

GALLIUM ARSENATE REMOVAL FROM WASTE WATERS

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Abstract

The aim of this paper is to study the loss of gallium (Ga) and arsenic (As) loss during the sedimentation of gallium arsenate (GaAsO_4) from waste solutions of GaAs epitaxial production by chloride method. The solid wastes of this semiconductor manufacturing process are removed from technological equipment by dissolution in an acidic etching solution. In order to recover valuable Ga and very toxic As from these waste solutions we proposed to precipitate them as gallium arsenate. Experiments have been conducted to determine the migration of the two elements in filtrate and washing solutions as a function of pH for both model and real industrial wastes. It has been determined the optimal interval of pH for sedimentation, the losses of Ga and As present 0,01-0,053%. For model solutions the sedimentation is optimal in the range of pH from 3,2 to 4,3, while in the case of real waste solution this interval is 3,6-5,0. Comparative evaluation of the precipitation efficiency revealed that for model solutions the arsenic loss during the precipitation is higher (0,5%), and this can be explained by a different ratio of initial Ga^{3+} and AsO_4^{3-} in model and real solutions. The results described in this paper provide important guidelines for the sedimentation of gallium arsenate from acidic waste solutions and indicate an overall efficiency of the process that could lead to savings in cost and process time for industrial effluent treatment technologies.

1. Introduction

The semiconductor gallium arsenide (GaAs) manufacturing processes generate large amount of solid wastes containing valuable gallium and toxic arsenic [1]. The dissolution of these wastes in specific etching solutions is an inevitable process. For instance in the case of growing GaAs layers from gaseous phase by chloride epitaxial method the technological equipment should be periodically treated with an etching solution to remove the solid deposit from the surface. Usually the solutions for etching contain a solubilizing and an oxidizing agent. In general it is desirable to use chemical agents which oxidize arsenic to +5 valence state, since the use of acids without oxidizer leads to generation of a highly toxic gas arsine AsH_3 . A number of chemicals have been used for these purposes, the most commonly used oxidants being hydrogen peroxide, hypochlorites, and nitric acid. The combination of the nitric with hydrochloric acid is especially attractive, since the resulted solution is characterized by a high etching activity and short reaction time. The dissolution process produces an acidic waste solution that may contain up to 2 mol/l of gallium(III) and arsenic(V). At such concentrations, the aqueous wastes require subsequent treatment for recovery of Ga and removal of As, prior to discharge of the waste from the manufacturing plant. For example, during the process of growing epitaxial GaAs semiconductor layers from

gaseous phase by chloride method the resulting waste solution from etching technological equipment in HCl/HNO₃ may contain up to 70% of the initial materials of high purity [2, 3]. The same category of liquid wastes results from dissolution of residual epitaxial GaAs plates in such acidic solutions. Since the aqueous waste itself contains gallium and arsenic of high semiconductor purity there is a critical need in developing appropriate technologies for their recovery. Recycling of such wastewater offers tremendous benefits from both reduced cost of production and environmental liability [1]. For example, gallium is particularly expensive and its recovery is economically advantageous to semiconductor manufacturers. However, there is a lack of technologies dealing with recovery of Ga and As from waste solutions containing g/l concentrations of these elements. It is clear that management of such hazardous wastes containing huge concentration of As is a very serious problem [4].

The environmental issues facing semiconductor industry have recently considerably expanded and become increasingly important concerns. For instance, the management and disposal of hazardous wastes, such as arsenic, receive significant attention because of strict regulation [4, 5]. Therefore, it is desirable to treat the wastewaters at the production plants, avoiding the costs and risks of eventual transportation to specialized mills. This strategy would permit to reduce production costs, conserve natural resources, and prevent pollution.

We propose a simple and robust method for recovery of both Ga and As from waste solutions derived from dissolution of GaAs in acidic solutions. This method involves the sedimentation of gallium arsenate (GaAsO₄) by adjusting the pH of the solution. The present study is devoted to the study of gallium arsenate sedimentation by titration of corresponding acidic solutions with an alkaline base (NaOH or KOH) and analysis of Ga and As removal at different pH, as well as the loss of these elements during the precipitation and washing of the sediment.

