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THE ROLE OF CHEMICAL PROCESSES IN THE TECHNOLOGICAL TREATMENT OF GALLIUM ARSENIDE UNDER CONDITIONS OF LOW-TEMPERATURE NON-EQUILIBRIUM PLASMA REDUCED PRESSURE IN CHLORINE

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The article considers the basic processes occurring in a laboratory reactor during plasmachemical treatment of gallium arsenide (GaAs) in chlorine plasma. The treatment of GaAs has a significant influence both on etching processes of semiconductor material and on the formation of the stationary concentration of chlorine in the reactor. The chlorine atoms act as the main chemically active particle (CAP) in etching GaAs. Along with the processes of chlorine atom formation we deal with the physical processes of their heterogeneous recombination on the inner surface of the glass reactor and on GaAs samples. The work demonstrates experimentally the exaggeration of the rate constants of interaction of chlorine atoms with GaAs without taking into account the stages of heterogeneous recombination of chlorine atoms on the surfaces bounding the plasma zone. We carry out gallium arsenide etching in a flow reactor at low plasma gas flow rates and the constant total pressure. In order to study the diagnostic purposes and experimental determination of rate constants of target processes of chemical and heterogeneous CAP recombination directly in the zone of the positive column of the glow discharge in chlorine we use a relaxation pulse technique.

Introduction

The chemical industry reached the high levels in use, modification and processing of a wide variety of raw materials. Materials industries form a raw materials supply system, while the textile industry provided the market with goods for public consumption. Moreover, preprogrammed products are gaining the market share. There emerging the materials changing their characteristics in response to external parameters. Electronic devices combining various means of communication and modern technologies are appearing. It is possible through the combined efforts of different sciences: physics, mathematics, cybernetics and chemistry. And chemistry and chemical technology are the general items for creation of new materials and technologies. The nanotechnologies are impossible without the chemical aspect of materials production using the principles of self-organization and assembly as a fundamental aspect of innovative development.

Problem statement and description of the experimental plant

GaAs is a prospective material for micro- and nanoelectronics products. It uses not only for microwave chips based on it but also for various sensors and transducers in various fields [1, 2]. The properties of these devices are directly depending on GaAs processing regimes. The etching process is the most important one. The precision etching of crystalline materials such as gallium arsenide is often carried out in plasma-chemical reactors. It is a process of high quality and accuracy because of the large number of process parameters. It is important to set the discharge current, pressure and flow of the plasma gas (in our case chlorine or its mixtures with inert or molecular gases) and the temperature of the sample and gas mixture correctly. Optimization of each of the parameters is a special research. We set the parameters as follows: pressure p = 100 Pa, discharge current I = 11 mA, flow rate of plasma-forming mixture q = 1.3 cm^3/s. The sample temperature varied in the range T = 300–600 K. The selected parameter values are the most commonly used for plants of this type. Moreover, fixing the parametres at a constant level made possible to study the kinetics of recombination processes without taking into account the additional degrees of freedom of the system.

In chlorine plasma the main etching particles of gallium arsenide are chlorine atoms and molecules [3]. The source of the chlorine molecules is the plasma gas itself. It is produced directly in the vacuum section of the plant by the decomposition of the calcined $CuCl_2$ salt. Table 1. Processes influenced on the formation of atoms.

Table 1. Processes of formation and death of chlorine atoms in a reduced pressure discharge in the presence of GaAs samples

