Effect of GaAs native oxide upon the surface morphology during GaAs MBE growth

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Abstract. The GaAs native oxide effect upon the surface morphology of the GaAs epitaxial layer was studied with taking into account the main growth parameters of MBE technology: substrate temperature, effective As$_4$/Ga flux ratio and growth rate. The MBE modes of atomically smooth and rough surfaces and surfaces with Ga droplet array formation were determined. The possibility of the obtaining of GaAs nanowires via GaAs native oxide layer was shown.

1. Introduction
The relevance of the experimental studies of the influence of GaAs native oxide on the GaAs epitaxial growth is caused by the need to solve a number of technical problems associated with the formation of nanoscale systems based on A$_3$B$_5$ semiconductors using different epitaxial growth techniques on pre-structured surfaces, including those based on the method of molecular beam epitaxy (MBE). However, most of the works are limited to the study of the GaAs oxide interaction with epitaxial layer and its influence on the morphology during the substrate surface treatment by thermal oxide removal in a growth chamber [1-4] in order to obtain an atomically smooth surface, which is very critical for the subsequent formation of self-organized nanostructures [5,6].

This paper presents the results of comprehensive experimental studies of the interaction of the GaAs native oxide with the substrate material, GaAs epitaxial layer, as well as growth components – Ga and As at a stages of heating, oxide removal and epitaxial growth.

2. Experiment
Experimental study of the interaction between GaAs native oxide, the surface of GaAs substrate and growth components was carried out using the MBE system STE35 (SemiTEq) with solid state sources. The deposition of GaAs was carried out from Ga and As$_4$ fluxes over the GaAs native oxide film on the GaAs(001) substrate without its prior removal by thermal desorption in the growth chamber. The thickness of oxide film was 3-5 nm [7, 8]. Effective deposition thickness of GaAs was 100 nm for all samples. The substrate temperature $T$ during MBE growth was varied from 450 to 650°C, and the effective As$_4$/Ga flux ratio $J_{As/Ga}$ – from 1 to 4. At low substrate temperatures (below 500°C) growth component feed was started when the substrate temperature reached the desired value. In the regions of the middle (500-600°C) and high (over 600°C) temperatures growth started at the....
beginning of the structural changes in the GaAs native oxide film, which was observed by RHEED. The set value of flux ratio was maintained in all temperature ranges. We used two growth modes: with Ga pregrowth deposition and without it. After growth, sources of Ga and As$_4$ were closed simultaneously, and the substrate was rapidly cooled. Then all samples were examined by SEM and AFM-based techniques.

3. Results and discussion
The experiments showed that in the mode without Ga predeposition at $J_{As/Ga} = 4$ and at high and low temperatures (below 550°C) rough surfaces formed, as shown in figure 1a, and RHEED dotted pattern was observed. The pits were 30-200 nm in diameter with density in a range $(3-7) \cdot 10^9$ cm$^{-2}$. At $T = 550$-600°C there were observed smooth surfaces with Ga droplets (figure 1b), which had a diameter of 50-200 nm, height – 10-20 nm and mean density – up to $(8-10) \cdot 10^9$ cm$^{-2}$.

Figure 1. SEM images of GaAs surface after GaAs deposition at: a) $J_{As/Ga} = 4$ and $T = 630°C$, b) $J_{As/Ga} = 40$ and $T = 590°C$, c) $J_{As/Ga} = 1$ and $T = 580°C$, d) $J_{As/Ga} = 1$ and $T = 500°C$. 
At the same time, reduction of As$_4$/Ga flux ratio to 1 led to the increase of Ga droplets in diameter and height to 200-500 and 100-120 nm, respectively, and to the decrease of density to $1 \times 10^7$ cm$^{-2}$ (figure 1c) at the same temperatures. All of these structures had a low crystalline pedestal at its base with diameter of up to 1 µm. At the other temperature modes we obtained results similar to previous case (figure 1d).

It should be noted, the droplets did not immerse into growth layer or did not dissolve one and remained on the surface during the GaAs MBE growth. Moreover, the Ga droplets had a liquid state even after cooling of samples to room temperature. This was confirmed by results of surface analysis via AFM techniques [9]. As shown in figure 2, droplets had a sharp phase contrast with the crystalline GaAs surface including its base. The spreading resistance mode showed the significant difference between the droplets and the other surface areas too.

![AFM images of surface with Ga droplets in different modes: a) non-contact mode, b) phase mode, c) contact mode, d) spreading resistance mode.](image)

Predeposition of 5-10 monolayers of Ga resulted in the smooth surface formation at high substrate temperatures (over 600°C), and in the growth of GaAs layers with pits and particles of metallic Ga at lower temperatures due to the excess Ga accumulation on the surface.

In all cases, the formation of pits or droplets is explained by the interaction between GaAs native oxide film, substrate and growth components [10]. Furthermore, being based on the experimental
results obtained, we proposed that at high temperature Ga droplets can act as nucleation centers for nanowire growth or as its initial stage. At some conditions GaAs native oxide film promotes to create a gallium excess and local supersaturation like SiO\textsubscript{x} film in [11]. But in the case of GaAs oxide it is difficult to keep these conditions for long time due to the instability of such films at high temperatures.

However, decreasing of the sample heating rate led to the formation of GaAs nanowires which was determined \textit{in situ} by the characteristic RHEED patterns [12]. As shown in figure 3, GaAs crystals had mean density of $5 \cdot 10^8 \text{ cm}^{-2}$, length $1-6 \mu\text{m}$ and diameter $60-200 \text{ nm}$ at an effective deposition thickness of 200 nm. The nanowires tilting relative to substrate caused by surface crystallographic orientation [13].

![Figure 3. GaAs nanowires obtained via GaAs native oxide layer: a) SEM image, b) dependence of the crystal length on its diameter (dots – experiment, line – approximation).](image)

Decreasing dependence of nanowire length on its diameter and comparison of crystal length and deposition thickness suggest the diffusion growth mode [14].

4. Conclusion

In summary, the experimental studies of effect of GaAs native oxide upon the surface morphology of GaAs epitaxial layer was carried out with taking into account the main growth parameters of MBE technology and the features of the interaction between GaAs native oxide, the surface of GaAs substrate and growth components. It was shown that there is a significant influence of the presence of the oxide film during growth on the morphology which depends primarily on the substrate temperature, heating rate and flux ratio. The possibility of the obtaining of different nanostructure types was shown during the MBE growth in the presence of GaAs native oxide film.

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