2. Experimental Section

2.1. Materials

Three model and one real waste solutions were considered for the present study. The three model waste solutions have been obtained by dissolution of GaAs plates in an acidic solution of nitric and hydrochloric acid and contain respectively 297.524, 244.586 and 92.425 g of GaAs in 1 litre of solution. The real waste solution results from etching technological equipment of GaAs epitaxial layers growing from gaseous phase from the Ga-AsCl₃-H₂ system. The other chemicals were analytical reagent grade and were used without any further purification. All solutions were prepared in deionised pure grade water. All glassware were cleaned with water and 1 N HCl and then rinsed with distilled water. KOH and NaOH stock solutions were standardized with a solution of hydrochloric acids (C_N=1.000 mol/l). The intermediate and secondary standards of working solutions were prepared freshly for each experiment. The separation of the sediment was performed using FILTRAK paper filters of medium porosity.

2.2. Procedure

2.2.1. Precipitation

The sedimentation experiments were carried out at 20±1 °C. The pH of the waste solutions was adjusted by adding either aqueous NaOH or KOH. An initial volume of 2ml of

the acidic solutions was added in 11 beakers, each of 50 ml. To each beaker 20 ml of deionised water was added to dilute the solutions in order to minimise the possible co-precipitation effects. Then to the first beaker a solution of the alkaline base was added gradually to the point of incipient precipitation. To the rest of the beakers a step-wise increased volume of the alkaline base was added under continuous stirring. For instance in the case of potassium hydroxide solution with a concentration of $T=0.05743$ g/l, this volume was in the range 0.3-0.7 ml, and it was individual for each acidic solution, function of the concentration of gallium and arsenic. These concentrations were preliminary measured by means of a spectrophotometric method [3]. The final volume of the solutions was adjusted to 50 ml with deionised water and the samples were left to equilibrate for 4 hours.

2.2.2. Filtration and Washing

The separation of the obtained gallium arsenate sediment was performed by filtration on the paper filters. The filters were preliminarily stored at $120\text{ }^{\circ}\text{C}$ for 40 min and weighted on a balance with a precision of 0.5 mg. The time of contact of the filters with the atmosphere is minimised and is maintained constant for each sample. The sediments were separated by filtration. The filtrate solutions have different values of pH and present the first source of gallium and arsenic losses during the sedimentation of GaAsO_4 . The obtained gallium arsenate sediment was washed with 50 ml of deionised water directly on the filter. The washing solutions present the second source of gallium and arsenic losses.

2.2.3. Drying of the sediment

The filters containing the gallium arsenate were dried at $120\text{ }^{\circ}\text{C}$ for 90 min and then weighted. The obtained gallium arsenate presents a white amorphous solid, slightly hygroscopic. The weighting is performed in the same conditions for all samples, during the same period of time, determined by the cooling the samples to room temperature in a desiccator. The weight of the gallium arsenate was determined as the difference of the weight of the filter with and without sediment.

3. Measurements

The weight of the samples was measured by means of a laboratory balance VLR-200 (class of precision - 2). The pH measurements of the solutions were performed with an 3310 pH meter by means of glass and Ag/AgCl electrodes, the later filled with saturated potassium chloride solution.

The concentrations of gallium (Ga) and arsenic (As) in solutions have been measured by atomic-absorption spectroscopy method. The measurements have been performed 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 a 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 utilisation of the computer controlled machine work and the analysis process. This method has found exhaustive use for determination of small concentrations of arsenic [6] and gallium [7] for determination of trace amounts of gallium by

tungsten metal furnace. The filtrate solutions contain 1-680 mg/l of gallium and 55-880 mg/l of arsenic, depending on the value of the pH of sedimentation. For this reason it is necessary to dilute the investigated solutions for using the described methods [8, 9]. The dilution of solutions is only of 5-20 times for atomisation method in flame, and of 100-1,000 times for thermal method and up to 10,000 times for hydride technique is necessary.