№	Process	Process scheme	Threshold energy; process rate constant
Processes of the chlorine atom formation:			
1	Dissociation of chlorine molecules by electron impact	$Cl_2 + e \rightarrow Cl + Cl + e$	2.5 eV
2	Dissociative electron attachment to chlorine molecules	$Cl_2 + e \rightarrow Cl_2^- \rightarrow Cl + Cl^-$	2.5 eV
3	Dissociative ionization of Cl_2	$Cl_2 + e \rightarrow Cl + Cl^+ + 2e$	15.7 eV
4	Ionization of chlorine molecules followed by ion-ion recombination	$Cl_2 + e \rightarrow Cl_2^+ + 2e$	11.50 eV
5	Ion-ion recombination	$Cl_2^+ + Cl^- \rightarrow 3Cl$	$(5–10)\cdot10^{-8}$ cm^3/s
6	Electron detachment from the negative chlorine ion	$Cl^- + e \rightarrow Cl + 2e$	3.4 eV
Chlorine atom death processes:			
7	Heterogeneous recombination of atoms on the reactor wall	$Cl \overset{\text{ст.}}{\rightarrow} 1/2\ Cl_2$	~10 s^{-1}
8	Volumetric (homogeneous) recombination	$Cl + Cl + Cl_2 \rightarrow 2Cl_2$	$10^{-31}–10^{-33}$ $cm^6\cdot s^{-1}$
9	Heterogeneous recombination on a GaAs sample	$Cl \overset{\text{GaAs}}{\rightarrow} 1/2\ Cl_2$	10–500 s^{-1}
10	Atomic chemical reaction with GaAs	$Cl + GaAs \rightarrow$ gallium chlorides	-
11	Molecular chemical reaction with GaAs	$Cl_2 + GaAs \rightarrow$ gallium chlorides	-

Under low-pressure gas discharge conditions, the concentration of chlorine atoms can reach 10^{16} cm^{-3} [4]. This level of atom concentration is a result of the processes of their formation and death (recombination) (see Table 1), including chemical interaction with GaAs. In order to assess the contribution of processes *7* and *9* compared to the target etch process *10* (see Table 1) we used samples of unilaterally ground gallium arsenide plates. We do not consider the death of atoms in the bulk (process *9)* because of its low probability under reduced pressure conditions.

The assessment of the various chlorine atom recombination processes is relevant due to the priority technological approaches to atomic level material processing (precision surface finishing). The uncontrolled consumption of CAP becomes an important aspect of recombination. The surface recombination (a process without a chemical reaction) in conjunction with ion fluxes to the surface confining the plasma zone can regulate the number of active centres on the surface of the treated material. Fig. 1. A vacuum diagram of the experimental plant.

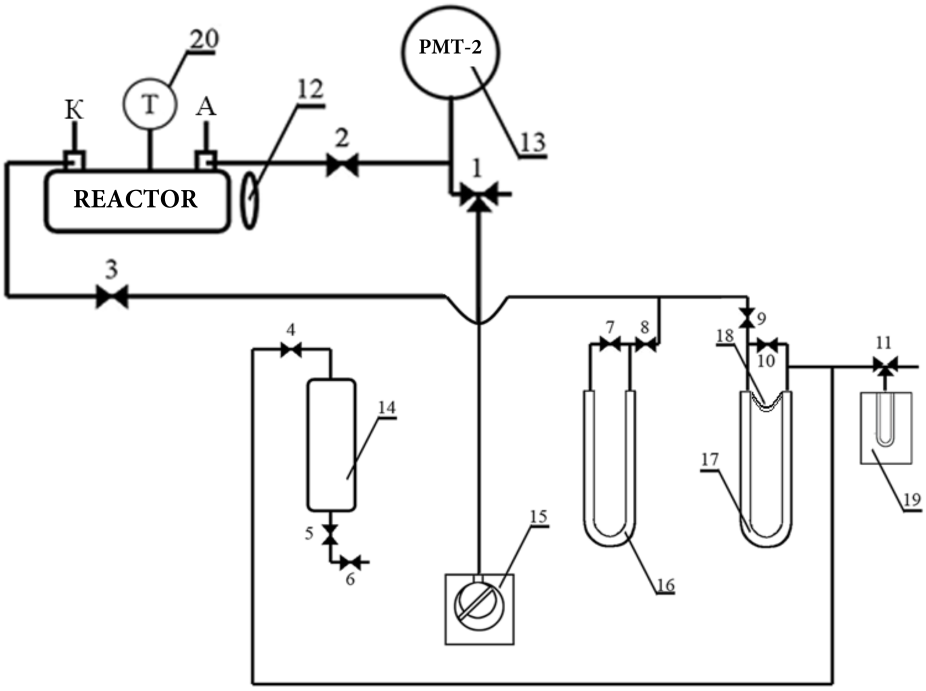

Fig. 1. Diagram of the vacuum part of the experimental plant: *1-11* two- and three-way vacuum cocks; *12* - split flange connection for loading samples into the reactor; *13* - gauge lamp PMT-2; *14* - cylinder for plasma gas; *15* - forevacuum pump VN-461; *16* - U-shaped oil pressure gauge; *17* - U-shaped oil rheometer for measuring gas flow rate; *18* - calibrated capillary for monitoring gas flow rate; *19* - heater for heating an ampoule with $CuCl_2$ to produce pure chlorine; *20* - temperature measuring sensor

