Technology of nanoplanar surface preparation of GaSb and InP substrates

A M Zhirnov¹, A E Marichev², V S Epoletov², N D Prasolov², R V Levin² and B V Pushnyi²

¹Saint Petersburg Electrotechnical University "LETI", Professora Popova street, 5, Saint-Petersburg, Russia
²Ioffe Institute, Politekhlicheska Street, 26, Saint-Petersburg, Russia

e-mail: artemzhi38@gmail.com

Abstract. In this work, we studied the surface quality dependence of GaSb and InP substrates prepared by various methods of pre-epitaxial preparation, specifically, etching, annealing, and growing a buffer layer. Our main goal was to obtain the most efficient method of pre-epitaxial treatment, which allows preparing substrates with the best surface quality. The experimental results were evaluated by the parameter of the average roughness of the substrate. As a result a combination of the methods of pre-epithelial preparation of GaSb and InP substrates was selected, which made it possible to obtain a root-mean-square surface roughness about 0.6–0.8nm.

1. Introduction

For the manufacture of devices based on quantum-size effects, it is necessary to grow semiconductor structures with thicknesses about few nanometers. The single-crystal substrate on which such structures for devices are grown should have a minimum root-mean-square roughness parameter. Reducing this parameter, as well as cleaning from external contaminants, is key objective of pre-epitaxial processing of the substrate. To use substrates that have a roughness of more than 2–3 nm, it is necessary to prepare them first in order to obtain a high-quality surface (close to an atomically smooth surface). That will allow to achieve high quality of the grown instrument structures and the possibility of use for “bonding”.

To obtain structures of the required quality, it is necessary to take into account many aspects of the growth process. Quantum-size effects appear only in sufficiently perfect and homogeneous structures with a thickness in the range of several nanometers. To obtain such films without internal and surface defects, it is very important to pay attention to the processing of the substrate surface and the removal of all traces of natural oxides and mechanical surface defects to a level of less than 1 nm.

For successful “bonding”, the surfaces of the structures used must be pre-treated to remove contaminants absorbed by the surface of the structure, as well as to remove the mechanically damaged surface layer. [1]

The aim of the work was to develop the technology of pre-epitaxial preparation of GaSb and InP substrates, which allows to obtain a nanoplanar surface close to atomically smooth.
2. Experimental
The effect of different etchants and their combinations on the surface roughness of the GaSb (Table 1) and InP (Table 2) substrates was investigated.

**Table 1. Methods and results of etching GaSb substrates in various etchants.**

| Sample | Etchant                          | Time | Rms-roughness |
|--------|----------------------------------|------|---------------|
| SL1    | HCl                              | 4 min| 11.6 nm       |
|        | HCl (H2O+H2O2+C4H6O4 (40%)+HF (25:25:22:1,5) | 1 min| 16.6 nm       |
| SL2    | HCl                              | 3 min| 16.6 nm       |
|        | HCl (H2O+H2O2+C4H6O4 (40%)+HF (600:40:20:2) | 5 min| 29.7 nm       |
| SL3    | HNO3+HF+CH3COOH (18:2:40)        | 40 sec| 36.8 nm      |

**Table 2. Methods and results of etching InP substrates in various etchants.**

| Sample | Etchant                          | Time | Rms-roughness |
|--------|----------------------------------|------|---------------|
| SL5    | HCl selective etchant            | 1 min| 42.8 nm       |
| SL6    | HNO3+HCl (1:1)                   | 1 min| 21.1 nm       |
| SL7    | H3PO4                            | 1 min| 11.3 nm       |
|        | (HBr + saturated H2O solution K2Cr2O7) (2:1) | 4 min| 9.8 nm        |
| SL8    | H3PO4                            | 1 min| 9.8 nm        |
| SL9    | H3PO4                            | 5 min| 9.5 nm        |

The experiments on substrate annealing were performed on the AIXTRON AIX-200 MOCVD system. At an annealing temperature in the range of 500-700°C, at a reduced reactor pressure of 76 Torr, in a stream of high-purity (dew point less than -100°C) hydrogen. For stabilization of the surface of InP substrates, phosphine (PH3) was added to the hydrogen flow.
Figure 1. Dependence of the surface roughness of GaSb substrates: a) from the annealing temperature for 2 min; b) from the time of annealing at a temperature of 650°C.

Figure 2. Comparison of the AFM image of the surfaces of GaSb substrates: a) before annealing; b) after annealing at 650°C for 8 minutes.

Samples were examined using an atomic force microscope (AFM) and a scanning electron microscope. The surface quality of the substrates was evaluated by the root mean square surface roughness (Rq) - measured by the AFM method.

3. Results
It can be seen from Tables 1 and 2 that one of the minimal values of the surface roughness of the substrates was obtained using concentrated HCl acids for GaSb and H3PO4 substrates for InP substrates, however, their etching rate is less than 50 nm / min (mainly the oxide film is removed) and this not enough to remove a thicker (~ 2-3 microns) surface mechanically disturbed layer. Therefore, it is preferable to use a combination of different etchants and the most suitable is SL2 method (Table 1) for GaSb substrates and SL9 (Table 2) for InP substrates.

