Effect of wet chemical treatment on the properties of GaAs FIB-modified surface

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Abstract. We present the results of studies of the effect of wet chemical treatment on the properties of a GaAs surface modified by a gallium focused ion beam. Our studies based on results of AFM, KpAFM and Raman spectroscopy measurements have shown that, during wet chemical treatment, the damaged areas disappear completely in the case of low accelerating voltages and small doses of ions. At the same time, large accelerating voltages lead to the formation of extended damaged regions, the complete removal of which requires a longer treatment or additional processing.

1. Introduction

Despite active research recently, the problem of positioning self-organizing nanostructures (quantum dots, nanowires, etc.) is still urgent [1 – 4]. Accurate control of the position of nanostructures, as well as their size, is necessary for a wide range of promising devices in nanoelectronics and nanophotonics [5 – 13]. The complexity of solving this problem is largely because in epitaxy the most common approach for ordering structures has become an approach based on surface modification by various methods: from conventional lithography to local techniques based on ion beam treatment and local anodic oxidation [2, 14 – 17].

However, any treatment of growth surface inevitably leads to degradation of its properties, including damage of crystal structure of surface and subsurface layer and surface contamination with unwanted impurities. At the same time, epitaxial synthesis is extremely demanding on the quality of the substrate surface. This requires the development of methods for the pre-growth treatment of modified surfaces, which would improve their quality for subsequent epitaxial synthesis. This is very important for obtaining electrically and optically active nanostructures.

In this paper we present the results of studies of the effect of selective wet chemical etching on the properties of GaAs (001) surfaces modified by the Ga+ focused ion beams (FIB).

2. Experiment

For experimental studies we formed regular arrays of nanoholes on the GaAs (001) surface (epi-ready substrate) using by the FIB technique at various modification mode. The accelerating voltage of the ion beam was 10 and 30 kV, the ion beam current was 0.3 pA for voltage of 10 kV and 10 pA – 30 kV which is due to the peculiarities of the FIB system [2]. The number of FIB passes was varied in the range from 1 to 300. After that, the samples were treated (etched) in an HCl solution for 3 min. Then all the samples,
including the control one (with only FIB modification), were study by atomic force microscopy (AFM), Kelvin probe AFM (KpAFM) and Raman spectroscopy to obtain information about changes in surface morphology, surface potential and crystal structure, respectively.

3. Results and discussion
The results of the AFM study showed that an increase in the accelerating voltage does not lead to significant changes in the depths of the nanoholes. Surface profiles at the Figure 1 show the depth of the nanoholes for the limiting FIB treatment modes is comparable (30 – 35 nm). Perhaps this is due to the significantly larger aspect ratio of the surface structures obtained at higher accelerating voltages and, accordingly, the limited capabilities of the AFM (probe radius). At the same time, the diameter of the nanoholes increases insignificantly, which is due to the large diameter of the ion beam at 30 kV. However, after wet chemical etching of prepared samples, the character of sample morphology is different for different FIB voltage. As can be seen from Figure 1, at low accelerating voltages, the diameter of the nanoholes did not change, but the depth decreased. At the same time, at 30 kV, the diameter decreased, and the depth increased. We attribute this to the fact that at low voltages, implanted Ga⁺ ions are accumulated in a thin subsurface area around nanohole.

![Figure 1. AFM profiles of GaAs surface morphology (a, b) and of potential distribution (c, d) for samples before (0 min) and after wet chemical treatment (3 min) obtained at different FIB-modes: 10 keV, 0.3 pA (a, c) and 30 keV, 10 pA (b, d).](image)

Considering the inevitable process of chemical etching of the unmodified GaAs surface, this leads to a decrease in nanohole depth. At the same time, at high voltages, the Ga⁺ ions penetration depth increases. This leads to the formation of extended damaged areas, which significantly increase the
surface structure depth during chemical etching. The unequal character of changes in the morphology of nanoholes formed at different voltages may indicate a different etching rate of damaged and original surface areas.

Analysis of the surface potential distribution by the KpAFM (Figure 1 (c, d)) showed that in the case of low accelerating voltages, the implanted Ga$^+$ ions are localized at the near surface layer, which leads to higher surface potential values (+0.06 V) in comparison with the points formed at higher voltages (+0.03 V), when ions are distributed over a larger volume of the substrate, but with a lower volume density. This leads to the fact that after wet chemical treatment in areas obtained at low accelerating voltages and implantation doses, potential peaks disappear, while at points with a high accelerating voltage, the potential value practically does not change staying at +0.03 V.

It should be noted that, in all cases, a system of concentric areas with different values and signs of the surface potential is formed around the nanohole. The size of the regions reaches 0.5 μm in diameter and weakly depends on the FIB modes and the morphology of the nanohole. We attribute this to the redistribution of mobile charge carriers in the near-surface GaAs layer due to the formation of a charged region of implanted Ga$^+$ ions. This assumption is supported by the fact that, after wet chemical etching, these regions disappear around the nanoholes formed by the ion beam at low accelerating voltages and remain around ones formed at high voltages (Figure 2). This also additionally confirms the formation of more extended damaged areas around nanoholes during processing with high-energy ion beams.

Figure 2. AFM images of GaAs surface morphology (a) and lateral distribution of surface potential (b) for sample after FIB treatment at 30 kV and subsequent wet chemical etching.

The KpAFM results are in good agreement with the Raman spectroscopic data. As can be seen from the Raman spectra in Figure 3, an increase in the Ga$^+$ ion implantation dose leads to a decrease in the intensity of the GaAs LO-phonon peak and the appearance of an extended region (shoulder) in the range 240 – 280 cm$^{-1}$. The formation of this region may be due to the presence of components of amorphous arsenic (peaks at 204, 205, and 252 cm$^{-1}$) and amorphous GaAs (peaks at 245 and 247 cm$^{-1}$), as well as TO-phonons of crystalline GaAs (265 cm$^{-1}$) [18 – 21]. It is also important to note that after FIB treatment, the intensity of the GaAs LO-phonon peak is practically equal to the intensity of the multicomponent shoulder at 240 – 280 cm$^{-1}$. This also indicates the presence of extended areas with a high degree of defectiveness around nanoholes. After wet chemical treatment, the relative intensity of the LO-phonon peak in GaAs sharply increases, and the GaAs TO-phonon peak clearly appears in the structure of the multicomponent shoulder. We attribute this to the predominant removal of the damaged area around nanoholes during the wet chemical etching. At the same time, the extent of the damaged GaAs layer is such that it is not completely removed during etching, leaving a significant contribution to the Raman signal even after chemical treatment.
Figure 3. Raman spectra from GaAs area with nanoholes obtained at 30 kV before (a) and after (b) wet chemical etching.

4. Conclusions
Thus, experimental studies of the effect of liquid chemical treatment and FIB modes of nanoholes formation on the morphology, surface potential, and defectiveness of near-surface layer in the modification region of GaAs substrate have been carried out. Based on the results of the analysis of samples by KP-AFM and Raman spectroscopy, we have shown the possibility of selectively removing damaged regions around GaAs nanoholes while maintaining its shape and size correlation using low accelerating voltages of the ion beam at the stage of surface structure formation. At the same time, the use of high-energy ion beams leads to the formation of extended regions around nanoholes while maintaining a relatively high defectiveness and built-in charge in GaAs substrate.

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