Impact of silicon wafer surface treatment on the morphology of GaP layers produced by plasma enhanced atomic layer deposition

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Investigations of atomic-layer deposition of GaP layers on Si substrates with different orientations and with different preliminary surface treatment have been carried out. The deposition of GaP was carried out by the method of plasma enhanced atomic-layer deposition using *in situ* treatment in argon plasma. It was shown that at the initial stage of the growth of GaP layers on precisely oriented (100) Si substrates and with misorientation, two-dimensional growth occurs both after chemical and plasma surface treatment. Upon growth on (111) substrates, after plasma treatment of the surface, a transition to three-dimensional growth is observed, at which the size of islands reaches 30−40 nm. The smallest root-mean-square roughness of the surface of the growing GaP layers (< 0.1 nm) was achieved for (100) substrates with a misorientation of 4°. The GaP layers grown on (100) substrates had a roughness of ∼ 0.1 nm, and on substrates with the (111) orientation — 0.12 nm. It was found that the surface treatment of Si substrates with the (100) orientation in hydrogen plasma leads to a slight increase in the surface roughness of growing GaP layers (0.12−0.14 nm), which is associated with the effect of inhomogeneous etching of silicon in hydrogen plasma. When treating the (100) silicon surface in argon plasma, the surface roughness does not change significantly in comparison with the chemical surface treatment. On the surface of substrates with preliminary deposition of an epitaxial Si layer with a thickness of 4 nm, the morphology of GaP layers is the same as in the case of using hydrogen plasma.

Keywords: PECVD, ALD, silicon, gallium phosphide

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1. Introduction

The development of solar power requires constant improvement of the characteristics of solar cells (SC), the most important parameter of which is the efficiency of solar energy conversion (efficiency). One of the most successful ways to increase the efficiency of solar cells is the use of heterostructures, which use a heterojunction between a wide-gap emitter and an absorbing material. An example of the successful application of this approach was the intensive development of SCs based on the *a*-Si:H/*c*-Si heterojunction. Using a thin layer (< 5 nm) of undoped amorphous hydrogenated silicon (*a*-Si:H) coated with a highly doped layer *a*-Si:H, made it possible to achieve efficiency value close to the theoretical limit for SC based on silicon [1]. The undoped layer *a*-Si:H provides the necessary passivation of the surface (low density of surface states), and the doped layers form the bands bending in the Si-substrate. However, *a*-Si:H is unstable when exposed to temperatures > 300°C, which imposes serious restrictions on other technological processes. Also, a significant disadvantage of *a*-Si:H use as a wide-gap emitter is the losses for absorption of a part of the solar radiation spectrum due to the high absorption coefficient in the short-wavelength region of the spectrum.

In recent years, attempts were made to search for new, wider-gap materials for creating the emitter with low absorption coefficient that provide good passivation of Si. Encouraging results were achieved using transition metal oxides and fluorides to create hole and electron contacts, respectively [2]. However, for structures based on these materials, the problem of temperature stability was not yet solved [3–5]. In this connection, $A^{III}B^{V}$ compounds, in particular gallium phosphide (GaP), are of particular interest. GaP is an undirect-band wide-gap semiconductor with the forbidden band width of 2.26 eV, which guarantees low absorption losses. Due to the small difference in the values of the constant lattice for GaP and Si (0.4%), it is possible to achieve a low concentration of defects at the GaP/Si interface. The large gap of valence bands at this interface ($\Delta E_V = 0.8-0.95$ eV) [6,7] limits the transport of holes generated in Si, which suppresses surface recombination. On the other hand, relatively small gaps of the conduction

bands ($\Delta E_C = 0.2-0.35$ eV) ensure efficient transport of electrons through the GaP/Si interface. Based on the band structure, the GaP/Si heterojunction is of primarily interest for the creation of photovoltaic converters based on Si of *p*-conductivity type [6,8]. Add that the task of creating efficient SCs based on Si of *p*-type is still relevant for low-orbit space applications due to their better radiation resistance [9].

