



Thermogravimetric study of GaAs chlorination between -30 and 900 °C

Fernando M. Tunez^{a,b,*}, Jorge A. Gonzalez^{a,b}, María del C. Ruiz^a

^a Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, 5500 Mendoza, Argentina

^b Instituto de Investigaciones en Tecnología Química (INTEQUI-CONICET), Universidad Nacional de San Luis, Argentina

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ABSTRACT

Gallium (as GaAs) is at present an essential part of electronic devices, and the recovery of this element from electronic wastes is fundamental for the metallurgic industry. In this work, with the aim of recovering Ga by chlorination, the following reaction was investigated:



A thermogravimetric study of the previous reaction was carried out, and the following variables were investigated: chlorine partial pressure, in the range between 0.2 and 1 atm, by dilution with N_2 and reaction temperature in the -29 °C to 900 °C interval. The thermodynamic calculations predicted that the reaction was feasible during the entire analyzed temperature range, and the experimental results were in agreement with the thermodynamic estimations. The results showed that the chlorination rate did not change significantly with temperature, but it increased with the chlorine partial pressure. It was found that AsCl_3 was partially evaporated at temperatures above 20 °C, while the GaCl_3 started evaporating at 100 °C. The experimental observations showed that the mechanism originating the reaction was different in each temperature range ranging between -30 and 160 °C, 200 – 400 °C, and above 500 °C. In the first case the reaction was caused by adsorption of Cl_2 on the solid surface. In the second case, the solid started reacting when little quantities of GaCl_3 and AsCl_3 vapor were injected in the entrance of the system, indicating that the chlorination kinetics responded to an autocatalytic mechanism. Above 500 °C, the reaction was caused without adding chlorination products. The results of the analysis by scanning electron microscopy and X-ray diffraction showed a preferential attack on one of the crystal planes of GaAs. Besides, the formation of Ga_2O_3 and GaAsO_4 was observed as a consequence of the presence of small quantities of oxygen accompanying Cl_2 .

The results showed that chlorination is a selective and economic methodology for the recovery of gallium from electronic wastes.

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1. Introduction

Gallium is a rare element with a natural abundance of 16 ppm. Although this mineral is more concentrated in gallite, it is mostly found in aluminosilicates such as bauxite, clays and zinc ores (for example, sphalerite). Gallium is mainly extracted from wastes obtained during aluminium processing, and also from electrolytic zinc condensers. Other extraction sources include ashes released from coal burning [1].

Gallium metal, alloys and compounds are used in a relatively reduced scale in industries such as the construction of machines, the production of electrical and electronic equipment (diodes, tran-

sistors, lasers, conductors coating), vacuum technology, and in the chemical industry for the catalyzers manufacturing [1].

Gallium has important applications in optoelectronics (LED's), telecommunications, aerospace technology, and many commercial and domestic devices such as computers and DVD's [1].

Gallium has found application in the Gallex Detector Experiment located in the Gran Sasso Underground Laboratory in Italy. In this experiment, 30.3 tons of gallium in the form of 110 tons of GaCl_3 – HCl solution are being used to detect solar neutrinos [2].

When gallium is used for glass painting, it forms a brilliant mirror and also wets the crystal and porcelain. The element adapts easily to form alloys of low fusion point (for example, eutectic alloys) with most metals.

Gallium arsenide (GaAs) is a valuable compound widely used in the manufacturing of advanced semiconductors for microwave transceivers, transistors, solar cells, lasers, laser diodes, compact discs and other electronic applications. This compound has several advantages in relation to other semiconductor materials, such as

* Corresponding author at: Instituto de Investigaciones en Tecnología Química (INTEQUI), Universidad Nacional de San Luis - CONICET, CC: 290, 5700 San Luis, Argentina. Tel.: +54 2652423789x116; fax: +54 02652426711.

E-mail address: fmtunez@unsl.edu.ar (F.M. Tunez).

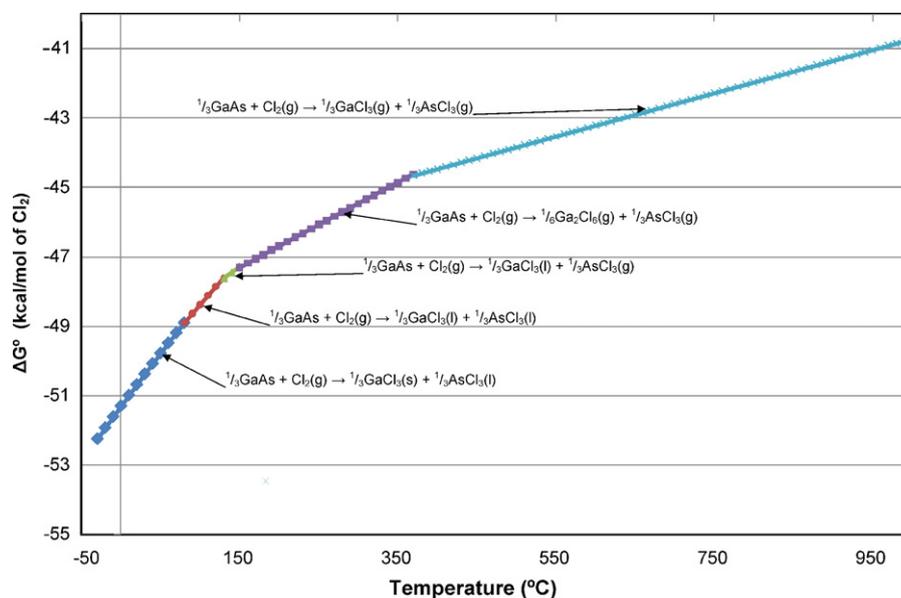


Fig. 1. Change of Gibbs free energy versus temperature for the GaAs chlorination reaction.

fast operation with low energy consumption, good radiation resistance and capacity to convert electrical signals into optical ones [1,3].

The manufacturing of electrical and electronic devices has rapidly developed, giving place to an increase in the production of wastes from these devices. The recycling of these wastes is an important issue not only because their reduction is necessary but also because valuable materials can be recovered. Besides, these kinds of wastes constitute a concern for the governments and also for the population due to their dangerous materials [4].

Electronic wastes are of diverse complexity due to their different materials and components and to the different processes used for the equipment manufacturing. The characterization of these wastes is of key importance for the development of a recycling system with a good cost-benefit relation between the system and the environment. The selective dismantling used to identify dangerous substances and/or valuable materials is an essential process in the recycling of these wastes [5].

Progress in the development of materials with application in different fields, ranging from medicine to aerospace industries, has made the production of high purity metals necessary. Several methods exist to produce rare and precious metals with a high purity degree; however, liquid–liquid extraction from metallic halides in solution and chlorides distillation are the most widely applied methodologies nowadays. In both cases, obtaining the metallic halides is the first stage of the process, and one of the most widely used techniques for this stage is the previous chlorination of materials such as metals, ores, metallic oxides or industrial wastes [6].

The use of chlorination in the metal extraction processes by means of pyrometallurgical and hydrometallurgical methods has received great attention in recent decades, and an increasing use of the chlorine chemistry is expected due to the advantages of this process [7]. According to Kubo et al. [8], the main advantages of the chlorination process in relation to other refinement methods for gallium recovery from GaAs can be summarized as follows: operation temperatures are low, most of the impurities can be effectively eliminated, high-purity metallic gallium can be obtained and the productivity increase is significant.

Several authors have reported the mechanism of the chlorination reaction of GaAs. Jenichen and Engler [9], using the functional density method, theoretically found that the most feasible reaction

mechanism involves adsorption of Cl_2 on the surface of GaAs and subsequent desorption of GaCl. Hung et al. [10] studied the chlorination of GaAs at low temperatures (110 K) using soft X-ray photoelectron spectroscopy and found that at low exposures of Cl_2 it dissociates itself and preferentially adsorbs on the atoms of As inducing the breaking of the bond Ga–As, generating subsequently gallium and arsenic chlorides. Bond et al. [11] using pulsed supersonic molecular beam scattering studied the reaction of Cl_2 with the surface of GaAs, and they observed that the reaction products depended on the flow of chlorine and temperature; at low flows of Cl_2 and high temperature, the formation of GaCl and As predominates, and at high flows of Cl_2 and low temperature, there is a predominance of GaCl_3 and AsCl_3 formation.

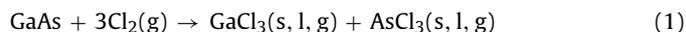
This paper presents the thermogravimetric study of GaAs chlorination with Cl_2 between -30 and 900 °C. The partial pressure of Cl_2 was varied between 0.2 and 1 atm. The purpose of the study is to provide data to facilitate elucidating the mechanism and kinetics of the reaction in working conditions so that these results can then be applied to the recovery of Ga.

2. Thermodynamic analysis

This section presents the thermodynamic calculations for the GaAs– Cl_2 system, which have been done for the temperature range used for the experimental essays. All the calculations were obtained using the HSC Chemistry for Windows, version 5.1 software [18].

The reactions that may occur between GaAs and Cl_2 have been theoretically and experimentally studied by several authors [9–17] under different temperature conditions, partial pressure and Cl_2 quantity in order to obtain components for electronic applications. The results of these investigations showed that the reaction products vary in their composition as well as in their aggregation state according to the working conditions.

