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Plasma Nanoscale Structuring of GaAs in a High-Frequency Discharge of Freon and Freon/Argon Mixtures

A. V. Dunaev*

Institute of Thermodynamics and Kinetics of Chemical Processes, Ivanovo State Institute of Chemical Technology, Ivanovo, 153000 Russia

**e-mail: dunaev-80@mail.ru*

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Abstract—The high-frequency discharge plasma in chlorine-containing gases is widely used in microelectronics and nanoelectronics technology for the purification and "dry" etching of the surface of semiconductor plates and integrated circuit functional layers. In this paper we have studied the surface quality (based on roughness data) of GaAs semiconductor structure after plasma chemical etching in plasma of Freon R12 and a Freon/argon mixture. Freon R12 is often used for etching Si, Ge, and other materials (GaAs, GaP, and InP), ensuring technologically acceptable interaction rates, and satisfies the requirements of anisotropy and selectivity. Mixtures of "active" gases with inert ones (He or Ar) are also widely used; they can act both as diluent gases and ion sources for the ion bombardment of samples to provide more ionic stimulation of desorption of reaction products that improve the useful properties of the surface with a slight decrease in etching rate.

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INTRODUCTION

Nowadays, the modern approach to the formation of micro- and nanostructures in electronics production are closely tied with technological approaches of treating metals and semiconductors with the latest research in the field of plasma technology and knowledge-intensive processes. For example, the use of plasma allows one to obtain unique new materials with desired properties that are difficult to obtain by conventional methods.

Chlorine-containing plasma is commonly used for etching A^3B^5 semiconductors [1]. This is due to the volatility of Group 5 halides; therefore, they are effectively removed from the surface into the gas phase. Group 3 halides, especially fluorides, have low volatility under technologically acceptable temperatures; therefore, "pure" fluorine-containing plasma is inapplicable for etching.

One crucial process is the formation of a topological relief on the surface of GaAs, which is one of the most promising materials of electronics for the future. This is explained by the combination of a large band gap and high carrier mobility, which allows one to create a wide range of GaAs-based high-speed devices. Furthermore, GaAs is the main material of quantum-based nanoelectronics based on heterotransitions in the AlGaAs system.

Here, we have studied Freon R-12 (CCl_2F_2). Freon R-12 (or dichlorodifluoromethane) is a colorless and odorless gas. Freon molecules are chemically inert; this gas is nonexplosive even when it is in contact with an open flame. Freon R-12 plays an important role in the plasma etching industry [2], since it dissociates into chemically active Cl and F atoms. With respect to technology, its use for etching mixtures containing an inert gas, in particular argon, are of great interest, which leads to a substantial improvement in the surface quality of samples [3] and allows one to reduce the reagent gas flow without substantially reducing the etching rate and the emission of toxic substances into the atmosphere.

Due to the increasing requirements for the surface quality after treatment, the question of adjusting methods after the etching operation remains acute. With respect for the relief studies, one of the most promising is atomic force microscopy (AFM), whose main advantages are the ability to obtain reliable data on the height of the microrelief, the absence of additional intermediate procedures, the ability to obtain nanometer resolution in air, etc.

The kinetics and mechanisms of GaAs plasma chemical etching in Cl_2, HCl, and mixtures of HCl with argon, chlorine, and hydrogen under the same external discharge parameters were studied [4, 5]. It was found that the HCl plasma is characterized by lower GaAs etching rates providing, however, significantly less surface roughness after treatment. With respect to the plasma of hydrogen chloride and mixtures thereof, is has been shown that the optimal com-

