GaN growth via HVPE on SiC/Si substrates: growth mechanisms

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Abstract. The article focuses on the study of GaN thin film growth via chloride epitaxy on SiC/Si hybrid substrate. SiC buffer layer was grown by a method of substitution of atoms, which allows one to reduce impact of mechanical stress therein on subsequent growth of III-nitride films. It is shown, that change in GaN growth conditions leads to change in its growth mechanism. Three mechanisms: epitaxial, spiral and stepwise growth are considered and mechanical stresses are estimated via Raman spectroscopy.

1. Introduction
Nowadays wide-bandgap semiconductors like GaN, AlN, SiC and others are becoming more widespread in view of huge prospects of their use in power electronics and LED technology, HEMT-transistors and much more [1-3]. However, large-scale production of such materials is still difficult, since certain problems arise during the growth of thin films of these semiconductors. In particular, today sapphire [4] is used mainly as substrates for the growth of GaN thin films and heterostructures, which has a number of drawbacks, due to which it is impossible to grow a defect-free film: sapphire has a large lattice mismatch and different coefficient of thermal expansion comparing to GaN [5]. Therefore, the search for new types of substrates, allowing one to obtain more structurally perfect GaN films, heterostructures and devices continues. In a series of papers [6,7] a method for the synthesis of SiC/Si substrates has been developed theoretically and put into practice, based on the chemical substitution of Si atoms for C atoms directly in the silicon substrate. It was demonstrated that SiC/Si substrates obtained by this method can be used for the growth of high-quality GaN layers. Moreover, use of silicon as a starting material will allow integrating wide-bandgap semiconductors into traditional silicon electronics. Therefore, it seems expedient to further study and optimize the growth of III-nitrides on SiC/Si substrates.

In addition to choosing a suitable substrate for the growth of GaN layers, a well-developed technique for their deposition is also required. One of such techniques, along with molecular-beam (MBE) [8] and metal-organic (MOCVD) [9] epitaxy, is chloride epitaxy (HVPE) [10].
\[ \text{GaCl} + \text{NH}_3 = \text{GaN} + \text{HCl} + \text{H}_2 \]  

which allows one to ensure a high growth rate of thin films and to simplify the mass production of GaN-based devices. In this paper, we investigate mechanisms of GaN growth via HVPE on SiC/Si substrates formed by the method of substitution of atoms [6] and influence of the growth conditions on growth mechanisms.

2. Experiments
The first stage of the experiment was the deposition of the SiC buffer layer on silicon substrates with an orientation of \langle{111} \rangle. In the growth process via method [7] the following parameters were used: growth temperature 1250°C, total pressure of the gas mixture 2 Torr, synthesis time 15 min, gas mixture flow 100 ml/min, silane fraction in the mixture 16%. We have grown three similar substrates. Then, buffer layers of AlN were deposited on the obtained SiC/Si samples via chloride epitaxy, and then GaN layers were grown in a single process. For the growth we used HVPE reactor of horizontal type, having symmetric parallelepiped shape, the pressure in which was close to atmospheric. It should be noted, that three samples were placed in different places of the reactor. The first one SH295-1 was the closest to the reactor inlet nozzle, the second SH295-2 was at the center of the reactor, and the third SH295-3 was near the outlet. In this connection we suppose, that growth conditions were the same for all samples except total supersaturation, since when the gas mixture arrive to the third sample, it has already reacted with the first sample and the second one, etc. Therefore, we consider, that supersaturation gradually decreased from the first sample to the third one. Deposition of AlN films occurred as a result of a gas-phase reaction between aluminum trichloride (AlCl\(_3\)) and ammonia, GaN deposition was carried out as a result of reaction (1). Growth temperature for AlN and GaN was 1050°C. NH\(_3\) flow was 1.5 l/min, flow of HCl through gallium was 200 ml/min during GaN growth, and the same through aluminum during AlN growth. After the growth process the samples were studied by optical microscopy, Raman spectroscopy and optical profilometry.

3. Results and discussion
The study showed that the growth mechanism of GaN depends essentially on the supersaturation. Figure 1 shows optical images of the samples surface demonstrating various growth mechanisms of GaN film: epitaxial growth, stepwise growth, and spiral growth.

