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Study of arsenic flux effect on thermal desorption of GaAs native oxide and surface morphology

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Abstract. In this paper we presents the results of studying the molecular arsenic flux effect on the processes of native oxide thermal desorption and the resulting surface morphology of GaAs(001) substrates. We have shown that the exposure of GaAs under As flux at the stage of oxide removal significantly modulates the decomposition of native oxide and its chemical interaction with substrate materials. Based on the obtained experimental results and analysis of possible chemical reaction in this system we have shown that in the presence of arsenic molecules on the surface, free gallium atoms bind with it and no longer participate in the decomposition of native oxide components. This leads to additional decomposition of the substrate materials as a result of its etching. As a result, nanoholes of lower density, but larger in size, are formed on the surface. We have also shown that a decrease in the oxide thickness leads to a decrease in the density and dimensions of the nanoholes.

Keywords: native oxide desorption, gallium arsenide, native oxide, molecular beam epitaxy, A3B5

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Материалы конференции
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Исследования влияния потока мышьяка на термическую десорбцию собственного оксида GaAs и морфологию поверхности

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Аннотация. В данной работе представлены результаты исследований влияние потока мышьяка на процессы термической десорбции собственного оксида и результирующую морфологию поверхности подложек GaAs(001). Показано, что экспозиция GaAs в потоке As на стадии удаления оксида существенно модулирует процессы разложения природного оксида и его химическое взаимодействие с материалами подложки, приводя к снижению плотности и увеличению среднего размера ямок, образующихся в результате травления. При этом уменьшение толщины окисла приводит к пропорциональному снижению плотности и размеров формирующихся углублений.

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Ключевые слова: десорбция собственного оксида, собственный оксид, молекулярно-лучевая эпитаксия, A3B5

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Introduction

One of the actively developing approaches to controlling the characteristics of A3B5 quantum dots is the use of substrate surfaces pre-structured in various ways [1–4]. Since not all modification methods provide for high-vacuum substrates transport between technological chambers for subsequent epitaxial growth, issues related to the inevitable oxidation of the surface and precise removal of the oxide to preserve the morphology formed at the previous stages become increasingly important. At the same time, despite the rather deeply studied processes of A3B5 semiconductors native oxide formation, its composition and methods for its removal, the question related to molecular arsenic effect on the oxide desorption processes and surface morphology remains open. For GaAs wafers used in epitaxial growth, native oxide is multicomponent. Excluding intermediate phases the oxide mainly consists of As_2O_5, As_2O_3 and Ga_2O_3 [5]. Therefore, the nature of thermal desorption will be determined by the individual chemical decomposition reactions of each component, which proceed at different temperatures. The goal of this work is to study the effect of arsenic flux on the GaAs native oxide thermal decomposition.

Materials and Methods

To study of molecular arsenic flux effect on the native GaAs oxide thermal desorption of, we used epi-ready GaAs(001) wafers with a nominal oxide thickness of ~ 3 nm [6] and epitaxial GaAs structures with oxide thickness of about 1 nm. The structure with a thin oxide layer was obtained by removing the oxide by the standard method, growing an atomically smooth buffer GaAs layer and oxidation in the atmosphere. In both cases native oxide was removed in the MBE growth chamber in two ways. The first method involved heating the substrate to 600 °C and exposing it to As_4 after complete oxide removal, following the standard MBE procedure [7]. The second method involved heating the substrate to 600 °C under the As_4 flux. The process was controlled by monitoring the reflection high-energy electron diffraction (RHEED). Then the samples were studied by SEM and AFM.

Results and Discussion

The AFM study showed that after the complete oxide removal with or without As_4 flux, the surface relief was highly developed and contained many holes of various shapes and sizes as it can be seen from AFM data on the Fig. 1.

We analyzed the geometric parameters of the obtained structures, their density, as well as the root-mean-square roughness (Table).

