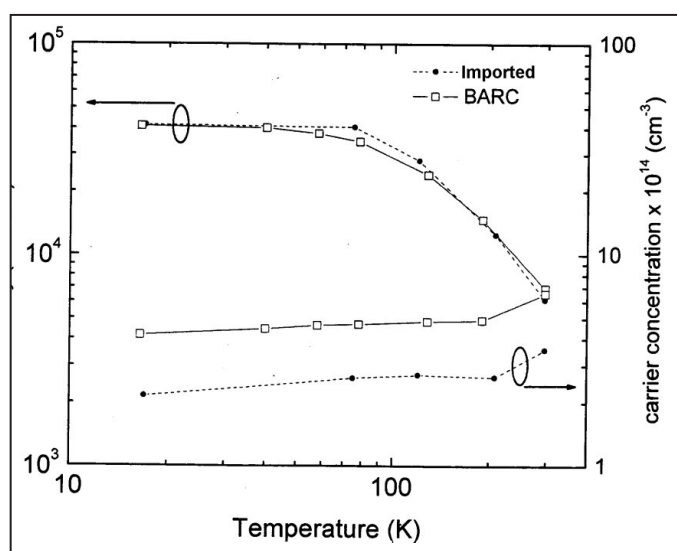


Figure.1 Comparison of Hall mobility data of BARC TMG vs Imported TMG (courtesy Prof. B. M. Arora, TIFR, Mumbai)

2.2 Organoindium compounds

Like trimethylgallium, trimethylindium is commonly used as precursors for MOCVD process. Trimethylindium is readily obtained either by the reaction between anhydrous indium trichloride and $MeMgI$ in diethyl ether or by treatment of Mg_3In with methyl iodide in diethyl ether. The ether adduct, $Me_3In.OEt_2$ (b.p. = 110-120 °C / 760 mm) can be used in synthesis of other methyl indium complexes^{12, 13}, on treatment with high boiling neutral nitrogen ligands gives $Me_3In.L$ ($L =$ neutral donor ligand). The latter on pyrolysis yields highly pyrophoric base free trimethyl indium (b.p. = 66-67 °C / 12 mm).

2.3. Organo-arsenic and -antimony compounds

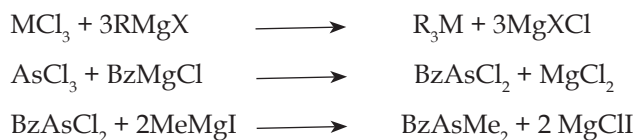
Inherent drawbacks of conventional Group-V precursors, like AsH_3 (extremely poisonous and pyrophoric gas and many fold excess requirement of the gas for deposition of GaAs due to high decomposition temperature) and SbH_3 (highly unstable at room temperature, poses storage problems), for their use in MOCVD process have led to the design and development of a wide range of precursors. The following considerations are kept in mind while developing alternate Group-V precursors:

- (i) A liquid with adequate volatility is preferred over a solid or gas.
- (ii) The precursor should be convenient to synthesize and purify and should be stable over a long period of time.
- (iii) A large temperature window between its evaporation and decomposition.
- (iv) Clean decomposition on pyrolysis without contaminating the deposited material.

The methyl derivatives of Group-V have higher M-Me ($M = As, Sb$) bond energy than the analogous isopropyl / allyl / benzyl (Bz) derivatives as all the latter compounds give stable free radicals on decomposition (bond energies : Me-H, Pr^i -H and allyl-H are 105.1, 95.1 and 86.3 kcal / mol, respectively). For antimonide materials (e.g., InSb, m.p. = 524 °C) low deposition temperatures are often required. In such cases use of expensive Me_3Sb is inadequate due to its high decomposition temperature. Isopropylantimony (Pr^i_3Sb) has emerged as a precursor of choice.¹⁴

At BARC, a number of organo-arsenic and -antimony precursors have not only been synthesized but their convenient purification processes have also been developed (Table 1).^{15,16} The compounds containing M- Pr^i ^{17,18}, M-Bz¹⁹ and M-allyl²⁰ linkages have been synthesized by the reactions of suitable metal halides with appropriate

Grignand reagent in diethyl ether or tetrahydrofuran (Scheme 1) and purified by distillation.¹⁷⁻²⁰



Scheme 1

The triorgano-arsenic and -antimony compounds readily form coordination complexes with palladium of composition, $[\text{PdCl}_2(\text{MR}_3)_2]$ (Figure 2) which can be purified conveniently to a high degree by recrystallization. The purified complexes are stable indefinitely under ambient conditions. These complexes on pyrolysis yield pure MR_3 as revealed by thermogravimetric analysis (Figure 4). Clearly these adducts not only allow to store air sensitive compounds under normal conditions but also offer a convenient route to purify these precursors.