We placed the GaAs sample on the inner wall of the reactor. A FLUKE 289 universal temperature meter, fitted with a calibrated thermocouple uses to measure the temperature of the sample. We measure the temperature on the outside of the reactor. The reactor placed in a resistance-type thermostat. In measuring the temperature of the samples, we assumed the temperature of the outer wall of the reactor is not significantly different from that of the inner wall [5]. The reactor was made of P-49 glass. The wall thickness is 0.65 mm. In order to study recombination processes in plasma we used relaxation pulse method (RPM) along with emission spectroscopy (ES) (to determine the rate constant of chemical interaction of chlorine atoms with GaAs) and absorption spectroscopy (AS) (to determine the rate constant of wall recombination of chlorine atoms - processes *7* and *9*, Table 1). Discussion of the methodological issues of implementing this methodology [6]. The total reactor load with gallium arsenide did not exceed 20%. It was necessary to eliminate the influence of the interaction products of GaAs with chlorine on the electrophysical parameters of the plasma.

During the experiments, especially at low temperatures when the volatility of the products of interaction between GaAs and chlorine was quite low, the surface of the sample could become contaminated with chlorides. This fact had to be taken into account in planning the experiments. Therefore, the time of each experiment lasted no longer than 10 sec. During this time at all temperatures the chloride contamination of the sample was minimal. Nevertheless, each batch of experiments started with the cleaning of the inner wall of the reactor and the samples. In order to dry the glass reactor we cleaned it with hydrofluoric acid, then with distilled water and finally with acetone. The criterion for the reactor inner wall cleanliness was the stable reproduction of the rate constant for the process of heterogeneous recombination (k_r^g) of chlorine atoms on molybdenum glass at a level k_r^g = 10–14 s^{-1} (process probability γ_r^g = 8–10^{-4}) at room temperature [7].

Results and discussion

The chlorine plasma as a rather simple plasma-forming medium. It allows us to study the processes of heterogeneous recombination of chlorine atoms and chemical interaction of chlorine atoms with different samples, including GaAs during the pause between current pulses. Chlorine atoms expended in the formation of interaction products (chlorides), providing the etching process. The higher the concentration of chlorine atoms in the reactor, the higher both the process speed 10 and the efficiency of the plasma treatment of materials. The chlorine atoms produced during discharge combustion (processes 1-6) and reached stationary concentration during 0.3-0.7 sec. On the contrary, processes 7-9 are non-target ones, as their only result is loss (recombination) of chlorine atoms with formation of initial Cl_2 molecule. Thus, plasma chemical treatment of GaAs will only be effective if the contribution of processes 7-9 is small.

The contribution of each of the above recombination processes considered by the processing experimental kinetic dependences (time dependences of changes in the concentration of chlorine atoms or molecules). We obtained them during the implementation of RPM, using emission and absorption spectroscopy. The rate constant is a quantitative measure of process efficiency. In our work process 10 diagnosed by the emission of atomic chlorine at the leading edge of the current pulse (emission wavelength 452.6 nm, transition $5p^2 p_{3/2}^0 \rightarrow 4s^2 p_{3/2}$). We obtained spectral kinetic relationships reflecting the time course of the chlorine atom concentration in the reactor by processing a series of experiments (RPM and ES). If the heterogeneous recombination of chlorine atoms on the surfaces confining the plasma zone were negligible, the constant obtained by treating this kinetic relationship corresponded to the dynamics of the process 10. In order to identify the efficiency of heterogeneous recombination, we also ignited the discharge in pulsed mode, realizing RPM, but together with AC.

The experimental dependencies of the radiation intensity of atomic chlorine were linearized in coordinates:

$$\ln(I_0 / I) = f(t), \tag{1}$$

where I_0 and I are the relative intensities of Cl (452.6 nm), t is time.

