Observation of the influence of complex SiC porous buffer layer on properties of GaN/Si(111) heterostructures

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Abstract. 1-μm-thick GaN layers were obtained in one growth procedure on compliant SiC/Si(111) substrates using plasma-assisted molecular beam epitaxy (PA MBE). Si(111) substrates were modified by the atoms substitution technique. Prior to the atoms substitution procedure, on the one substrate, the transition porous Si layer (por-Si) was performed. The GaN layer grown on this substrate revealed better surface morphology and structural quality, less threading dislocation density, and as a result, showed lower free carrier concentration and higher carrier mobility. Moreover, the XRD study revealed less strain level in the GaN layer grown on the por-Si layer.

1. Introduction
The problem of integrating III-N technology with the most established Si technology is one of the most urgent problems facing the state of art science and technology. For decades, there have been numerous attempts to solve the well-known problem of III-nitride material family, i.e., defects and dislocations which occurs due to a high lattice and thermal expansion coefficient (TEC) mismatch between Si and GaN (~17% and ~54%, respectively) [1]. One of the most common ways to suppress defect generation the process is the use of complex multi-periodic superlattices based buffer layers [2] but this results in a complication of growth procedure and significantly increases the end-device cost. SiC substrates seem to be more suitable for III-N based devices fabrication due to their higher thermal conductivity $k_{3H-SiC}=3.6$ W/(cm×°C), less lattice mismatch $\sim$3.4% (with the account of rotation) and insignificant TEC mismatch ($\sim$0.4°K$^{-1}$) [1] but SiC substrates are also expensive. The possible solution to this problem may be the use of the transition SiC buffer layer.

In this paper, we continue to develop a novel approach to the formation of III-N layers on silicon substrates using a transition nanoporous Si sublayer. We modified the previously described porous Si layer [3] by using the atoms substitution technique [4] to achieve 3H-SiC / por-Si / Si (111) compliant substrate. In one growth procedure, we form a 1-μm-thick GaN layer on 3H-SiC / por-Si / Si (111) substrate and observe that the GaN layer which was formed on the first one revealed better optical, physical, and structural properties.

2. Experimental
Both samples were grown in one growth procedure by plasma-assisted molecular beam epitaxy using a Veeco Gen 200 setup. Prior to the growth, the substrate with a preformed por-Si layer formed as
described in [5] as well as conventional Si(111) substrate underwent atoms substitution technique. The nucleation layer with 3-dimensional surface morphology was grown at the equal nitrogen and gallium fluxes \( F_{Ga} = F_{N} \sim 0.05 \, \mu \text{m/hour} \) at the growth temperature \( T_{s} = 650^\circ \text{C} \). The upper laying high-temperature 350-nm-thick GaN layer was formed at \( T_{s} = 700^\circ \text{C} \) and metal-rich conditions \( F_{Ga} \sim 0.4 \, \mu \text{m/hour} \) and \( F_{N} \sim 0.05 \, \mu \text{m/hour} \). The top GaN layer was grown at the \( T_{s} = 650^\circ \text{C} \) and less metal-rich conditions \( F_{Ga} \sim 0.2 \, \mu \text{m/hour} \) and \( F_{N} \sim 0.05 \, \mu \text{m/hour} \) up to GaN thickness of \( \sim 1 \, \mu \text{m} \). The surface morphology was studied scanning electron microscopy (SEM). Crystalline quality was evaluated using the X-ray diffraction (XRD) analysis. Optical properties were studied by means of PL, Raman, UV spectra analysis. Carrier concentration and type of conductivity were determined by means of Hall Effect technique applying Van der Pau method.

3. Results

The cross-section SEM image confirms the revealed reasonable quality of the obtained layer and layer–substrate interface. Both interfaces have a porous structure independent of either using of por-Si sublayer or not. However, as can be seen from Figure 1 (a, b) the depth of the porous region in the substrate is considerably greater for the sample grown on SiC/por-Si/Si substrate.

![Cross-section SEM image of samples grown on SiC/por-Si/Si (a, c) and SiC/c-Si (b, d) substrates at the different magnification.](image)

The results of the electro-physical measurements are listed in table 1. Both samples revealed n-type conductivity.

| Sample                  | Charge carrier concentration, cm\(^{-3}\) | Mobility, cm\(^2\)/Vs |
|-------------------------|------------------------------------------|------------------------|
| GaN/SiC/c-Si(111)       | \(-1.8 \times 10^{19}\)                  | 52                     |
| GaN/SiC/por-Si(111)     | \(-9.2 \times 10^{17}\)                  | 990                    |

The structural quality of both samples was estimated using high-resolution X-ray diffraction on the basis of inverse q-space mapping of the samples (see Figure 2). Measured lattice parameters \( a \) and \( c \) of both samples are presented in Table 2.