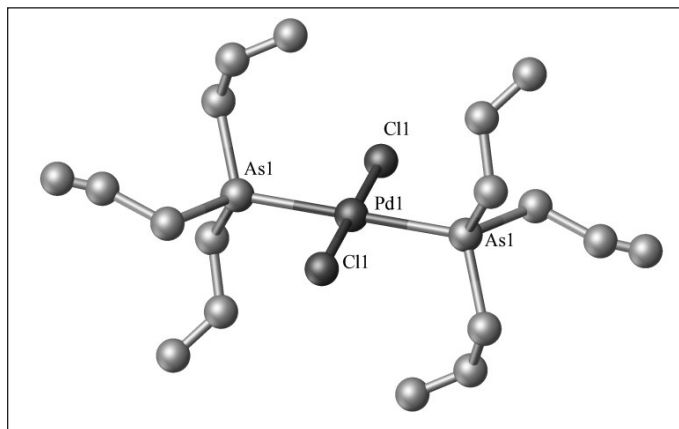


Figure-2. Molecular structure of $\text{trans-}[\text{PdCl}_2\{\text{As}(\text{CH}_2\text{CH}=\text{CH}_2)_3\}_2]$ (redrawn from Ref. 20)

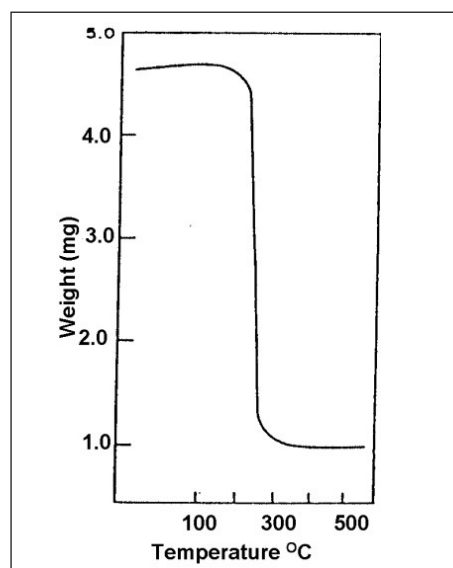


Figure-3. TG pattern for $[\text{PdCl}_2(\text{AsPr}^i)_2]$ (adapted from Ref. 18)

Table 1: Boiling points of triorgano-arsenic and -antimony compounds

Compound	Nature	b.p. (°C / mm)
Pr^i_3As	Colourless liquid	49-56 / 3
$(\text{CH}_2=\text{CHCH}_2)_3\text{As}$	Colourless liquid	52-53 / 2.5
$(\text{CH}_2=\text{C}(\text{Me})\text{CH}_2)_3\text{As}$	Colourless liquid	53-55 / 2.5
Me_2AsBz	Colourless liquid	44-45 / 2
Pr^i_3Sb	Colourless liquid	48 / 3
Bu^i_3Sb	Colourless liquid	85-90 / 3-4
$(\text{CH}_2=\text{CHCH}_2)_3\text{Sb}$	Colourless liquid	70-73 / 2
$(\text{CH}_2=\text{C}(\text{Me})\text{CH}_2)_3\text{Sb}$	Colourless liquid	68-70 / 2

3. Single source molecular precursors

Conventional MOCVD approach requires volatile molecular precursors such as hydrides (e.g., AsH_3 , H_2Se , etc) or simple alkyl (e.g., Me_3Ga , Me_2Cd , etc) derivatives. Although these derivatives have been used routinely for deposition of thin films of II-VI and III-V materials, there are several disadvantages in their use. These include (i) pyrophoric nature, (ii) most of the hydrides are toxic gases, (iii) over pressure and excess of precursors are usually required, (iv) only limited number of materials can be prepared.²¹

To overcome the above mentioned disadvantages, another approach to prepare numerous compositions of materials is the use of single source molecular precursor. This approach eliminates handling of pyrophoric toxic gases; avoids use of excess starting material for maintaining stoichiometry of the material, low temperature growth of delicate materials. Control of impurity incorporation in the thin film is possible by appropriate design of precursor molecules. The low volatility of these precursors, however, can be circumvented by employing alternate CVD processes, like MOVPE and AACVD.