A first analysis involves to study the feasibility of a gallium and arsenic chlorides formation from GaAs. Fig. 1 shows the results of the calculation of the Gibbs free energy variation for the following global reaction:



The analysis of Fig. 1 permits to conclude that the reaction between GaAs and Cl_2 is feasible at all the studied temperature

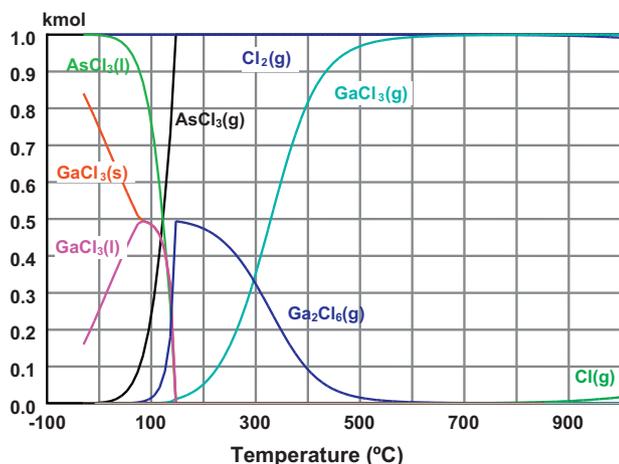


Fig. 2. Equilibrium composition in pure chlorine.

range, showing greater spontaneity as temperature decreases. The changes in the graph slope indicate phase changes of the reaction products. It is important to emphasize that between 150 and 360 °C the formation of the gaseous gallium trichloride is more feasible as dimmer Ga_2Cl_6 .

The equilibrium compositions at different temperatures and Cl_2 amounts was used to present the thermodynamic analysis for the reaction between GaAs and Cl_2 .

The equilibrium compositions were obtained assuming that from the elements constituting the reagents used, all the species available in the software database may be formed: $\text{As}(\text{g})$, $\text{As}_2(\text{g})$, $\text{As}_3(\text{g})$, $\text{As}_4(\text{g})$, $\text{AsCl}_3(\text{g})$, $\text{Cl}(\text{g})$, $\text{Cl}_2(\text{g})$, $\text{Cl}_3(\text{g})$, $\text{Cl}_4(\text{g})$, $\text{Ga}(\text{g})$, $\text{Ga}_2(\text{g})$, $\text{GaAs}(\text{g})$, $\text{GaCl}(\text{g})$, $\text{GaCl}_2(\text{g})$, $\text{GaCl}_3(\text{g})$, $\text{Ga}_2\text{Cl}_2(\text{g})$, $\text{Ga}_2\text{Cl}_4(\text{g})$, $\text{Ga}_2\text{Cl}_6(\text{g})$, $\text{AsCl}_3(\text{l})$, $\text{Ga}(\text{l})$, $\text{As}(\text{l})$, $\text{GaCl}_3(\text{l})$, $\text{As}(\text{A})$ (amorphous arsenic), $\text{As}(\text{Y})$ (yellow arsenic, cubic), $\text{Ga}(\text{s})$, $\text{As}(\text{s})$, $\text{GaAs}(\text{s})$, $\text{GaCl}_3(\text{s})$.

Fig. 2 shows the equilibrium composition for the $\text{GaAs}-\text{Cl}_2$ reacting system in the temperature range ranging between -30 and 1000 °C obtained considering a total pressure of the system of 1 atm. The initial reagents were $\text{GaAs}(\text{s})$ and $\text{Cl}_2(\text{g})$. The quantity of $\text{Cl}_2(\text{g})$ was higher than the stoichiometric. Since the experimental assays were carried out with excess Cl_2 , the estimates were performed with excess Cl_2 in relation to the reaction using the largest quantity of Cl_2 (reaction (1)). The composition was in the same figure it can be observed that in all the analyzed temperature range, the reaction products are gallium trichloride and arsenic trichloride which are formed according to reaction (1), with different aggregation states depending on the temperature.

Fig. 3 shows the equilibrium composition in relation to Cl_2 quantity. This diagram was calculated at a total pressure of 1 atm, with pure Cl_2 at 85 °C, starting with one mol of GaAs and increasing the quantity of Cl_2 . It can be observed that as $\text{GaAs}(\text{s})$ is consumed and $\text{GaCl}_3(\text{l})$ and $\text{As}(\text{s})$ are produced; when all the GaAs has been consumed, the formed As starts reacting with the Cl_2 producing $\text{AsCl}_3(\text{l})$.

While Fig. 2 provides a thermodynamic estimation of the species that may exist in equilibrium at different temperatures when GaAs reacts with Cl_2 in excess, Fig. 3 shows the thermodynamic evolution of the reaction in relation to the amount of the present chlorine, which might be useful to elucidate the most probable reaction mechanism.

Fig. 4 shows the partial pressure variation in relation to temperature for the three products that may be formed by the reaction between GaAs and Cl_2 . AsCl_3 vapor pressure reaches 10^{-3} atm at 58 °C, where as Ga_2Cl_6 reaches this pressure at 118 °C, and GaCl_3 , at 125 °C.

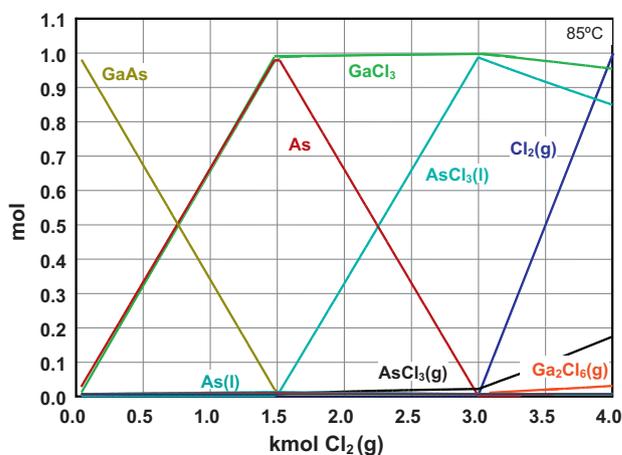


Fig. 3. Effect of Cl_2 quantity at 85 °C.

The formation of small amounts of oxygenated compounds, such as Ga_2O_3 and GaAsO_4 was observed (see Section 4.2.1) in the experimental phase when working at a temperature above 300 °C. In order to investigate this phenomenon, the analysis of the compounds thermodynamic feasibility to be formed from the chlorination products of the gallium arsenide was carried out.

The results shown in Fig. 5a indicate that the reactions of the compounds formation are thermodynamically feasible at almost all the studied temperature range, except for the reaction of the Ga_2O_3 formation which is spontaneous up to 810 °C. Also, the predominance diagrams (p_{O_2} versus p_{Cl_2}) presented in Fig. 5b and c for Ga and As, respectively, show that Ga and As oxygenated compounds predominate over those chlorinated at 25 °C.

3. Experimental

3.1. Materials

The materials used were GaAs Sigma–Aldrich with a purity of 99.999%, gaseous chlorine INDUPA Argentina with a purity of 99.5% and N_2 , as gas for dilution and purge, AGA ARGENTINA with a purity of 99.9%.

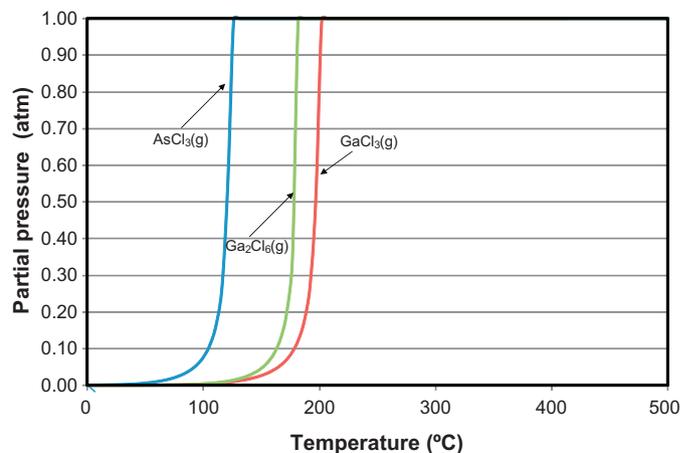


Fig. 4. Partial pressure of equilibrium versus temperature for AsCl_3 , Ga_2Cl_6 and GaCl_3 .

