Electronic structure and optical characteristics of the hybrid GaN/por-Si heterostructures

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Abstract. GaN/Si(111) heterostructures grown by plasma-assisted molecular beam epitaxy on routine Si(111) substrates and compliant por-Si/Si(111) substrates without using AlN buffer layer was studied by using various structural and spectroscopy methods of analysis. XPS study revealed that the layer is grown on the compliant substrate of por-Si being closer to the stoichiometric composition. The shift of the A1(LO) mode in the Raman spectrum confirms the lattice-matched growth type on the compliant substrate in comparison with the routine c-Si substrate. The experimentally determined value of the optical bandgap width for the epitaxial GaN layer grown on por-Si substrate exceeds that of the layer grown on single-crystalline silicon c-Si by 0.1 eV

1. Introduction

III-N films on Si templates and nanorods are of great importance due to the low-cost and high availability of Si substrates. Usage of compliant Si(111) substrates with nanoporous Si layer (por-Si) helps to decrease the cost of III-N based devices in comparison with ones, grown on heteroepitaxial 6H-SiC, c-Al₂O₃, and native GaN substrates. Furthermore, employing compliant substrates helps to suppress processes of cracking and misfit dislocations generation, which are related to large lattice and thermal mismatches (17% and 54% for GaN on Si(111), respectively [1]). As it was shown in our previous work [1] by using plasma-activated molecular-beam epitaxy (PA MBE) growth technique and compliant substrates it is possible to grow thick crack-free GaN layer at room temperature (RT) directly on Si substrate. In this paper, we report on the results of the analysis and comparison of GaN/c-Si(111) and GaN/por-Si(111) substrates.

2. Experimental

GaN layers were grown using an original 3D GaN buffer layer as described in [1], on the routine c-Si(111) and compliant por-Si(111) substrates. The samples were studied using X-ray photoelectron spectroscopy (XPS), Raman and ultraviolet (UV) spectroscopy. XPS spectra were obtained by using
the SPECS brand spectrometer, Raman spectra by using a Renishaw 1000 microscope equipped with the x50 NPlan lens. Perkin Elmer LAMBDA 650 setup equipped with the URA module been used for measurement of the UV properties of both samples.

3. Results

The elemental composition of the GaN films grown on the two substrates was determined by XPS. For the analysis, the electrons in the working chamber were accelerated up to 10 kV and the investigated area was 750 x 750 μm, with a microanalysis penetration depth of ~0.25 μm. This experiment demonstrated that the main elements in the film were gallium and nitrogen, with the layer grown on the compliant substrate of por-Si being closer to the stoichiometric composition. The XPS Ga 2p3/2 spectra of the investigated samples are presented in figure 1. The thin film of the high structural quality single-crystalline GaN 3 μm thick layer obtained by the MBE technique on the substrate of Al₂O₃ using standard technology was utilized as a reference sample [2].

![Figure 1. XPS Ga 2p spectra of the reference sample GaN, GaN/c-Si(111) and GaN/por-Si(111) samples.](image1)

Raman scattering spectra of the investigated samples are presented at figure 2. As evident from the experimental data, the same set of Raman modes is present in the spectra of both samples. The most intensive mode is related to the longitudinal optical phonon from a single-crystalline substrate Si (LO), with three low-intensive vibrations in the Raman spectra at 430 cm⁻¹, 617 cm⁻¹ and 675 cm⁻¹ related with Si. Regarding the response from the epitaxial layer, one can observe E₁(TO) and A₁(LO) phonons in the spectra of both samples allowing for the GaN phase with wurtzite symmetry arranged at ~564 cm⁻¹ and 730 cm⁻¹, respectively, as well as an additional mode characteristic of wurtzite GaN at 301 cm⁻¹.

![Figure 2. Raman spectroscopy graph for the GaN/c-Si(111) and GaN/por-Si/Si(111) nanorods.](image2)
Special attention should be paid to the fact that the position of A1(LO) mode in the spectrum of the heterostructure grown on the “compliant” substrate of por-Si is shifted by 4 cm⁻¹ relatively to its position in the Raman spectrum of the structure grown on the crystalline silicon. Moreover, the A1(LO) mode in the first case is less than half-width.

The optical properties of the samples in the UV and visible ranges (190–900 nm) were investigated by reflection spectroscopy, a technique that was demonstrated previously to be efficient for the study of thin films grown on the bulk substrates. [3, 4–6]. Using the proposed technique and experimental reflection-transmission spectra of the sample obtained under different angles of radiation incidence, it was possible to calculate the refractive index of the samples by the interference pattern for the wavelength coinciding with the interference maximum/minimum, thereby determining the dispersion of the refractive index in a wide range of wavelengths [5, 6]. The refractive index dependence on wavelength is presented at figure 3.