Metal chalcogenides represent an important family of semiconductor materials which are core in numerous electronic devices. During the past few years our group has developed numerous single source molecular precursors for metal chalcogenides and have demonstrated their utility not only for deposition of thin films but also for the preparation of metal chalcogenide nanocrystals. Precursors for I-VI, II-VI, III-VI, IV-VI and V-VI materials have been developed. A few representative examples are given below.

3.1 Precursors for I-VI materials

Copper, silver and gold complexes derived from pyridyl / pyrimidyl selenolate / tellurolate have been synthesized.²²⁻²⁴ The homoleptic complexes $[\text{M}(\text{Epy})]_n$ (M

= Cu or Ag) are oligomeric species (Figure 4). They have been employed for the preparation of metal selenide nano-crystals as well as for deposition of metal chalcogenide thin films.²² Dark-red to black copper chalcogenide thin films on glass substrate have been deposited by AACVD using tetranuclear copper chalcogenolates, $[\text{Cu}\{\text{EC}_5\text{-H}_3(\text{Me-3})\text{N}\}]_4$ (E = Se or Te). Copper selenide films correspond to the orthorhombic form of Cu_5Se_4 while the copper telluride films are cubic phase of $\text{Cu}_{1.85}\text{Te}$. The deposited films comprise of uniform grains of high phase purity and are continuous in nature (Figure 5).²²

3.2 Precursors for II-VI materials

The II-VI materials are an important class of semiconductors. Their optical properties, highly dependent

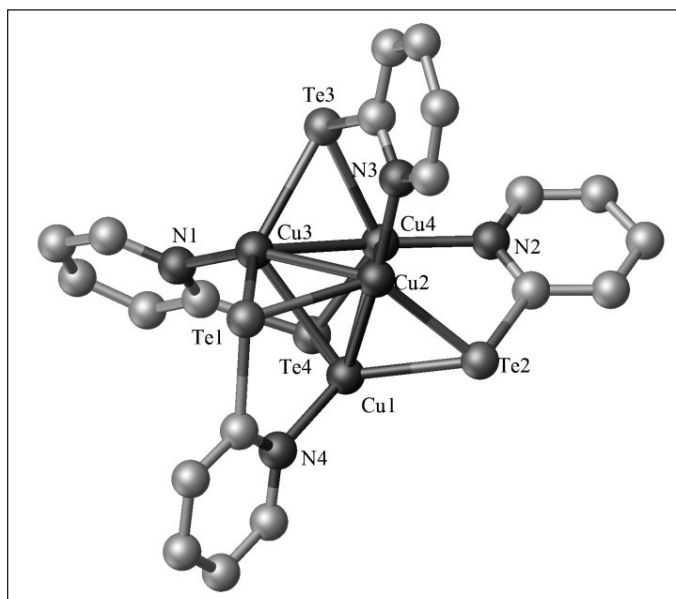


Figure-4. Molecular structure of $[\text{Cu}\{\text{TeC}_5\text{H}_3(\text{Me-3})\text{N}\}]_4$ (Redrawn from Ref. 22)

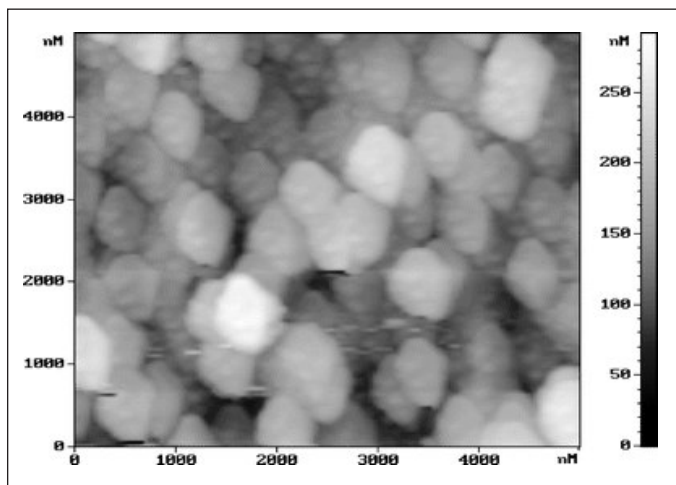


Figure-5. AFM image of $\text{Cu}_{1.85}\text{Te}$ thin film (adapted from Ref 22)

