METHOD OF STUDY GALLIUM AND ARSENIC LOSSES IN TECHNOLOGY OF GALLIUM ARSENATE OBTAINED FROM WASTES

S. Baranov, J. Redwing[*], O. Bogdevici[**], B. Cinic, and D. Izmailov[**]

Scientific and Engineering Center «Informinstrument» SA, Chisinau, Republic of Moldova,
**Department of materials science and Engineering, Penn State University USA,*
***Accredited Experimental Laboratory "GeoLab» GGI, Academy of Science, Republic of Moldova.*

Corresponding author: Simion Baranov. *Office Tel.: 24-11-13, 24-52-72,*
E-mail: sbaranov@mail.md
H. Tel.: 56-28-72

Abstract

Having the goal to recover gallium (Ga) and arsenic (As) from technological wastes derived from the process of growing epitaxial gallium arsenide structures, it is proposed to extract gallium arsenate ($GaAsO_4$) by precipitation and filtration of the sediment. In this paper it is proposed to measure the concentrations of Ga and As by means of the atomic absorption spectrometer AAnalyst 800 directly in the filtrate solution. We compare the results obtained by two methods of elemental Ga and As atomization: flame and thermal atomization. The values of Ga and As concentrations in filtrate are function of pH for solutions containing 1-680 mg/1 of Ga and 55-880 mg/1 of As. The developed method can be used to study and further optimize the technological process.

Introduction

It is known [1] that using epitaxial technologies for production of semiconductor devices the most part of the initial materials consumed during the process are deposited on the surface of the technological equipment inside the reactor, generating solid wastes. For instance, during the process of gallium arsenide layer growing by a gaseous transport chemical reaction [2] about 70% initial Ga and As are deposited in the cold part of the reactor. The sediment is then chemically treated by an acidic solution to prepare the next technological cycle, being transformed in this way into liquid wastes. One of the developed technological processes of wastewater treatment at the place of their formation [2] consists of the recovery of gallium and arsenic as solid gallium arsenate ($GaAsO_4$). Gallium and arsenic concentrations in these liquid wastes achieve values of 30-120 g/l and can be determined by the spectrophotometrical method [3]. The determination of these elements in the sediment is problematic due to diverse factors. The errors of the gravimetric method to determine the weight of the sediment are considerable and can be also caused by co-precipitation of the other elements, present in initial acidic solution. In this paper it has been proposed and described a solution of the problem by direct measurement of gallium and arsenic concentrations in the filtrate solution after removal of $GaAsO_4$, using the Atomic Absorption Spectrophotometer Aanalyst-800. This method has found exhaustive use for determination of small concentrations of arsenic [4] and gallium [5] for determination of trace amounts of gallium by tungsten metal furnace.

Gallium ion concentrations (Ga^{3+}) are determinant for gallium arsenate sedimentation process from the waste solutions under investigation. For this reason the measurements of

gallium as well as arsenic concentrations in the filtrate solution after removal of gallium arsenate are important and can be used to study and further optimize the technological process of wastewater treatment.

1. Materials and Sample Preparation

1.1. Sedimentation of the gallium arsenate.

For the presented study we considered the model waste solutions obtained by dissolution of stoichiometric gallium arsenide GaAs in aqua regia, the acidic solution being used for chemical etching of the technological equipment [2]. The gallium and arsenic concentrations in the model waste solution were proved to be higher than the corresponding values in real wastewaters, 108 g/l for Ga and 101 g/l for As. The concentration of these elements in the real wastewaters is within 30-60 g/l. The process of gallium arsenate sedimentation has been controlled by the variation of the pH of the solution. The weight of the sediment obtained after filtration was determined by using a gravimetric method. The filtrate solution after the removal of the gallium arsenate represents the object under investigation. This solution contains gallium in the form of Ga^{3+} and arsenic in the form of AsO_4^{3-}, whose concentrations characterize the losses of gallium and arsenic during the technological process, or in other words, the quality of the process of gallium arsenate removal.

1.2. Preparation of the samples

The samples for the investigation have been prepared from the solution rested at once after filtering process of the precipitation. The concentrations of Ga and As in the filtrate varied in the diapason of 1-680 mg/l for Ga and 55-880 mg/l for As depending on value of pH. The filtrate was limpid when visually investigating and didn't contain any solid particles. Before measurement the samples were well mixed by shaking up and they were diluted with micropipette in a measuring vessel for a necessary time (K). The ones with higher concentrations were deluted twice.