However, when speaking about SC manufacturing at industrial level, the synthesis technology is of great importance, it should provide, on the one hand, high productivity and the ability to carry out the process at relatively low temperatures, and, on the other hand, a high quality of the interface. In this relation scalable low-temperature technologies for the formation of thin layers are of great potential interest, such as plasma-chemical deposition (PCD), atomic layer deposition (ALD), or their combination, which make it possible to carry out deposition over large areas.

Previously, a large amount of research on the GaP growth on silicon substrates by the plasma-chemical ALD method [10–12] was carried out, which showed the perspectivity of this direction of research. In particular, a method of plasma-chemical ALD with additional intermediate treatment in hydrogen plasma [10] was developed, and the effect of plasma treatment on the electrophysical properties of the Si-substrate [11] was shown. The successful doping of GaP with silicon to obtain the *n*-conductivity type [13] was also demonstrated, which makes it possible to obtain an efficient photoconverting structure on the silicon *p*-substrate. Besides, the possibility of two-dimensional epitaxial growth of GaP on Si (100) substrates with a misorientation 4° in direction [110]was demonstrated using the plasma-chemical ALD method with *in situ* annealing in Ar-plasma [14]. However, further investigation of the growth mechanism at the initial stages is still required. It is necessary to determine the effect of the plasma treatment used on the surface morphology of the growing layer. Studies of the effect of substrate orientation are also required. As a rule, when creating SCs based on Si a textured surface is used, which is formed by anisotropic chemical etching of substrates with orientation (100). The textured surface of Si- wafers is a pyramid with an average size of 5 μm with faces oriented in the direction [111], therefore, during SC the formation the growth of GaP layers should occur on the surface (111). Thus, the study of the initial stages of plasma-chemical ALD of GaP layers on Si substrates with different orientations and with different pretreatment of the surface is an urgent problem, this paper is focused on this problem solution.

2. Experimental part

A series of experiments was carried out relating atomic deposition of GaP layers on Si substrates with different orientations and different pretreatment of the surface. The deposition was carried out on precisely oriented polished Si-substrates (100) and (111), as well as on Si-substrates (100) with misorientation 4° in direction [110]. For all types of substrates, immediately before the start of the deposition process, the natural oxide was removed by chemical treatment in a 10% HF/H_2O solution.

Then, immediately after the chemical treatment the substrates were placed in the lock chamber of the Oxford Plasmalab 100 PECVD plasma-chemical deposition unit. After the lock chamber evacuation the substrates were transferred to the growth chamber on a substrate holder (24 cm in diameter) preheated to temperature of 380°C and kept for 30 min. Before deposition of the GaP layer four series of experiments were carried out: without plasma treatment, with treatment in hydrogen plasma, with treatment in argon plasma, and with preliminary deposition of a thin Si epitaxial layer.

Surface treatment of Si-substrates in pure hydrogen plasma was carried out at a pressure of 0.5 Torr, HF (13.56 MHz) power of discharge 100 W for 1 min. Surface treatment was carried out similarly in pure argon plasma at a pressure of 0.5 Torr, a power of 100 W for 1 min. The process of preliminary deposition of Si layer with thickness of 4 nm was carried out under conditions that ensured initial epitaxial growth on the surface of GaP substrates [15]. The deposition occurred at a flow ratio of silane to hydrogen 1/50, a power of 100 W, and a pressure of 1.9 Torr.

Further, immediately after surface treatment at a temperature of 390°C the process of plasma-chemical atomic layer deposition was carried out in the previously developed mode using *in situ* treatment in argon plasma, which provides epitaxial growth of GaP layer [14]. For the growth of GaP layers, the organometallic compound Ga — trimethylgallium (TMG) and phosphine (PH_3), respectively, were used as a source of Ga and P atoms. The process of plasma-chemical atomic layer deposition of GaP, which consists of cyclic alternating feeding of trimethylgallium and phosphine into the reaction chamber, was carried out at a temperature of 390°C. The decomposition of PH_3 takes place in a glow discharge plasma with a power of 200 W and a pressure of 0.35 Torr. After each deposition step, the chamber was purged with Ar stream. Before the step of Ga deposition, carried out due to the thermal decomposition of TMG, the surface of the growing layer was activated using Ar-plasma with power of 200 W for 10 s. The TMG was supplied to the chamber using a carrier gas — hydrogen, providing TMG concentration in mixture with hydrogen at a level of 8%. For each series the deposition process consisted of 20 cycles to provide the resulting GaP layer thickness ~ 4 nm.

