



Modified matrix volatilization setup for characterization of high purity germanium



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ABSTRACT

Modified matrix volatilization (MV) method has been described to characterize high purity germanium material of 7 N (99.99999%) purity. Transport of both, the chlorine gas generated in-situ in this method and the argon gas (carrier) is fine controlled by means of a mass flow controller. This enabled both uniform reaction of chlorine gas with the germanium matrix and smooth removal of germanium matrix as its chloride. This resulted in improvement in the reproducibility of the analytical results. The use of quartz reaction vessel has led to the reduction in the process blank levels. The combined effect of these modifications in the MV setup has resulted in very consistent and low process blanks and hence improved detection limits of this method. Applicability of the method has been expanded to rare earth elements and other elements after examining their recoveries. The quantification is done by using inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) and continuum source graphite furnace atomic absorption spectrometry (CS-GFAAS). In the absence of certified reference materials for high pure germanium, the accuracy of the method is established by spike recovery tests. The precision of the method has been found to vary from 1 to 30% for concentrations between 1 and 30 ng g⁻¹. The limits of detection (LOD) for the target analytes are found to be between 18 and 0.033 ng g⁻¹.

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1. Introduction

High pure germanium (Ge) finds many applications in gamma ray spectroscopy, electronics industry, and medicine. The electronics industry uses germanium semiconductor materials in the form of transistors, high-speed integrated circuits (SiGe), solar electrical parts, etc. High pure germanium also finds applications in extremely sensitive infrared detectors, gamma-ray detectors and phosphor agents in fluorescent lamps, fiber-optics systems, and polymerization catalysts [1–4]. Additionally, Ge substitute offer certain advantages over GaAs: high crystallographic perfection, high mechanical strength, and the ability to recycle germanium. These factors have led to a wide use of Ge wafers as a substrate for GaAs for telecommunication satellites [5]. Generally, refining method is used to make at least 6 N (99.9999%) purity germanium. The impurities present in the germanium samples can act as traps for electron-hole pairs and also produce deep-level states in the band-gap which can act as recombination centers or carrier traps, thereby degrading the performance of semiconductor devices [6,7].

In view of the above applications, it is essential that the analysis of high purity germanium meet the challenges and highest demands in the global market. Few analytical techniques have been developed for the determination of trace constituents in high pure germanium. Among them, neutron activation analysis (NAA) [8,9], photoelectron spectroscopy [10], atomic absorption spectrometry (AAS) [11–13], atomic emission spectrometry (AES) [14] and spark source mass spectrometry [11] are the analytical techniques used for the characterization of high pure germanium.

Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive and multi-elemental analytical technique, it can determine the concentrations of impurities at trace and ultra-trace levels but can tolerate solutions containing only up to a maximum of 0.1% total dissolved solids [15–17]. This drawback demands the separation of the Ge matrix from its impurities. Chemical separation of the matrix from all other minor or trace constituents is not possible in a single step. Many separation procedures found in the literature are suitable only for a group of elements at a time. Thus, trace element group separations using co-precipitation, solvent extraction, and ion exchange methods are often required.

A distillation method was used to separate the germanium matrix as GeCl₄ from its impurities [18]. Later, a closed-vessel microwave assisted volatilization of Ge and Se as their chlorides in the presence of aqua regia vapors and determination by ICP-MS was reported [19]. Besides, two different matrix separation procedures

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were reported [20] for the determination of critical impurities such as Cr, Cu, Fe, Ni, and Pb in a germanium matrix by using GF-AAS. One procedure [20] involves cloud point extraction which uses the ammonium pyrrolidine dithiocarbamate (APDC)-Triton X-114 system, and another procedure [20] uses a matrix volatilization technique for the removal of the germanium matrix with chlorine gas and determination by GF-AAS. However, only a few impurity elements (Cr, Cu, Fe, Ni, Pb) were quantified by both the procedures and compared their results and reported [20]. Later, nearly 40 impurities were quantified in high pure germanium of 6 N purity using the matrix volatilization method and reported [21].

Recently, Niemela et al. [22], published a procedure on the determination of trace impurities in germanium oxide by ICP-MS, Electro thermal – AAS, ICP-Optical emission spectrometry (OES) after matrix volatilization. But only fifteen impurity elements were quantified. These authors used the open-vessel digestion and open-vessel evaporation of germanium matrix which attracted the external contamination. Hence the procedure can be applicable only up to the purity of around 6 N even after using quartz digestion vessel. Recently, Petrova et al. [23], reported another procedure on the analysis of high purity germanium oxide by AAS, however only seven elements were reported. The procedure involves germanium separation through reactive evaporation in the form germanium tetrachloride in an open system and offers an analysis of around 6 N purity material only. As the purity of the germanium increases the process blank levels of an analytical method restricts the quantification of the impurities in high pure materials. To our knowledge, as of now there are no reports in the literature about the determination of impurities in high purity germanium greater than 6 N purity by wet chemical methods.