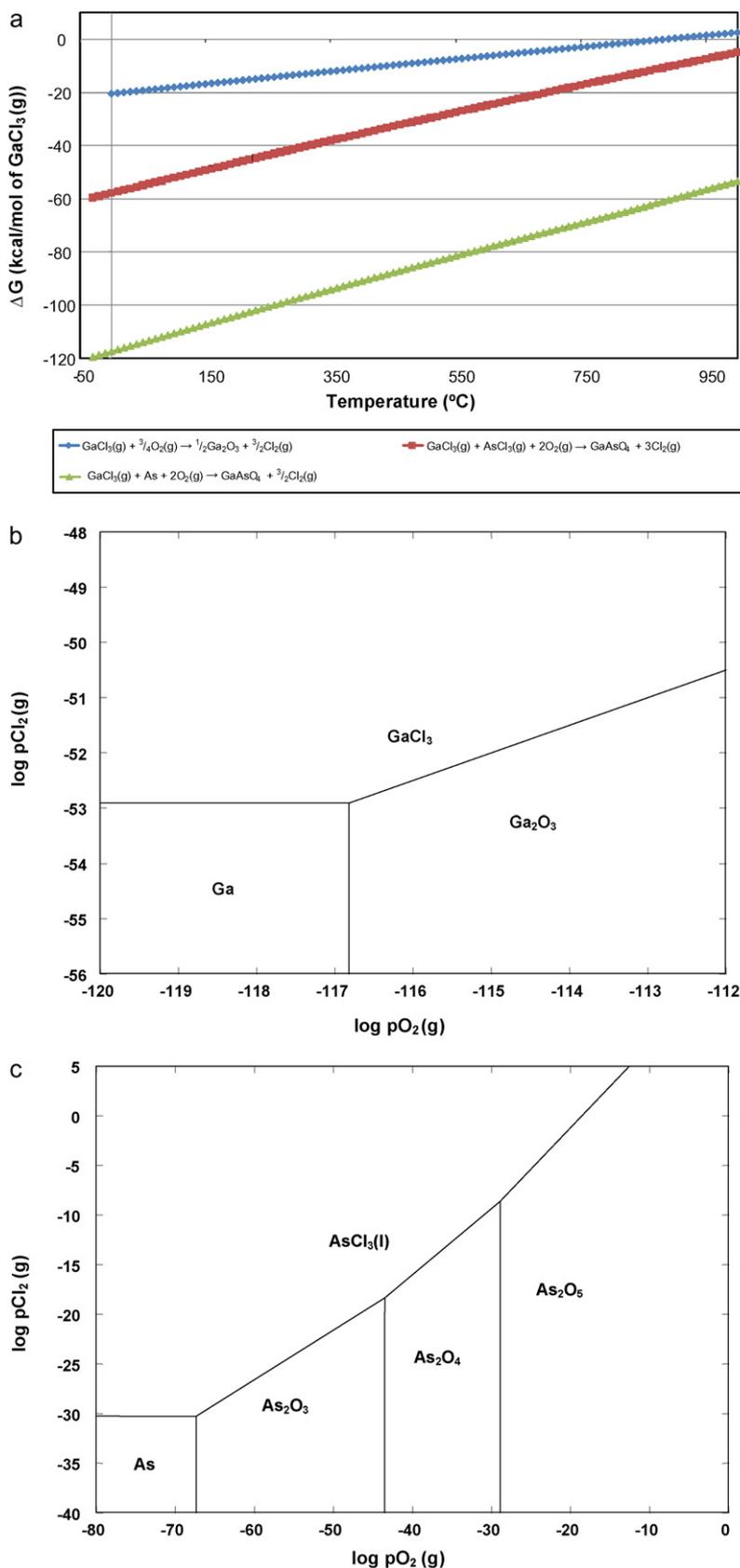


Fig. 5. (a) Change of Gibbs free energy in relation to temperature for the reactions which include the formation of oxygenated compounds. (b) Predominance diagrams ($p\text{O}_2$ versus $p\text{Cl}_2$) for Ga. (c) Predominance diagrams ($p\text{O}_2$ versus $p\text{Cl}_2$) for As.

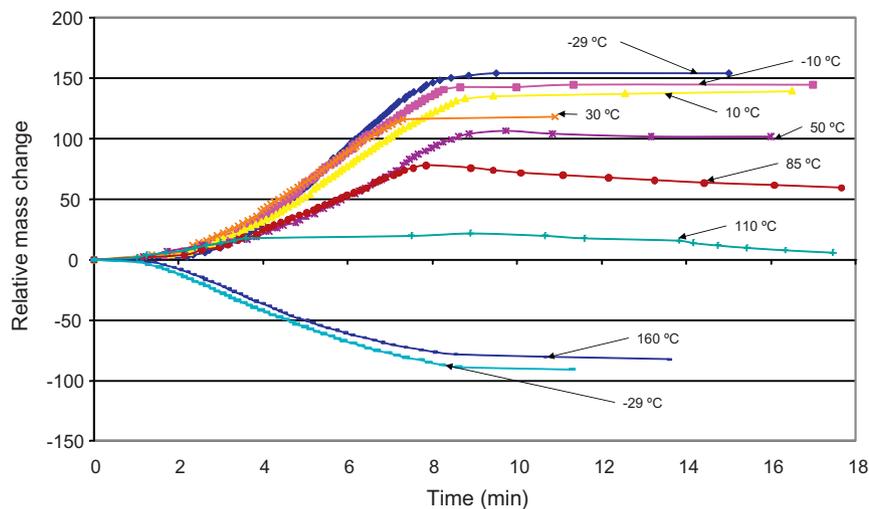


Fig. 6. Isothermal chlorination of GaAs with pure Cl_2 , in the temperature range between -30 and 200 °C.

3.2. Experimental equipment and procedure

The monitoring of the chlorination reaction was performed using thermogravimetry. An experimental equipment capable of working in corrosives and no corrosives atmospheres, developed in our laboratory [19], was used for this purpose.

The analyses of the chlorination wastes were carried out using X-ray diffractometry (XRD) in a Rigaku equipment model D-Max III C; X-ray fluorescence (XRF) using a Philips equipment model PW 1400; scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) using a LEO 1450VP microscope and a coupled EDAX Gemini 2000 energy dispersive spectrometer (EDS) and atomic absorption spectrometry (AAS) using a Shimadzu 6800 AA equipment.

The experimental procedure for the thermogravimetric study of GaAs chlorination was as follows: the sample, previously ground and classified to a particle size of $-40+90$ mesh, was placed in a previously weighed quartz crucible, then the crucible with the sample was supported in a thermobalance. In each experiment a mass of solid reagent of approximately 50 mg was used.

After being placed in the thermogravimetric system, the sample was thermostated for 30 min in an N_2 current of 50 ml/min. Once the working conditions were stabilized, the N_2 flow was turned off and a Cl_2 current of 50 ml/min was introduced in the thermogravimetric system at the corresponding partial pressure by dilution with N_2 ; time was measured from this moment, and data of mass change were collected. When the experiment was finished the Cl_2 gas flow was turned off and the thermogravimetric system was purged with N_2 . In all the essays the thermostatisation and purge

times were standardized in an N_2 environment. After that, the crucible with the chlorination wastes was removed, and the wastes were prepared for analysis. The effluent gases from the reactor were treated by H_2SO_4 and NaOH traps.

4. Results and discussion

Isothermal essays at different temperatures and partial pressures of chlorine were carried out until complete conversion of GaAs in order to study the influence of both variables on the chlorination reaction.

The thermogravimetric analysis of the GaAs– Cl_2 system is presented separately for temperature ranges lower and higher than 200 °C.

4.1. Thermogravimetric analysis between -30 and 200 °C

4.1.1. Temperature effect

The effect of temperature on the reaction between GaAs and pure $\text{Cl}_2(\text{g})$ was analyzed from thermogravimetric measurements. Fig. 6 shows the results of the time evolution of relative mass changes. There is an induction time of approximately 1 min at all the studied temperatures whose origin will be discussed in Section 4.3. The maximum relative mass changes obtained from Fig. 6 are shown in Table 1 close to the expected values for the temperatures at which aggregation states of reaction products can be assumed. For other temperatures the mass change contribution of vaporization process of reaction products) cannot be theoretically predicted

Table 1
Mass percentage changes expected in relation to the aggregation state of the products.

Reaction	Maximum theoretical mass change (5%)	Temperature (°C)	Maximum experimental mass change (%)	x
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{s}) + \text{AsCl}_3(\text{l})$ (1)	148.15	-29	154.59	
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + \text{AsCl}_3(\text{l})$ (2)	148.15	-10	144.81	
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + (1-x)\text{AsCl}_3(\text{l}) + x\text{AsCl}_3(\text{g})$		10	139.58	0.06
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + (1-x)\text{AsCl}_3(\text{l}) + x\text{AsCl}_3(\text{g})$		30	118.23	0.23
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + (1-x)\text{AsCl}_3(\text{l}) + x\text{AsCl}_3(\text{g})$		50	101.89	0.36
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + (1-x)\text{AsCl}_3(\text{l}) + x\text{AsCl}_3(\text{g})$		85	78.02	0.55
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{l}) + \text{AsCl}_3(\text{g})$ (3)	21.73	110	21.96	
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow (1-x)\text{GaCl}_3(\text{l}) + x\text{GaCl}_3(\text{g}) + \text{AsCl}_3(\text{g})$		160	-82.32	0.88
$\text{GaAs} + 3\text{Cl}_2(\text{g}) \rightarrow \text{GaCl}_3(\text{g}) + \text{AsCl}_3(\text{g})$ (4)	-100	200	-94.55	

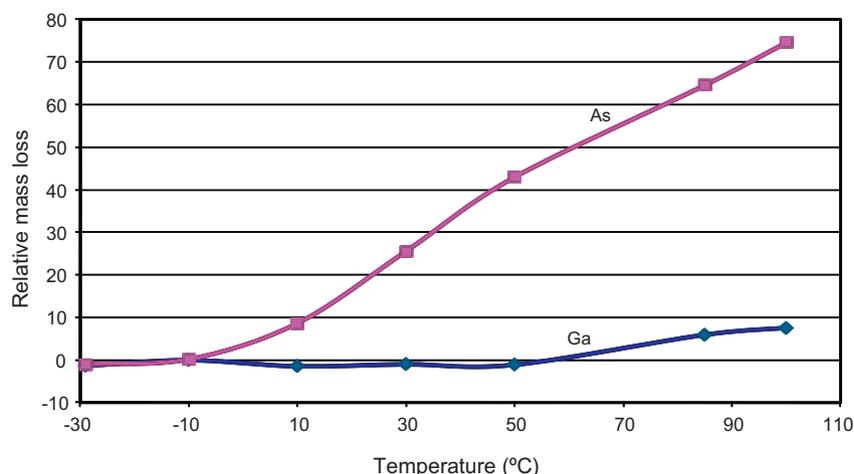


Fig. 7. Ga and As loss in the chlorination essays at different temperatures.

