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GaN heterostructures with diamond and graphene

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Abstract

The full performance of GaN devices for high power applications is not exploited due to their self-heating. Possible solutions are the integration of materials with high heat conductivity i.e., single crystalline diamond and graphene layers. We report the growth of single crystalline (0001)-oriented GaN thin films on (100), (110) and (111) diamond single crystals studied by transmission electron microscopy (TEM) in cross-sections. As for graphene, we show a high quality GaN layer that was deposited on patterned graphene layers and 6H-SiC. The atomic structures of the interfaces in the heterostructure are studied using aberration-corrected scanning TEM combined with energy dispersive x-ray and electron energy-loss spectroscopy.

Keywords: GaN, graphene, diamond, electron microscopy

(Some figures may appear in colour only in the online journal)

Introduction

Nitride-based (e.g. GaN, InGaN and AlGaN) thin films (III-nitrides) are applied not only in various optoelectronic devices and sensors, but also in high power devices, typically in transistors. Concerning their performance, the most difficult technical problem is the extraction of the dissipated heat during their operation. For III-nitride growth it would be advantageous to use substrates with excellent heat conductivity in order to avoid the self-heating of high power devices. Probably the best candidates are diamond and graphene with their superior thermal conductivities ($2000\ Wm^{-1}K^{-1}$ for diamond and $5000\ Wm^{-1}K^{-1}$ for graphene). A review paper on the thermal properties of carbon-based materials including diamond, graphene and few layer graphene (FLG) can be found in [1]. However, very few III-nitride epitaxial growth experiments have been reported on diamond and even fewer on graphene. Probably the first growth experiment using metal organic chemical vapour deposition (MOCVD) was carried out by Hageman *et al* [2] on single crystalline diamond and resulted in poor quality GaN. Dreumel *et al* also grew polycrystalline GaN on nanocrystalline diamond/Si template [3] and later oriented GaN crystals on polycrystalline diamond substrates [4]. The epitaxial growth of GaN is difficult due to the high lattice misfit in the GaN/diamond system. Recently we have shown that single crystalline (0001) GaN films can be grown on (111) diamond substrates [5]. The thermal management of heterostructures containing graphene or related materials includes: lithographically patterned graphene oxide in light-emitting diodes (LEDs) [6]; transferable GaN layers deposited on ZnO-coated graphene layers [7], and thermal heat-escaping channels of graphene layers prepared on top of AlGaN/GaN transistors [8]. We also reported [9] that nitride layers can be grown by MOCVD on patterned graphene/SiC templates.

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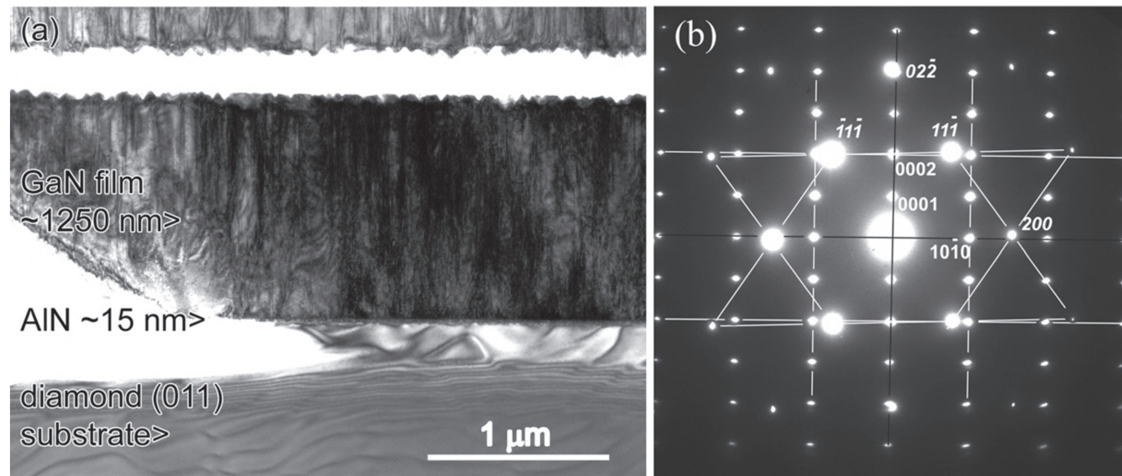

Figure 1. Microstructure of GaN/AlN (0001) layers on diamond (110) substrate without nitridation treatment. (a) BF TEM image of the GaN film showing the high density of IDs in the GaN layer; (b) SAED pattern of the nitride layers and diamond. The reflections of hexagonal nitride layers and cubic diamond are marked by four and three digit indices, respectively.