on shape and size, are exploited in a wide range of opto-electronic devices such as light emitting displays, photovoltaic and bioengineering applications.

A wide range of single source molecular precursors for zinc, cadmium and mercury sulfide²⁵, selenide^{26, 27} and telluride²⁸ have been designed and developed. They have been used primarily for the preparation of II-VI nano-crystals. The facile cleavage of C-Se linkage in selenocarboxylate has been exploited for the preparation of M-Se nanocrystals. The zinc and cadmium selenocarboxylates, $[\text{M}(\text{SeCOAr})_2(\text{tmeda})]$ (M = Zn or Cd; Ar = Ph or *p*-tol) (Figure 6), which contain monodentate M-Se bonded selenocarboxylate, undergo clean decomposition to give phase pure M-Se. For instance, thermolysis of $[\text{Cd}(\text{SeCO tol})_2(\text{tmeda})]$ in HDA at 230 °C yields red nano-crystals (~ 15 nm) of cubic phase of CdSe. The absorption maximum of the latter is blue shifted (680 nm) with respect to the bulk CdSe ($\lambda_{\text{max}} = 713\text{nm}$).²⁶ Similarly thermolysis of $[\text{Cd}(\text{Tepy})_2]$ affords hexagonal phase of CdTe, size of which can be controlled by thermolysing it in different solvents. The yellow (1 nm) of CdTe is obtained by pyrolysis in TOPO while in HDA red (4 nm) nano-crystals are formed [28].

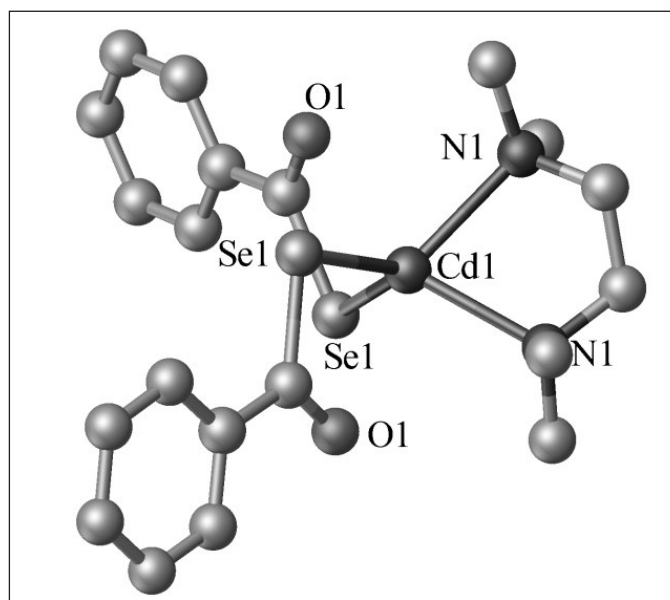


Figure-6. Molecular structure of $[\text{Cd}\{\text{SeC}(\text{O})\text{Ph}\}]_2(\text{tmeda})$ (Redrawn from Ref. 26)

3.3 Precursors for III-VI materials

A variety of gallium and indium 1,1-dithiolate²⁹ and selenolate complexes³⁰ have been synthesized for the preparation of binary sulfide / selenide and ternary CuInSe_2 . The octahedral complex, $[\text{In}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}]_3$, which crystallizes with water molecules, on thermolysis in

coordinating solvents yields In_2Se_3 which could be isolated either in hexagonal (from TOPO or HDA) or rhombohedral (from OA) phases. When thermolysis of a 1:1 mixture of $[\text{In}\{\text{SeC}_5\text{H}_3(\text{Me-N})\text{N}\}_3]$ and $[\text{Cu}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}_4]$ in HDA, TOPO or OA at 330°C is carried out, black powder of tetragonal CuInSe_2 (Figure 7) is readily formed.³⁰