but empirically quantified through the calculation of the stoichiometric coefficient x , as shown in last column of Table 1. Also, at low temperatures, absorption of Cl_2 (b.p. = -34.04°C , [2]) in liquid chlorides must be taken into account. Finally, chlorides vaporization could be enhanced by a local temperature rising due to reaction exothermic effect. Therefore, chemical equations (1), (2) accounts well for reaction at -29°C and -10°C , respectively, and reaction at 10°C deviates slightly from mass changes predicted by equation (2) indicating a low contribution ($x \approx 0$) of $\text{AsCl}_3(\text{l})$ vaporization. As the temperature rise from 30°C , the increasing x values indicates the enhancing contribution of $\text{AsCl}_3(\text{l})$ vaporization. In fact, for experiments carried out at 50°C and 85°C (Fig. 6), once reaction finished, a continuous mass decreasing corresponds to $\text{AsCl}_3(\text{l})$ vaporization as unique phenomenon.

Total mass change after chlorination at 110°C is accounted for total vaporization of AsCl_3 (chemical equation (3)) which, despite temperature is lower to its boiling point (130°C [2]), can be explained from the exothermic effect above mentioned. The experiments at highest temperatures are interpreted taking into account $\text{GaCl}_3(\text{g})$ or $\text{Ga}_2\text{Cl}_6(\text{g})$ formation which is partial at 160°C and is nearly total at 200°C .

Also reaction residues were quantified by atomic absorption measurements and results are shown in Fig. 7 as Ga and As rel-

ative mass loss. Fig. 7 quantitatively agree with the increasing $\text{AsCl}_3(\text{l})$ vaporization at temperatures greater than 10°C , and partial $\text{GaCl}_3(\text{l})$ vaporization for the highest temperatures, as determined from thermogravimetric measurements.

4.1.2. Effect of the partial pressure of Cl_2

Figs. 8–10 the results of the thermogravimetric essays carried out to investigate the effect of the Chlorine partial pressure, p_{Cl_2} , (using N_2 as inner diluent gas) at -20 , 20 and 85°C , respectively. For all tested temperatures, the greater p_{Cl_2} , the greater the reaction rate (with the only exception shown in Fig. 10 for the two highest p_{Cl_2}). However, a detailed analysis is not easy because chlorination reaction is overlapped with chlorides evaporation. Therefore, any reaction order calculation, for example, will be falsified by other processes. Moreover, observed maximum relative mass changes indicates that contribution of chlorides vaporization seems to be dependent, not only on temperature (x value in Table 1) but also on p_{Cl_2} . The net effect for lower p_{Cl_2} is some combination of N_2 dilution, that enhances the heat dissipation and reduces the mentioned exothermic effect on chlorides vaporization, and a lowering in chlorination rate enhances the relative contribution of chlorides vaporization. This complexity is also confirmed by the (unexpected)

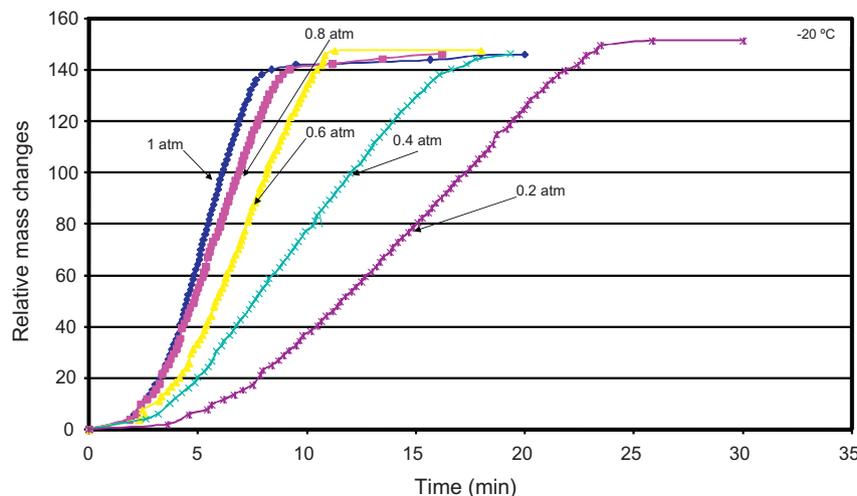


Fig. 8. Influence of Cl_2 partial pressure of at -20°C .

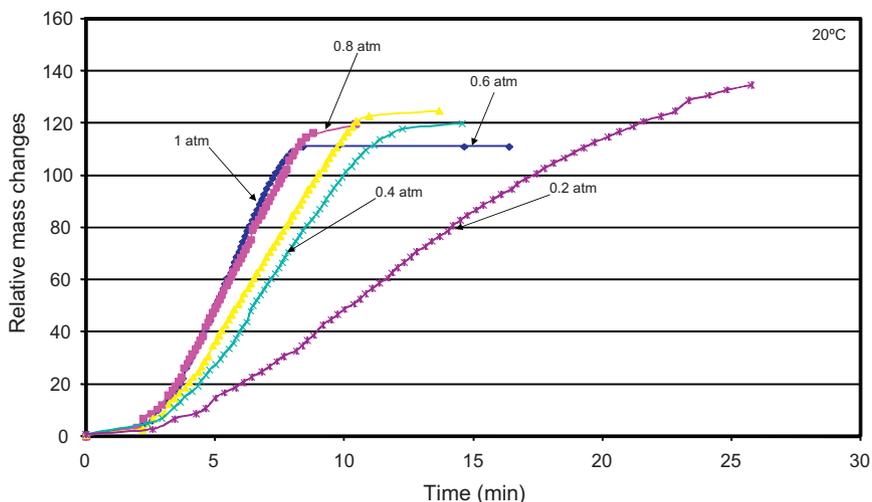


Fig. 9. Influence of Cl_2 partial pressure at 20°C .

inverse dependence of reaction rate process with $p\text{Cl}_2$ observed at 85°C as above mentioned from Fig. 10.

4.2. Thermogravimetric analysis between 300 and 900°C

4.2.1. Temperature effect

Chlorination performed at this temperature range exhibits a particular behavior. For the tested temperatures below 600°C reaction does not start unless small amounts of a $\text{GaCl}_3(\text{g})$ – $\text{AsCl}_3(\text{g})$ mixture is added. Therefore, for the experiments at 300°C and 500°C , those chlorides were injected in Cl_2 flow and supply was finished once reaction was started.

Fig. 11 shows the results of the thermogravimetric study of the GaAs chlorination with pure chlorine at temperatures between 300 and 900°C . According to the thermodynamic predictions analyzed in Section 2, all the products of the GaAs chlorination are in gaseous state in this temperature range, and in a flow system, they may be carried away by the gaseous current and then condensed outside the reaction zone. Consequently, the expected relative mass loss might be 100%.

Fig. 11 shows that chlorination rate does not practically depend on temperature; induction time changes inversely with tempera-

ture and, excepting for the two highest temperatures, solid residues remain (see Section 4.2.3). After chlorinations, solid residues of white color were observed deposited, not also in crucible, but also in reactor walls.

Fig. 11 also shows that solid residues remain, except in the essays performed between 800 and 900°C . It was observed in the experimental study that the residues were deposited in the crucible and also in the reactor walls. The residues observed in this figure, according to the analyses carried out using SEM, EPMA and XRD, correspond to compounds containing Ga, O and As. These data indicate that the GaAs chlorination was complete, and consequently the masses found at the end of the reaction were due only to these oxygenated compounds. The formation of these residues, whose origin, composition and structure will be discussed in detail in Section 4.2.3, might be due to the reactions between the products of the GaAs reaction and small amounts of O_2 present in the Cl_2 (Fig. 5).

4.2.2. Effect of the Cl_2 partial pressure

Figs. 12 and 13 show the effect of $p\text{Cl}_2$ on reaction rate at 300°C and 500°C , respectively. The effect of $p\text{Cl}_2$ on reaction rate is less prominent as $p\text{Cl}_2$ decreases. In all cases, final relative mass change indicates variable amounts of solid residues. At both temperatures,

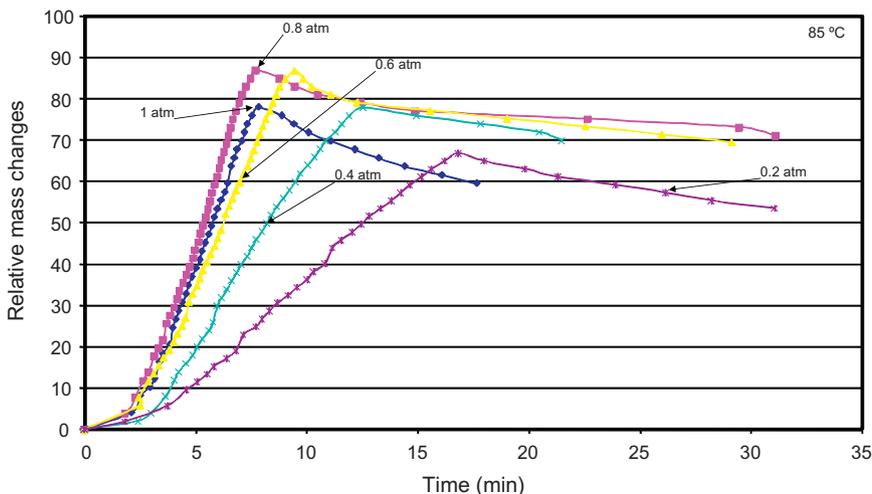


Fig. 10. Influence of Cl_2 partial pressure at 85°C .