In the present study, we show the successful growth of high quality N-face GaN thin films deposited on (i) single crystalline diamond and (ii) patterned graphene and (0001) 6H-SiC. Both material systems were studied in cross-sectional geometry using conventional transmission electron microscopy (TEM) and aberration-corrected TEM operated at 200 and 300 kV. The preparation of electron transparent specimens of diamond- and graphene-containing samples for TEM characterization represented a significant challenge due to the hardness of diamond and the sensitivity of the graphene layers to the ion energies used during the milling process. We used a conventional mechanical and Ar ion milling (Technoorg–Linda model) process to prepare the diamond samples. Low energy ion milling was carried out on specimens embedded into a Ti supporting ring [10]. The graphene-containing cross-sections were prepared using a focused ion beam (FIB) in a dual-beam system using ion energies of 30 and 5 keV. A Pt/C protective layer was deposited onto the surface of the GaN using electron and ion beams with thicknesses of 0.5 and 2.5 μm, respectively. The FIB lamella was fixed onto a standard Cu Omniprobe grid using Pt/C layer deposition. The ion beam-induced surface damage was then reduced by using low energy (0.5 keV) focused Ar ion milling at an incident angle of 10° in a Fischione Nanomill 1040 system.

Bright-field (BF), dark-field images and selected area electron diffraction (SAED) patterns were taken using a Philips CM 20 microscope working at 200 keV. High-resolution TEM studies were performed using JEOL 3010 and FEI Titan electron microscopes at 300 keV.

Single crystalline GaN on diamond

In the first part of this paper we report on the microstructure of GaN thin films that were grown on (100) and (110) diamond single crystal substrates by plasma-assisted molecular beam epitaxy (PAMBE), employing a nitrogen radio frequency (RF) plasma source [11]. Then we will discuss the nitride layers grown by MOCVD on patterned FLG/SiC. Cross-sectional TEM studies showed that pre-treatment (nitridation) of the diamond surface with the nitrogen beam improved the structural quality of the grown epilayers by reducing the threading dislocation density and eliminating the formation of inversion domains. The chemical mapping of the nitride/FLG/SiC structure was carried out using energy dispersive x-ray spectroscopy (EDXS).

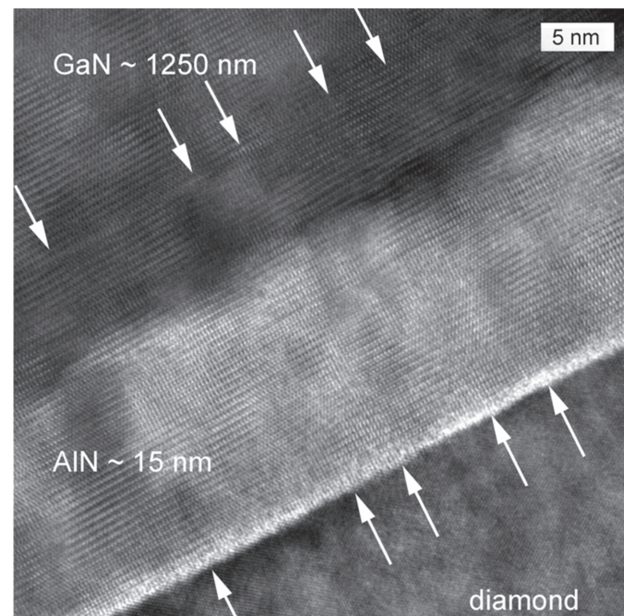

Figure 2. High-resolution TEM image of the GaN/AlN/diamond interfacial region showing a high density of IDs (some of them are marked by arrows) in the GaN/AlN layers. The IDs formed even on the surface of diamond.

Figure 3. GaN/AlN layers grown on nitrided diamond (110) surface. (a) BF TEM image. (b) high-resolution TEM image showing active layers in the top region.