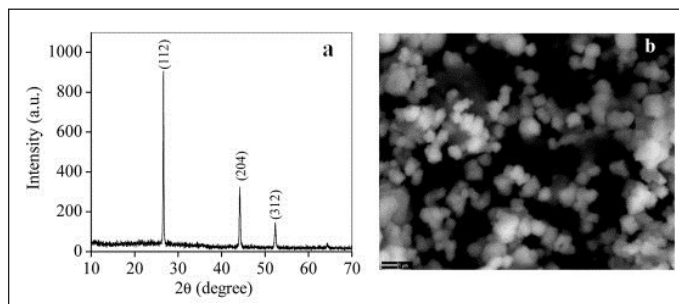


Figure-7. a) XRD pattern and b) SEM image of CuInSe_2 obtained by thermolysis of $[\text{Cu}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}_4]$ and $[\text{In}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}_3]$ in TOPO at 330°C (adapted from Ref 30)

3.4 Precursors for IV-VI materials

Diorganotin pyridyl chalenolate complexes have been developed as single source molecular precursors for tin sulfide³¹ and selenide³² thin films. Tin chalenolate thin films have been deposited from $[\text{R}_2\text{Sn}\{\text{SC}_4\text{H}(\text{Me}_{2-4,6})_2\text{N}_2\}_2]$ and $[\text{Bu}^t_2\text{Sn}(\text{SeC}_5\text{H}_4\text{N})_2]$ by AACVD at 530°C on a glass substrate. The Sn-Se films appear as rectangular sheets with continuous grain boundaries. The I-V characteristic shows Ohmic behaviour of the films. These films exhibit photo response and there is 20% increase in the current with fast switching (Figure 8).³²

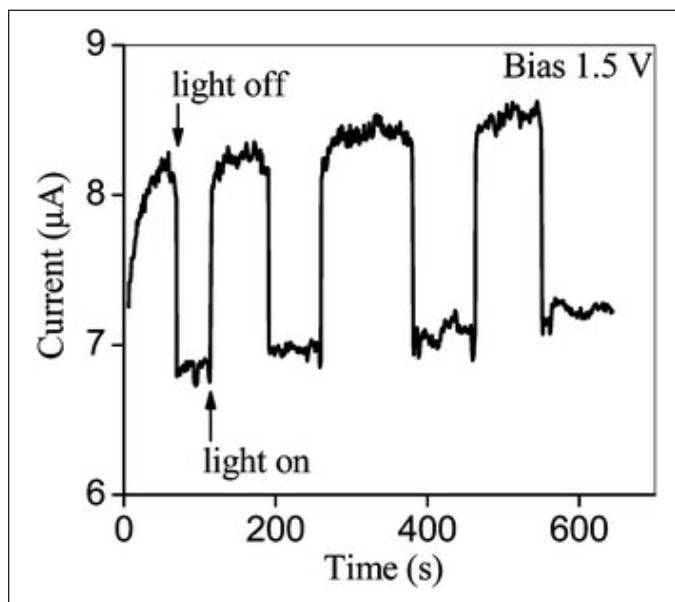


Figure-8. Photo-response of the SnSe thin film deposited from $[\text{Bu}^t_2\text{Sn}(2\text{-SeC}_5\text{H}_4\text{N})_2]$ at 490°C with a bias voltage of 1.5 V (adapted from Ref. 32).