![Figure 3](image.png)

**Figure 3.** Dispersion of the refractive index for GaN/c-Si(111) and GaN/por-Si(111) heterostructures.

The experimental transmission-reflection spectra obtained at the incidence angle of electromagnetic radiation of ~67° within the wavelength range 190–900 nm were transformed to the absorption spectra to reveal the features of the optical absorption in the samples. Using Kramers-Kronig relations [7], the optical density of the samples was calculated, then the dependences of (D•hν)² on the quanta energy hν were obtained (see figure 4).
Graphical analysis of the obtained data revealed separate parts with the linear dependence of \((D\cdot h\nu)^2\). Linear extrapolation of these to zero value of energy makes it possible to determine the energy of direct transitions characteristic for these samples.

4. Discussion

Fabrication of the GaN/Si templates is an actual technological issue. Well known Ga-Si interaction leads to deterioration of the GaN – Si interface, high density of threading dislocations results in low efficiency of optoelectronic and power semiconductor GaN-based devices. As well as we achieved a thick GaN layer directly on Si substrates with reasonable quality, we studied its optical properties by variable spectroscopy methods. As can be seen from figure 1 decomposition of all Ga 2p spectra into their components demonstrated that the reference sample mainly represented a GaN phase (main peak at \(E_b = 117.8\ eV\)), with a small amount of metallic gallium (116.5 eV) and its oxide Ga\(_2\)O\(_3\) (119 eV) on its surface. The contribution of the side components in the decomposition of the experimental XPS spectra was enhanced for GaN layers grown on the silicon substrates. Analysis of the spectra shows that in the spectrum of GaN grown on the crystalline silicon, metallic Ga component weight is roughly equal to Ga\(_2\)O\(_3\) component weight when for the sample grown on por-Si layer Ga\(_2\)O\(_3\) more intensive. We associate this fact with more pronounced surface micrelief for GaN/por-Si layer, which formed due to growth features of 3D GaN buffer layer on the nanoporous Si layer. Growths on the porous layer led to the formation of a self-organized array of nanocolumns isotropically distributed on the substrate surface and further their coalescence in 2D layer with periodical surface micrelief. Thus, the presence of the surface micrelief increases the oxidation process for GaN/por-Si sample.

Special attention should be paid to the fact that the position of \(A_1(LO)\) mode in the spectrum of the heterostructure grown on the “compliant” substrate of por-Si is shifted by \(4\ cm^{-1}\) relatives to its position in the Raman spectrum of the structure grown on the crystalline silicon. Moreover, the \(A_1(LO)\) mode in the first case is less than half-width. This shift can be explained if we assume that the growth of the GaN layer was matched by the crystal lattice parameter with the porous sublayer in the plane of growth.

**Figure 4.** Dependences of \((D\cdot h\nu)^2\) or on the quanta energy for the samples of GaN/c-Si(111) and GaN/por-Si(111) heterostructures.
and undergoing considerable distortion along the direction of growth, but of better crystalline quality than the layer obtained on c-Si.

It is evident that the value of the refractive coefficient for the epitaxial GaN layer grown on c-Si and the compliant substrate of por-Si (see figure 3) monotonously increases with a decrease in the wavelength. Meanwhile, within the wavelength range of 330–430 nm (~3.75–2.9 eV), an extreme up-rise of the refractive coefficient was observed for both samples (figure 9), indicating the close arrangement of the fundamental absorption edge for the epitaxial film at this wavelength [8, 9]. The value of the refractive index of the GaN layer grown on c-Si in the same spectral range is, on average, 10% higher than for the layer grown on the “compliant” substrate of por-Si. Moreover, based on the shape of the dispersion function, it is possible to assume that its extreme maximum and, hence, the energy position (value) of the fundamental absorption edge for GaN/por-Si sample is shifted towards the higher energies relative to the similar value of the sample GaN/c-Si.

Graphical analysis of the obtained data (figure 4) revealed separate parts with the linear dependence of $(D\cdot h\nu)^2$. Linear extrapolation of these to zero value of energy makes it possible to determine the energy of direct transitions characteristic for these samples. Analysis of the obtained information (see Figure 10) for both samples showed the characteristic appearance of two direct transitions. The first is related to the direct allowed interband transition of $\Gamma_6V - \Gamma_1C$ GaN. In fact, the energy of this transition coincides with the reference value of the optical bandgap width in GaN. The second is the direct allowed transition with an energy of ~1.7 eV, which coincides with that of the bandgap width in SiN and agrees with the X-ray diffraction and Raman spectroscopy data concerning formation of an amorphous phase of silicon nitride in the epitaxial film. Thus, the use of a “compliant” Si substrate is an appropriate approach for the formation of semiconductor instrumental heterostructures based on GaN by an MBE PA technique.

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