Figure 4. Selected area diffraction pattern of GaN grown on (001) diamond.

Single crystalline diamond substrates with sizes of approximately $5 \times 5\ \mathrm{mm}^2$, prepared by Element6 (www.e6.com) were used. GaN thin films with thickness of about 1 μm were grown on single crystal diamond substrates by PAMBE. Two sets of experiments were carried out: in the first set, a thin AlN nucleation layer with thickness of approximately 15 nm was directly grown on diamond, at 780 °C, under stoichiometric growth conditions, without any prior treatment of the diamond surface, followed by the thick GaN layer, grown at 700 °C, grown under metal-rich conditions. In the second set of experiments, the diamond surface was exposed to a nitrogen beam (nitridation), and then an AlN nucleation layer, with thickness of about 100 nm was grown, under the same growth conditions as the first set, followed by the thick GaN layer. The temperature of the nitridation was varied from 125 °C to 750 °C, while the duration time was varied from 1 min to 60 min

The optimal conditions for the nitridation treatment of the diamond substrates were selected according to our previous experience of the effects of exposure to a nitrogen plasma source beam on sapphire [12] and GaAs substrates [13, 14]. A nitrogen plasma beam can be very reactive and may result in roughening of the substrate surfaces at high substrate temperature. In the case of sapphire substrates, it was found that low temperature nitridation did not result in formation of an interfacial AlN layer but improved the smoothness of the substrate surface and the abruptness of the substrate/epilayer interface. This is attributed to the removal of contaminants from the substrate surface by reaction with the active species of the nitrogen plasma source. However, a sufficiently long time, such as 60 min, may be needed to assure the cleaning of the substrate surface at low temperature.

Figure 1(a) shows a cross-section of the GaN film deposited on (110) diamond, without the nitridation treatment. (The surface roughness of the GaN layer should not be considered here, since it is a result of the chemical etching carried out in order to determine the polarity of the grown layers). A large number of threading dislocations, as well as inversion domains (IDs), were formed in the GaN layer. The SAED pattern in figure 1(b) reveals the single crystalline growth of the III-nitride layers on the diamond {110} substrate, with an epitaxial relationship of (0002)GaN//(02$\underline{2}$) diamond and (10$\underline{1}$0)GaN//(400)diamond.

The high-resolution TEM study of the GaN/AlN/diamond interfacial region (shown in figure 2) revealed a high density of IDs that formed even at the AlN/diamond interface. Those IDs then propagated to the top surface of the nitride layers. Although the grown nitride layers are epitaxial to the