For all structures the surface morphology was studied using atomic force microscopy (AFM). The measurements were carried out on NT-MDT NTegra Aura unit in the semicontact mode, using NT-MDT HA_NC probes with a resonant frequency of ~ 235 kHz and a tip radius of < 10 nm. For all samples, the scan size was 500×500 nm (512×512 dots). RMS roughness was measured using the Gwyddion software package.

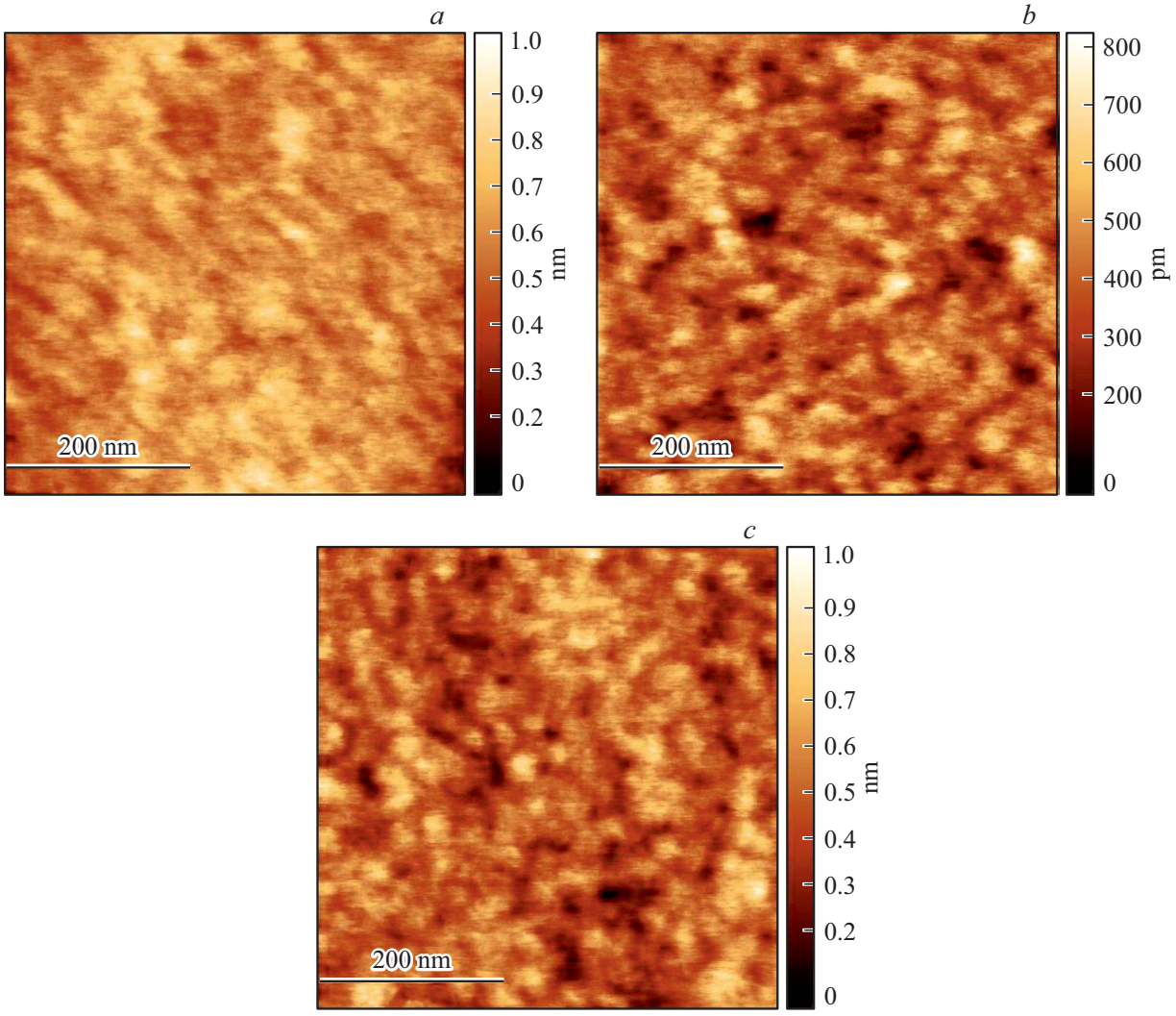

Figure 1. Surface morphology of the GaP layer deposited without pretreatment in plasma on Si substrates with the orientation: (100) with misorientation 4° in the direction [110] (*a*), (100) (*b*), (111) (*c*).

RMS roughness for GaP layers

Substrate orientation	Surface treatment			
	W/o treatment, pm	In H_2 plasma pm	In Ar plasma, pm	Si thin layer, pm
(100) 4° in direction [110]	95	147	68	140
(100)	97	114	113	114
(111)	121	198	206	122

3. Results and discussion

The surface morphology image obtained by AFM for GaP layers deposited without plasma treatment is shown in Fig. 1. GaP layers deposited on Si-substrates with different orientations have a very smooth surface. The values of root-mean-square surface roughness given in the Table are at the level of 0.1 nm. Thus, at the initial stage two-dimensional growth of GaP is observed on the surface of