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Plasma assisted molecular beam epitaxy of thin GaN films on Si(111) and SiC/Si(111) substrates: Effect of SiC and polarity issues

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ABSTRACT

The paper focuses on growth of GaN thin films via plasma assisted molecular beam epitaxy on SiC/Si(111) substrate formed by atom-by-atom substitution method. A comparison with GaN film grown in the same process directly on Si(111) substrate is performed. The films were studied by ellipsometry, electron diffraction and Raman spectroscopy. The results of these measurements are used to compare polarity of the films, crystalline properties, quality and residual elastic stresses in GaN films grown on Si and SiC/Si substrates. It is shown that SiC buffer layer has a positive effect on the structural quality of growing GaN thin films. It was found that use of SiC/Si(111) substrate leads to formation of N-polar film, whereas Ga-polar film is formed on Si(111).

1. Introduction

To date there are a lot of studies devoted to epitaxial growth of thin films of wide bandgap semiconductors, in particular, gallium nitride (GaN) [1–3]. The main interest in this material is results from the potential of its practical application in power electronics (HEMT-transistors), LED technology, chemical sensors, detectors of UV-irradiation, and much more [4–6]. For epitaxial growth of GaN the most commonly used substrate is sapphire [7] which though inexpensive, has a number of significant shortcomings. Firstly, sapphire has a larger thermal expansion coefficient than that of GaN, resulting in biaxial stresses arising during the cooling which in turn leads to cracking of the films [7]. Secondly, mismatch of sapphire and GaN lattices is about 16%, which also leads to a high concentration of misfit dislocations. To reduce the effect of these shortcomings different buffer layers of other semiconductors are often used, for example AlN [8] as well as multilayer structures [9], but the density of defects in the growing films still remains quite high (10^9–10^{10} cm^{-2}) [7]. In this regard, the search for new substrates for the growth of gallium nitride films continues. Silicon carbide (SiC) [7,10,11] and silicon (Si) [12,13] stand out among other materials. The advantage of the first one is the similarity of the lattice parameter (the mismatch with GaN ~3% [7]), and high thermal conductivity, but SiC monocrystalline substrates are extremely expensive. Silicon is less suitable for the growth of GaN, but it is cheap and its technological processing has been worked out for decades. In a series of studies summarized in reviews [14,15] authors proposed a method that allows one to combine the advantages of both semiconductors and obtain a cheap high-quality SiC buffer layer on a silicon substrate. The method proposed in [14] is technologically simple, inexpensive, and allows growing of SiC films on silicon substrates of any orientation and any type of conductivity. To date, a reactor has been developed for the growth via this method and using it epitaxial SiC layers were obtained on Si substrates up to 6 in. in diameter [16]. The scheme of the reactor, a detailed description of the growth technology and peculiarities of the method can be found in the review [15], as well as detailed study of the samples at all stages of the growth process.

The originality of the method is that unlike the growth of SiC thin film through a conventional deposition onto the top of the Si substrate, SiC is directly formed in the substrate via chemical reaction between Si and carbon monoxide (CO). As a result, part of silicon atoms in the substrate is being substituted by carbon atoms, thus, the subsurface layer of silicon being converted into SiC. At the same time due to the peculiarities of the method [14] during the growth of SiC buffer layer the elastic energy is being relaxed, and SiC film is almost not subjected to mechanical stresses, which has a positive effect on the quality of subsequent layers. Also it should be noted that using the atom-by-atom substitution method allows obtaining a desired polytype of SiC layers: cubic or hexagonal. Thus, the study and optimization of GaN growth processes on SiC/Si substrates made by substitution of atoms is promising from viewpoint of producing inexpensive high-quality thin GaN

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films and devices based on them.

For deposition of gallium nitride films, along with the metalorganic chemical vapor phase epitaxy (MOCVD) [17] and hydride vapor phase epitaxy (HVPE) [18], which are widely used in commercial manufacturing of devices, molecular beam epitaxy (MBE) is also used [19]. Reactive nitrogen in this process can be obtained both by thermal cracking of ammonia (NH_3-MBE) [20,21] and by activation of N_2 in plasma (PA-MBE) [22]. The advantage of the latter method is the ability to grow films at low substrate temperatures and in the absence of hydrogen. Also as has been shown in [19] the method allows growing GaN films of different polarity, which is defined by the type of the substrate and by growth conditions.

This article is a continuation of the series of papers [18,23,24] aimed at study of optimal conditions for the epitaxial growth of GaN on SiC/Si(111) substrates by various methods, in which authors have already considered MOCVD [23] and HVPE-processes [18]. The impact of SiC buffer layer on the growth of GaN by plasma assisted molecular beam epitaxy is studied, and comparison with the films of GaN, grown on silicon without SiC buffer layer is performed. A special attention is paid to the polarity of the GaN films, since during our studies we have noticed, that use of SiC/Si buffer layers leads to change in GaN polarity comparing with GaN film grown on Si substrate. This discovery is one of the main reasons for writing this article. The samples were studied by electron diffraction, Raman spectroscopy, SEM, and ellipsometry and were etched in KOH to study polarity issues.

2. Experimental details

For the growth of GaN films we used semi-insulating ($R > 10{,}000\ \Omega * cm$) Si substrates (111) without deviation from the basic direction ⟨111⟩ and hybrid SiC/Si(111) substrates made by substitution of atoms [7] on the Si(111) substrates ($R > 2000\ \Omega * cm$). We suppose that difference in the concentration of dopants, since it is of the same order for both samples, does not greatly affect the growth of GaN. Table 1 shows the conditions of the synthesis of SiC buffer layer. The film thickness according to the ellipsometry was equal to 72 nm. From our previous studies [14,25] on the SiC/Si surface morphology, crystalline quality and structure, it follows that the film is epitaxial and has no twinnings at the surface. Fig. 1 demonstrates reflection high-energy electron diffraction pattern of the SiC/Si sample (111) to get acquainted with the quality of the film.