4. Results and Discussion

Three different model and one real waste solutions have been selected for the gallium arsenate sedimentation studies. The purpose for selecting those solutions was to study the effect of concentration of the dissolved gallium and arsenic, as well as their ratio. The results of the sedimentation of the gallium arsenate from acidic wastes are shown in Fig. 1. As expected, at higher concentrations of Ga(III) and As(V) the quantity the gallium arsenate sediment is higher. The interval of pH for optimum sedimentation for the solution with the concentration of GaAs 2.06 mol/l is between 3.2 and 4.4 with 3.1% loss from the weight of the sediment. At the concentration of GaAs 0.64 mol/l this interval is between pH 3.2 and 5.0 with the same amount of loss of the sediment.

Precipitation of gallium arsenate from the wastes solutions

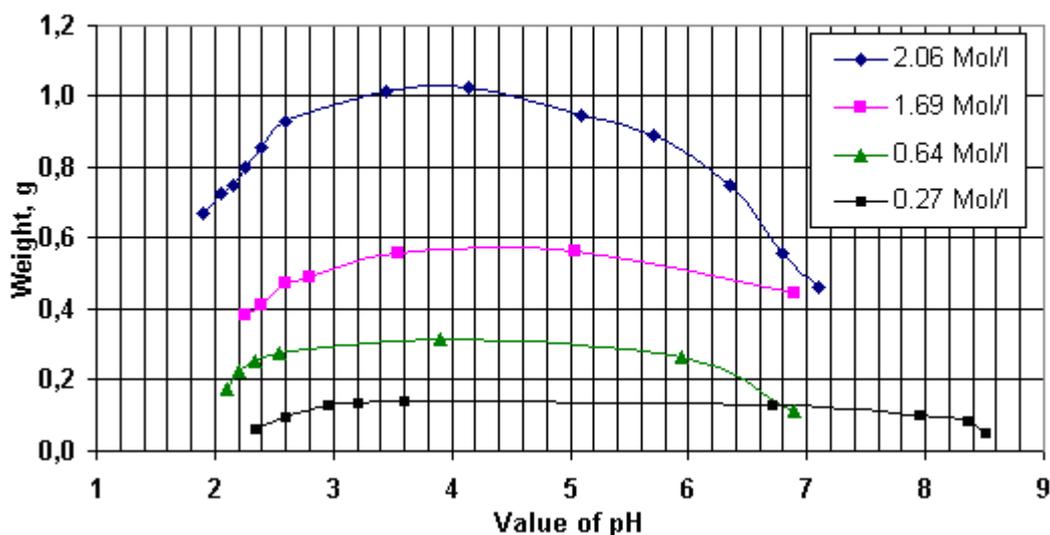


Fig.1. Precipitation of gallium arsenate from waste solutions

For the real waste solution with a concentration of Ga 0.27 mol/l the highest removal was obtained at a pH between 3.6 and 6.7, but the losses are smaller than 1% from the total weight. To be noted that the ratio of Ga to As in the real waste solution is close to 2:1, while in the model solutions this ratio is 1:1. The efficiency of the precipitation is higher for the more diluted solutions. The weight of the sediment obtained in the range of optimal pH values is about 20% higher as the calculated for anhydrous gallium arsenate. This increase in mass can be explained by the hygroscopic properties of the obtained gallium arsenate, that can incorporate water molecules, as well as co-precipitate other ions presented in solutions.

The experiments were conducted with both KOH and NaOH solutions, the results are identical in both cases. The loss of gallium and arsenic calculated from gravimetric measurements presents a general characteristic of the precipitation process, but does not contain information about absolute losses of these elements. The atomic absorption method

permits to measure directly the concentrations of Ga and As, both in filtrate and washing solutions.