In this paper we report a method for the determination of impurities in high purity germanium of 7 N purity using ICP-QMS and GF-AAS by modified matrix volatilization method. The process blank levels of earlier reported matrix volatilization procedure [21] are significantly reduced with the use of quartz reaction vessel and also by fine controlling the transport of chlorine gas by means of a mass flow controller. The work reported in this paper is a substantial improvement over the previous method [21]. Its analytical applications are demonstrated in detail in this article. The reported method is useful for chemical characterization of higher purity (7 N) germanium materials. It is an improved application in an area of materials science. The quantification is performed by ICP-QMS as the levels of many of the impurities are at sub parts per billion levels. The elements that suffer from potential spectral interferences due to discharge gas and germanium matrix have been identified in ICP-QMS analysis and are quantified by an alternative

sensitive analytical technique, GF-AAS. Salient features of the modified matrix volatilization method are reported.

2. Experimental

2.1. Instrumentation

An inductively coupled plasma quadrupole mass spectrometer (VG Plasma Quad 3 ICP-QMS, V.G. Elemental, Winsford, Chesire, UK) was used for the analyte determinations. The operating conditions of ICP-QMS were optimized for maximum sensitivity using a 10 ng mL⁻¹ tuning solution of Be, Co, Rh, In, and Bi in 2% (v/v) HNO₃ introduced at a flow rate of 0.7 mL min⁻¹ using a peristaltic pump (REGLO Digital MS-4/12, ISMATEC, Switzerland). The instrumental parameters of the ICP-QMS and typical measurement parameters are listed in Table 1. Sample introduction was carried out by pneumatic nebulisation using a Mein hard[®] concentric nebulizer and a double-pass Scott-type spray chamber cooled to 5 °C using a NESLAB recirculating chiller, and a Fassel-type torch. Rhodium was used as the internal standard for all the samples. Mass spectra were obtained in the peak jumping mode. A 3 mL screw cap PFA (perfluoroalkoxy) containers are cleaned using Evapo-Cleaner (Analog, Junior Evapo Clean, France) with the 250 mL of concentrated HNO₃ and 250 mL of concentrated HCl at 75 °C for about 4 h and then are cleaned further with Millipore water 3 to 4 times and then used for the germanium samples.

The analytes, Fe, Ga, As, Sr, Ag, Sb were determined by using CS-GFAAS (Contra AA 700, Analytik Jena AG, Jena, Germany). A transversely heated graphite tube, MPE 60 auto sampler and xenon short arc lamp in hot-spot mode operated at 300 W as a continuum radiation source were used. A high resolution double monochromator consisting of a prism and an echelle grating monochromator, providing a spectral bandwidth per pixel of ca. 2 pm at 200 nm was used. A linear charge coupled device array detector total 588 pixels, out of which 200 pixels were used for the determination of dispersed radiation. The analyte's absorptions were measured using the central pixel (CP) ± 1 pixels i.e., over a spectral interval of approximately 6 pm. Argon with a purity of 99.99% was used as the purge gas in all stages, except during atomization step. Sample volume is 10 µL. Optimized furnace programs used for the determination of these elements is given in Table 2. Fast heating for pyrolysis process is required to expel the unwanted matrix and to retain the analyte. This program has been established by instrument manufacturer and given in the instrument manual. Absorption measurement was made at the analytical wavelength 248.327 nm for Fe, 287.424 nm for Ga,

Table 1
Optimized instrumental parameters of ICP-QMS.

Parameter	Optimum value
Plasma RF power	1350 W
Reflected power	< 0.8 W
Torch type	Fassel (VG)
Coolant argon flow rate	13.4 L min ⁻¹
Auxiliary argon flow rate	0.88 L min ⁻¹
Nebulizer gas	0.92 L min ⁻¹
Sample uptake rate	0.7 mL min ⁻¹
Ni sample cone orifice	1.0 mm
Ni skimmer cone orifice	0.7 mm
Detector Mode	Dual Mode (PC/Analog)
Scanning mode	Peak jump
Number of replicates	3
Dwell time	100 ms per channel
Isotopes used	⁷ Li, ⁹ Be, ¹¹ B, ²⁶ Mg, ²⁷ Al, ⁴⁵ Sc, ⁴⁹ Ti, ⁵⁰ V, ⁵³ Cr, ⁵⁵ Mn, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁴ Zn, ⁷¹ Ga, ⁸² Se, ⁸⁵ Rb, ⁸⁸ Sr, ⁹³ Nb, ⁹⁴ Zr, ⁹⁸ Mo, ¹⁰² Ru, ¹⁰⁷ Ag, ¹⁰⁸ Pd, ¹¹¹ Cd, ¹¹⁵ In, ¹²⁰ Sn, ¹²¹ Sb, ¹²⁸ Te, ¹³⁸ Ba, ¹³³ Cs, ¹³⁹ La, ¹⁴⁰ Ce, ¹⁴⁶ Nd, ¹⁵² Sm, ¹⁵³ Eu, ¹⁵⁸ Gd, ¹⁵⁹ Tb, ¹⁶⁴ Dy, ¹⁶⁵ Ho, ¹⁶⁶ Er, ¹⁶⁹ Tm, ¹⁷⁴ Yb, ¹⁷⁵ Lu, ¹⁸¹ Ta, ¹⁸⁴ W, ¹⁸⁷ Re, ¹⁹³ Ir, ¹⁹⁵ Pt, ¹⁹⁷ Au, ²⁰² Hg, ²⁰⁵ Tl, ²⁰⁸ Pb, ²⁰⁹ Bi.

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