Epitaxial synthesis of single-domain gallium phosphide on silicon

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Abstract. The aim of the work is to investigate different approaches for the growth of planar gallium phosphide layers on silicon by molecular beam epitaxy. Atomic force microscopy and reflection high energy electron diffraction were used to study surface morphology and estimate the film domain structure. Developed growth technique with the use of a low-temperature AlGaP/GaP seeding layer allowed us to achieve atomically flat pseudomorphic single-phase GaP on Si(001).

1. Introduction
Gallium phosphide is a promising buffer layer material for the monolithic integration of III-V on silicon since it has a 0.37% lattice mismatch with Si at 300K. The common problems of GaP/Si heteroepitaxy are caused by the difference in the symmetry of the film and the substrate, surface energy mismatch, and chemical interaction between Si, Ga and P [1]. The migration enhanced epitaxy (MEE) method is commonly proposed to obtain single-domain GaP buffer layers [2,3]. This technique consists of alternating exposure of the structure under molecular III and V groups fluxes at the low growth temperature. However, it brings numerous drawbacks including poor reproducibility, wearing out of the molecular source shutters and inefficient surface smoothness.

In this letter, we optimize the growth technique and developed a new simple approach to obtain single-domain and atomically-flat GaP layers on Si(001).

2. Experimental
Heterostructures were synthesized with the use of Veeco GEN-III molecular beam epitaxy (MBE) setup with cracking sources of phosphorus (we used P₂ molecules - the temperature of a cracker zone is 900°C) and arsenic (we used As₄ molecules - the temperature of a cracker zone is 600°C). Silicon wafers were cleaned using the Shiraki technique [4] before the loading into the MBE chamber. The temperature of the substrate was controlled using a thermocouple calibrated by direct comparison with an optical pyrometer. The crystal structure and surface morphology were monitored during the growth using reflection high-energy electron diffraction (RHEED).

Beam equivalent pressure (BEP) was measured by Bayard-Alpert gauge. At a growth temperature (T_growth) of 580°C the stoichiometric ratio of V/III fluxes in our MBE setup is 6 since at lower values of phosphorus fluxes Ga droplets accumulate on the substrate surface.
We carried out the GaP surface morphology analysis by atomic force microscopy (AFM) using a Bruker Bioscope Catalyst.

3. Optimization of a substrate preparation

We used boron-doped p-type vicinal silicon (001) substrates (0.3–3 Ohm·cm) with a misorientation of \(4\pm0.5^\circ\) toward \(\langle 110\rangle\). According to published data, annealing of vicinal substrates with an azimuth of misorientation along one of two mutually perpendicular directions of Si(001) surface dimers can form a system of biatomic steps on the Si surface repeating the III-V (001) surface symmetry [5-8]. We could archive biatomic steps with the standard thermal annealing under residual \(P_2\) and \(P_4\) pressure below \(2\times10^{-9}\) Torr since phosphorus can diffuse deep into the substrate [9], replace and prevent diffusion of surface silicon atoms [10].

Another factor affecting the Si(001) surface quality is the annealing temperature. The high temperature promotes the surface step rearrangement and facilitates the surface chemical reaction between P with Si. The following method was developed: initial annealing for 10 min at 850°C - the minimum temperature necessary for desorption of the surface oxide prepared by the Shiraki method, and subsequent annealing for 30 min at 800°C to smooth the surface. As a result, we observed (2x1) surface reconstruction RHEED pattern, which corresponds to the biatomic steps on the Si surface.

(001)-oriented surface provides predominant adatom diffusion along surface dimer rows, affecting the shape of the growing GaP layer [11]: antiphase regions are elongated in mutually perpendicular directions. As soon as a dominant domain is formed, the growth rate of the antiphase domain is limited due to the adatom diffusion anisotropy. As a result, the antiphase domain has a smaller thickness. Thus, the presence of antiphase boundaries on the GaP/Si(001) surface can be judged from the analysis of AFM images [12,13].

4. Formation of single-domain GaP

It was found that the growth of GaP layers at a stoichiometric ratio of molecular fluxes (V/III~6) induce the surface pit formation due to the chemical interaction of Ga and Si. The V/III ratio ~8 is optimum since the roughness increases at larger fluxes of the V group due to the suppression of Ga adatom diffusion.

Sample 1 was synthesized as the initial sample (figure 1 (a)). At the initial stage of heteroepitaxy, it is necessary to achieve uniform nucleation of the growing GaP layer over the entire surface of the substrate. We used low-temperature seed layers for this purpose. The temperature should be in the range of GaP nucleation with a single polarity [14]. Given that we cooled the substrate to 440°C for GaP seeding growth after the oxide annealing.