As observed in Fig. 2, in the filtrate solution resulted from the model waste samples the total concentrations of arsenic in the investigated pH range are between 0.5 and 0.9 mol/l, while the gallium concentrations are between 36 mg/l to 120 mg/l with the highest removal between pH 3.2 and 4.3.

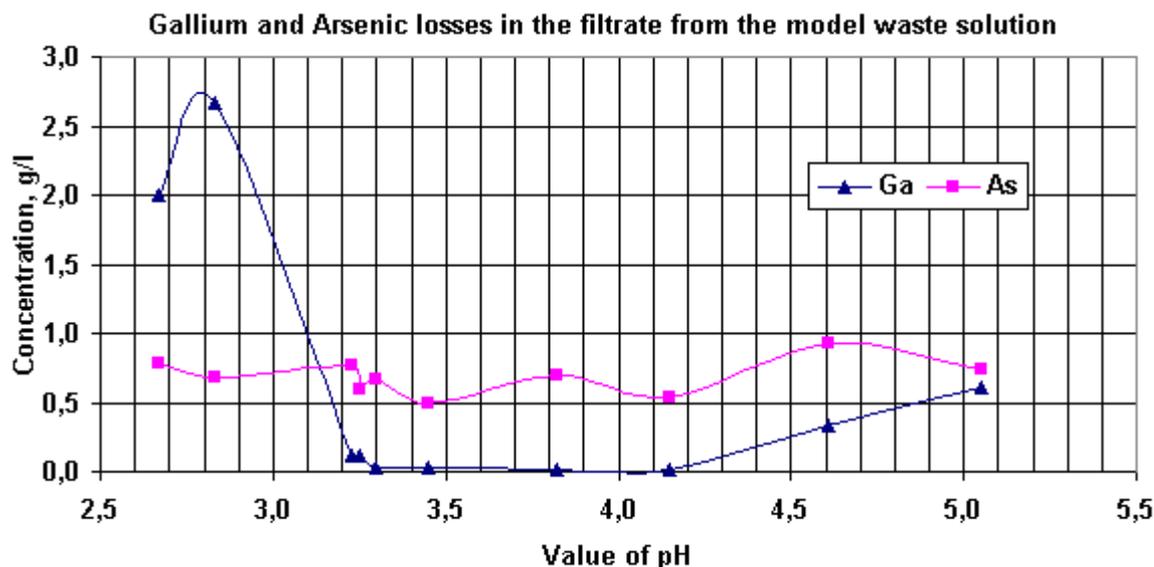


Fig. 2. Ga and As losses in the filtrate from the model waste solution

It is clear that for the real waste solution the composition of the sediment is different from stoichiometric, and can be formulated as $\text{Ga}(\text{AsO}_4)_x$. The occurrence of both stoichiometric and non-stoichiometric gallium arsenates has been previously reported [10-12]. A possible reason for the increase of gallium concentrations in the filtrate at pH higher than 4.3 may be formation of soluble Ga species. The speciation of gallium(III) solution chemistry and formation of hydroxo-complexes is well documented [13].

The solution chemistry of gallium(III) is very sensitive to pH due to hydrolysis reactions. For instance, Ga(III) solutions with more than 0.1 g/L or 1.4 mM Ga, one or more polynuclear species, such as $[\text{Ga}_{26}(\text{OH})_{65}]^{13-}$, can exist at pH above 3. Below 0.01 g/L or 0.14 mM Ga, four mononuclear complexes are reported: GaOH^{2+} ($\text{pK}_{a1}=3.09$), $\text{Ga}(\text{OH})_2^+$ ($\text{pK}_{a2}=3.55$), $\text{Ga}(\text{OH})_3$ ($\text{pK}_{a3}=4.40$) and $\text{Ga}(\text{OH})_4^-$ ($\text{pK}_{a4}=6.0$) [13]. In our case the existence of soluble polynuclear Ga(III) complexes is very likely and this can explain the increase of Ga(III) concentration in the filtrate at pH higher than 4.3. The same conclusion may be made based on the results of the measuring gallium concentrations in washing solutions.

