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Surface treatment of gallium arsenide after etching in C_2F_5Cl-plasma

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In the work four different methods for surface treatment of gallium arsenide after etching in chloropentafluoroethane (C_2F_5Cl) plasma were presented; the stoichiometry of the upper layer, roughness, and the presence of impurities were studied. The most optimal of the methods is a combination of *ex situ* etching in hydrogen plasma followed by removal of the upper layer by liquid etching in $NH_4OH/H_2O_2/H_2O$. By this method, it is possible to remove almost all contaminants, both from the surface and from the side walls of the profile with an acceptable level of roughness.

Keywords: chloropentafluoroethane, plasma-chemical etching, gallium arsenide, surface.

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The progress in GaAs-based microelectronics is attributable to certain advantageous features of gallium arsenide, namely a direct band gap and a high electron mobility [1]. GaAs transistors are radiation-resistant and may operate at microwave frequencies [2,3]. This turns them into useful components of modern satellite communication and navigation systems. Vertical channel positioning is used to raise the current level in such transistors [4]. A channel of this kind may be formed by plasma-chemical etching in chlorine-containing plasma. This method is characterized by high anisotropy and the lack of side etching [5–7]. At the same time, stoichiometry violation may occur in the GaAs structure under the influence of plasma particles, making epitaxial regrowth of the channel infeasible. Thus, the problem at hand is to establish such pre-growth conditions (stoichiometry of a near-surface layer, impurity level, roughness) under which vertical etching in chlorine-containing plasma and epitaxy are compatible.

It has been demonstrated in our previous study that the etching of gallium arsenide in inductively coupled chloropentafluoroethane (C_2F_5Cl) plasma has a polishing effect and does not produce a damaged near-surface layer [8]. However, the surface of GaAs became contaminated with impurity elements that were left there following an incomplete removal of residual freon. Impurities were concentrated both at the bottom of etched grooves and on their side walls. This may complicate considerably the process of subsequent epitaxial regrowth of the obtained structures. Within this context, four different methods for cleaning the GaAs surface after etching were proposed: liquid processing in $NH_4OH/H_2O_2/H_2O$, *in situ* plasma-chemical etching in chlorine plasma, *ex situ* plasma-chemical etching in hydrogen plasm, and thermal annealing in a flow of arsine [9]. The residual impurity concentration and the mean-square surface roughness were evaluated. Liquid etching of a surface layer to a shallow depth performed after the primary plasma-chemical etching should contribute to the removal of impurities and stoichiometry correction. Plasma-chemical processing of GaAs in hydrogen and chlorine plasma offers gentle removal of impurities from a surface by etching them away with the formation of volatile products. The minimum capacitive discharge power (10 W) sufficient to maintain stable plasma in the reactor was chosen for this purpose in order to minimize the impact on the structure. The processing time was adjusted with account for the GaAs etching rate in the given regime.

It is known that gallium arsenide produces an oxide film, which interferes with epitaxy, in the atmospheric environment [9]. In view of this, it was decided to examine the method of *in situ* GaAs surface processing (without exposure of the sample to air) and the technique of thermal annealing directly in the epitaxial growth system (for removal of the oxide).

Plasma-chemical etching of gallium arsenide wafers with the (001) orientation was performed first in accordance with the procedure detailed in [10]. Equipment provided by the Center for Collective Use „Physics and Technology of Micro- and Nanostructures" (Institute for Physics of Microstructures, Russian Academy of Sciences) was used. The surface of GaAs after etching in C_2F_5Cl plasma was analyzed via secondary-ion mass spectrometry (SIMS) (a „TOF.SIMS-5/100" mass spectrometer), scanning electron microscopy (SEM) (an „Evo 10" microscope), and atomic force microscopy (AFM) (an NTEGRA PRIMA scanning probe microscope). A quartz reactor and an Epiquip VP-502RP setup were used to perform thermal annealing of GaAs in a flow of arsine. Plasma-chemical etching of GaAs in hydrogen plasma was carried out using an Oxford PlasmaLab 80 system.

