Epitaxial GaN layers synthesized on Si (111)

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Abstract. Realization of epitaxial synthesis of high quality gallium nitride layers on silicon substrates is driven by the high potential of GaN-on-silicon technology for fabrication of high efficiency and relatively low-cost electronic devises. Growth process of GaN layers on Si substrates by molecular-beam epitaxy is complicated by differences in thermal expansion coefficients and lattice parameters causing large number of defects and dislocations. Another issue is mutual diffusion of Si and Ga. To improve the quality of GaN layers high temperature nitridation of silicon substrates was applied. We used Raman spectroscopy and Hall measurements to study the effect of nitridation. The shift of $E_{2870}/g_{2892}$ phonon mode allowed to calculate biaxial stress and this indicated stress relaxation in GaN epitaxial layers. P-type conductivity was observed in GaN/Si(111) structures and nitridation was proven to reduce carrier concentration. Thus, high temperature nitridation of Si substrate led to stress relaxation and decrease of Ga diffusion into substrate.

1 Introduction

Gallium nitride (GaN) is considered to be an excellent material for the development of power electronics replacing silicon (Si). Due to the wide bandgap, the size of electronic devices based on GaN can be lessen and such devices can operate at the high temperatures [1]. Reduction in the world energy consumption can be achieved if this material is used [2]. Mechanical properties, chemical stability, good thermal conductivity and high breakdown field are other reasons for the structures based on GaN to more and more penetrate the market [3]. The GaN based electronic components have already been applied for VR/AR technologies [4], LIDARs [5], microLED displays [6], electric vehicles [7] and charging devices [8]. Other area of GaN application is sensors [9]. AlGaN/GaN transistors-based sensors utilized for chemical and biological detection owing to stability to moisture and chemicals, superior biological compatibility which is important for direct contact with living organisms such as micro-organisms and cells. These sensors can be applied for biophysical and medical research, environmental monitoring and other analytical task [10].

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In addition, optical transparency of these structures in the visible range allows combining electronic and microscopic control of sensing.

Molecular-beam epitaxy (MBE) is one of the widespread technologies for the production of the GaN epitaxial layers, however a proper substrate of the synthesis of GaN have not been chosen. GaN layers grown on GaN substrates studies by Lui et al proved that it is a promising technology option for high frequency and high power applications [11], however the cost of GaN substrates is too high. So gallium nitride layers are commonly synthesized on silicon carbide (SiC), sapphire (Al₂O₃) and silicon (Si). Despite less than 4% difference in lattice parameters of GaN and SiC, the production on silicon carbide substrates is still expensive. Prices of Al₂O₃ substrates are lower than SiC, the thermal conductivity of this material is not enough for high power devices. Silicon is recognized as one of the most promising material for substrates for gallium nitride films due to the well-known advantages allowing the production of large size single crystalline substrates with high mechanical strength and excellent thermal conductivity [12]. Thus, heat dissipation of GaN on Si devices can be excellent and their price can be lower than its competitors [13]. Although over the past decades many studies have been devoted to the improvement of the quality of epitaxial GaN layers grown on Si substrates, the appearance of stress after cooling from growth temperature and diffusion of silicon and gallium are still difficulties for production [12,14].

One of the ways to reduce the number of dislocations is a nitridation of silicon substrate in a flow of activated nitrogen species, which can be carried out immediately before the GaN growth process in order to form an ultra-thin silicon nitride layer on a surface of Si substrate.

Recently the effect of nitridation was studied for GaN /p-Si (100) grown by MBE and the structural and morphological characterizations were investigated by using the high resolution X-ray diffraction, atomic force microscopy, Raman and photoluminescence spectroscopic studies. The results of these measurements allowed making a conclusion about the strain free nature and reasonably good crystallinity of the films [15].

The material quality of the GaN layers grown on undoped Si (111) were studied as a function of nitridation time and temperature via Micro-Raman and photoluminescence (PL) measurements. It was observed that the quality of silicon nitride affects the properties of GaN layers and demonstrated that FWHM of PL spectra decreased with rising nitridation time at 700°C but nitridation at low temperature (530°C) resulted inferior optical properties [16].

At the same time it was established that the shift of the nonpolar E₂GaN phonon mode is sensitive to the presence of impurity atoms causing internal stress of the GaN lattice [17] and to make realistic far going conclusions, it is important to obtain the accurate strain value.

The results of investigations of the effect of the initial conditions of nitridation of the Si(111) substrate during plasma assisted molecular-beam epitaxy (PA MBE) were presented in ref. [18]. It was experimentally established that the optimal initial condition for high-quality GaN epitaxy on Si(111) substrates is high temperature (T = 850°C) nitridation of the Si(111) substrate carried out immediately before GaN growth.

Here we present the complete investigation of the GaN layers structural and optical properties grown with nitridation and without it.