For washing solutions, as shown on Fig. 3, the concentrations of arsenic at pH higher than 4.3 increase to a value of 0.26 g/l, and at pH 5.05 reach 0.73 g/l and are higher than in the filtrate 0.61 g/l, while at the more acidic pH the As concentrations are in the range 58-90 mg/l.

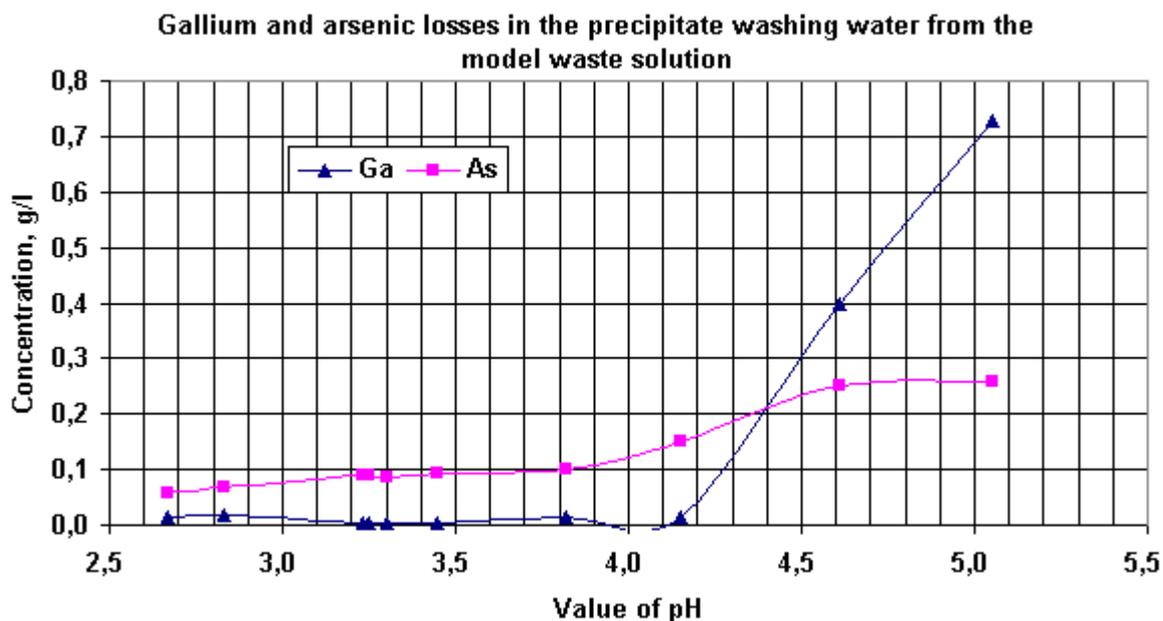


Fig. 3. Ga and As losses in the precipitate washing water from model waste solution