All epitaxial GaN layers were grown by PA MBE [22] on the Veeco Gen 200 set-up, which allows using multiple substrates in a single growth process. The set-up is equipped with ten ports for Knudsen sources of the third group elements and doping elements, and also for activated nitrogen plasma source. To activate the nitrogen, we used high-frequency (13.56 MHz) plasma source RFN 50/63 (Riber). The substrate temperature was monitored in situ by infrared pyrometer.

The silicon substrate was chemically pre-treated by Shiraki method [26], which includes liquid chemical etching to remove carbon-containing structures from the silicon surface, formation of a thin protective oxide film and subsequent removal of it in high vacuum. Before the growth the Si(111) substrates were annealed in the growth chamber at $T_S = 850\ ^\circ C$ for 30 min to remove SiO_2 layer. Removal of the SiO_2 was controlled by an appearance of clear (7 × 7) reflection high-energy electron diffraction (RHEED) pattern.

Table 1
Conditions of the synthesis of SiC buffer layer.

Parameter	
Si	p-type
Growth temperature, C	1250
Growth time, min	15
Total pressure of the gas mixture ($CO + SiH_4$), Torr	1.8
Flow of the gas mixture, ml/min	100
Content of the silane (SiH_4) in the mixture, %	16

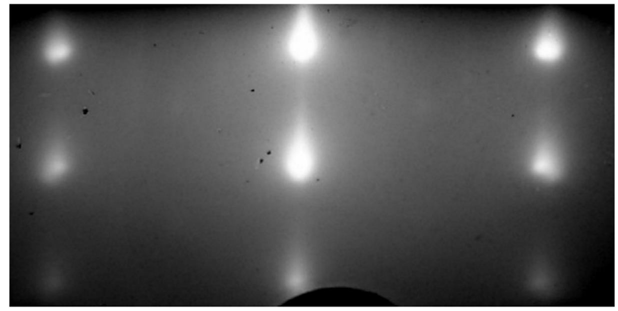

Fig. 1. Electron diffraction pattern of the SiC/Si(111) sample.

In all experiments for growth of epitaxial GaN films on Si (111) and SiC/Si(111) substrates two-step deposition was used. Firstly "low temperature" buffer layers LT-GaN of 200 nm thickness were grown at temperature $T_S = 650\ ^\circ C$ and stoichiometric conditions $F_{Ga} = F_N \sim 0.1$ ML/s. Then the growth temperature and Ga flow was increased to values $T_S = 730\ ^\circ C$ and $F_{Ga} \sim 0.6$ ML/s for the growth of "high temperature" layers of HT-GaN/LT-GaN of 600 nm thickness. Despite the fact that the typical buffer layer for high-quality GaN growth is aluminum nitride [27], we used LT-GaN, since the growth of GaN directly on Si and SiC substrates is interesting for study of Ga-Si interdiffusion processes, which may result in formation of unintentional p-type conductive layer at the GaN/Si(111) interface and melt-back etching of Si (111) substrate. However, detailed study of this issue will be presented in next paper. Also, the SiC/Si substrate grown by the method of atoms substitution is quite new, and the processes of GaN growth on it are not well studied yet.

After that the samples were studied via ellipsometry, SEM, Raman spectroscopy, electron diffraction and were etched in KOH to determine GaN polarity.

3. Results and discussion

The thickness of GaN films on the sample GaN/Si(111) according to electron microscopy and ellipsometry was exactly as expected ~800 nm (see Fig. 2a), while the thickness of GaN on the GaN/SiC/Si (111) sample was slightly less ~780 nm. Ellipsometry (Fig. 3a, b) also shows that the sample GaN/Si(111) is slightly more transparent than the sample GaN/SiC/Si(111). Fig. 2b also demonstrates pores, arised during the formation of SiC layer in silicon [14], which provide a relaxation of the elastic stresses. Detailed studies of the porous structure that appears in the Si near-surface layer, and a SiC/Si interface, in particular via TEM method, are presented in [14,27,28]. It should be noted that the main impact of the SiC/Si buffer layer on GaN growth in comparison with SiC grown on Si by convenient methods is namely the presence of these pores. Because of them, the contact area of the silicon substrate and the buffer layer of silicon carbide is significantly reduced (up to 90%) and the substrate is mechanically "detached" from the SiC layer. This phenomenon allows one to successfully overcome the difference in coefficients of thermal expansion and lattice parameters between silicon and silicon carbide. More detailed description of the pore impact on the growth of subsequent layers can be found in [7,14].

Crystalline quality of both samples was studied by means of reflection high-energy (50 keV) electron diffraction. Fig. 3(c, d) show the electron diffraction patterns. As can be seen in Fig. 3c, there are rings (though not clearly visible) indicating the presence of polycrystalline phase in the sample GaN/Si(111). At the same time Kikuchi lines clearly seen in Fig. 3d prove that GaN film grown on SiC/Si substrate is monocrystalline.

The samples were also examined by X-ray diffraction. The half-width (FWHM) of the rocking curve for the sample GaN/Si(111) was equal to 53′, while that of 36′ for the GaN film grown on SiC/Si(111),