The dependence described the normalized intensity of the I_{tr} radiation passed through the plasma reactor by the DDS-30 lamp.

$$I_{\mathrm{tr}} = 1 - e^{-k_r t}, \tag{2}$$

where k_r is the rate constant of the process of heterogeneous recombination of atoms in a chlorine plasma.

The rate constant of the process described by equation (1) is the tangent of the slope of this experimental relationship.

The probability of processes of heterogeneous recombination of chlorine atoms on GaAs and on the glass wall of the reactor is different. Two processes, 7 and 9, respectively (see Table 1) described the heterogeneous stage of recombination of chlorine atoms on the materials limiting the plasma zone. We consider both these two processes by means of a balance equation written for the positive column zone of the glow discharge in chlorine in the pause between current pulses:

$$k_r^g S_\Sigma = k_r^g(\mathrm{GaAs}) \cdot S(\mathrm{GaAs}) + k_r^g(\mathrm{Gl}) \cdot S(\mathrm{Gl}), \tag{3}$$

where k_r^g - is experimentally fixed rate constant of process of heterogeneous recombination of chlorine atoms on materials, limiting plasma zone; S_Σ - is area of internal surface of reactor within positive column of glow discharge (301.44 cm^2; k_r^g (GaAs) and k_r^g (Gl) - are rate constants of processes of heterogeneous recombination of chlorine atoms on gallium arsenide and glass respectively; S(GaAs) and S(Gl) - are accordingly total areas of gallium arsenide samples, placed in the zone of positive column of discharge, and internal surface area of reactor not occupied by GaAs samples: $S(\mathrm{Gl}) = S_\Sigma - S(\mathrm{GaAs})$.

We obtain the calculated data from equation (3) for the rate constant of heterogeneous recombination of chlorine atoms on gallium arsenide:

$$k_r^g(\mathrm{GaAs}) = \frac{k_r^g S_\Sigma - k_r^g(\mathrm{Gl}) S(\mathrm{Gl})}{S(\mathrm{GaAs})}. \tag{4}$$

According to the work, the rate constant of the process of heterogeneous recombination of chlorine atoms on the glass wall of the reactor is practically independent of temperature and remains constant over a wide temperature range (325–600 K). Thus, we can neglect by its temperature dependence and considered constant over the entire temperature range investigated (k_r^g (Gl) = 14 s^{-1}). In contrast, we can observe this dependence for monocrystalline gallium arsenide. We obtained it from experimental data (*PIM* and *AC*) and using calculations of equation (4). Fig. 2 shows the results.

The constants we obtained increase over the whole temperature range investigated, although in some works there is a decrease in the probabilities of chemical (heterogeneous recombination) of atoms (radicals) with increasing temperature [8-10]. This fact is explained by the conditions of the experiment. Thus, the methodology for identifying the probabilities of heterogeneous processes involves investigations in the afterglow zone of the discharge. Under these conditions, interaction products (e.g. chlorides in the case of chlorine or chlorine-containing plasma-forming media) form on the surface of the samples as the temperature increases. In our experiments, we placed the sample in the zone of the positive column of the low-pressure glow discharge. It purified by ion streams intensely bombarding the GaAs surface. We recorded the formation of products on the surface of the sample to be treated (the volatility of gallium chloride is not the same at different temperatures). In order to prevent the influence of products of plasma chemical interaction between GaAs and chlorine, at each batch of experiments we subjected the samples to multistage cleaning consisting of their dispersion washing in distilled water and sequential treatment in orthoxylene and acetone followed by drying at a temperature of not 45–65 °C.

It allows us to determine process rate constants directly for pure GaAs surfaces. In our opinion, it is more relevant for the purposes of material processing at the micro- and nanoscale.