2. Spectrophotometer

For the determination of Ga and as losses in the process of gallium arsenate synthesis the atomic-absorption spectroscopy method was used. Measures have been done by an atomic-absorption spectrophotometer AAnalyst-800 (Perkin-Elmer, USA), supplied with a flame atomizer with pneumatic nebulizer and interchangeable burner heads, the thermo-electric atomizer transversely-heated graphite furnace THGA incorporating an electromagnet for longitudinal Zeeman-effect background correction and flow injection system FIAS-400. As line radiation source we have used the hollow cathode HCL lamp for determination of Ga and the electrode less discharge EDL lamp for determination of arsenic. A P-E firm AA Win Lab 4.1 program with utilization of Pentium III computer controlled the machine work and the analysis process. The instrumental parameters for both elements are shown in table 1.

Table 1. Instrumental Parameters

	Flame		THGA		FI-MHS
	As	Ga	As	Ga	As
Wavelength (nm)	193,7	287,4	193,7	287,4	193,7
Lamp	EDL	HCL	EDL	HCL	EDL
Lamp current (mA)	380	20	380	20	380
Background correct.	Deuterium Lamp		Zeeman corrector		
Atomizer	Air-acetylene flame		Electrother. Atomizer		Quartz cell
Signal Processing	Time Average		Peak Area		Peak Height
Sample Volume, µl	500		20		500
Atom. Temperat. ^{0}C	2000-2300		2000	2300	900
Reagents, modifiers	-		$Pd + Mg(NO_3)_2$		$NaBH_4$
Gas	Air-C_2H_2		Ar		Ar
Analyses Time, sec	6		180		30
Sampling	Manual		Automat AS-800		Aut. AS-90
Calibration Method	Zero-Intercept, Nonlinear				

3. Methods of technological solution analysis

Depending on the investigation technology selection the samples were brought in an atomizing source (flame, cuvette, hydride system) and they were analyzed in automatic rate at the Aanalyst-800. By means of calibration graph preliminary built, the machine gives out in automatic rate for every sample on the display screen the following parameters: C_i – the concentration of determine element in the analyzing dilute solution (g/l); SD – the standard deviate of concentration (g/l); RSD – the relatively standard deviate (%). After every ten samples the stability of calibration graph is verified and if it is necessary, the last samples are recurred. The obtained data are used to calculate the concentrations taking into account the dilution coefficient $C_m = C_i * K$.

By choosing the optimal conditions of Ga analyzing advantages and shortcomings of two atomization possibilities – flame and thermal have been appreciated. Possibilities of hydride technique have been supplementary estimated. Characteristic Mass and Linear of caliber diagrams for study variant are shown in table 2.

Table 2. Characteristic Mass and Linear.

		Flame, mg/l	THGA,µg/l	FI-MHS, µg/l
As	Char. Mass	1,4	1,5	0,1
	Linear	100	150	20
Ga	Char. Mass	3,0	2,5	-
	Linear	100	200	-

As follows from tab. 2 the hydrid method is characterized by the highest relative sensibility but the flame atomization method – by the least one. Selection of the method for technological solution analyses depends on the reproduction and precision obtained at the measuring results. In this investigation there is excess of Ga and As in large pitch

concentrations, therefore it would be interesting to carry out some parallel experiments of the same samples with diverse methods and to estimate the advantage of them.

4. Results and Discussion

Table 3 shows the results obtained by different technologies and certainly different dilution of initial samples.

Table 3. Concentration of Ga and As in the solution by different dilution degree

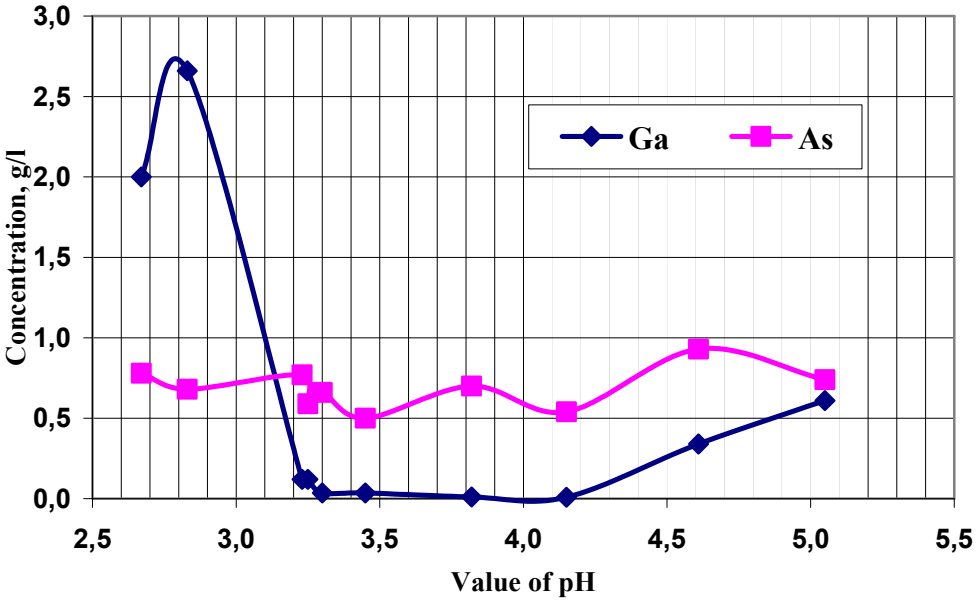
Element	Sample	Flame			THGA		
		K_{dill}	$C_{mg/l}$	$C_{mg/l}$ K	K_{dill}	$C_{\mu g/l}$	$C_{mg/l}$
Ga	142	1	73,43	73,43	1000	76,0	76,0
		20	3,803	76,06	500	127,3	63,65
		10	7,521	75,21			
	143	20	35,22	704,0	10000	59,3	593,0
		10	68,68	686,8	5000	97,4	485,0
	146	20	<2	<2	20	54,0	1,08
		10	<2	<2	10	99,2	0,99

