



Wet sulfur passivation of GaSb(1 0 0) surface for optoelectronic applications

E.V. Kunitsyna*, T.V. L'vova, M.S. Dunaevskii, Ya.V. Terent'ev, A.N. Semenov,
V.A. Solov'ev, B.Ya. Meltser, S.V. Ivanov, Yu.P. Yakovlev

Ioffe Physical-Technical Institute RAS, 26 Politekhnicheskaya st., 194021 St Petersburg, Russia

ARTICLE INFO

Article history:

Available online 11 March 2010

PACS:

81.05.Ea
81.65.Rv
81.65.Cf
78.55.Cr
68.37.Ps
73.40.Kp

Keywords:

GaSb
Passivation
Annealing
Photoluminescence
AFM
LPE
MBE

ABSTRACT

A comparative analysis of the properties of the non-passivated and S-passivated GaSb(1 0 0) surfaces has been performed through PL, AFM and RHEED characterization. The samples treated with a 1 M Na₂S aqueous solution demonstrate an increase in the 5 K PL intensity. According to AFM data, the annealing of the S-passivated GaSb(1 0 0) leads to the formation of the clean flat (1 0 0) surface. Moreover, after annealing the PL intensity of the S-passivated GaSb(1 0 0) surfaces decreases by 20%, whereas for the non-passivated samples it drops by more than a factor of 4. The method of wet sulfur passivation has shown great effectiveness in pre-epitaxial processing for LPE and MBE growth of the GaSb-related materials for optoelectronics.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Recently the III–V compound semiconductors have become the subject of extensive investigations because of the progress in developing IR lasers, photodiodes, solar cells and thermophotovoltaic converters [1–5]. The GaSb-based optoelectronic devices for the 2–4 μm spectral range are of great interest for a wide range of applications, such as high-resolution laser diode spectroscopy of gases and molecules, optical fiber communication, ecological monitoring, medicine, energy production and etc.

As is known, the performance of optoelectronic devices is strongly influenced by the electronic and chemical properties of heterostructure surfaces and interfaces. The inherent problem of the GaSb-related technology is high chemical activity of the material which causes the quick growth of surface oxides. Different kinds of treatment and many chemical compounds have been proposed to solve the problem [6–8]. However, knowledge on the GaSb surface and interface phenomena is scarce, as compared with GaAs material. Considerable advances in the processing technology,

including passivation techniques are required. Wet sulfur passivation of GaSb(1 0 0) surface before liquid phase epitaxy (LPE) and molecular-beam epitaxy (MBE) opens up new avenues for developing the optoelectronic devices.

We present a strategy to change the chemical and electronic surface properties through the passivation in the aqueous solutions of sodium sulfide (Na₂S·9H₂O). In our case, the water-based technique has been chosen consciously. For epitaxial growth of the GaSb-related heterostructures, an antimony-rich GaSb(1 0 0) surface is preferable in order to avoid the emergence of gallium clusters and microdrops on the surface under annealing. It was shown in [9] for GaAs(1 0 0), that the arsenic depletion of the surface layer under annealing results in emergence of Ga clusters forming then microdrops. The arsenic evaporation rate from the Ga microdrops is higher than Ga and As evaporation rates from the surface. It leads to strong damage of the GaAs(1 0 0) surface accompanied by occurrence of small pits. Recently, a comparative study of GaSb(1 0 0) passivation in aqueous and nonaqueous solutions by Liu et al. [10] corroborated the fact that the GaSb(1 0 0) material after aqueous Na₂S treatment demonstrates the Sb-rich surface, whereas nonaqueous Na₂S treatment yields Sb-poor surface.

In this paper, such fundamental aspects of the GaSb(1 0 0) surface pre-epitaxial processing as passivation and annealing are discussed. The effect of influence of the passivation in the

* Corresponding author. Tel.: +7 812 2927956; fax: +7 812 2970006.
E-mail address: kunits@iropt9.ioffe.ru (E.V. Kunitsyna).

strong alkaline Na_2S solutions ($\text{pH} \sim 13.9$) on the properties of the GaSb(100) surface has been studied through PL, AFM and RHEED characterization.

2. Experimental

The experiments were performed with Te-doped n-GaSb(100) samples ($n = (1-3) \times 10^{17} \text{ cm}^{-3}$, $\mu = 5720 \text{ cm}^2/\text{V} \times \text{s}$ at $T = 80 \text{ K}$), which have usually served as substrates for LPE and MBE growth of the GaSb-related heterostructures. The sample surfaces were degreased with acetone and then were treated with the Na_2S aqueous solutions ($\text{pH} \sim 13.9$). The treatment time was determined through the photoluminescence (PL) spectroscopy data (see Section 3).

For all measurements the n-GaSb(100) substrates prepared according to the conventional technique for LPE and MBE were used as a reference for the passivated samples. After cleaning by immersion in boiling and cold acetone, the reference substrates were etched with $\text{CrO}_3/\text{HF}/\text{H}_2\text{O}$, and then treated with $\text{HCl}:\text{H}_2\text{O}$. Finally, the substrates were washed in deionized water and blown dry with nitrogen.

To investigate the processes of the interaction between (100) surfaces of GaSb and Na_2S aqueous solutions with molarity of $M = 0.6-2.4$, a part of the wafer was covered by a SiO_2 protecting layer. After exposure in the solution the samples were washed in deionized water and dried in nitrogen flow. Then, the SiO_2 film was removed in the $\text{HF}:\text{H}_2\text{O}$ solution, and the etching depth was determined by profilometer.