3.5 Precursors for V-VI materials

The V-VI materials are direct band gap, highly anisotropic layered semiconductors and exhibit high thermo electric power and good photovoltaic properties. In our group a number of single source molecular precursors for antimony and bismuth sulfide and selenide nanocrystals and thin films have been developed.³³⁻³⁵ Both classical and organometallic bismuth(III) 1, 1-dithiolates, $\text{Bi}(\text{S}^0\text{S})_3$ and $\text{RBi}(\text{S}^0\text{S})_2$ ($\text{R} = \text{Me}$ or Ph ; $\text{S}^0\text{S} = \text{S}_2\text{COR}$, S_2CR) have been synthesized.^{33,34} Homogeneous black Bi_2S_3 films on glass and silicon wafers have been deposited employing $[\text{PhBi}(\text{S}_2\text{Ctol})_2]$ by AACVD. The SEM image shows that these films³³ comprise of micron sized fibrous Bi_2S_3 . The selenolate complexes, $[\text{Sb}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}_3]$ and $[\text{Bi}\{\text{SeC}_5\text{H}_3(\text{Me-3})\text{N}\}_3]$ (Figure 9) have been used for deposition of metal selenide thin films on glass substrate. The antimony precursor yields orthorhombic phase of Sb_2Se_3 . The films grew preferentially in (221) direction.³⁵ The films comprise of nano-wires. The bismuth precursor gave different compositions of bismuth selenides depending on the deposition parameters.

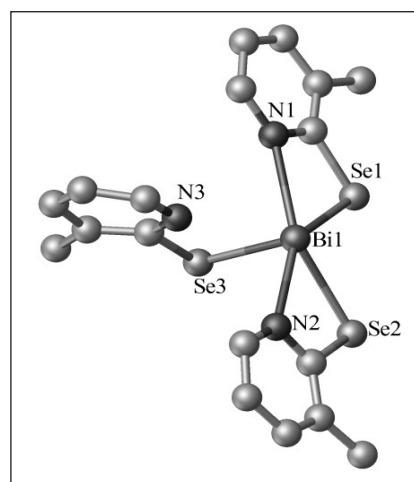


Figure-9. Molecular structure of $[\text{Bi}\{\text{Se-C}_5\text{H}_3(\text{Me-3})\text{N}\}_3]$ (Redrawn from Ref. 35)

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References

1. C.H. L. Goodman, *J. Cryst. Growth*, 75 (1986) 1.
2. S. Kishino, The silicon crystal in semiconductor technology, "Main Group Elements & Their Compounds", pp 77-89 (1996), Ed. V.G. Kumar Das, Narosa, New Delhi.
3. H. M. Manasevit, *Appl. Phys. Lett.*, 12 (1968) 136; H. M. Manasevit and W. I. Simpson, *J. Electrochem. Soc.*, 116 (1969) 1725.