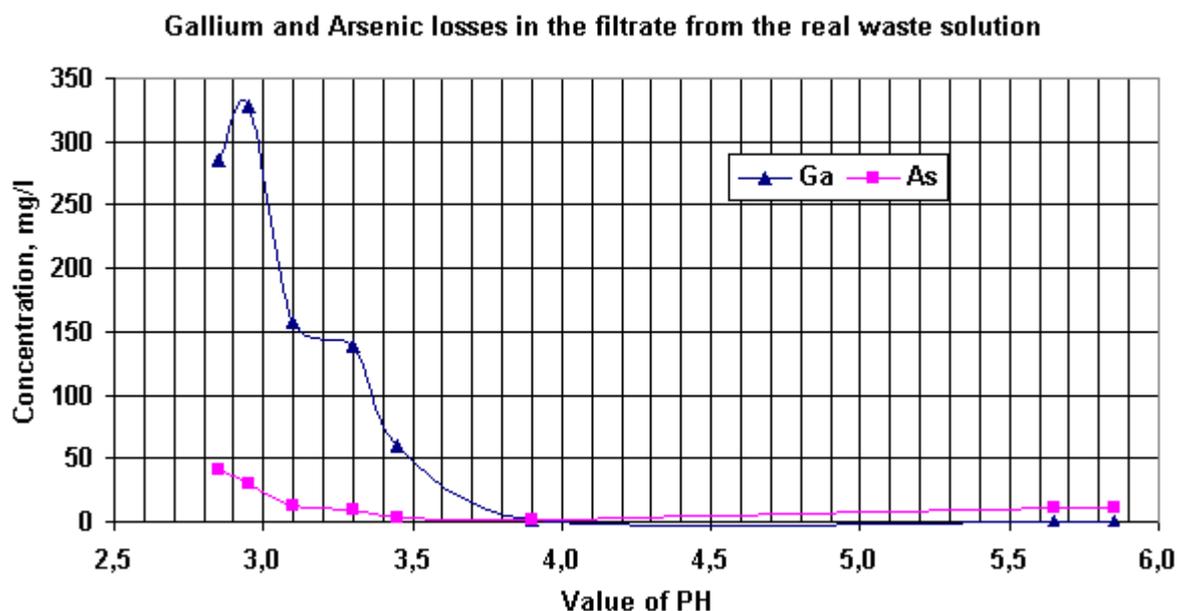


Fig. 4. Ga and As losses in the filtrate from the real waste solution

The effect of pH on the removal of gallium and arsenic from the real waste solution with the ratio Ga/As=2:1 is presented in Fig. 4. It can be seen from the figure that the concentrations of these elements in filtrate are smaller, probably due to their lower content in initial solution. The concentrations of As in filtrate decrease with pH from 42 mg/l to 2.2 mg/l at pH=3.9. The gallium concentrations also diminish from 328 mg/l to 1.7 mg/l at pH=3.9., but the beginning of the optimal sedimentation is at a slightly higher pH, 3.5 versus 3.2 for model solutions. A possible reason for this behaviour may be the different ratio of gallium to arsenic in solution.

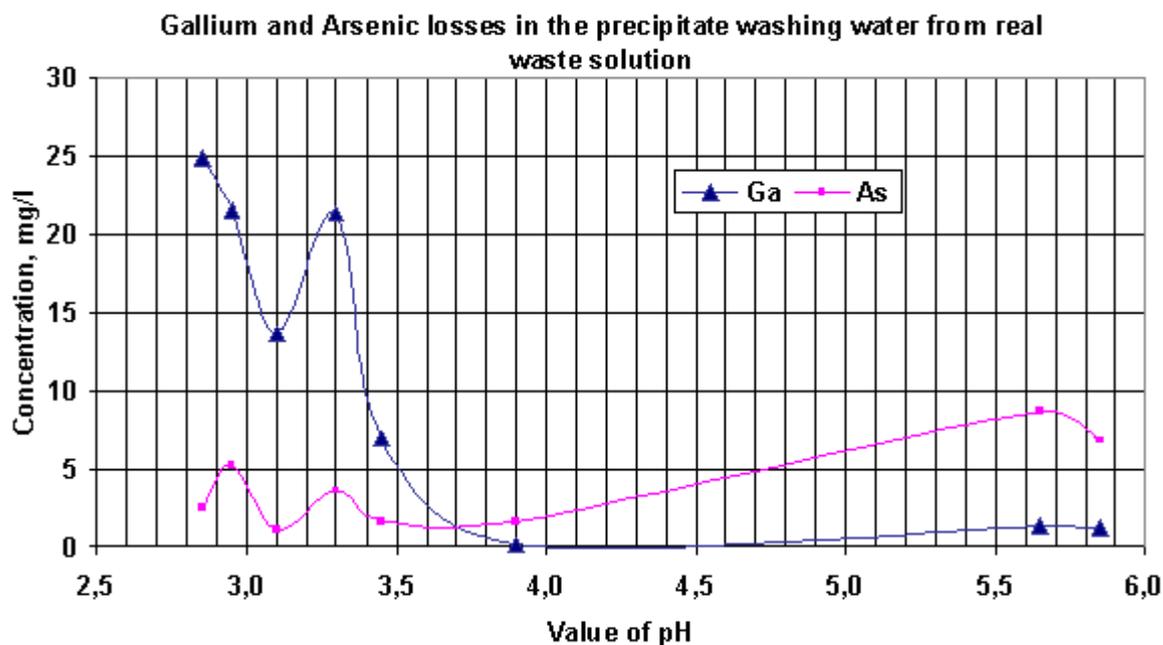


Fig. 5. Ga and As losses in the precipitate washing water from real waste solution