Subsequently, GaSb substrates prepared using the SL2 method were annealed in a hydrogen stream. The objective of high-temperature annealing is to heat substrate to a certain temperature and held for a certain time. At high temperature, the energy of atoms on the surface of the substrate
increases, which contributes to their migration. Migration leads to a redistribution of the material over the surface and its subsequent smoothing, i.e. roughness reduction.

Typical surface roughness of the substrate GaSb after etching was 17 nm. Annealing was performed in the temperature range 500 - 700°C in the time interval from 2 to 8 minutes in a stream of hydrogen (speed 5.5 slpm). At the first stage, to determine the optimal annealing temperature, the substrates were kept for 2 minutes in the temperature range 500–700°C (Fig. 1a). As can be seen from fig. 1a, the optimal annealing temperature is 650°C, at which the smallest roughness of 7.5 nm was observed. At the second stage, the optimal annealing time was determined at a temperature of 650°C, and the substrates were annealed for 2–8 minutes (Fig. 1b). It can be seen from the dependence (Fig. 1b) that, with an increase in the annealing time, the surface roughness decreases, and the smallest obtained roughness at the annealing temperature of 650°C is 1 nm. Figure 2 a) and b) show AFM images of the surfaces of GaSb substrates, before annealing and after annealing at 650°C for 8 minutes. AFM images show changes in surface topography after annealing.

A similar dependence of the change in surface roughness was also observed for indium phosphide substrates, except that it was necessary to add a stabilization flow of phosphine (PH3) in the proportion H2 + PH3 (1000: 1) to the hydrogen flow and a lower annealing temperature to 600°C.

In the course of the study, results were obtained that made it possible to formulate the most suitable and reproducible pre-epitaxial preparation methods for gallium antimonide and indium phosphide substrates conducted at room temperature.

The sequence of pre-epitaxial preparation of GaSb substrates:
1. to remove natural oxide - etching GaSb substrates in concentrated HCl for 1 min, followed by washing with deionized water for 30 sec;
2. to remove a mechanically disturbed layer - etching for 3 min in an etchant H2O + H2O2 + 40% aqueous solution of C4H6O4 + HF (25: 25: 22: 1.5), followed by washing with deionized water for 1 min;
3. etching in HCl for 5 minutes, followed by washing with deionized water for 3 minutes;
4. centrifuge drying at 500 rpm;
5. annealing the GaSb substrates in a stream of hydrogen at 650°C for 8 minutes.

The sequence of pre-epitaxial preparation of InP substrates:
1. to remove natural oxide - etching InP substrates in H3PO4 for 1 min followed by washing with deionized water for 30 sec;
2. to remove a mechanically disturbed layer - etching for 1 min in an etchant (HBr + saturated aqueous solution of K2Cr2O7) (2: 1), followed by washing with deionized water for 1 min;
3. etching in H3PO4 for 3 minutes, followed by washing with deionized water for 3 minutes;
4. centrifuge drying at 500 rpm;
5. annealing of InP substrates in a mixture of H2 + PH3 flows (1000: 1) at 600°C for 6 minutes.

The pre-epitaxial preparation of GaSb substrates allowed us to obtain such Rq as 1.0–1.2 nm with a defect density of less than 10³cm–2. For InP substrates, the surface Rq was 1.0 nm with a defect density of less than 10³cm–2. These results are superior to those obtained in earlier similar studies, where Rq for GaSb substrates was 3.2 nm. [2]

After preparing of the substrates, an undoped buffer layers of GaSb on GaSb and InP on InP were grown. Growth was performed by gas-phase epitaxy from organometallic compounds. The optimal layer thickness in both cases is 500 nm. The growth of the buffer layer made it possible to reduce the Rq of the surface of the GaSb and InP substrates from 1.0–1.2 nm to 0.6–0.8 nm.

The photoluminescence method was used to study the effect of annealing on the luminescent properties of the layers. As the example there is analysis of the photoluminescence spectra of buffer layers grown on GaSb substrates (Fig. 3). It shows that annealing for 2 minutes at a temperature of 600°C improves the surface quality of the grown structures and contributes to an increase in the radiation intensity by about a factor of 5 in comparison with an unannealed buffer layer. Regardless of the thickness of the grown buffer layer, the intensity of the main (interband) peak does not change in the annealed samples.
4. Conclusion
In this work, various methods of pre-epitaxial preparation of GaSb and InP substrates were studied, specifically, etching, annealing, and growing a buffer layer. The surface quality was estimated by the parameter of the average roughness of the substrate. The technology of pre-epithelial preparation of GaSb and InP substrates were determined, which made it possible to obtain a root-mean-square surface roughness about 0.6–0.8 nm.

On the prepared by the presented technology substrates, InAs / GaSb quantum-dimensional heterostructures were grown and Bonding operations on InP were performed.

The conducted studies suggest the effectiveness of the proposed method for surface treatment of GaSb and InP substrates. A wide range of studies and tests in the field of semiconductor optoelectronics is possible on substrates processed by these methods.

Acknowledgments
This work was partially supported by the Russian Foundation for Basic Research (grant № 20-08-00982, Semiconductor laser-radiation photovoltaic converters for the wavelength range of 1500-1750 nm).

References
[1] Moriceau H et al. 2007 Solid State Phenomena 121 29
[2] Luca S, Santailler J, Rothman J, Bell J, Calvat C, Basset G, Passero A. Khvostikov V, Potapovich N and Levin R 2006 ASME J. Sol. Energy Eng. 129 304