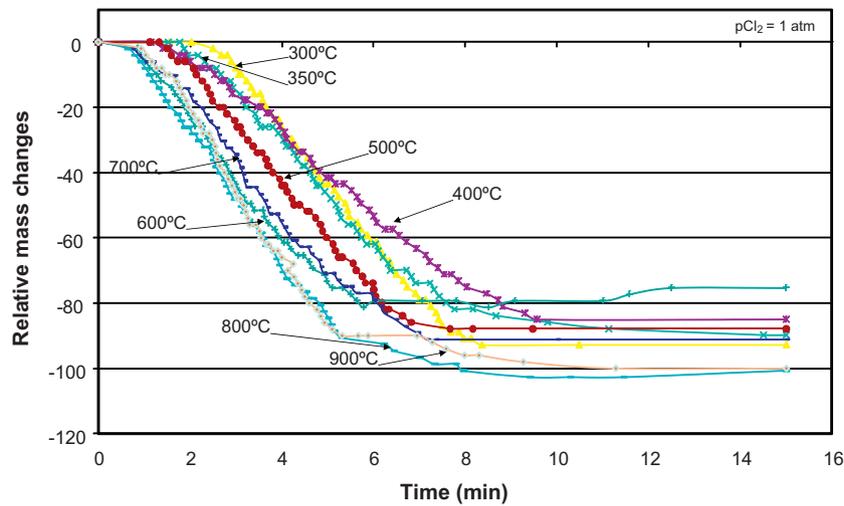


Fig. 11. GaAs isothermal chlorination with pure Cl₂, between 300 and 900 °C.

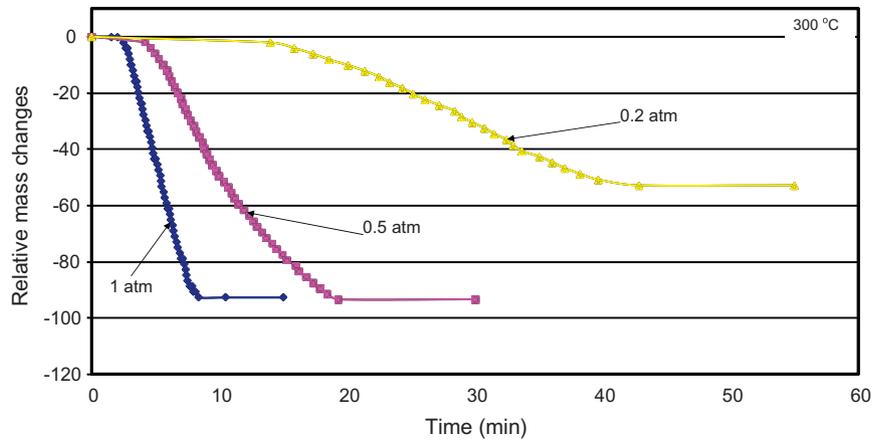


Fig. 12. Influence of Cl₂ partial pressure at 300 °C.

these solid residues were black or white, respectively, at lower or higher pCl₂ (see Section 4.2.3).

4.2.3. Characterization of the solid residues

Solid residues of chlorinations performed at temperatures between 300 °C and 900 °C were analyzed by XRD, SEM and EPMA.

Fig. 14 shows the X-ray diffractograms of residues after reaction with pure Cl₂ at 300 °C, 350 °C and 400 °C and it can be clearly observed that solids in all cases are amorphous. The SEM images and EPMA analyses on these solids were all similar. Fig. 15 shows results corresponding to residue obtained at 350 °C. Solid particles exhibits irregular surfaces and are composed by As, Ga and O. This last result is consistent with the above mentioned white color of

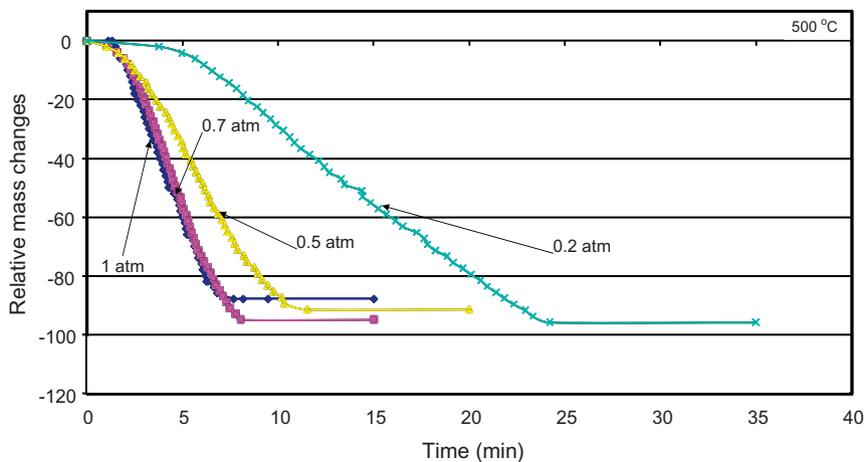


Fig. 13. Influence of Cl₂ partial pressure at 500 °C.

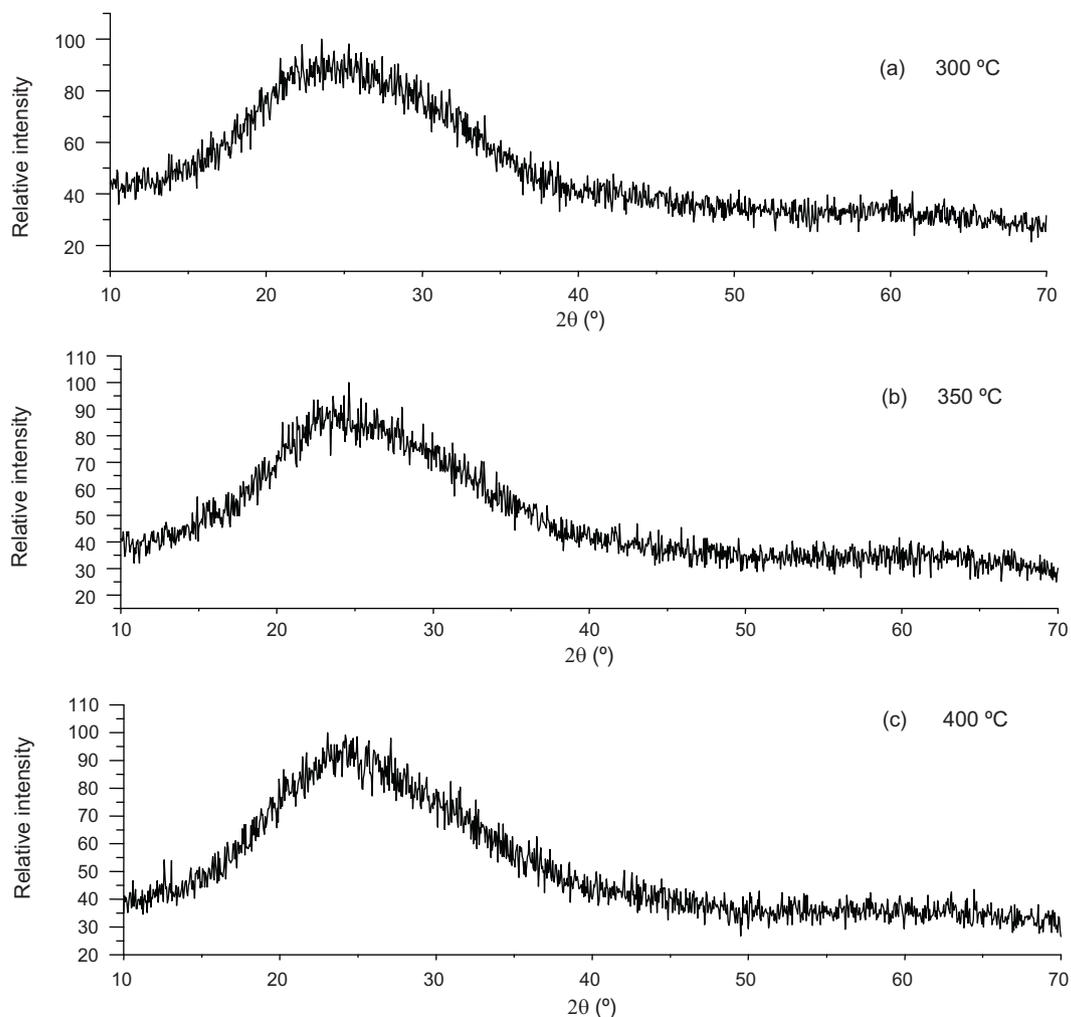


Fig. 14. Diffractograms of the residues from the essays with pure Cl_2 . (a) 300 °C; (b) 350 °C; (c) 400 °C.

residues observed at high $p\text{Cl}_2$ if it is assumed residues formed by As/Ga oxides.

