Preparation of a silicon surface for subsequent growth of dilute nitride alloys by molecular-beam epitaxy

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Abstract. This article discusses the process of preparation of a silicon surface for subsequent growth of dilute nitride alloys by molecular-beam epitaxy. The method of preparation of Si (100) and Si (111) substrates was developed. This method provides reproducible high-quality silicon surface for molecular-beam epitaxy of Si-GaP heterostructures. As a result, it managed to reduce the evaporation oxide temperature below 800 °C, which is an important parameter for the MBE technology.

1. Introduction

The pre-growth preparation of substrates is one of the most important steps in the formation of structures of molecular-beam epitaxy (MBE) technology for opto- and microelectronics, since the presence of chemically pure, structurally perfect, atomically smooth surface is a prerequisite for producing epitaxial layers of device quality. Nowadays the most common methods of surface cleaning are the high-temperature annealing and the formation of a protective layer on the surface, subsequently removed in ultra-high vacuum thermally.

High-temperature annealing (850-1200 °C) found wide application in silicon MBE, as it allows to obtain a surface of the necessary growth quality. However, high-temperature heating causes unwanted diffusion of impurities and the appearance of a near-surface p-type layer, thereby changing the doping profile of the structures. In addition, the growth of such crystal defects as dislocations and packing defects, the appearance of extended microsteps and pits of thermal etching is observed [1]. Thus, the use of a relatively low-temperature (not higher than 900 °C) pre-epitaxial preparation method, using the passivation effect of the Si surface with nonstoichiometric SiO₂ or hydrogen, is more preferable and, accordingly, more common.

The main impurity remaining on the surface of the semiconductor substrates after degassing in the ultra-high vacuum (UHV) is carbon, which moreover, at temperatures above 700 °C, reacts chemically with silicon and form a hard-to-remove SiC, so the passivation layer must have carbon-photophobic properties. Also, it must be sufficiently resistant to the action of chemically active contaminants that are always present in the environment, easily forms during the chemical preparation of the substrates and completely removes from the surface with moderate warming along with traces of residual contaminants.

The objective was to prepare the silicon surface for subsequent growth of dilute nitride alloys by MBE.

2. Experiment

Based on the methods proposed in the works [2,3] the method of preparation of Si (100) and Si (111) substrates was developed.

The procedure of the chemical treatment of substrates consists of the following operations (HNO₃ ~ 70%; HF ~ 46%; H₂O₂ ~ 30%; NH₄OH ~ 28%; HCl ~ 36%; distilled deionized water with a resistance of at least 15 MΩ·cm):

1. Washing off traces of organic contaminants by boiling first in CCl₄, then in acetone.
2. Oxidation of the upper layer of silicon in boiling nitric acid and bleeding of the formed SiO₂ in a solution of hydrofluoric acid (HF:H₂O = 1:3) for 20-30 seconds (this operation is repeated several times).
3. Boiling in a peroxide-ammonia solution (NH₄OH:H₂O₂:H₂O = 1:1:3) for 10 minutes, followed by removal of contaminants together with silicon oxide in a solution of hydrofluoric acid.

4. Formation on the surface of a thin protective oxide by boiling in peroxide-acid solution (HCl:H₂O₂:H₂O = 3:1:1) for 10 minutes.

5. Final washing with deionized water and drying with ethanol in centrifuge.

Samples prepared in this way were immediately loaded into the MBE chamber, where they were before the final stage of pre-epitaxial preparation in the conditions of UHV. The pre-epitaxial preparation of the silicon surface was tested on a SUPRA-32 (Riber) whose growth module contains an electron-beam evaporator to obtain the required Si flux.

Directly before the growth experiments, the substrate was sequentially degassed at the temperatures of 400 and 750 °C for 60 and 40 minutes, respectively, after which, at a temperature of 750 °C in a weak Si stream (~1 · 10¹³ atoms·cm⁻²·s⁻¹) or a layer of silicon oxide was removed from the surface only thermally at a temperature of 800 °C for 15-20 minutes.

In order to test the quality of the prepared surface the control layers of Si were grown by MBE at a temperature of (600 ÷ 650) °C (optimal for silicon MBE) and thickness from several hundred to several thousand angstroms. Processes of the pre-growth preparation and growth under vacuum were monitored in-situ by reflection high-energy electron diffraction (RHEED) and ex-situ by atomic-force microscopy (AFM).

3. Results and discussion

According to AFM, silicon plates initially had an atomically smooth surface (figure 1). This is indicated by the image of the surface relief in the AFM pictures and the profile parameters characterizing the surface rms = 3 Å, peak-peak = 20 Å.

![AFM image of the original surface Si (100)](image)

Figure 1. AFM image of the original surface Si (100) rms = 3 Å, peak-peak = 20 Å.

After chemical treatment, the morphology of the substrate surface did not change. According to the AFM, chemical preparation also does not lead to coarsening of the surface relief in the nanoscale range (rms = 3 Å, peak-peak = 20 Å). The presence of a pattern of elongated diffraction reflections on this
surface (figure 2), corresponding to the Si lattice, indicates that the surface of the substrates is atomically smooth and that the thickness of the formed SiO$_2$ layer does not exceed several monolayers (for Si (100) surface $1\text{ML} \approx 6.8 \times 10^{14} \text{atoms/cm}^2$).

![Figure 2](image)

**Figure 2.** The RHEED image from the Si (100) surface after chemical preparation.

In UHV conditions, chemically prepared substrates were sequentially degassed in a growth module at 450 °C for 60 minutes and 750 °C for 40 minutes until the pressure in the growth chamber stabilized at a minimum level ($3\div9 \times 10^{-10}$ Torr). Removal of the protective oxide thermally at 800 °C ($t \approx 10^{-15}$ minutes), or by heating at 750 °C in a stream of Si atoms ($\sim 1 \times 10^{13} \text{atoms} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, $t \approx 15-20$ minutes), according to RHEED, it is possible to obtain an atomically-smooth structurally-ordered silicon surface (figure 3).

![Figure 3](image)

**Figure 3.** The RHEED image from the Si (100) (a) and Si (111) (b) substrates after removal of the oxide layer. The electron energy is 10 keV. The azimuth of the incidence of the electron beam [011] and [112] for (100) and (111) surfaces, respectively.

Control Si layers with a thickness of 100 to 5000 Å were grown on the prepared substrates at temperatures from 350 °C to 750 °C and deposition rates of 1.0 Å/s. All the samples showed linear (2x2) and (7x7) diffraction for Si (100) and Si (111) substrates, respectively, with well-defined long narrow strands with presence of a superstructure and Kikuchi lines, which indicates a two-dimensional nature of the surface, its structural order and absence of microroughnesses (figure 4).
Figure 4. AFM image of the Si[500Å]Si(100) structure. \( \text{rms} = 3 \, \text{Å}, \text{peak-peak} = 10 \, \text{Å} \).

Grown structures demonstrate good morphological surface quality, without sharp jumps of relief, significant changes in the level of the average relief and areas of the heterogeneous roughness. The surface roughness is less than 1 nm. As a result, it managed to reduce the eviction oxide temperature below 800 °C, which is an important parameter for the MBE technology.

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