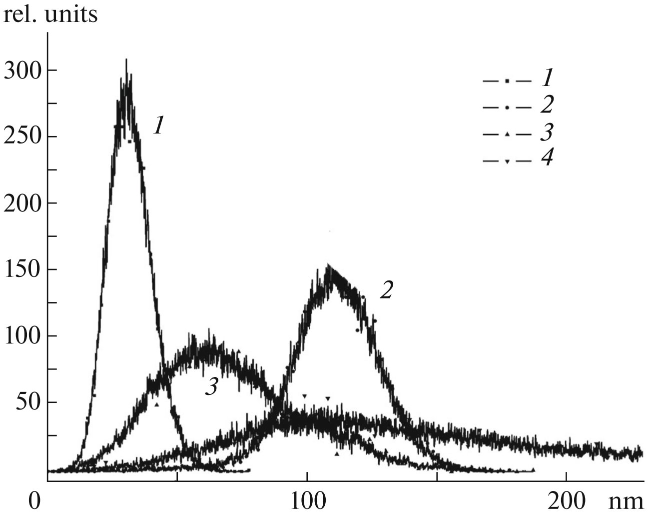

Fig. 1. Histogram of the distribution of roughness (σ) on the surface of the GaAs sample treated in the Freon R12 plasma: *1*—$W_{\rm rf} = 950$ W, $W_{\rm bias} = 0$ W, $P = 1.4$ mTorr, $\tau = 30$ s; *2*—$W_{\rm rf} = 950$ W, $W_{\rm bias} = 0$ W, $P = 1.4$ mTorr, $\tau = 150$ s; *3*—$W_{\rm rf} = 950$ W, $W_{\rm bias} = 300$ W, $P = 1.4$ mTorr, $\tau = 30$ s; *4*—$W_{\rm rf} = 950$ W, $W_{\rm bias} = 300$ W, $P = 1.4$ mTorr, $\tau = 150$ s.

bination of etching rate and surface roughness is achieved in a mixture of hydrogen chloride and argon by the effective purification of the surface from argon atoms. Such a situation is natural in the case of a high-frequency discharge in the studied plasma-forming media.

The aim of this work was to identify general rules of changes in the surface roughness (as processing quality index) of the semiconductor structure after etching in high-frequency plasma of Freon R-12 and mixtures thereof with argon for further use of the results in the technology of formation of topology on gallium arsenide plates.

EXPERIMENTAL

To study the plasma-chemical processes in conditions of a high-frequency discharge, we used a Platran-100HT installation. It was designed for the plasma chemical etching of semiconductor materials and metal films. The installation allows the treatment of plates with 100 mm in diameter and smaller plates from 0.3 to 2 mm in thickness.

The system was pumping out using a mechanical rotary vane (Leybold BCS, capacity 30 m^3/h) and a turbo-molecular (TMP 803 LMTC, capacity 803 L/s) pumps to provide the pressure of the residual gases on the order of 10^{-6} Torr. Operating pressure in the reactor was controlled using a pressure sensor with an upper range limit of 0.1 Torr. The plasma gas flow rate was measured and controlled using a flowmeter with an upper range limit of 500 cm^3/min. The temperature control system provides automatic stabilization of the substrate temperature by controlling the coolant flow rate. In our experiments, the power of discharge was constant and equal to 950 W; the plasma gas flow rate was 20 cm^3/min (~1.4 mTorr). The etching time varied from (30–150 s) every 30 s. Sample parties were treated without the bias potential on the substrate holder and at the maximum possible bias of 300 W.

Argon was used as the gas-mixture component. Pure argon was used (MRTU 51-77-66); the main gas content was no less than 99.985%.

The samples subjected to etching were pieces of polished GaAs plates (with a thickness of 400 μm and an area of 1 cm^2). The surface relief of the samples was controlled using a Solver P47-PRO atomic force microscope, which allows one to study the surface of the samples at sites up to 50 × 50 μm. The semicontact scanning method was used.

RESULTS AND DISCUSSION

We carried out a comparative study of plasma-chemical etching of GaAs at different parameters in order to identify the optimum flow of the process. Our experiments have shown that, even after prolonged (over 10 min) exposure of GaAs in the CCl_2F_2 (Freon R 12) media without discharge, the change in the sample weight is at a level of error of weighted measurements, suggesting that the interaction between molecules CCl_2F_2 with gallium arsenide did not proceed or proceeded at a very low rate. Therefore, starting CCl_2F_2 molecules can be eliminated from the set of reactive species in the plasma-etching conditions.