Fig. 16 shows the X-ray diffractograms of residues after reaction with pure Cl_2 at 500 °C and 700 °C. residues are clearly crystalline solids. Solid obtained at 500 °C is a mixture of Ga_2O_3 [21,22] and GaAsO_4 [23]. At 700 °C an additional, and unknown, crystalline phase also appears.

The formation of oxygenated species during chlorinations is explained from O_2 traces presence in commercial Cl_2 , originated at its industrial production. The appearance of these oxides, inside and outside the crucible, likely indicates they are originated by the oxidation of the $\text{GaCl}_3(\text{g})$ and $\text{AsCl}_3(\text{g})$ which are feasible reactions according to Fig. 5. This assumption is also supported by the fact GaAs does not react with air below 800 °C (results not shown).

Fig. 17 shows X-ray diffractograms of residues obtained after chlorinations for $p\text{Cl}_2 = 0.2$ atm at 300 °C and 500 °C. XRD peaks allow to identify both solids as GaAs [24], which explain the above mentioned black color of residues observed at low $p\text{Cl}_2$. The diffractogram of the residue obtained at 500 °C shows a high preferred orientation effect of planes (220). Likely Cl_2 through a selective attack promotes changes in crystallites enhancing morphological importance of those planes. Fig. 18 shows the SEM observations of residue obtained at 300 °C compared with starting GaAs confirm a localized reactivity on solid particles.

The absence of oxygenated compounds is consistent with the low O_2 content for $p\text{Cl}_2 = 0.2$ atm.

Finally, the residues composition dependence on $p\text{Cl}_2$ (some combination of GaAs and As–Ga–O compounds) explain the variable limit for mass loss for experiments carried out with low $p\text{Cl}_2$ (Figs. 12 and 13) and the incomplete products vaporization for experiments with pure Cl_2 (Fig. 11) due to formation of non reactive As–Ga–O compounds after complete GaAs chlorination.

4.3. Reaction mechanism

GaAs chlorination shows two main behaviors depending on temperature. As mentioned, chlorination were performed in a simple experimental procedure at all temperatures, except for the range between 300 °C and 500 °C. For this temperatures the reaction does not start when Cl_2 reaches GaAs, unless small amounts of a mixture of reaction products ($\text{GaCl}_3(\text{g})$ – $\text{AsCl}_3(\text{g})$) are added. This last feature corresponds to an autocatalytic behavior.

Any mechanism proposal must explain autocatalytic and non autocatalytic behaviors at each temperature range, and the observed induction time variation with experimental conditions. Each temperature range will be separately discussed.

4.3.1. Low temperature range (–30 °C and 200 °C). Non catalytic behavior

A first step proposal in chlorination process could be supported on experimental [11,14] and theoretical [15] studies which conclude the $\text{GaAs}(\text{s})$ – $\text{Cl}_2(\text{g})$ interaction, at room temperature, yields the formation of $\text{GaCl}(\text{g})$ and $\text{As}_2(\text{g})$ or $\text{As}_4(\text{g})$. Therefore, Ga is firstly

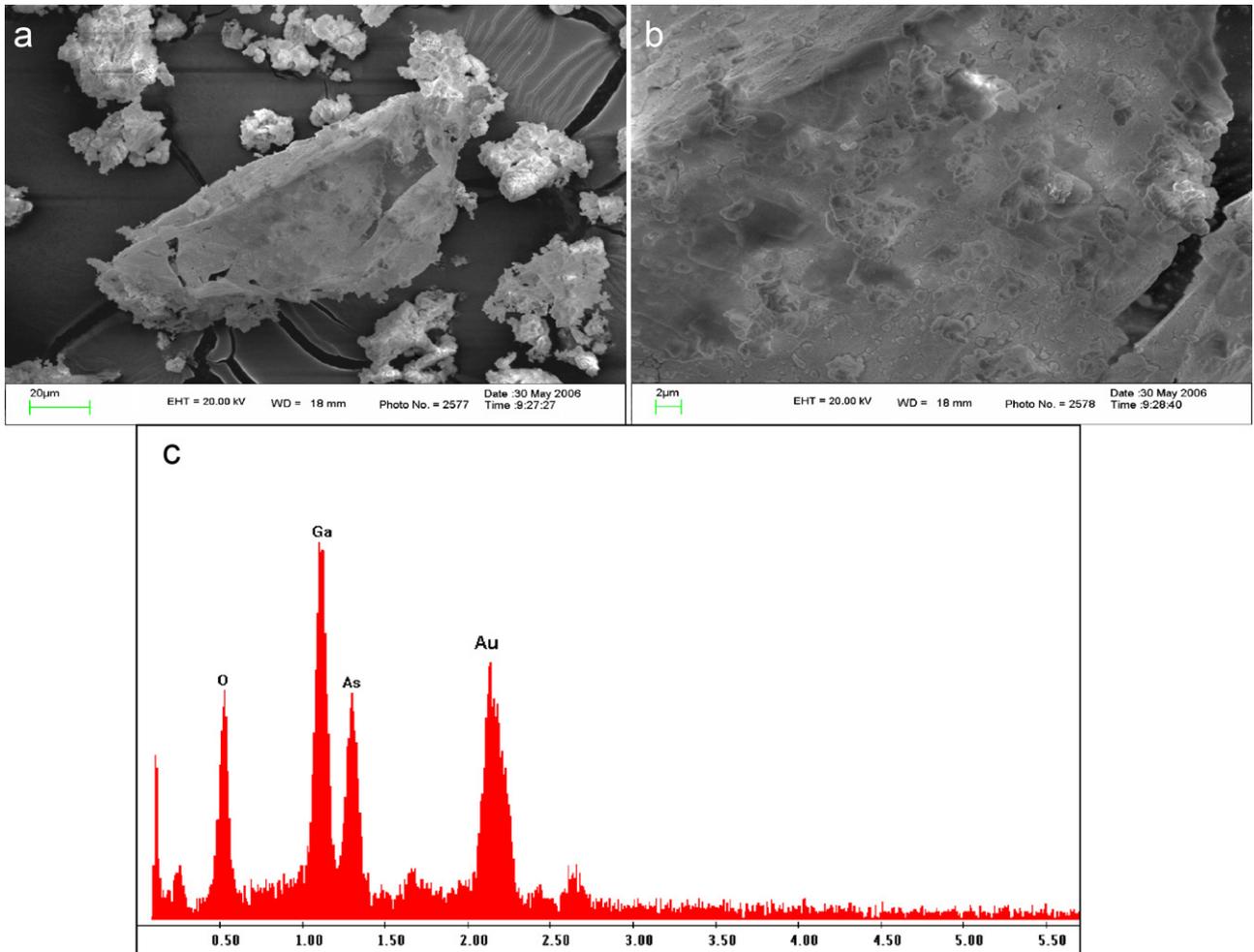


Fig. 15. SEM micrographs of the residue from the essay carried out at 350 °C with pure Cl₂. (a) Residue particle; (b) enlarged surface of the particle; (c) residue analysis of the essay carried out at 350 °C with pure Cl₂.

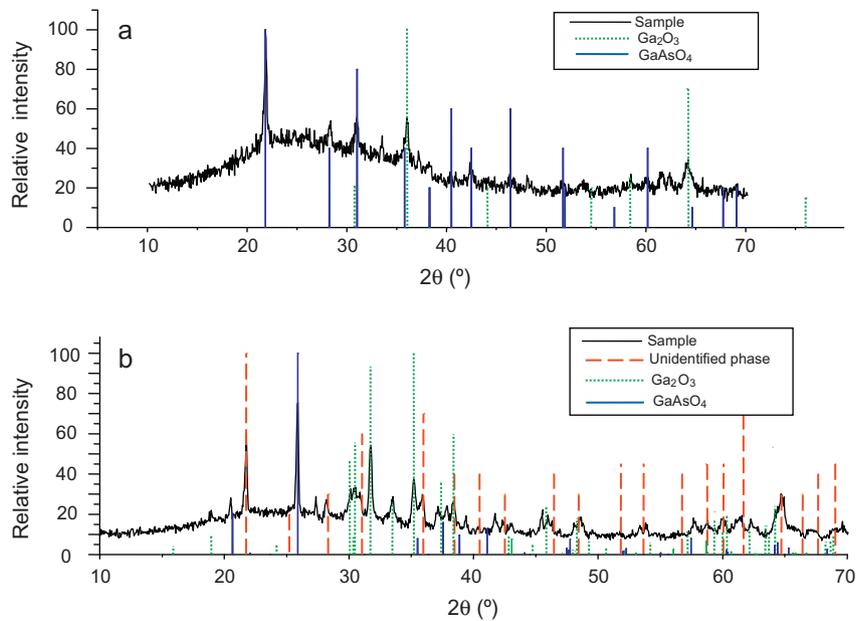


Fig. 16. Diffractograms of the residues from the essays carried out with pure Cl₂. (a) 500 °C; (b) 700 °C.