Before the start of GaP growth, we exposed the substrate under the phosphorus growth flux to form P-Si surface bonds. Then, the group III source shutter was opened for a low-temperature GaP seeding layer synthesis with a calculated thickness of 3.4 nm. After that, without interrupting the growth, the substrate temperature was heated at a rate of 40°C/min to 580°C. The high mobility of adatoms at high temperatures helps to smooth the surface and improve the crystalline quality of the growing layer. We chose the growth time to obtain a total layer thickness of 33.4 nm. This is 3 times lower than critical, which means that there should be no defects in the crystal structure related to the relaxation of elastic stresses [15].
Figure 1. Sample 1 (a) and 2 (b) schemes and AFM images.

We synthesized a series of samples to show optimal growth conditions from the point of view of crystal quality and to determine the antiphase domain suppression factors. On the surface of sample 1 one can distinguish the dominant domain with an atomically smooth surface and pits of antiphase regions (depth ~8 nm, diameter ~50 nm). Earlier, we found that a growth temperature higher than 600°C and lower than 540°C deteriorates the surface morphology.

It was noted [16], that exposure of Si under the arsenic improves the quality of the GaP buffer layer since phosphorus can diffuse into Si, while As rather terminates the surface. The surface of sample 2 (figure 1 (b)) was exposed under the As flux. However, in sample 2 there is no dominant domain and the surface roughness is higher in comparison with sample 1.

Figure 2. Sample 3 (a) and 4 (b) schemes and AFM images.

Sample 3 (figure 2 (a)) has a larger thickness of the low-temperature layer while maintaining the total thickness. It has a smoother surface of dominant domain and lower defect density compared to sample 1 (table 1). The short diffusion length and high nucleation density at low temperatures favor the overgrowth of the antiphase domains at the initial moment of growth. In this case, the growth rate of antiphase domains is suppressed due to the small lateral size, which increases the difference between dominant and antiphase areas thicknesses.

| Sample number | Sample description | The proportion of the dominant phase | The difference between areas thickness, nm |
|---------------|--------------------|-------------------------------------|------------------------------------------|
| 1             | initial            | 0.83                                | 8.2                                      |
| 2             | As initialization  | 0.55                                | 8.7                                      |
| 3             | ↑ h seeding layer  | >0.98                               | 23.5                                     |

It was found that growth interruption during the sample heating adversely affects the layer. Sample 4 (figure 2 (b)) was grown with the growth interruption between the low temperature and high-
temperature layers. One can find that surface pits are formed through the entire thickness of the GaP layer. We assume that the uniform integrity of the low-temperature GaP layer was broken at the temperature rise. Thus, the opened Si surface does not overgrow during the subsequent high-temperature growth.

![Figure 3. The sample 5 (a) and 6 (b) schemes and AFM images.](image)

It was also noted [16], that the use of a low-temperature AlGaP buffer layer improves the quality of growing layers. The AlGaP/Si heterointerface has an atomically sharp boundary when GaP/Si mutually diffuses and has an island growth mode. We synthesized sample 5 (figure 3 (a)) with an AlGaP seeding layer thickness of 0.8 nm, followed by low-temperature GaP. It has a lower roughness than sample 3 (figure 2 (a)) with a single low-temperature GaP seeding layer.

To study films with increased thickness we grew sample 6 (figure 3 (b)) using an optimized synthesis technology. It differs from the sample 5 by the low-temperature and high-temperature layer thickness. Near ⅓ of the pits overgrow along with the structure's growth, but the remaining ones almost unchanged their depth.

5. Conclusions

Influence of the growth conditions and seeding layer formation techniques on the GaP growth on Si(001) was studied: namely the effect of the growth interruption between the low-temperature and high-temperature growth stages, the role of AlGaP seeding layer thickness, and influence of the Si surface pre-growth exposure under the As and P flux on the GaP layer structure and morphology were revealed.

Judging from the analysis of the AFM and RHEED data we can conclude that pre-growth exposure under P flux and the use of a thick low-temperature seeding layer result in the most effective antiphase boundary annihilation. However, threading pit-like defects remain at the GaP surface. We note that one of the effective approaches to suppress the formation of such defects is to not interrupt the growth during sample heating upon transition to high-temperature growth.

Acquired information allowed us to suggest a novel method of growth single-phase GaP buffer layer on Si without the use of MEE technique.

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