Si-substrates, regardless of their orientation. The two-dimensional growth is also confirmed by the results of transmission electron microscopy for a GaP/Si multilayer structure deposited on Si (100) with misorientation 4°, which are shown in Fig. 2. GaP layer deposited on Si-substrate inherits the structure of the substrate and has a uniformly distributed thickness of 3 nm, i.e. at the initial stage two-dimensional epitaxial growth of GaP takes place.

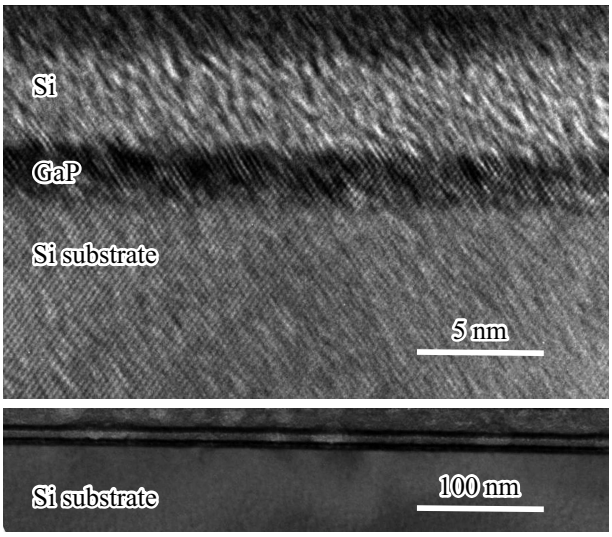

Figure 2. TEM of the cross section of GaP/Si-structure deposited on Si (100) substrate with misorientation 4° in the direction [110].

At the next stage the influence of Si surface treatment in hydrogen plasma was studied. The surface morphology of GaP layers deposited after treatment in hydrogen plasma is shown in Fig. 3. It can be seen that the roughness of the GaP layers deposited on substrates with (100) orientation increases by 1.2–1.5 times. The rms value is 0.11 nm for a precisely oriented surface and 0.15 nm for a vicinal surface. At the same time, for GaP layers deposited on substrate with the (111) orientation, the roughness increases more significantly. On the AFM image (Fig. 3, *c*) one can observe the formation of individual grains with a size of 10–20 nm, indicating an island growth mechanism.