Based on theoretical calculation we expected that the arsenic flux would initiate additional chemical interaction with different oxide components such as As_xO_y and Ga_xO_y oxides, with activation temperature of ~ 200 and 560 °C [8] (hereinafter, stoichiometric coefficients are not shown for ease of understanding).

$$As_2O_5 + As_4 = AsO \tag{1}$$

$$As_2O_3 + As_4 = AsO \tag{2}$$

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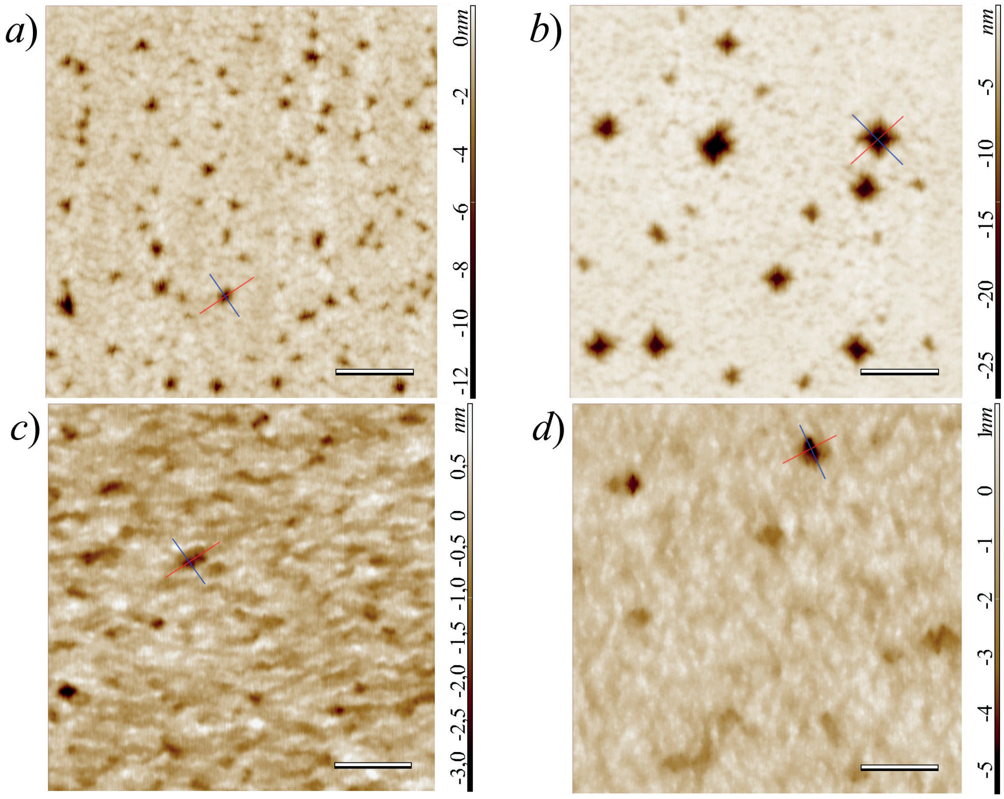

Fig. 1. AFM images of the GaAs surface after removing oxide of various thickness: 3 nm (*a*-*b*) and 1 nm (*c*-*d*) without (*a*, *c*) and with (*b*, *d*) As flux. Scalebar is 200 nm

Table

GaAs surface parameters after native oxide removal

№ sample	Oxide thickness, nm	Arsenic flux	Density, μm^{-2}	Average (maximum) depth, nm	Average (maximum) diameter, nm	RMS roughness
#a	3		77	6.3 (12)	17 (48)	0.832
#b	3	+	30	11 (26.5)	41 (105)	2.236
#c	1		30	3 (4)	30 (56)	0.404
#d	1	+	14	4.8 (5)	36 (75)	0.566

$$Ga_2O_3 + As_4 = Ga_2O + AsO, \tag{3}$$

This set of reactions should theoretically contribute to the native oxide layer thinning and suppress its reactions with substrate material, preventing its decomposition and morphology disturbance. However, we got the opposite results.

As can be seen from the presented data, the removal of native oxide of epi-ready GaAs(001) wafers (thick oxide layer) in As flux leads to a noticeable (twofold) decrease in the density of holes formed as a result of the interaction of the oxide with the substrate material, which worsens the surface morphology, as well as to an increase in holes geometric dimensions (depth and diameter) (Fig. 1, *a*, *b*). A decrease in the oxide thickness leads to a sharp (by several times) decrease in the density of holes and their sizes (Fig. 1, *c*, *d*).