2 Methods

To study the effect of nitridation undoped GaN epitaxial layers were grown on semi-insulating Si(111) substrates by PA-MBE on a Veeco Gen 200 industrial type set-up [18]. Before the growth process, the silicon substrates were cleaned by Shiraki method [19] and
annealed for 30 min at the temperature of \( T_0 = 850 \, ^\circ C \) in the growth chamber to remove SiO\(_2\) layers.

The silicon substrate for sample A was nitridized in the growth chamber of Veeco Gen 200 set-up for 30 min at the temperature of \( \sim 850 \, ^\circ C \) immediately before GaN growth start, while sample B was grown without nitridation. Growth of GaN layers on both Si(111) substrates consisted of two steps presented in table 1: synthesis of high temperature (HT) GaN on low temperature (LT) GaN. The schematic view of the structure of sample B is presented in figure 1, assuming that nitridation led to the formation of ultra-thin Si\(_x\)N\(_y\) layer.

### Table 1. The stages of growth process.

|                | LT - GaN | HT - GaN |
|----------------|----------|----------|
| Substrate temperature | 650 °C   | 730 °C   |
| Gallium flux    | 0.1 ML/s | 0.6 ML/s |
| Nitride flux    | 0.1 ML/s | 0.1 ML/s |

![Schematic illustration of the samples A and B grown under the same conditions with the exception of the Si\(_x\)N\(_y\) nucleation layer in sample B (highlighted by the dashed lines).](image)

Fig. 1. Schematic illustration of the samples A and B grown under the same conditions with the exception of the Si\(_x\)N\(_y\) nucleation layer in sample B (highlighted by the dashed lines).

Optical and mechanical properties of these samples were investigated by means of Raman spectrometer Horiba Jobin-Yvon LabRam HR800 with with an excitation wavelength of 532 nm and Hall measurement on an Ecopia HMS-3000 set-up.

### 3 Results and Discussion

The thickness of GaN layer was \( \sim 860 \, \text{nm} \) (Sample A) and \( \sim 770 \, \text{nm} \) (Sample B) according to the ellipsometry. The room-temperature Raman spectrums were obtained for the Si(111) substrate and samples A and B. Several Raman measurements were conducted from different spots of each sample and showed that the spectra of both GaN/Si (111) layers contained the same phonon modes. Frequencies of these modes for each sample presented in table 2.

It is known that the position of \( E_2^1 \) GaN phonon is sensitive to biaxial deformation in the epitaxial layers. Using formula (1) for shift of the phonon frequency (\( \Delta \omega \)) with respect to its position in unstrained GaN stress \( \sigma \) can be calculated, according to [20].
\[ \Delta \omega = 4.2 \sigma \]  

(1)

For this calculation, it is essential to know the precise value of the unstrained sample \( \omega_0 = 566.65 \text{ cm}^{-1} \), which was corrected in [17]. It should be noted that, the value \( \omega_0 = 568 \text{ cm}^{-1} \) is still applied by some researchers, although it was proven incorrect.

Table 2. Frequencies of phonon modes in both samples

|                | Sample A        | Sample B        |
|----------------|-----------------|-----------------|
| Si             | 520.2 cm\(^{-1}\) | 520.2 cm\(^{-1}\) |
| \( E_2 \) GaN  | 142.5 cm\(^{-1}\) | 142.3 cm\(^{-1}\) |
| \( E_0 \) GaN  | 563.9 cm\(^{-1}\) | 564.1 cm\(^{-1}\) |
| \( A_1 \) GaN  | 731.6 cm\(^{-1}\) | 732.9 cm\(^{-1}\) |

Fig. 2. Raman spectra of both samples. Arrows demonstrate GaN phonon modes.

For investigated GaN layers the shift of these phonon modes can be attributed to the tensile deformation. Thus, the stress was 0.65 and 0.6 GPa for sample A and B respectively.

The continuum band intensity near the \( E_2 \) phonon mode proved p-type conductivity of both GaN samples and can be associated with the holes transitions in the valence band. This conductivity was attributed to unintentional doping of Si(111) substrate by Ga atoms, which takes place due to Ga-Si interdiffusion. The intensity of \( E_2 \) mode normalized on its integrated intensity rises with the increase of hole density as it was demonstrated by Harima at al in [21]. According to our calculations, nitridation led to the decrease of hole density.
The electrical characterization of the grown GaN/Si(111) samples confirmed p-type conductivity in them. Hall measurements demonstrated hole density $2 \times 10^{19} \text{cm}^{-3}$ and $7.6 \times 10^{18} \text{cm}^{-3}$ in sample A and B respectively.

4 Conclusions

1. High quality of investigated GaN epitaxial layers on Si(111) substrate was observed.
2. It was demonstrated that both samples had p-type conductivity associated with holes transitions in valence band.
3. High temperature nitridation ($T = 850^\circ \text{C}$) was proven to reduce Ga diffusion into Si substrate.
4. Stress relaxation in epitaxial layers was observed due to substrate nitridation.

The work at AU was supported by the Ministry of Education and Science of the Russian Federation state assignment numbers 0791-2020-0006 and 0791-2020-0008.

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