On the one hand, preliminary pregrowth treatment in hydrogen plasma is often used to remove the oxide layer from the surface of substrates [16], which is of great practical interest for the development of technology in which the interoperational time, when oxidation of Si surface occurs after treatment in HF solution, can be increased. Additional treatment in hydrogen plasma was also used

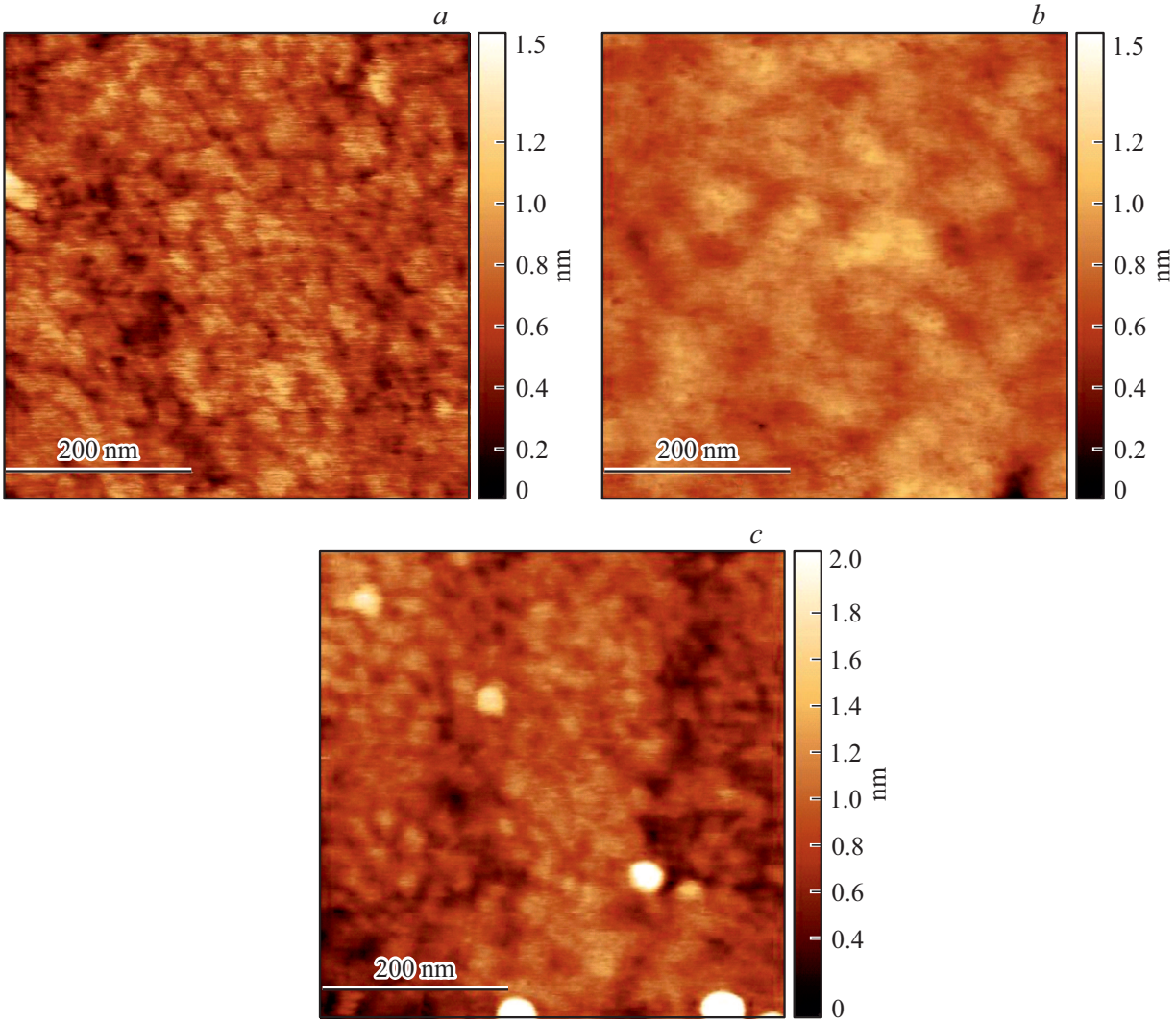

Figure 3. Surface morphology of the GaP layer deposited with pretreatment in H_2 plasma on Si substrates with the orientation: (100) with misorientation 4° in the direction [110] (*a*); (100) (*b*); (111) (*c*).