It can be observed that the presence of arsenic flux on the surface has about the same effect as increasing the thickness of the oxide. In both cases the depth and diameter of the formed holes increase. It is important to note that as the geometric size of the holes increases, their faceting becomes more pronounced. The hole geometry analysis (orientation of the planes relative to the base cuts and the plate surface) allowed us to determine that the holes are facetted by planes {111} which is typical for droplet etching [9].

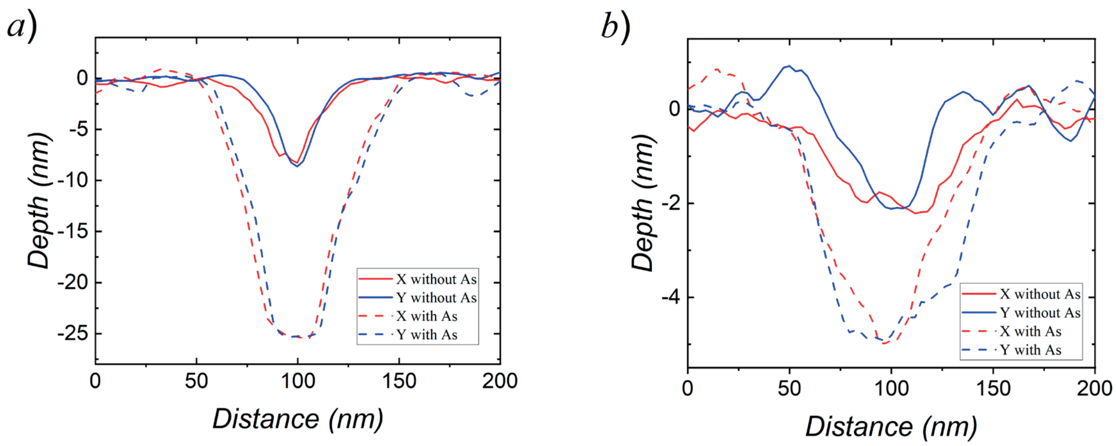

Fig. 2. Profile of holes of the obtained structures: the thickness of the oxide is 3 nm (*a*), the thickness of the oxide is 1 nm (*b*)

We attribute this behavior of the system to the fact that the addition of As molecules at the stage of oxide removal leads to the binding of Ga atoms released as a result of the thermal decomposition of GaAs (with an activation temperature of about 530 °C) in already open areas of the substrate surface, which prevents their migration to areas with oxide:

$$Ga + As_4 = GaAs \quad (4)$$

This leads to suppression of the main mechanism of thermal desorption of the oxide (5) at high temperatures – decomposition of Ga_2O_3 which is the main component of GaAs native oxide.

$$Ga_2O_3 + Ga = Ga_2O \quad (5)$$

Thus, at the surface areas masked by oxide, the removal of Ga_2O_3 becomes possible only due to the enhanced decomposition of the substrate material directly under the oxide (6-7), which leads to the accumulation of excess Ga, followed by the formation of nanosized droplets and activation of the droplet etching of the substrate material.

$$GaAs + Ga_2O_3 = Ga_2O + AsO \quad (6)$$

$$GaAs + Ga_2O_3 = Ga_2O + As_4. \quad (7)$$

The proposed mechanism explains well the formation of holes with much larger geometric dimensions and lower density. A decrease in the total density of holes with a decrease in the thickness of the oxide layer can be associated with the suppression of the interaction reactions between the oxide components (Ga_xO_y and As_xO_y) at earlier stages, leading, in turn, to a decrease in the content of the thermally stable Ga_2O_3 phase in the oxide film.

Conclusion

Thus, we have experimentally shown that the exposure of GaAs surfaces to an arsenic flux at the stage of removal of native oxide leads to a significant deterioration of the initial GaAs substrate morphology. Based on the obtained data, we assumed that this effect is based on the binding of Ga atoms formed on the substrate during its thermal decomposition with arsenic species. This slows down the decomposition of the main component of native GaAs oxide, Ga_2O_3, due to its interaction with metallic Ga. In turn, this leads to an increase in the processes of decomposition of the substrate material. It is also shown that the mechanism of droplet etching of the material leads to the formation of faceted nanoholes. We have also shown that the interaction of molecular arsenic with Ga-containing components can be neglected. The results of the work can be used in the development of both methods for protecting epitaxial surfaces and methods for their nanoscale structuring of substrates for the subsequent production of self-organizing nanostructures.

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