![Image](image1.png)

**Figure 1.** Optical image of GaN/AlN/ SiC/Si samples growing by different mechanisms. As the total supersaturation decreases, the growth mechanism changes from epitaxial (a) and stepwise (b), to spiral one (c).

In epitaxial mode (SH295-1) film grows uniform in thickness and does not have expressed defects on the surface. Its average roughness (rms) is 15 nm according to optical profilometry. On the GaN sample growing by a stepwise mechanism (SH295-2) average distance between the steps is of the order of 10-20 \(\mu\)m, and their height is 200-300 nm according to optical profilometry. GaN sample growing in conditions of lower supersaturation (SH295-3) demonstrate growth due to screw dislocations and growth spirals are clearly visible on the surface. Characteristic sizes of the spirals are
40-70 microns in diameter, and 250-400 nm in height according to optical profilometry (Fig. 2). The height of the individual steps of the spiral is much smaller than in the case of stepwise growth and is of the order of 25-40 nm (Fig. 2b).

The change in growth mechanism seems to be related to change in supersaturation and agrees with previous results on crystal growth. In [11] it was shown that at low supersaturations growth occurs mainly due to screw dislocations, whereas with increasing supersaturation, concentration of adatoms on the surface becomes sufficient for 3D and 2D nucleation. The question arises about the samples SH293-1, and SH293-2. It seems that stepwise growth should occur at higher supersaturations than flat epitaxial growth, and this is not fully understood. One of possible reasons is a small inhomogeneity in the temperature at the center (SH295-2) and along the edges of the reactor (SH295-1, SH295-3), which affects reaction rate near the center.

The Raman spectra of the samples are shown in Figure 3. The spectra contain GaN bands (567.5 cm\(^{-1}\), 734 cm\(^{-1}\), AlN (658 cm\(^{-1}\)), Si (521 cm\(^{-1}\)), and SiC band (796 cm\(^{-1}\)) of low intensity due to the small thickness of the film. Using the Raman spectra mechanical stresses arised in GaN films grown via different mechanisms were estimated. For evaluation we used spectral position of 567.5 cm\(^{-1}\) gallium nitride band, which is depicted in the inset in Fig. 3.

The evaluation was carried out using the formula [12]:

\[
\Delta \omega_{\text{GaN}} = 4.3 \sigma \text{ cm}^{-1}/\text{GPa}
\]

where \(\Delta \omega_{\text{GaN}}\) is the deviation from the band position at unstressed state (567.5 cm\(^{-1}\))[12], and \(\sigma\) is the mechanical stress. Obtained stress values for the sample SH295-1 is 200-250 MPa, for SH295-2 is 100-150 MPa, for SH295-3 is 250-300 MPa. It should be noted that on the sample SH295-3
demonstrating spiral growth, fewer cracks were visually observed than on the other two samples. We suppose increased elastic stresses in this sample are associated with this fact, since elastic energy remains stored instead of being used for the formation of cracks.

![Figure 3. Raman spectra of the samples. Inset demonstrates position of GaN band (567.5 cm⁻¹) on a larger scale.](image)

4. Conclusions
In this paper the growth of GaN via the method of chloride epitaxy is considered. A series of samples of thin GaN films were grown in a single process on SiC/Si substrates obtained by the method of substitution of atoms. It is found that while supersaturation increases, the growth mechanism of GaN changes from growth via screw dislocations (growth spirals are observed on the surface), to epitaxial growth (the surface remains relatively smooth), and stepwise growth (on the surface there are clearly discernible parallel steps). Using optical profilometry characteristic sizes of the spirals were estimated to be ~ 40-70 μm in diameter and 250-400 nm in height. The height of the steps of the growth spirals is about 25-40 nm. The characteristic height of the steps during stepwise growth is about 200-300 nanometers and are equal to about 300 MPa, whereas this sample is the least cracked. The results can be used in further findings of optimal growth conditions of GaN on SiC/Si substrates via HVPE.

Acknowledgments
This study was supported by Russian Science Foundation (RNF grant N 14-12-01102). Part of the results were obtained unique scientific facility “Physics, chemistry, and mechanics of crystals and thin films” (IPME RAS, St. Petersburg, Russia).

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