Element	Sample	Flame			FI-MHS		
		K_{dill}	$C_{mg/l}$	$C_{mg/l}$ K	K_{dill}	$C_{\mu g/l}$	$C_{mg/l}$
As	173	10	5,416	54,16	1000	54,81	54,81
		5	11,04	55,20	2000	28,61	57,22
	167	10	65,66	656,6	10000	52,0	520,0
		5	136,9	684,5	5000	99,8	499,0
	179	20	11,55	231,0	500	54,36	271,8
		10	24,28	242,8	200	132,5	265,0
		5	52,35	261,75			

As follows from tab.3 the results for Ga in flame analysis with 10-20 time dilution are in a good agreement with the results obtained in thermal atomization with 500-1000 time dilution and they are very different at K=5,000-10,000 (sample 143). If the initial sample contains less than 2 mg/l of Ga the analysis in flame isn't carried out, a more sensitive method of thermal atomization with 10-50 time dilution is used. The results for As are well agreed with both methods at the 5-20 time dilution for flame one and the 200-2000 time delusion for hydride technique. The FI-MHS method also gives lower results for higher dilute time (5,000-10,000 sample 167). The experimental errors represent 12 % and are more significant when the dilution factor is over 5000-10000.

In the figure the measured gallium and arsenic concentrations in the filtrate solutions depending on the value of pH are shown. The concentration value represents the mean quantity of two measurements by different methods. As it is clear from the figure the least of gallium losses at the precipitating gallium arsenate from oxide solution with stoichiometric GaAs is obtained in space 3.2-4.2 of pH value.

Gallium and arsenic losses in the filtrate of the model waste



5. Conclusions.

In this paper it was shown the opportunity of using the atomic absorption spectrometer AAnalyst 800 to investigate the gallium and arsenic losses in technological process of precipitation and filtration the gallium arsenate. The filtrate in this process contains 1-680 mg/l of gallium and 55-880 mg/l of arsenic, depending on the value of pH. For this reason it is necessary to dilute the investigated solutions for using those measuring methods. So the dilution of solutions only of 5-20 times for atomization method in flame, of 100-1,000 times for thermal method and up to 10,000 times for hydride technique is necessary. The investigated method can be used to study and further optimize the technological process.

Acknowledgement

The research described in this publication was made possible in part by Award No. MP2-3048 of the Moldovan Research and Development Association (MRDA) and the U.S. Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF). Any opinions, findings and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the MRDA or CRDF.

References

[1] EPA 600/R-02/089, Reduction of Arsenic Wastes in the Semiconductor Industry. www.epa.gov/ORD/NRMRL/Pubs/600R02089/600R02089.htm.
[2] S. Baranov, B. Cinic, V. Stavila, Waste Formation in Epitaxial Production of GaAs From Processing Technological Equipment in The Etching Solution. Proceeding of the 3rd

International Conference on "Microelectronics and Computer Science", p.130-133, sept.26-28, 2002, Chisinau, Moldova.

[3] J. Redwing, S. Baranov, V. Stavila, B. Cinic. Study of the Waste Formation Process in Etching Solution Derived From Manufacture of Epitaxial GaAs Structures. Scientific Analects of State University of Moldova, ISBN 9975-70-305-4, series "Physics and Mathematics Sciences", pp.129-133, 2003

[4] P. Palfy, E. Vircicova, L. Molnar Processing of arsenic waste by precipitation and solidification. Waste Management 19, 1999, pp. 55-59.

[5] A. Uzawa, H. Minamisawa, T. Okutani, Determination of trace amounts of gallium by tungsten metal furnace atomic absorption spectrometry after preconcentration on activated carbon impregnated with 8-quinolinol. Analytical Sciences (2000), 16(10), 1085-1088. CODEN: ANSCEN ISSN:0910-6340. CAN 133:343943 AN 2000:776598 CAPLUS

[6] D.M. Christie and J.R. Chelikowsky, Electronic and structural properties of $GaAsO_4$, Journal of Physics and Chemistry of Solids. pp. 617-624, Issue 5, v. 59, 1998.