The method of liquid etching of GaAs in $NH_4OH/H_2O_2/H_2O$ to a shallow depth (~ 150 nm) turned out to be one of the best of the examined

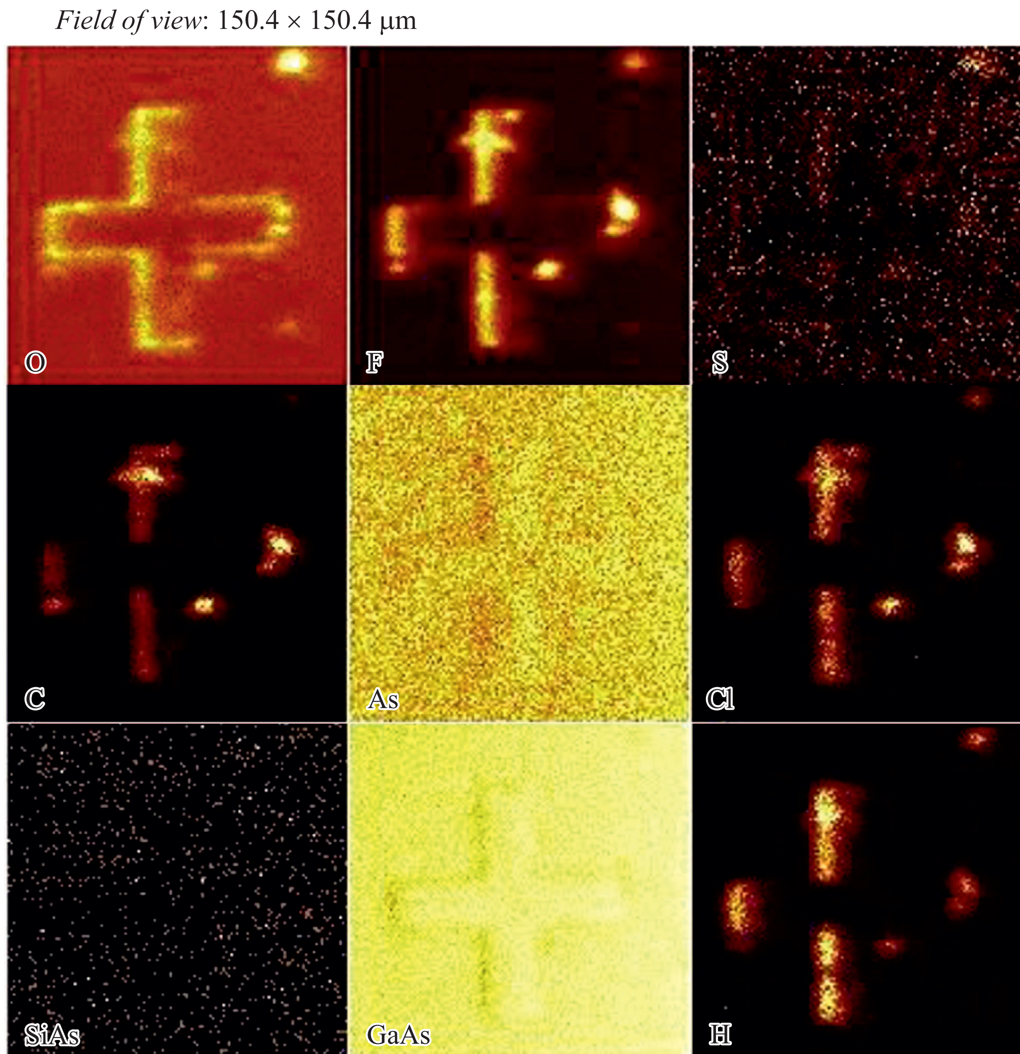

Figure 1. Distribution of secondary ions of elements over the surface of gallium arsenide (determined by SIMS) after additional liquid etching in $NH_4OH/H_2O_2/H_2O$.

techniques. It helped reduce the concentration of impurities without increasing the surface roughness. The brighter the regions of maps illustrating the distribution of secondary ions of elements (Fig. 1) are, the higher is the residual concentration of impurities in these regions. Since etched and non-etched regions are almost indistinguishable in secondary ions of As and GaAs (the cross is barely discernible), it may be concluded that the stoichiometric composition of the surface of gallium arsenide is preserved in the course of liquid processing. This method provides an opportunity to remove the thin upper contaminated layer without underetching. However, it does not allow one to clean a sample completely, since a certain amount of impurities remains on the side walls of the profile.