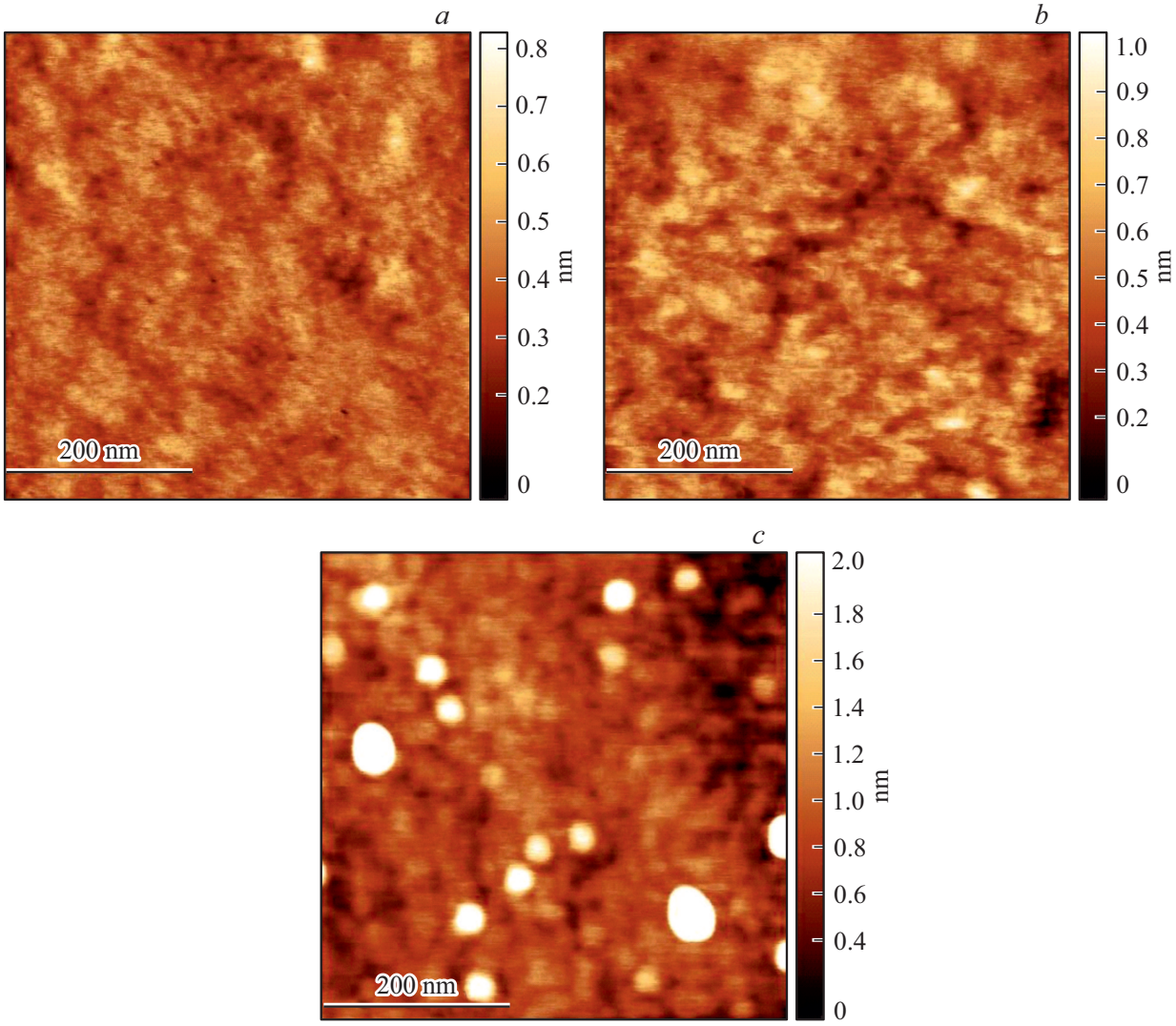

Figure 4. Surface morphology of the GaP layer deposited with pretreatment in Ar plasma on Si substrates with the orientation: (100) with misorientation 4° in the direction [110] (*a*), (100) (*b*); (111) (*c*).

