Processes of formation of epitaxial arrays of self-catalytic GaP nanowires on Si (111)

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Abstract. This study is devoted to the investigation of the effect of growth conditions (growth temperature, values of molecular beam fluxes) on the formation of self-catalytic GaP NW on Si(111), namely surface density, orientation and NW morphology. Nanowire arrays were grown on Si (111) by the plasma-assisted molecular beam epitaxy. It was determined that an increase of the temperature and a decrease of the Ga flux, while maintaining the V/III ratio, reduces the inclined NWs and parasitic islands nucleation probability.

1. Introduction

Epitaxial III-V semiconductor nanowire arrays (NW) are a promising material for modern optoelectronics. When forming NW by the vapor-liquid-solid mechanism, the most extensive possibilities for controlling the morphology of NW arrays are opened when using catalytic particles of third-party materials - usually a droplet of Au, pre-deposited on the growth substrate. However, the catalyst material can be embedded in the lattice of a growing NW, resulting in deep-level defects that reduce the lifetime of charge carriers and increase the probability of non-radiative recombination. The formation of NWs by a self-catalytic mechanism, when using an element of the III-group of the NW itself as a catalyst (for example, Ga for GaP) excludes III-V compound contamination, but imposes serious restrictions on the range of possible growth parameters and, as a result, the morphology of the formed NWs. [1]

Gallium phosphide is an indirect band gap semiconductor with Eg=2.27 at 300K, which is almost lattice-matched() with silicon. In addition application of GaP in optoelectronic devices is limited by its indirect bandgap structure and thus low quantum efficiency.[2] However, recently it was theoretically predicted that GaP in the metastable wurtzite crystal phase should demonstrate pseudo-direct band behaviour [3, 4]. In fact, Au-assisted wurtzite GaP NW grown by MOVPE demonstrated bright PL response at room temperature.[5] Also, GaP NW’s can also find applications in high-thermal loads and high-radiation environments, such as space, due to its wider bandgap and higher radiation hardness in comparison with Si and one of the highest thermal conductance among other semiconductors.

In this work, we study the effect of growth conditions (growth temperature, values of molecular beam fluxes) on the formation of self-catalytic GaP NW on Si (111), namely surface density, orientation and NW morphology.
2. Materials and methods
Epitaxial GaP NW’s arrays were synthesized on a p-Si(111) substrate using the PA-MBE Veeco GEN-III machine. Prior to the loading into the MBE chamber, the silicon substrates were cleaned using a modified Shiraki technique. Silicon oxide was obtained by wet chemical oxidation by boiling in a NH$_4$OH:H$_2$O$_2$:H$_2$O(1:1:3) solution. The growth temperature was measured using a pyrometer and a thermocouple. After loading and degassing, the substrates were annealed at temperatures of 770-800 °C, which is ~40 °C less than the deoxidation temperature. Thus, GaP NW formation occurs on the silicon surface oxide layer, which prevents the direct interaction of gallium adatoms with the silicon and facilitates the formation of non-wetting Ga droplets. Ion gauge-based beam flux monitor (BFM) was used to control the equivalent pressure of Ga and P$_2$ molecular beams. NWs growth was performed at temperatures of 610-630 °C and V/III ratios are 6 and 24.

![Figure 1. Schematic representation of GaP NW.](image)

The morphology of synthesized NW’s arrays was studied using a scanning electron microscope (SEM) (Zeiss SUPRA 25-30-63).