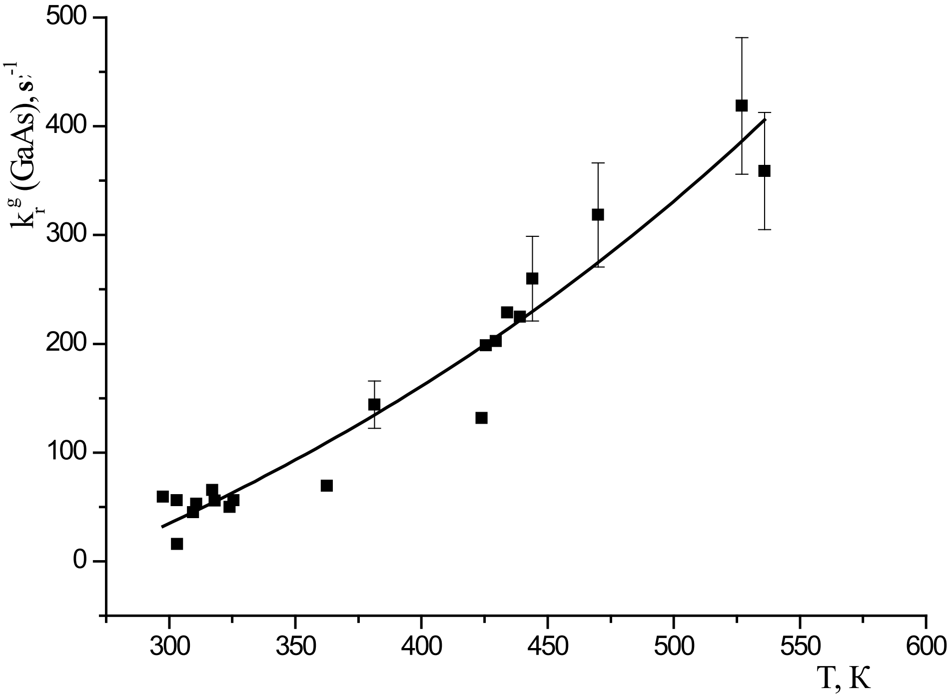

Fig. 2. Temperature dependence of the rate constant for heterogeneous recombination of chlorine atoms on gallium arsenide

By Fig. 2, the data correspond to the values of rate constants of processes of heterogeneous recombination of chlorine atoms on GaAs taking into account the partial loading of the reactor with the investigated samples. But a detailed examination of the kinetic scheme of the process has led us to suggest that these data may be exaggerated. The RPM methodology together with AC does not take into account the change of concentration of chlorine molecules. It can occur not only due to processes 7 and 9 (heterogeneous recombination) and due to process 11 (interaction of Cl_2 with GaAs). It impossible to separate these processes directly within RPM, so we proposed the following solution to this problem. We created such conditions in the discharge. So, during the discharge combustion, practically all the molecular chlorine dissociated to form atoms. We can achieve these conditions by introducing oxygen into the discharge zone. For example, [11] shows the degree of dissociation of Cl_2 in a mixture of chlorine and oxygen in equal ratios by changing the electrophysical parameters of the plasma increases up to 95%. Thus, in chlorine-oxygen plasma the process 11 will not affect the obtained absolute values of rate constants of processes of heterogeneous recombination of chlorine atoms on the surfaces bounding the plasma zone. Fig. 3 correlates with these data.