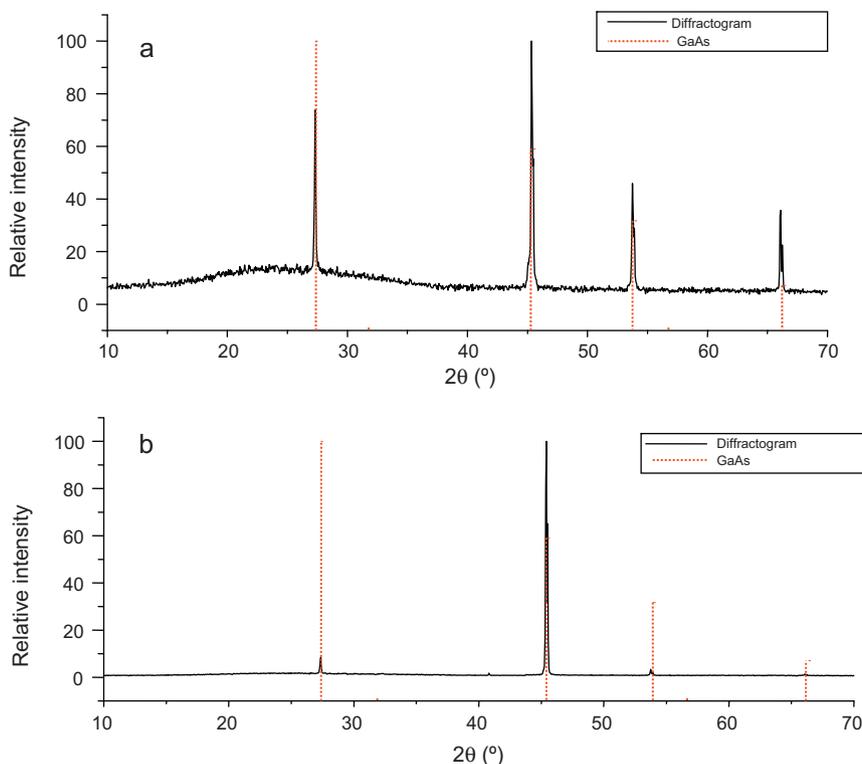
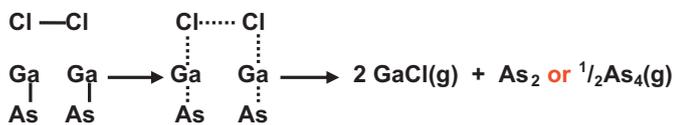


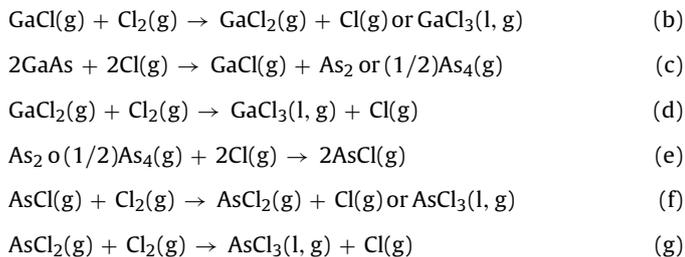
Fig. 17. Diffractograms of the residues from the essays with a Cl_2 partial pressure of 0.2 atm. (a) 300 °C; (b) 500 °C.

chlorinated instead As is. Then initiation includes adsorption of Cl_2 on As atoms of GaAs. Adding possible propagation steps, a mechanism could be expressed as:

Stage 1 (initiation)



Stage 2 (propagation)



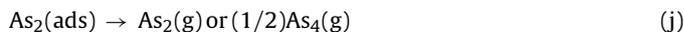
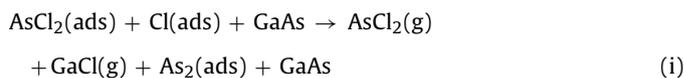
Assuming control by stage 1, the decrease of induction time as temperature increases (Fig. 6) can be explained based on an increasing rate on $\text{GaCl}(\text{g})$ formation, due to the break of Ga–As is favored, which faster increase Cl radicals concentration through the first propagation step, b.

Finally, reaction is sustained due to formation of the very active $\text{Cl}(\text{g})$ radicals at several of propagation steps, two of them (d, g) also accounts for GaCl_3 and AsCl_3 products formation.

4.3.2. Medium temperature range (300 °C and 500 °C). Catalytic behavior

As temperature increases Cl_2 adsorption on GaAs could be enough unfavorable to avoid the effective participation of step

a. The addition of reaction products must generate the reaction initiation. Singh and Krout [20] found that AsCl_3 reacts with GaAs forming $\text{GaCl}(\text{g})$, $\text{GaCl}_2(\text{g})$ and $\text{As}(\text{g})$ at this temperature range, therefore the following steps, can be added:



where Cl radicals are directly formed the initiation step, h. This accounts for decreasing induction time with increasing temperature (Fig. 11) at 300–500 °C range due to acceleration of Cl radicals concentration. Besides, the increase of induction time with decrease of p_{Cl_2} (Figs. 12 and 13) suggests the simultaneous participation of step d whose rate will proportional to $\text{Cl}_2(\text{g})$ concentration. Therefore, once reaction starts catalyzed by gaseous products supply, also propagation steps associated the non autocatalytic regime also operate.

4.3.3. High temperature range (600 °C and 900 °C). Non catalytic behavior

For this temperature range again direct contact between GaAs with $\text{Cl}_2(\text{g})$ is enough to produce chlorination without needing to add reaction products. However for this temperature range step a cannot be considered as for autocatalytic regime. For highest temperature dissociation of $\text{Cl}_2(\text{g})$ can occur. Fig. 19 shows a calculation of amounts of equilibrium species in a $\text{Cl}_2(\text{g})$ – $\text{N}_2(\text{g})$ mixture at several temperatures. This diagram shows that the concentration of atomic chlorine $\text{Cl}(\text{g})$ is almost null at low temperatures, and as the temperature increases, its molar fraction also increases, and above 500 °C, it is higher than 10^{-5} . This concentration could be enough to make important step b as a first propagation one. The

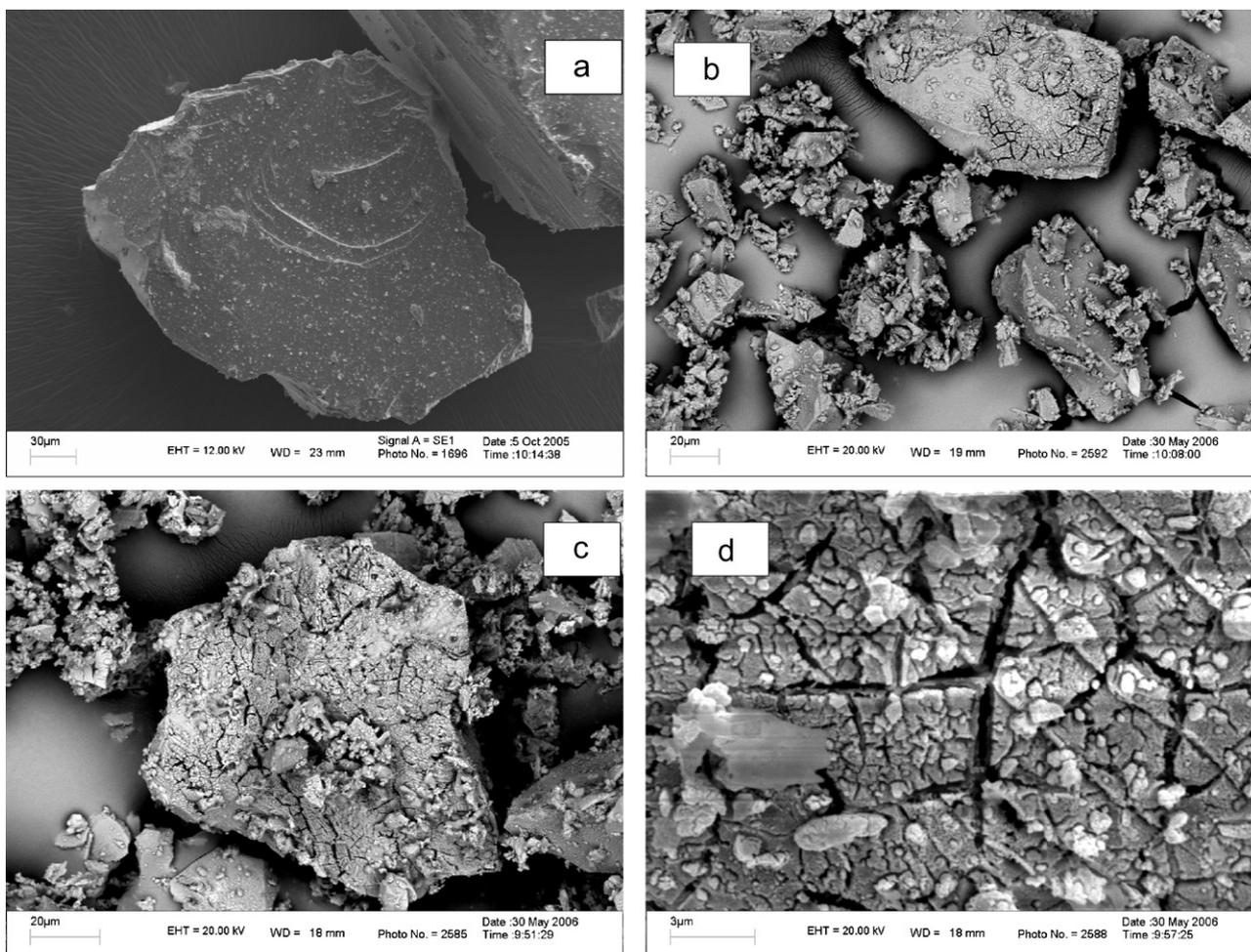


Fig. 18. SEM micrographs of GaAs particles partially attacked at 300 °C and a Cl₂ partial pressure of 0.2 atm. (a) Original particle of GaAs; (b) residue particles; (c) enlarged zone of one of the particles; (d) surface of an attacked particle.