4. V. K. Jain, *Bull. Mater. Sci.*, 28 (2005) 313.
5. V. K. Jain, *J. Chem. Sci.*, 118 (2006) 547.
6. V. K. Jain, *J. Indian Chem. Soc.*, 85 (2008) 123.
7. G. Kedarnath and V. K. Jain, *IANCAS Bulletin*, April (2007) 112.
8. G. B. Stringfellow, *J. Cryst. Growth*, 75 (1986) 91.
9. N. Kushwah, M. K. Pal, M. Kumar, A. P. Wadawale, D. Manna, T. K. Ghanty and V. K. Jain, *J. Organomet. Chem.*, 781 (2015) 65.
10. L. M. Dennis and W. Pantode, *J. Am. Chem. Soc.*, 54 (1932) 182.
11. K. B. Bhatt, S. M. Chopade, D. Dutta, V. K. Jain, N. Prasad and A. Y. Shah, BARC/2002/R/001.
12. M. K. Pal, N. Kushwah, D. Manna, A. Wadawale, V. Sudarsan, T. K. Ghanty and V. K. Jain, *Organometallics*, 32 (2013) 104.
13. N. Kushwah, M. K. Pal, A. Wadawale, V. Sudarsan, D. Manna, T. K. Ghanty and V. K. Jain, *Organometallics*, 31 (2012) 3836.
14. S. H. Li, C. A. Larsen and G. B. Stringfellow, *J. Electronics Materials*, 20 (1991) 457.
15. K. P. Chaudhari, P. P. Phadnis, H. Mahalakshmi, S. S. Garje and V. K. Jain, BARC/2003/I-004 (for Organoarsenic precursors)
16. K. P. Chaudhari, P. P. Phadnis, H. Mahalakshmi and V. K. Jain, BARC/2002/R/013 (for organoantimony precursors)
17. P. P. Phadnis, V. K. Jain and B. Varghese, *Appl. Organomet. Chem.*, 16 (2002) 61.
18. P. P. Phadnis, V. K. Jain, A. Knoedler and W. Kaim, *Z. Anorg. Allg. Chem.*, 628 (2002) 98.
19. P. P. Phadnis, V. K. Jain, A. Klein, M. Weber and W. Kaim, *Inorg. Chim. Acta*, 346 (2003) 119.
20. P. P. Phadnis, V. K. Jain, A. Klein, T. Schurr and W. Kaim, *New J. Chem.*, (2003) 1584.
21. P. O'Brien and S. Haggata, *Advanced Materials for Optics and Electronics*, 5 (1995) 117.
22. R. K. Sharma, G. Kedarnath, V. K. Jain, A. Wadawale, C. G. S. Pillai, M. Nalliath and B. Vishwanadh, *Dalton Trans.*, 40 (2011) 9194.
23. G. K. Kole, K. V. Vivekananda, M. Kumar, R. Ganguly, S. Dey and V. K. Jain, *Cryst. Eng. Comm*, 17 (2005) 4367.
24. R. K. Sharma, A. Wadawale, G. Kedarnath, D. Manna, T. K. Ghanty, B. Vishwanadh and V. K. Jain, *Dalton Trans.*, 43 (2014) 6525.
25. G. Kedarnath, V. K. Jain, S. Ghoshal, G. K. Dey, C. A. Ellis and E. R. T. Tiekink, *Eur. J. Inorg. Chem.*, (2007) 1566.
26. G. Kedarnath, L. B. Kumbhare, V. K. Jain, P. P. Phadnis and M. Nathaji, *Dalton Trans.*, (2006) 2714.
27. R. K. Sharma, A. Wadawale, G. Kedarnath, B. Vishwanadh and V. K. Jain, *Inorg. Chim. Acta*, 411 (2014) 90.
28. G. Kedarnath, V. K. Jain, A. Wadawale and G. K. Dey, *Dalton Trans.*, (2009) 8378.
29. S. Ghoshal and V. K. Jain, *J. Chem. Sci.*, 119 (2007) 583.
30. R. K. Sharma, G. Kedarnath, N. Kushwah, M. K. Pal, B. Vishwanadh, B. Paul and V. K. Jain, *J. Organomet. Chem.*, 747 (2013) 113.
31. A. Tyagi, G. Kedarnath, A. Wadawale, V. K. Jain, M. Kumar and B. Vishwanadh, *RSC Advances*, 5 (2015) 62882.
32. R. K. Sharma, G. Kedarnath, A. Wadawale, C. A. Betty, B. Vishwanadh, B. Paul and V. K. Jain, *Dalton Trans.*, 41 (2012) 12129.
33. K. R. Chaudhari, N. Yadav, A. Wadawale, V. K. Jain and R. Bohra, *Inorg. Chim. Acta*, 363 (2010) 375.
34. K. R. Chaudhari, A. Wadawale, S. Ghoshal, S. M. Chopade, V. S. Sagoria and V. K. Jain, *Inorg. Chim. Acta*, 362 (2009) 1819.
35. R. K. Sharma, G. Kedarnath, V. K. Jain, A. Wadawale, M. Nalliath, C. G. S. Pillai and B. Vishwanadh, *Dalton Trans.*, 39 (2010) 8779.



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Sr. No.	Name and Affiliation	Name of Award/Honor	Conferred by
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2.	A. K. Tyagi, Chemistry Division, BARC	ISCA Platinum Jubilee Lecture Award in Materials Science	Indian Science Congress Association
3.	B. T. Thaker, Retired Prof. of Chemistry, Veer Narmada South Gujarat University, Surat	Dr. Lakshmi Gold Medal Award	R.T.M. Nagpur University, Nagpur
4.	D. Khushalani TIFR, Mumbai	Fellow of Royal Society of Chemistry	Royal Society of Chemistry
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6.	M. R. Pai Chemistry Division, BARC	Member of National Academy of sciences,	National Academy of sciences, Allahabad
7.	S. Verma, IIT Kanpur	Platinum Jubilee Lecture Award (Chemical Sciences), Prof A K Lala Memorial Lecture, ISCB Award for Excellence in Chemical Sciences, DarshanRanganathan Memorial Lecture, Shri Deva Raj Chair Professor	Indian Science Congress Association IIT Bombay Indian Society of Chemists and Biologists Chemical Research Society of India IIT Kanpur
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