| Sample                       | Lattice parameters, Å | Deformation \( \varepsilon_{\text{xx}} \) | Stress \( \sigma \), MPa |
|------------------------------|-----------------------|------------------------------------------|--------------------------|
| GaN/SiC/c-Si(111)            | \( a = 5.1813\) \( c = 3.1835\) | \(-1.8 \times 10^{-3}\)                   | -854                     |
| SiC                          | \(-\)                   |                                        |                          |
| Si                           | \(-\)                   |                                        |                          |
| GaN/SiC/por-Si(111)          | \( a = 5.1894\) \( c = 3.1933\) | \(1.3 \times 10^{-3}\)                   | 614                      |
| SiC                          | \(-\)                   |                                        |                          |
| Si                           | \(-\)                   |                                        |                          |
Figure 2. Q-space maps measured around (0002) GaN and (111) SiC sites for GaN/SiC/c-Si (a, c) and GaN/SiC/por-Si/c-Si (b, d). Cross-sections of the (0002) GaN and (111) SiC sites for GaN/SiC/c-Si (e, j, k) and GaN/SiC/por-Si/c-Si (f, l, m).

The PL spectra of the samples (see Figure 3) demonstrates two emission areas localized near 3.4 eV and broad emission band within the yellow-green range of the spectrum (500 – 600 nm) more intensive for GaN/por-Si/Si(111) heterostructure.

Figure 3. The PL spectra of the samples.

The maximum of emission the GaN/SiC/c-Si(111) sample is arranged at ~364.6 nm (3.4 eV) when maximum emission the GaN/SiC/por-Si(111) is arranged at ~363.1 nm (3.41 eV). This shift in energy (~0.01 eV) is related to different values of the internal stress in the films. It is also should be noted that both peaks revealed the same FWHM ~0.007 eV corresponding to reasonable crystalline quality.

Raman scattering spectra of the GaN films grown on SiC/c-Si and SiC/por-Si/Si templates and SiC film formed on the c-Si substrate are presented in Figure 4.
Measured transmission–reflection spectra of the samples are listed in Figure 4 (a, b). Based on these spectra the dispersion of the refractive index was calculated (see Figure 4 (c)). We obtained transmission–reflection spectra at the incidence angle of the electromagnetic emission close to 90°. Next, using Kramers–Kronig relation [6], the optical density D for the samples was calculated and the functional dependence $(D \cdot h\nu)^2$ on the quantum energy $h\nu$ was plotted.

![Figure 4](image1.png)

**Figure 4.** The Raman spectra of the GaN/SiC/c-Si (a), GaN/SiC/por-Si (b) samples and SiC/c-Si template (c).

![Figure 5](image2.png)

**Figure 5.** The transmission–reflection spectra of the samples (a, b), calculated refractive index of the samples (c), GaN/SiC/por-Si (b) samples and SiC/c-Si template (e), $(D \cdot h\nu)^2$–$h\nu$ dependence for both samples (d, e).

4. Discussion

From the SEM image of the samples, it can be seen that the depth of the porous region in the substrate is considerably greater for the sample within the por-Si layer. In this case when the SiC layer is formed diffusion of CO gas into the depth of the crystal proceeds by Si vacancies keeping in mind that...
due to its developed surface their amount in the bulk of porous layer is much greater than in crystalline silicon.

A significant increase in the mobility of free carriers along with a simultaneous decrease in their concentration, we associate with an increase in the crystalline perfection of the GaN layer in the sample grown on the por-Si layer. This fact is confirmed by the XRD study of the crystalline perfection of both samples.

XRD analysis revealed that the SiC layer formed on both substrates is characterized by a cubic lattice structure related to the substitution of the atoms technique in the base single-crystalline c-Si substrate which has a cubic crystalline structure. Using high-resolution X-ray diffraction on the basis of inverse q-space mapping of the samples we calculate crystal lattice parameters for all of the layers. The comparison of the reference GaN lattice parameters – \( a_{\text{GaN}}=0.31892 \text{ nm} \) and \( c_{\text{GaN}}=0.51860 \text{ nm} \) [7] and measured parameters (see Table 2) revealed that GaN layers grown on a substrate with and without por-Si transition layer has a different type of internal stress. The GaN/SiC/por-Si(111) sample have tensile internal stress level and GaN/SiC/Si(111) – compressive. This fact may be explained by a smaller size of nucleation islands which formed at the initial stages of each GaN monolayer growth for the sample grown on the por-Si layer. The smaller sizes of nucleation islands led to a higher tensile stress generation due to their coalescence, [8]. Analysis of the cross-sections of the sites (0002) for GaN and (111) – for SiC in the plane and in the direction of growth which is presented in Figure 2, revealed that cross-sections have roughly same FWHM in the plane of growth, however, FWH of GaN/SiC/por-Si sample in growth direction is 15% more narrow. This can indicate that in the case of heterostructure growth on the porous substrate as compared with the substrate of single-crystalline silicon a percentage of the vertical dislocations in the GaN layer is considerably lower while the contribution of the horizontal dislocations remains approximately the same.