Fig. 5 shows the losses of Ga and As during the washing of the sediment obtained from real wastes. It can be seen from the figure that in the range of pH 2.75-3.50 the character of dependence of Ga concentrations in solutions is similar, the absolute values diminish, however, due to dilution 1:1 at washing. The concentrations of arsenic diminish as well, but the dependence is not the same any more. At higher pH values the concentration of Ga (1.30 mg/l) is over the respective in filtrate (0.30 mg/l) with even a higher ratio than the corresponding value in the case of model samples. In contrast to this, As concentrations in this interval of pH values have the same behaviour as in the case of model solutions. To sum up, the precipitation experiments with model and real solutions proved that the interval of optimal removal of gallium arsenate is different in the two cases.

Results of the efficiency of gallium and arsenic removal in the process of gallium arsenate sedimentation at optimal values of pH are presented in Table 1.

Table 1. The efficiency of gallium arsenate sedimentation.

Element	pH range	Concentration, g/l	Losses at filtration, mg/l	Losses at washing, mg/l	Total losses, mg/l	Total losses, %
Ga	3.2-4.3	143.4	65.5	10.1	75.6	0.053
Ga	3.6-5.0	18.96	1.7	0.15	1.85	0.010
As	3.2-4.3	154.1	655.0	119.5	774.5	0.500
As	3.6-5.0	10.19	1.6	1.6	3.8	0.037

As can be seen from Table 1, the total losses of Ga are function of initial concentration of this element and constitute 0.01-0.053%. The corresponding As losses during the precipitation from the real waste solution are of the same order that those of Ga and present 0.037%. Contrary, the removal of As from model solutions is less efficient and the losses present about 0.5%. There is a difference of one order between the losses of Ga and As, it

seems that there is no correlation with the initial concentrations of these elements, and probably it is connected with the ratio of Ga to As at the precipitation and co-precipitation of the species existing in solutions.

It is known that some high-pressure modifications of gallium arsenate present promising electronic materials [14-16] with useful opto-electronic and piezoelectric properties in a large range of temperature, between 15 and 1073K. A study is in course to reveal the respective properties of the obtained material from our sedimentation experiments. In parallel we are currently developing a technology of processing the obtained gallium arsenate in order to recover pure gallium and arsenic. The obtained filtrate and washing solutions still contain huge quantities of As and in order to remove the contaminant from the resulting wastewater one of the available commonly used technologies can be used, for instance precipitation and adsorption by iron(III).

5. Conclusions

The precipitation of gallium arsenate may be considered as a serious option for removal of both gallium and arsenic from acidic aqueous wastes of GaAs semiconductor industry. The sedimentation from the real waste with a ratio of Ga to As of 2:1 is particularly effective with the optimal pH range of the process between pH 3.6-5.0. In the case of three model solutions with a ratio Ga:As=1:1 this interval is between 3.2-4.3. The losses of Ga and As present 0.01 to 0.053% in the optimal conditions, with a mention that in the case of model solutions the loss of As is higher and constitutes about 0.5%. The obtained results are promising and showed that removal of gallium arsenate from acidic solutions can be performed with losses less than 0.5%. The obtained gallium arsenate can be further processed to isolate pure gallium and arsenic, while the remaining waste solution can be treated with a conventional technology for arsenic removal. Implementation of this process may have a positive role on the waste minimisation and pollution prevention within industrial process of GaAs layers production.

Acknowledgements

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.

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