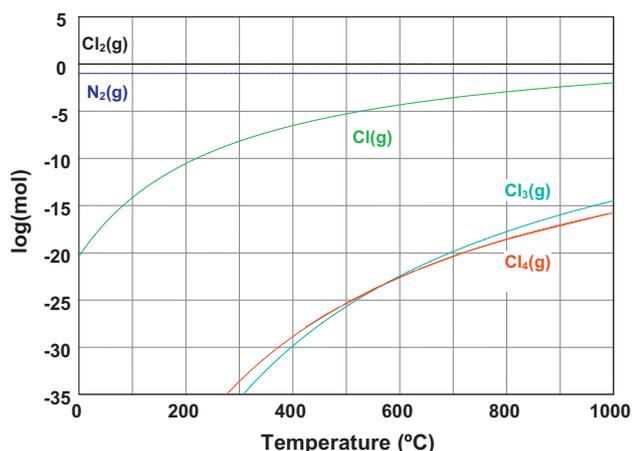


Fig. 19. Equilibrium diagram of the chlorine species at different temperatures and a Cl₂ pressure of 0.9 atm.

decreasing on induction time observed for increasing temperature for highest range (Fig. 11) can be explained from Fig. 19 because of concentration of Cl radicals increases with temperature.

5. Summary

GaAs chlorination with Cl₂ is feasible under several conditions, forming different products according to the environment to which

the system was exposed. The variation of Gibbs standard free energy versus temperature between –30 and 1000 °C shows, for all the proposed reactions that they are thermodynamically feasible in the established direction.

GaAs chlorination with Cl₂ is quite favorable in the temperature range between –30 and 900 °C, and it occurs at a high reaction rate, even at low temperatures. The system, at the studied temperature range, presents three intervals according to the way the reaction starts. Between –30 and 200 °C, the reaction starts by chlorine adsorption on the GaAs surface and the subsequent breakdown of the bond between Ga and As. Between 300 and 500 °C, the behavior is autocatalytic, requiring the presence of a reaction product such as AsCl₃ for the reaction to begin. Above 500 °C, there is a direct reaction between Cl₂ and GaAs due to the formation of atomic chlorine. The reaction temperature has little effect on the chlorination rate although it influences notably the induction times and determines if the reactions products volatilize or remain as solid or liquid residues into the crucible.

In the temperature range between –30 and 200 °C, the reaction is completed in approximately 8 or 9 min. Between –30 and 110 °C, the reaction causes a mass gain, whose magnitude varies according to the working temperature. These mass gains are due to different factors: adsorption of Cl₂ on the sample at –30 °C; at a higher temperature solid and/or liquid products are formed, and a partial evaporation of some species occurs, which is produced by the exothermic effect of the GaAs chlorination reaction. The Cl₂ partial pressure for the different studied temperatures has a marked

influence on the chlorination rate, varying the required time to complete the reaction between about 8 min at higher partial pressures and 25 min for the lowest. Also, as in the isothermic essays at constant pressure, the influence of the exothermic effect produced by the chlorination reaction is observed, which causes a partial evaporation of some reaction products, producing a difference between the mass changes expected and those observed.

The chlorination rate of GaAs with pure Cl₂ (1 atm) in the temperature range between 300 and 900 °C is slightly affected by the reaction temperature. Between 300 and 700 °C, and after the reaction is finished, solid residues constituted by Ga₂O₃ and GaOAs₄ remain. The formation of these compounds is due to the interaction in gaseous phase of the trichloride of Ga and As from the chlorination of GaAs and the O₂ contained in the used Cl₂.

The effect of the partial pressure of Cl₂ on the chlorination rate at 300 and 500 °C is noticeable. The chlorination at 300 °C is completed in approximately 8 and 42 min, working with 1 and 0.2 atm of Cl₂, respectively. The residues of the chlorination at 0.2 atm contain only GaAs because the reaction stops due to a lack of products in the vapor phase which may continue catalyzing the chlorination reaction.

The reaction mechanism depends on temperature range. At all temperatures steps b–j operates. At temperatures between –30 °C and 200 °C, step a must be added as the initiation one. At temperatures between 300 °C and 500 °C, the initiation step involves the step h. Finally, at temperature between 600 °C and 900 °C, the initiation step is Cl₂(g) thermal dissociation.

6. Conclusions

The results obtained permit to state that GaAs chlorination is a viable methodology to recover Ga and As from GaAs. At low temperature, Ga and As chlorides are in solid and/or liquid state, and the pressure vapor diagrams versus temperature indicate that separation by distillation is feasible.

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References

- [1] R.R. Moskalyk, Gallium the backbone of the electronics industry, *Miner. Eng.* 16 (2003) 921–929.
- [2] D.R. Lide, *Handbook of Chemistry and Physics*, CRC Press Inc., Florida, 2006–2007.
- [3] W.S. Lim, S.D. Park, B.J. Park, G.Y. Yeom, Atomic layer etching of (100/111) GaAs with chlorine and low angle forward reflected Ne neutral beam, *Surf. Coat. Technol.* 202 (2008) 5701–5704.
- [4] J. Cui, L. Zhang, Metallurgical recovery of metals from electronic waste: a review, *J. Hazard. Mater.* 158 (2008) 228–256.
- [5] J. Cui, E. Forsberg, Mechanical recycling of waste electric and electronic equipment: a review, *J. Hazard. Mater.* B99 (2003) 243–263.
- [6] J.E. Hoffmann, Advances in the extractive metallurgy of selected rare and precious metals, *JOM* 43 (1991) 18.
- [7] P.K. Jena, E.A. Brocchi, Metal extraction through chlorine metallurgy, *Mineral Process Extractive Metallurgy Review* 16 (1997) 211.
- [8] S. Kubo, M. Yukinobu, O. Yamamoto, G. Nabeshima, J. Okajima, Recovery of high purity gallium metal from gallium-arsenide scrap, in: J.H.L. Van Linden, D.L. Stward Jr., Y. Sahai (Eds.), *In the Second International Symposium-recycling of Metals and Engineered Materials*, TMS, 1990, pp. 505–513.
- [9] A. Jenichen, C. Engler, Etching of GaAs(100) surfaces by HCl: density functional calculations to the mechanisms, *Surf. Sci.* 475 (2001) 131–139.
- [10] W. Hung, S. Wu, C. Chang, Low-temperature chlorination of GaAs(100), *J. Phys. Chem.* 102 (1998) 1141–1148.
- [11] P. Bond, P.N. Brier, J. Fletcher, W.J. Jia, H. Price, P.A. Gorry, Reactive scattering study of etching dynamics: Cl₂ on GaAs(100), *Surf. Sci.* 418 (1998) 181–209.
- [12] L. Jalabert, P. Dubreuil, F. Carcenac, S. Pinaud, L. Salvagnac, H. Granier, C. Fontaine, High aspect ratio GaAs nanowires made by ICP-RIE etching using Cl₂/N₂ chemistry, *Microelectron. Eng.* 85 (2008) 1173–1178.
- [13] W.S. Lim, S.D. Park, B.J. Park, G.Y. Yeom, Atomic layer etching of (100)/(111) GaAs with chlorine and low angle forward reflected Ne neutral beam, *Surf. Coat. Technol.* 202 (2008) 5701–5704.
- [14] F. Stietz, J.A. Schaefer, A. Goldmann, Chemisorption of chlorine on GaAs(100) surfaces studied by high-resolution electron energy-loss spectroscopy, *Surf. Sci.* 383 (1997) 123–129.
- [15] T. Ohno, Theory of adsorption of Cl₂ molecules on GaAs(001) surfaces, *Surf. Sci.* 357 (1996) 322–326.
- [16] Y.N. Park, J.K. Kim, J.H. Lee, Y.W. Joo, H.S. Noh, J.W. Lee, S.J. Pearton, N₂ effect on GaAs etching at 150 mTorr capacitively-coupled Cl₂/N₂ plasma, *Microelectron. Eng.* 87 (2010) 548–552.
- [17] F.M. Tunez, M. del C. Ruiz, J.A. González, Kinetics of chlorination of GaAs, in: *2nd Mercosur Congress on Chemical Engineering EMPROMER*, 2005.
- [18] *HSC Chemistry for Windows*, versión 5.1, Outokumpu Research, Finland, 2002.
- [19] F.M. Tunez, J. González, M. del C. Ruiz, Equipo experimental de laboratorio para realizar termogravimetrías en atmósferas corrosivas y no corrosivas, *PO60100450* (2007).
- [20] N.K. Singh, R. Krout, Thermal and electron-induced reactions of AsCl₃ on GaAs(100), *Surf. Sci.* 442 (1999) 442–454.
- [21] Card N° 20-0426, JCPDS Powder Diffraction File (2003).
- [22] Card N° 76-0573, JCPDS Powder Diffraction File (2003).
- [23] Card N° 89-4432, JCPDS Powder Diffraction File (2003).
- [24] Card N° 32-0389, JCPDS Powder Diffraction File (2003).