Thermal annealing in a flow of arsine, which was performed for 10 min at 700°C, facilitated the removal of trace fluorine and chlorine (and, to a lesser extent, hydrogen and carbon) from the GaAs surface, while the oxygen content remained unchanged. Arsine was needed in order to preserve the surface layer stoichiometry [9].

Residual oxygen, chlorine, and fluorine were removed almost completely in 5 min of *ex situ* plasma-chemical etching of GaAs in hydrogen: volatile products forming in the process were pumped out of the reactor. It is important to note that the oxygen content remained unchanged over the entire surface (processing was performed after the removal of a mask). At the same time, although a low-power capacitive discharge was used, the roughness level still grew slightly (to 1.4 nm within an area of 25 μm^2; see Fig. 2) after cleaning of GaAs in H_2 plasma. Regions with large local inhomogeneities were also present on the surface.

The method of *in situ* etching in chlorine plasma at a low capacitive power turned out to be the worst. The near-surface layer stoichiometry was violated after the interaction with plasma, and the roughness level increased considerably

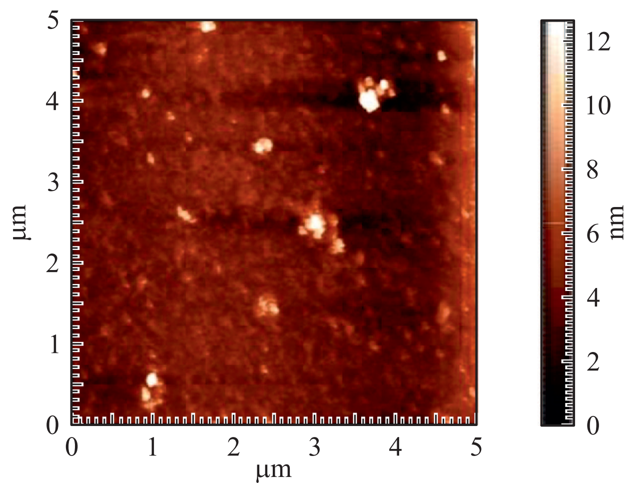

Figure 2. Surface relief of gallium arsenide after additional processing in hydrogen plasma (AFM image).

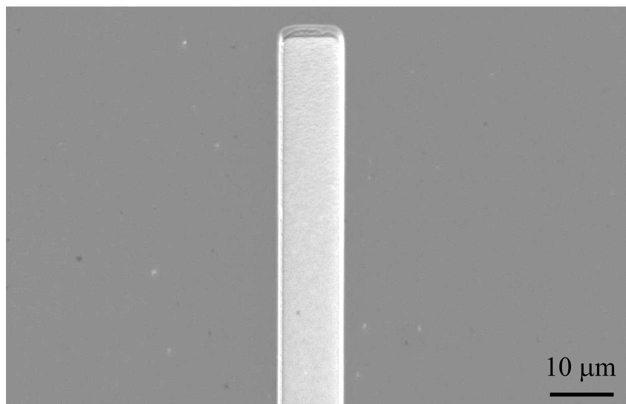

Figure 3. SEM image of the etched surface of gallium arsenide after processing in chlorine plasma. It is seen clearly that the etched groove has a rough bottom.

(Fig. 3). A strong topological contrast between the region etched in Cl_2 plasma (bottom of the groove) and the remaining part of the surface is seen in Fig. 3.

This processing also resulted in a many-fold increase in the concentration of all impurities on the surface of gallium arsenide both on the side walls and at the bottom of etched elements. It should be noted that the majority of these impurities were most likely already present in the reactor after primary etching. Since the reaction chamber was not cleaned, subsequent processing facilitated the transfer of these particles to the GaAs surface (even though the discharge power was low).

Thus, a combination of *ex situ* etching in hydrogen plasma at a low power and subsequent processing in a $NH_4OH/H_2O_2/H_2O$ solution is the best among the above-discussed techniques for GaAs cleaning after etching in C_2F_5Cl plasma.

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Conflict of interest

The authors declare that they have no conflict of interest.

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