in the process of cyclic plasma chemical deposition of GaP layers to remove excess phosphorus [10]. On the other hand, it is known that treatment in hydrogen plasma can lead to etching the silicon [17]. The deterioration of the surface morphology observed in this paper is most likely associated with the effect of etching Si in hydrogen plasma. In addition, it was previously shown that the use of high-power hydrogen plasma leads to the formation of defects in the Si near-surface region [11], which worsens the photoelectric properties of GaP/Si-heterostructures. Thus, we can conclude that the treatment of Si-substrates in hydrogen plasma has a negative effect on the surface morphology of growing GaP layers.

In addition to treatment in hydrogen plasma, the influence of Ar plasma on the surface of the growing GaP film is of great interest, since its use in the ALD regime makes it possible to achieve the best structural properties of GaP [14]. The results of morphology measurements with AFM for layers deposited after exposure to Ar-plasma are shown in Fig. 4.

For both precisely oriented and vicinal surface (100), in contrast to hydrogen plasma the Ar plasma does not lead to deterioration of the GaP surface morphology. In the case of vicinal surface even a slight decrease in the root-mean-square roughness to 0.68 nm is observed. Such an effect can be associated with local heating of the Si surface immediately before GaP growth, as it was suspected in [18]. The most significant result is that the action of Ar plasma does not lead to etching of Si (100), and, therefore, the growth mode using Ar-plasma can be used to form nucleation layers for the subsequent epitaxial growth of $A^{III}B^{V}$ compounds on silicon. For the surface (111) the action of Ar-plasma leads to the effect similar to hydrogen plasma. Grains with size of 20–30 nm are visible on the surface, indicating the three-dimensional growth of GaP. Note that for the surface (111) the action of H_2 or Ar plasma leads to a sharp change in the