As was already mentioned, one essential aspect of the etching in technology is the surface quality (roughness) after etching. The indicator of average square roughness of a nontreated plate is σ ~2 nm. Figure 1 shows the distribution histogram of the average surface roughness on the etched samples in the mentioned plasma forming gas (freon) depending on the exposure time. The surface roughness of the sample σ varied from 7 to 14 nm at the treatment time 30–150 s (curves *1* and *2*, respectively). The growth of the value of σ of the surface is characteristic of the sample treatment in the plasma of halogen gases and is suitable in terms of increasing the time of the interaction between the reactive particles of the plasma medium and the semiconductor plate [6].

In the absence of the bias potential, the energy of the ions is not sufficient to result in the efficient gasification of etching products or destruction of the polymer film. It contributes to the formation of a masking layer on the surface, which prevents the access of chemically active species. It seems that the limiting step in the process is the diffusion of fluorine and chlorine atoms to the surface of the solid phase (semiconductor) or fracture of the masking surface layer. Increasing the bias power to 200–300 W and the

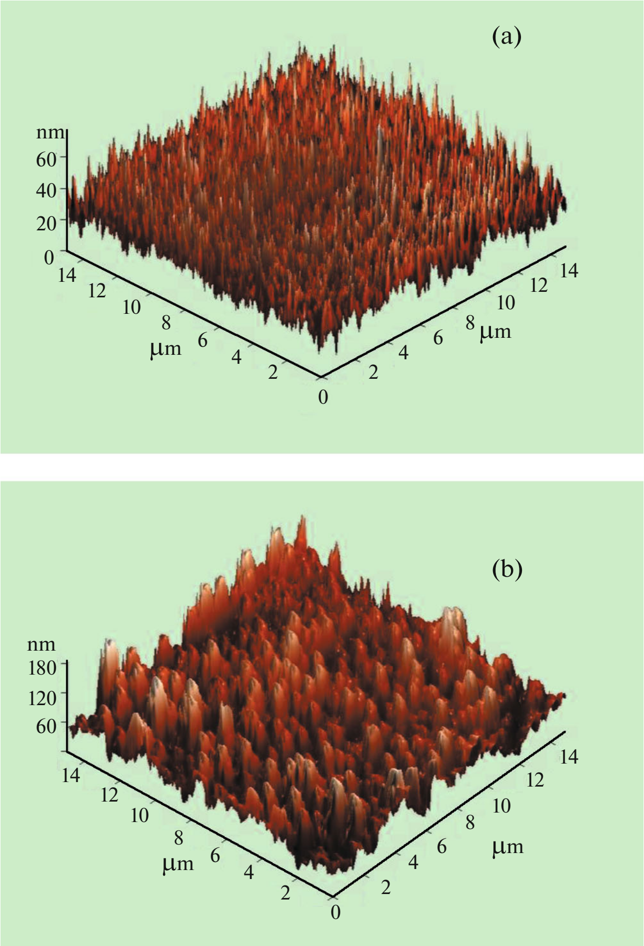

Fig. 2. (Color online) Surface of GaAs etched in the Freon R-12 plasma. $W_{rf} = 950$ W, $P = 1.4$ mTorr, $\tau = 30$ s: (a) $\sigma = 7$ nm, $W_{bias} = 0$ W; (b) $\sigma = 20$ nm, $W_{bias} = 300$ W.