From the PL spectra of the samples, we can calculate the centers of the emission peaks for both samples. The maximum of emission the GaN/SiC/c-Si(111) sample is arranged at \( \sim 364.6 \text{ nm} \) (3.4 eV) when the maximum emission the GaN/SiC/por-Si(111) is arranged at \( \sim 363.1 \text{ nm} \) (3.41 eV). This observation confirms that the GaN layer is of hexagonal symmetry but not the cubic one (in the latter case exciton emission would be of about 3.2 eV). As showed in [9] the bandgap of GaN is related directly with the stress level in the layer.

\[
E_g (\text{GaN}) = 3.4285 + 0.211 \sigma 
\]  

(1)

Using the formula (1) and calculated peak positions we can estimate the stress and strain levels in both samples as \( \sigma_{\text{c-Si}} = -1.32 \text{ GPa} \) and \( \sigma_{\text{por-Si}} = -0.66 \text{GPa} \). Stress and strain levels are directly proportional to each other with the coefficent of film modulus which is 478 GPa for GaN [10] – thus the deformations in the layers are \( \varepsilon_{xx,c-Si} = -2.7 \times 10^{-3} \) and \( \varepsilon_{xx,por-Si} = -1.3 \times 10^{-3} \). This data is not in good agreement with the XRD data analysis and this fact is under study.

From the Raman spectra of the samples presented in Figure 4, it can be seen that for the sample grown on the c-Si substrate the most intensive vibration is Si(LO) \( =531 \text{ cm}^{-1} \) and three low-intensive modes in the range of 430 cm\(^{-1}\), 617 cm\(^{-1}\) and 675 cm\(^{-1}\) associated with vibrations of atoms in silicon. As for the sample grown on the por-Si layer, two Si\(_{h,01}\) = 529 cm\(^{-1}\) and Si\(_{h,02}\) = 515 cm\(^{-1}\) are not the most intensive. This is connected with the fact that under the formation of the porous sublayer stoichiometry of the crystal lattice is violated due to the formation of nanocrystals in por-Si. The decrease of Si crystallite size results in the shift of the phonon mode Si(LO) localized in the Raman spectrum near 531 cm\(^{-1}\). Thus, in the considered case two modes with the frequencies of 515 cm\(^{-1}\) and 529 cm\(^{-1}\) are present in the spectrum of GaN/SiC/por-Si/c-Si heterostructure, meaning the formation of silicon nanocrystals with a size of 5 – 20 nm within the porous layer. As for Raman scattering from the epilayer layer spectra of the samples of both types involve vibrations characteristic of GaN with hexagonal symmetry. The Raman spectrum of the structure grown on SiC/c-Si only E\(_2\) (high) GaN vibration mode is observed while in the spectrum of SiC/por-Si/c-Si heterostructure both active vibrations of E\(_2\) (high) \((\sim 565 \text{ cm}^{-1})\), A\(_1\) (LO) \((\sim 730 \text{ cm}^{-1})\) are observed as well as E\(_1\) (TO) mode \((\sim 560 \text{ cm}^{-1})\). The occurrence of the E\(_1\) (TO) mode of GaN arranged near 559 cm\(^{-1}\) is related to nanocrystalline
GaN structure. The total width at half of the maximum (FWHM) for $E_2$(high) mode in both of the spectra is less than ~6.2 cm$^{-1}$, indicating at a good crystalline quality of GaN layer.

The obtained from UV transmission – reflection spectra revealed a slightly higher (+7%) value of the refractive index in the GaN layer grown on the template with the por-Si layer. Analysis of $(D\cdot h\nu)^2$- $h\nu$ dependence (Figure 5 (d, e)) allows revealing certain regions with a linear dependence of $(D\cdot h\nu)^2$ on the quantum energy. That may specify the presence of direct allowed transitions within this spectral range. Linear extrapolation of these spectral regions to the zero value of optical density enables the determination of the energy of direct transitions characteristic of the investigated samples of heterostructures. Energies of the direct allowed inter-band transitions determined from the graphical dependencies for both of the samples are presented in Table 3.

| Sample                        | Transitions and the features in UV spectra |
|-------------------------------|--------------------------------------------|
| GaN/SiC/c-Si(111)             | $2.31$ $1.81$                               |
| GaN/SiC/por-Si(111)           | $2.40$ $-$                                   |

It should be noted that the energies of direct transitions in GaN film grown on the templates of both types determined according to the described technique are in the range of the visible yellow luminescence (2.30 eV – 2.40 eV). Its appearance is quite often attributed to the defects of gallium (vacancies) bound with oxygen, and inherent to those that are found in the majority of GaN epitaxial layers with n-type conductivity. At the same time, a transition in the range of 1.86 eV can be attributed to SiN sublayer.

Summarizing all of the ideas presented above and based on the obtained experimental results, technological data, and on the information from the available literature, we think that the use of SiC/por-Si templates as substrates for the following growth of GaN films has a several unquestionable advantages as compared with the conventional ones. The application of nanoporous por-Si allows one to improve the structural and morphological properties of the epitaxial GaN layer as well as to achieve its unique optical and electro-physical characteristics.

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