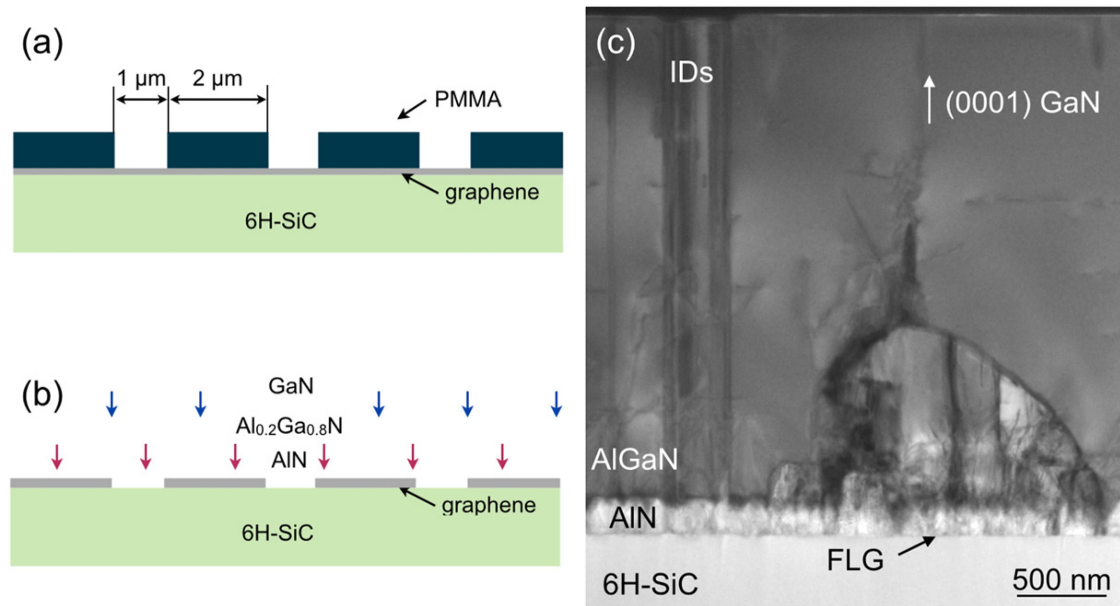

Figure 5. (a), (b) Schematic figure of the patterning process and growth. (c) Low magnification BF TEM overview of the heterostructure. FLG and ID indicate the few layer graphene and inversion domain, respectively.

diamond substrate, the large number of defects, especially the high density of IDs, will limit their device applications.

Figure 3 shows an overview of the nitride structure that was grown on the (110) diamond substrate, nitrided prior to AlN growth for 60 min at 150 °C. The AlN nucleation layer was 90 nm thick. It was found that the thick GaN layer is free of IDs, and only threading dislocations could be observed. Thus, we can conclude that the nitridation of the diamond surface, prior to the growth initiation, significantly affects the formation of crystal defects such as threading dislocations and IDs. Single polarity GaN films were achieved on the nitrided diamond substrates. The polarity of the layer was determined by convergent beam electron diffraction which proved the nitrogen polarity of the layers. Finally, in order to obtain a two-dimensional electron gas (2DEG) heterostructure, a thin AlN layer was grown on top of a thick GaN layer, followed by a 30 nm GaN cap layer. These layers were uniform and flat (figure 3(b)).

In our earlier work on (111) diamond [5] we performed a detailed high-resolution analysis of the interface between nitride and diamond and found no additional phase(s) on the diamond surface after nitridation. Most probably, the nitridation could clean the surface of diamond through the active nitrogen species, as it was shown for NH_3 in the case of SiC [15].

On (001)-oriented diamond two different domains of GaN were grown with a common *c*-axis parallel to the surface normal (figure 4). The epitaxial relationships are the following: (0002)GaN//(400)diamond and $(11\underline{2}0)$GaN//$(02\underline{2})$diamond, or $(10\underline{1}0)$GaN//$(02\underline{2})$diamond. Knowing that the epitaxial configuration on (111) diamond [5] is the same as in the case of (110) we can conclude that on all three orientations the grown GaN film is *c*-axis oriented.

GaN grown on patterned graphene

The integration of graphene into III-nitride thin films is very challenging due to the lack of chemical reactivity between graphene and the growing nitride (only polycrystalline material could be obtained with very weak bonding when we carried out MOCVD growth of nitride layers on SiC completely covered by graphene). Recently, we proposed a simple patterning process [9] of graphene layers grown on a 6H-SiC substrate using polymethyl methacrylate (PMMA) and electron beam lithography prior to standard nitride growth using MOCVD, as shown in figures 5(a) and (b). The unmasked graphene layers were removed by high density plasma etching using an Ar (89%) and O_2 (11%) mixture. The PMMA mask was dissolved by acetone. The patterned structure allowed us to nucleate AlN directly on bare SiC with strong bonding and with transfer of the epitaxial orientation to the regions growing above the graphene. The graphene layers were prepared on the Si-terminated side of 0001-oriented 6H-SiC single crystals by a high temperature sublimation technique [16]. Figure 5(c) shows a BF TEM image of the heterostructure. The dislocation density in the GaN layer is $\sim 10^9$ cm^{-2}. The GaN layer forms a smooth surface and contains IDs that reach the surface forming a little pit. Detailed analysis of the interface between the graphene layers and the 6H-SiC showed that the chemical etching of the lithographically patterned graphene/SiC removed not only the graphene from the window regions, but also a few layers of the topmost 6H-SiC. IDs were formed in GaN grown directly on 6H-SiC, as shown in figure 5(c). It is striking that the GaN layer is defective above the intact graphene layers, with a crystallographic orientation that is different from that of the single crystalline

