Talanta 159 (2016) 14–22

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

An improved matrix separation method for characterization of ultrapure germanium (8N)

M.A. Reddy, R. Shekhar*, Sunil Jai Kumar

National Centre for Compositional Characterization of Materials (NCCCM) Bhabha Atomic Research Centre, Hyderabad 500062, India

ARTICLE INFO

Article history:
Received 15 April 2016
Received in revised form
1 June 2016
Accepted 2 June 2016
Available online 3 June 2016

Keywords:
Ultrapure germanium
Chemical analysis
Matrix volatilization
ICPMS
GFAAS
Detection limits

ABSTRACT

An improved matrix separation method has been described to characterize ultrapure germanium of 8N (99.999999%) purity. In this method, temperature of the reaction vessel in which in-situ generated chlorine gas reacts with germanium solid material directly is optimized to quantitatively remove Ge matrix from all its impurities. Optimized reaction temperature has been found to be 230 ± 5 °C. Recovery studies on more than 60 elements have been carried out at the optimized temperature. Recoveries of all the analytes except As, Se, Sn, Hg, Tl are found to be quantitative. The method has been examined for various amounts of Ge material and found to be suitable even for 10 g of Ge sample and provides low parts per billion and trillion levels of process blanks. Determination of concentrations of impurities has been done by inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) and high resolution continuum source graphite furnace atomic absorption spectrometer (HR-CS-GFAAS). In the absence of certified reference materials for ultrapure germanium, accuracy of the proposed method is established by spike recovery tests. Precision of this method is found to vary from 7% to 50% for concentrations between 4 and 0.004 ng g^{-1}. Limits of detection (LOD) for the target analytes are found to be between 6 and 0.011 ng mL^{-1} or 1.8–0.003 ng g^{-1} for the proposed procedure. The method has been successfully applied for that characterization of ultrapure germanium material of 8N purity.

1. Introduction

Electronics industry uses germanium semiconductor materials in the form of transistors, high-speed integrated circuits (SiGe), solar electrical parts, etc. High pure germanium (Ge) finds many applications in gamma ray spectroscopy, electronics industry, medicine and phosphor agents in fluorescent lamps, fiber-optics systems, and polymerization catalysts [1–4]. Ultrapure germanium finds applications in extremely sensitive infrared detectors, gamma-ray detectors. 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 6N (99.9999%) purity germanium. Impurities present in the germanium materials 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 analysis of ultrapure germanium meet the challenges and highest demands in the global market. Few analytical techniques have been developed for the determination of trace constituents in 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 pure germanium.

Inductively coupled plasma mass spectrometry (ICP-MS) is a sensitive and multi-elemental analytical technique and it can determine 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 germanium matrix as $GeCl_4$ 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

---

* Corresponding author.
E-mail address: shekhar_raparthi@rediffmail.com (R. Shekhar).

http://dx.doi.org/10.1016/j.talanta.2016.06.007
0039-9140/

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, ^{26}Mg, ^{27}Al, ^{45}Sc, ^{49}Ti, ^{50}V, ^{52}Cr, ^{55}Mn, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{71}Ga, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{93}Nb, ^{94}Zr, ^{98}Mo, ^{102}Ru, ^{107}Ag, ^{108}Pd, ^{111}Cd, ^{115}In, ^{120}Sn, ^{121}Sb, ^{128}Te, ^{133}Cs, ^{138}Ba, ^{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, ^{192}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi.

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] involved cloud point extraction which used the ammonium pyrrolidine dithiocarbamate (APDC) - Triton X-114 system, and another procedure [20] used 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 6N 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 6N even after using quartz digestion vessel. Recently, Petrova el al. [23], reported another procedure on the analysis of high purity germanium oxide by AAS, however only seven elements were reported. The procedure involved germanium separation through reactive evaporation in the form germanium tetrachloride in an open system and offers an analysis of around 6N 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. More recently a modified matrix volatilization method was reported for the determination of impurities in high purity germanium of purity up to 7N [24]. This method [24] was applied to an ultrapure germanium (8N) material and found that Ge matrix was not at all separated from its impurities. Hence the reported procedure [24] was not applicable for the analysis of ultrapure germanium materials as the matrix separation from its impurities is very essential to quantify all the impurities present at very very low levels. In the literature also there are no procedures available to analyse such ultrapure germanium materials using wet chemical methods.

Therefore, in this paper we report an improved matrix separation method which enables the quantitative separation of Ge matrix of ultrapure germanium (8N) also from its impurities. Percentage of separation of matrix has been studied as a function of reaction temperature to achieve quantitative separation of Ge matrix. Applicability of this method has been studied on various amounts (weights) of germanium material. Recovery studies of more than 60 elements are examined using this method. Its analytical applications are described in detail in this article. The reported method is found to be useful for chemical characterization of ultrapure germanium (8N) materials. 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 proposed method are reported.

2. Experimental

2.1. Instrumentation

Concentrations of impurities in ultrapure germanium were determined by an inductively coupled plasma quadrupole mass spectrometer (VG Plasma Quad 3 ICP-QMS, V.G. Elemental, Winsford, Chesire, UK). 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) HNO_3 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 and typical measurement parameters of ICP-QMS are listed in Table 1. Sample introduction was carried out by pneumatic nebulisation using a Meinhard concentric nebulizer and a double-pass Scott-type spray chamber cooled to 5 °C using a NESLAB recirculating chiller. 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 were cleaned using Evapo-Cleaner (Analog, Junior Evapo Clean, France) with the mixed acid solution of 250 mL of concentrated HNO_3 and 250 mL of concentrated HCl at 75 °C for about 4 h and further cleaned with Millipore water 3–4 times and used for the germanium sample analyses. In ICP-QMS analysis, the isotope of iron ($^{56}Fe^{+}$) and arsenic ($^{75}As^{+}$) were suffered from isobaric interferences due to formation of poly atomic ions, $^{40}Ar^{16}O^{+}$ and $^{40}Ar^{35}Cl^{+}$ respectively. The list of interference free isotopes used for quantification of impurities by ICP-QMS is given in Table 1.

The isobaric-interfered analytes such as Fe, Ga, Sr, Ag, Sb were determined by HR-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