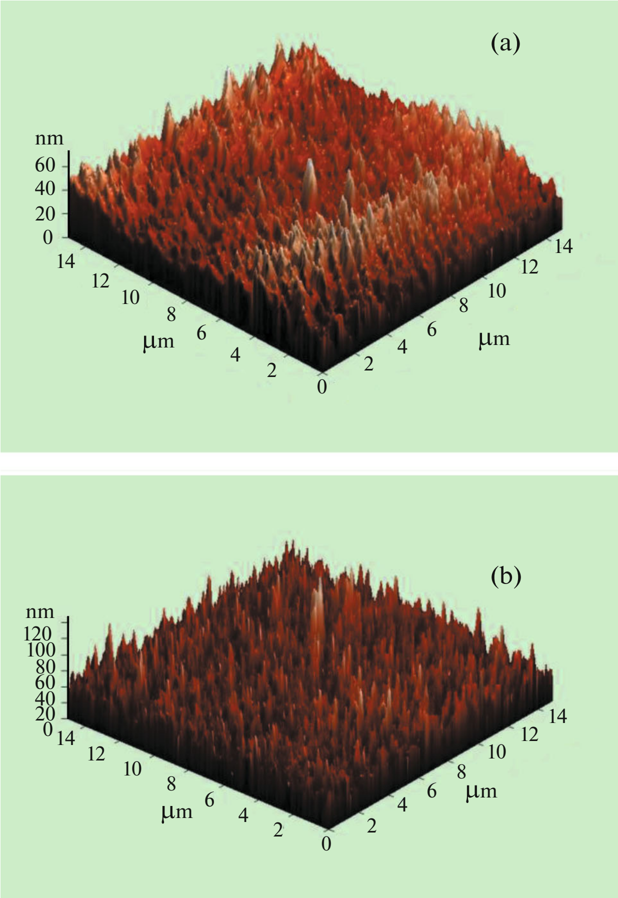

Fig. 3. (Color online) Surface of GaAs etched in the Freon R-12 + Ar plasma. $W_{rf} = 950$ W, $P = 1.4$ mTorr, $\tau = 90$ s: (a) $\sigma = 6$ nm, $W_{bias} = 0$ W; (b) $\sigma = 10$ nm, $W_{bias} = 300$ W.

accompanying growth of the energy of physically active particles lead to increasing rates of ion-stimulated desorption of the reaction products and the destruction of the surface layers of the material to ensure the complete purification of the treated surface.

In the light of the above, a higher etching rate is expected when compared to that in pure Freon without the bias and therefore a large surface roughness of the semiconductor surface under the same treatment times. This can be seen in the histogram (Fig. 1, curves *3* and *4*) and microimages of GaAs (Fig. 2). Even after the 30-s treatment, the value of σ is 20 nm, which is almost 3 times greater than the roughness of the etching without applying the potential to the substrate holder. After 150 s of plasma-chemical interaction with the surface of the sample, the value of σ is ~65 nm.

It can be assumed that, with a further increase in the treatment time (150 s), the rate of spontaneous chemical interaction will further increase, resulting in an extremely rough surface with traces of structure fracture and redeposition of the material and the reaction products on the sample surface. This is not acceptable for technology of the modern microelectronics and nanoelectronics. On the other hand, it explains the possibility to avoid the requirement for long-term treatment of gallium arsenide in the plasma-chemical reactor.

Regarding the R-12/Ar medium, the surface quality, under all conditions being equal and minor losses in etching rates, is considerably better. For example, the magnitude of σ after 90 s of plasma etching is only ~6 nm, whereas that in plasma without argon impurity is 11 nm, which can be used in technology of micro- and nanostructures. Figures 3 and 4 show the histogram of the average roughness distribution on the etched sample surface in a Freon/argon plasma mixture (R12 + Ar).

The surface of the GaAs samples treated in an HCl/Ar mixture in a DC glow discharge was studied in [3, 5]. The authors indicated that the quality of the surface is higher than that of the "pure" hydrogen

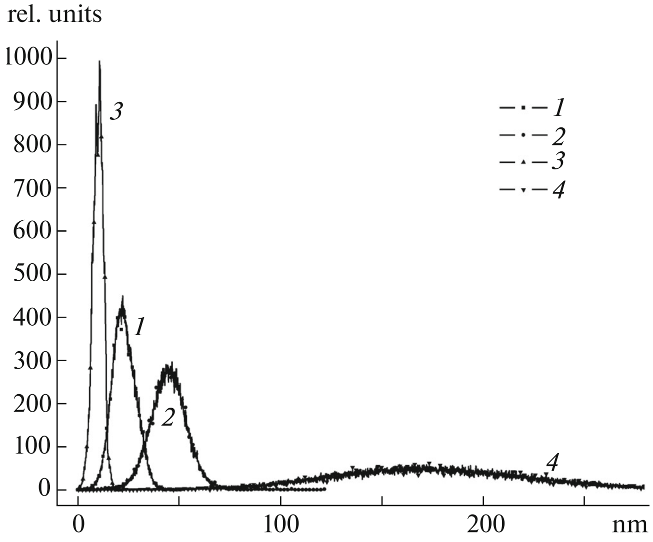

Fig. 4. Histogram of the distribution of roughness (σ) on the surface of the GaAs sample treated in the Freon R12 + Ar plasma: *1*—W_{rf} = 950 W, W_{bias} = 0 W, P = 1.4 mTorr, τ = 30 s; *2*—W_{rf} = 950 W, W_{bias} = 0 W, P = 1.4 mTorr, τ = 150 s; *3*—W_{rf} = 950 W, W_{bias} = 300 W, P = 1.4 mTorr, τ = 30 s; *4*—W_{rf} = 950 W, W_{bias} = 300 W, P = 1.4 mTorr, τ = 150 s.