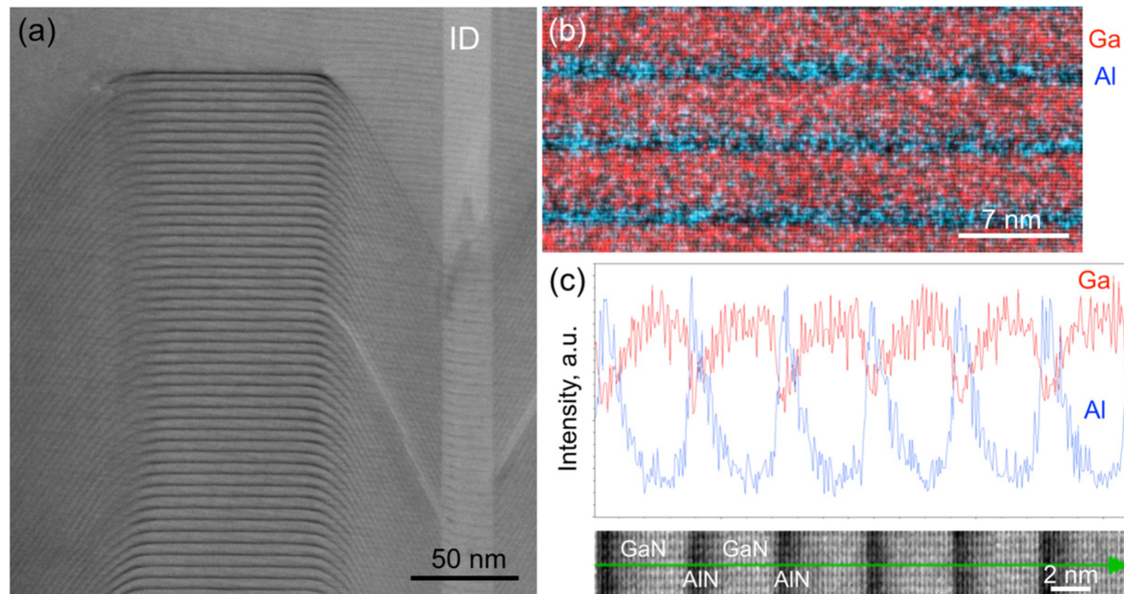

Figure 6. (a) HAADF STEM image of the AlN/GaN superlattice formed between the AlN buffer layer and GaN. (b) HAADF STEM image overlapped with Ga and Al distribution extracted from EDXS spectrum imaging experiment. The inner ADF detector semi-angle used was 69 mrad. (c) The distribution of Ga and Al across the layers extracted from EDXS and the corresponding HAADF STEM image.

GaN above the graphene-free SiC stripes. The single crystalline GaN overgrows the polycrystalline GaN by self-assisted lateral epitaxial overgrowth, thus reducing the dislocation density.

The AlN buffer layer (figure 5(c)) is rough and the morphology suggests that it was nucleated and grown over the graphene in a 3D way. Therefore, it is not surprising that the AlGaN layer grown on the buffer is also composed of hillocks (figure 6(a)). However, our electron microscopy study revealed the fact that this layer, which is a homogeneous and flat ternary layer in the control sample (without graphene) is decomposed into superlattices. The analytical investigations (figures 6(b) and (c)) show that the superlattice layers are pure AlN and GaN layers. Also, the thickness of the individual AlN (1–1.2 nm) and GaN layers (3.6 nm) fits with the available amount of the metals in the nominal $Al_{0.2}Ga_{0.8}N$ composition. The formation mechanism of the AlN/GaN superlattices is not completely understood. However, most probably this is connected to some carbon species originating from the graphene layers and being present in the 'ternary' layer. A similar effect was observed when a small amount of carbon was introduced into carbon–indium co-doped GaAs grown by MOCVD [17].

Conclusions

In conclusion, GaN thin films of high structural quality were grown on (110) single crystal diamond substrates by PAMBE using a 15–90 nm AlN nucleation layer. The optimized growth samples exhibited a single epitaxial relationship of GaN (0001) on diamond (110) with single N-face polarity. The formation of IDs was successfully eliminated by introducing a diamond nitridation treatment. This solution is effective for the heat dissipation problem of GaN based high-electron-mobility transistors (HEMTs) as was proved by Alomari *et al* [18]. The second solution based on graphene layers is also very promising and thermal reflectance measurements are in progress to prove that.

Acknowledgments

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