3. Results and discussion
3.1. Influence of Ga pre-deposition on the surface density.
Our studies reveal that in order to achieve a higher yield of GaP vertical nanowires on SiOx/Si(111) surface, there is no need to use a separate stage for the formation of a catalytic droplet. We assume that catalytical droplets can be self-assembled at the initial growth stage even if both group-III and group-V fluxes simultaneously reach the sample surface. On the Figure 2 presented below one can find SEM images of samples grown at similar growth conditions (V/III is 6, T is 610 °C, t is 5 min) but using different nucleation techniques. In the first sample growth was initiated by simultaneous opening of group V and III-shutters while the second sample was started with Ga predeposition with an equivalent thickness of 1 nm at the growth temperature. And the second one was grown using 30 second P pre-exposure prior to the opening of the Ga shutter. One can observe that NW nucleation density is higher and their diameter is less if we do not use any preliminary droplet deposition. In both cases density of in-plane grown nanoislands is higher than the density of NW and some of them demonstrate a Ga-droplet on their sides. If we keep in mind that structures were grown at stoichiometric V/III ratio, the appearance of the VLS in-plane growth can be an illustration that a too large catalytic droplet is formed in both cases or contact angle value is too small and as a result Ga-droplet wets the surface oxide. Formation of vertical NW without preliminary Ga deposition demonstrates that the Ga droplets can be self-organized in single step growth. In addition, the Ga predeposition, only worsens the NW yield, due to excessive increase of the catalytic droplet size. Notably, nucleation density is reduced in several orders of magnitude during the growth on the phosphorus preexposed SiOx/Si(111) surface.
We assume that self-organized growth of Ga droplets can occur at the beginning of the growth even in presence of group-V flux, as the phosphorus diffusion length on SiO$_x$/Si(111) at chosen growth temperature is negligible due to high desorption. However, one can suggest that the chosen V/III ratio should greatly affect this process.

3.2. Influence of change of growth temperature and Ga flux on the surface density of NWs arrays.
In this section, we discuss the effect of the growth temperature and the Ga flux on the surface density and yield of vertical NWs. An increase of the growth temperature from 610 to 630 °C (samples I and II, respectively) (beam equivalent pressure(BEP) P/Ga is 24, Ga flux 2 a.u.) leads to a sharp increase in the surface density of vertical NWs and decrease in the density of inclined NWs, while the island density remains approximately unchanged (see Figure 3). It follows from this that an increase in temperature favors the formation of nuclei with the GaP(111)B orientation.

Figure 2. a), c) side and top view on the sample grown by simultaneous opening of group V and III-shutters b), d) side and top view on the sample grown with the Ga droplet predeposition.
Figure 3. a), b) Diagrams of the axial and radial growth rates of GaP NWs arrays grown at various synthesis parameters c), d) Diagrams of the surface density and equivalent thickness of GaP NWs arrays grown at various synthesis parameters.

Also, an increase of temperature leads to a decrease of the NW diameter by 30% (see Figure 3). This effect can be explained by a decrease in the amount of Ga adatoms arriving to the catalyst droplet due to the increased Ga desorption. Due to the negligible phosphorus adatom diffusion length, the amount of phosphorus arriving into the Ga-droplet during VLS-growth is determined by its dimensions. Thus, the reduction of Ga droplet dimension and consequent decrease of the NW diameter can balance the incoming Ga and P fluxes.

Notably, twofold decrease in the absolute BEP of Ga (to 1 a.u.) and P while maintaining the constant V/III flux ratio (sample III), sharply suppress the nucleation of parasitic islands nucleation rate.

It can be noted that despite the doubled growth time the equivalent thickness of GaP in sample III is reduced as compared to sample II due to the increased fraction of desorbed P. At the same time, the fraction of material in the form of islands in comparison with sample II decreased: the equivalent thicknesses of vertical NWs in a doubled time (sample III) decreases by ≈ 2 times, and of islands ≈ 3 times.

4. Conclusions
In conclusion, we would like to note that an increase of temperature can effectively suppress the nucleation of inclined NWs, and a decrease in the Ga flux can effectively suppress parasitic islands. It was shown that droplets of the required morphology (size and contact angle) necessary for the nucleation of NWs can form self-organized with the simultaneous opening of the Ga and P source shutters. In the case of Ga preliminary deposition, the density of the array of vertical NWs decreases.

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