chloride plasma. Since the rate of spontaneous chemical interaction in the mixture is lower, the resulting surface roughness should be lower as well. This suggests that in the mixture the ion stimulated desorption occurs much more efficiently and the "masking" effect of the surface of the reaction products is less pronounced. It follows that inert gases such as argon can act both as gas diluents (reducing the concentration of active particles, increasing the anisotropy of the process, and reducing the working gas flow rate) and ion sources for additional ion stimulation of the desorption of reaction products. This is true for a Freon/argon mixture in high-frequency discharge conditions.

Surface roughness (σ) depending on the etching time in the "pure" Freon R-12 and a mixture of argon with Freon (R-12/Ar) with the bias potential applied and without it

R-12			
W_{rf} = 950 W, W_{bias} = 0 W		W_{rf} = 950 W, W_{bias} = 300 W	
t, s	σ, nm	*t*, s	σ, nm
30	7	30	20
90	11	90	
		28	
150	14	150	65
R-12/Ar			
W_{rf} = 950 W, W_{bias} = 0 W		W_{rf} = 950 W, W_{bias} = 300 W	
t, s	σ, nm	*t*, s	σ, nm
30	3.5	30	3.7
90	6	90	10
150	10	150	41

It is believed that, at low bias power (0–50 W), the diffusion of chlorine and fluorine atoms to the surface of the solid phase or degradation of the surface of the masking layer is the limiting step of the plasma chemical interaction. Qualitatively, a similar situation results from, for example, etching of copper in the chlorine plasma [7] in temperature ranges not providing purification of the surface from the reaction products.

Increasing the bias power to 200–300 W, as in the case with the "pure" Freon, and the concomitant increase in energy of physically active particles leads to a growth in the rate of the ion-stimulated desorption of the reaction products and the degradation of the material surface layers, ensuring the complete purification of the treated surface. Thus, a higher etching rate than that in a Freon/argon mixture without a bias and, therefore, a large surface roughness of the semiconductor surface under the same processing times are expected. This can be seen on GaAs micrographs in Fig. 3. At the same 90 s treatment, the value σ is ~10 nm, which is almost two times greater than the etching roughness without applying the potential to the substrate holder.

These data are comparable to those obtained for "pure" HCl and a mixture thereof with Ar in a glow discharge of direct current, which is indicative of plasma of Freon R12 and a mixture of R12 + Ar being a very effective tool for the plasma etching of GaAs maintaining the quality of the surface characteristic of hydrochloric chemistry.

The data on the surface quality (roughness) of gallium arsenide after high-frequency etching in Freon R-12 and mixtures thereof with argon depending on time with the bias and without it are shown in the table.

CONCLUSIONS

Our conclusions are the following: a high-frequency discharge initiated in a gas atmosphere of Freon R-12 and a mixture of Freon and argon is an effective instrument for the dimensional structuring of the surface of gallium arsenide balancing between etching rates acceptable for techniques, purity of the process, and uniform sample surface. It is shown that increasing the bias power to 200–300 W and the concomitant growth of energy of physically active particles leads to an increase in the rate of ion-stimulated desorption of the reaction products and the destruction of the surface layers of the material to ensure the active purification of the treated surface of the semiconductor. The average roughness of the samples in the studied range of parameters varied from 3.5 to 65 nm, depending on the type of plasma-forming gas. Thus, one can determine the quality of the future semiconductor structure by adjusting parameters such as treatment time, the power of the bias potential, and the type of plasma medium.

Thus, Freon and a mixture of Freon with argon are promising plasma-forming media and can be effectively used in microelectronics and nanoelectronics.

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