The GaSb(100) surface electronic and optical properties were characterized through PL spectroscopy using grating monochromator supplied with nitrogen-cooled InSb photovoltaic detector. The photoluminescence was excited by emission of semiconductor laser diode operating in cw mode at the $\lambda = 809 \text{ nm}$. The excitation density in light spot with diameter of 0.5 mm on the sample was about $10 \text{ W}/\text{cm}^2$. The measurements were performed at $T = 5 \text{ K}$ using lock-in amplifier.

The surface relief of non-passivated and S-passivated samples was investigated using the atomic-force microscope (NT-MDT, Russia) at atmospheric conditions. The AFM measurements were carried out in the contrast mode with the use of Si_3N_4 microcantilevers as a probe. The spring constants were 0.16 and 0.68 N/m, and the radius of the curvature of the tip was less than 20 nm. The AFM topography images were processed with the SPM Image Magic program.

Two kinds of annealing treatments of the GaSb(100) samples were performed: in H_2 atmosphere in the LPE system (SDO125 setup, Russia) and under ultra-high vacuum (UHV) conditions ($<10^{-9} \text{ Torr}$) in the MBE chamber (EP 1203 setup, Russia). The reconstruction of both non-passivated and S-passivated GaSb(100) surfaces under UHV annealing was controlled by reflection high-energy electron diffraction (RHEED).

The GaSb-related heterostructures were grown by LPE [11] and MBE [12] on the GaSb(100) substrates. The structural perfection of GaSb/GaInAsSb interfaces was analyzed by transmission electron microscopy (TEM) on a JEM-100C microscope in the cross-sectional geometry, as well as X-ray diffraction using a TRS-1 high-resolution two-crystal diffractometer.

3. Results and discussion

The study of etching dynamics of the GaSb(100) surfaces in the Na_2S aqueous solutions ($M = 0.6-2.4$) indicated that the etching process is nonuniform. As seen in Fig. 1, the etch rate decreases with the etching time for the solutions with different molarity. Our results on etching behavior of the GaSb(100) surface in Na_2S

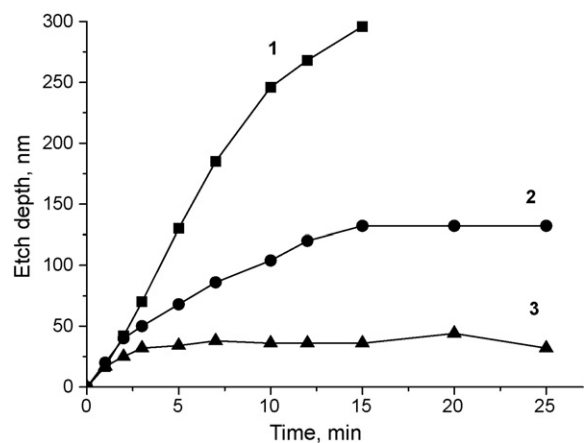


Fig. 1. Etch depth of n-GaSb(100) vs time of treatment with aqueous solutions of sodium sulfide ($\text{Na}_2\text{S}:\text{9H}_2\text{O}$) with molarity: 0.6 M (1); 1 M (2); 2.4 M (3).

solutions confirm that for this material the mechanism of the passivation includes two competitive processes, namely layer-by-layer etching and formation of the passivating coating. In short period of time the Na_2S treatment removes the undesirable native oxides and reduces the surface recombination velocity. The thin sulfur monolayer is formed, but does not protect the surface against etching. Then, after stopping an etching process a stable oxide-free sulfur protective layer is formed. We interpret our results in terms of the suggested chemical model. The treatment of GaSb with the strong alkaline Na_2S solutions initially produces the (100) Sb-terminated surface covered with chemisorbed SH^- groups, while residual Ga atoms are bounded with OH^- anions. This stage corresponds to an electron passivation only. Further removal of the OH^- anions with Ga atoms takes place in form of H_2GaO_3^- . With increasing the duration of the treatment, the SH^- groups are replaced by S^{2-} anions bounded with surface Sb atoms in bridge-site configuration. As a result of the sulfur passivation, the GaSb(100) surface is covered with an oxide-free sulfur protective layer. The 0.6 M Na_2S aqueous solution produces deep etching of the semiconductor (see Fig. 1, curve 1). At the same time, in the case of the molarity of 2.4 M the etch stage is too short (see Fig. 1, curve 3), which means that the solution leaves a lot of elemental sulfur physisorbed on the surface. This phenomenon may then provoke sulfur diffusion in the material under annealing. It follows from the aforesaid, that the 1 M Na_2S solution is more suitable for the passivation of the GaSb(100) surface in this study.

In the case where the sulfur passivation is applied for the treatment of the semiconductor substrates before epitaxy, determining the optimum time of the treatment plays an important role. On the one hand, this time should be long enough for the formation a chemisorbed sulfur monolayer on the GaSb(100) surface. On the other hand, the treatment should not provide the physisorbing of a thick layer of elemental sulfur on the surface. In our case, PL spectroscopy is the suitable method for investigation of electronic and optical properties of the GaSb surfaces, as well as for evaluation of the passivation efficiency of the Na_2S aqueous solutions. The optimum duration of crystal surface treatment with a sulfide solution is determined by the PL intensity maximum. Fig. 2 presents the 5 K PL spectra of the GaSb(100) samples treated with the 1 M Na_2S aqueous solution for different times. All spectra exhibit a dominant peak at 0.784–0.787 eV, which is connected with the direct interband transitions at 5 K. First, the sulfide treatment leads to a considerable increase in the PL intensity by a factor of 7.6. The PL intensity maximum is observed upon the treatment for 4 min. We believe, that this time is sufficient for the formation of the continuous chemisorbed sulfur monolayer on the GaSb(100) surface. Then,

Download English Version:

<https://daneshyari.com/en/article/5360227>

Download Persian Version:

<https://daneshyari.com/article/5360227>

[Daneshyari.com](https://daneshyari.com)