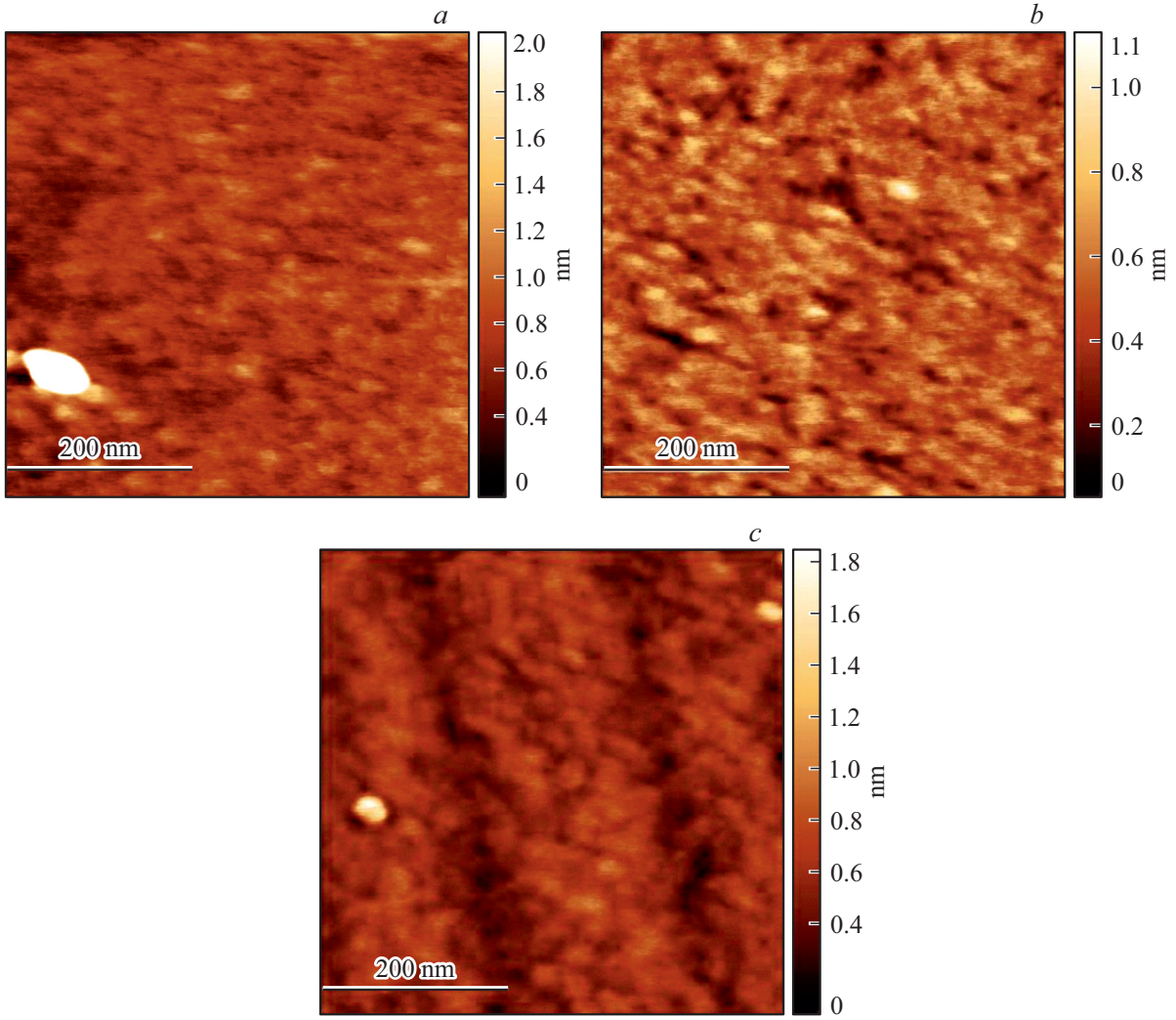

Figure 5. The surface morphology of the GaP layer deposited after the deposition of the Si layer on the substrates with the orientation: (100) with misorientation 4° in the direction [110] (*a*), (100) (*b*), (111) (*c*).

growth mechanism with an increase in the root-mean-square roughness by ~ 2 times.

However, a completely different picture is observed when using a pre-deposited epitaxial Si layer, as shown in Fig. 5. In this case, the surface of the GaP layer deposited on Si (111) is smoother compared to the treatment in H_2 or Ar plasma. The absence of granular structure allows us to conclude that GaP grows in two dimensions. For surface (100) the picture completely repeats the situation with the treatment in hydrogen plasma. During the growth of the epitaxial Si layer, a very strong dilution in hydrogen is used and, therefore, the surface of the Si-substrate is additionally exposed to hydrogen plasma, which explains the result obtained.

4. Conclusion

Thus, the investigations of the initial growth conditions showed that the smallest root-mean-square surface roughness of the growing GaP layers (< 0.1 nm) was achieved for (100) substrates with a misorientation 4°. The GaP layers grown on precisely oriented (100) substrates had a roughness of ~ 0.1 nm, and on substrates with the orientation (111) — 0.12 nm. It was found that surface treatment of Si-substrates with (100) orientation in hydrogen plasma leads to a slight increase in the surface roughness of growing GaP layers (0.12–0.14 nm), which is associated with the effect of inhomogeneous etching of silicon in hydrogen plasma. When surface (100) of silicon is treated in argon plasma, the surface roughness does not change significantly in comparison with chemical surface treatment. When using an intermediate epitaxial Si layer, the morphology of the GaP layers is similar to the situation with the use of hydrogen plasma, which is also associated with the effect of etching in hydrogen plasma due to the high concentration of hydrogen during epitaxial silicon growth. It was shown that at the initial stage of GaP layers growth on Si-substrates, precisely oriented (100) and with misorientation, two-dimensional growth occurs both

after chemical and plasma surface treatment. During growth on (111) substrates after plasma treatment of the surface, a transition to three-dimensional growth is observed. During 20 cycles the size of the islands reaches 30−40 nm.

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Conflict of interest

The authors declare that they have no conflict of interest.

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