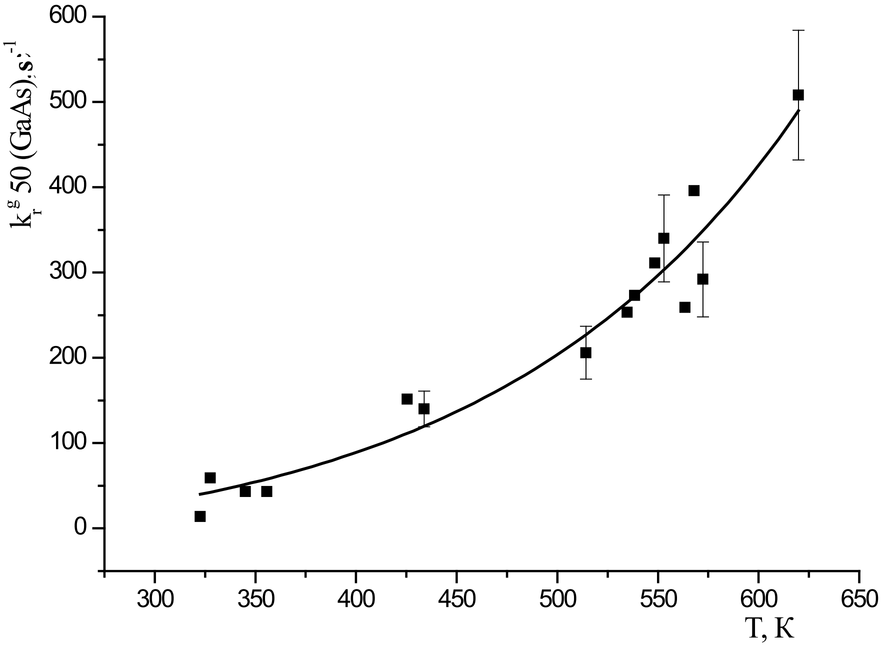

Fig. 3. Temperature dependence of rate constant for heterogeneous recombination of chlorine atoms on gallium arsenide in a chlorine-oxygen mixture in the ratio 50% Cl_2 to 50% O_2 in the plasma-forming mixture

Comparison of the results shown in Fig. 3 and 4 suggest the temperature dependence of the rate constant for the process of heterogeneous recombination of chlorine atoms on gallium arsenide in a plasma chlorine-oxygen mixture gives more accurate data with respect to process 9. These data allows us to define the rate constant of the chemical interaction of GaAs with atomic chlorine. For this purpose we use RPM in conjunction with ES as the variation of the pulse technique. It is sensitive only to changes in the concentration of atomic chlorine.

In order to obtain spectral kinetic dependences of chemical interaction processes of chlorine atoms with GaAs we use the approach with useful signal accumulation for decreasing the signal/noise ratio.

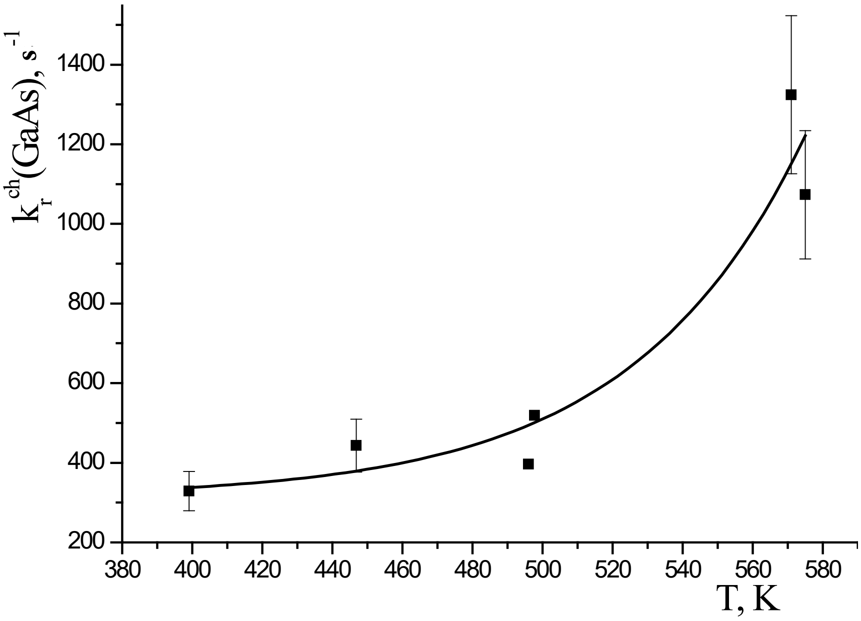

Fig. 4. Temperature dependence of the rate constant of the chemical interaction of chlorine atoms with gallium arsenide

Conclusion and recommendations

The work quantifies the processes occurring in chlorine plasma during the treatment of gallium arsenide. We obtained independently the rate constants of processes of heterogeneous recombination (death) of chlorine atoms on surfaces limiting plasma zone and chemical interaction of atomic chlorine with GaAs. The data derived from independent experiments. The samples to be treated were placed directly in the plasma zone. It allows us to obtain the experimental data for sample surfaces not contaminated by products of gallium arsenide interaction with chlorine. The results of the work can be applied for the formulation of process routes using plasma chemical treatment of gallium arsenide and for purposes of mathematical modelling, usually preceding expensive experiments with samples containing rare-earth elements.

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