Optical and structural properties of microcrystalline GaN on an amorphous substrate prepared by a combination of molecular beam epitaxy and metal–organic chemical vapor deposition

2016 Jpn. J. Appl. Phys. 55 05FB03
(http://iopscience.iop.org/1347-4065/55/5S/05FB03)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 133.6.201.6
This content was downloaded on 03/04/2016 at 23:29

Please note that terms and conditions apply.
Optical and structural properties of microcrystalline GaN on an amorphous substrate prepared by a combination of molecular beam epitaxy and metal–organic chemical vapor deposition

Jung-Wook Min1, Hyeong-Yong Hwang2, Eun-Kyu Kang2, Kwangwook Park3, Ci-Hyun Kim2, Dong-Seon Lee2, Young-Dahl Jho2, Si-Young Bae4*, and Yong-Tak Lee2*

1Department of Physics and Photon Science, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea
2School of Information and Communications, Gwangju Institute of Science and Technology, Gwangju 61005, Republic of Korea
3National Renewable Energy Laboratory, Golden, CO 80401, U.S.A.
4Department of Electrical Engineering and Computer Science, Nagoya University, Nagoya 466-8550, Japan

Received November 20, 2015; accepted January 15, 2016; published online April 1, 2016

Abstract

Microscale platelet-shaped GaN grains were grown on amorphous substrates by a combined epitaxial growth method of molecular beam epitaxy (MBE) and metal–organic chemical vapor deposition (MOCVD). First, MBE GaN was grown on an amorphous substrate as a pre-orienting layer and its structural properties were investigated. Second, MOCVD grown GaN samples using the different growth techniques of planar and selective area growth (SAG) were comparatively investigated by transmission electron microscopy (TEM), cathodoluminescence (CL), and photoluminescence (PL). In MOCVD planar GaN, strong bound exciton peaks dominated despite the high density of the threading dislocations (TDs). In MOCVD SAG GaN, on the other hand, TDs were clearly reduced with bending, but basal stacking fault (BSF) PL peaks were observed at 3.42 eV. The combined epitaxial method not only provides a deep understanding of the growth behavior but also suggests an alternative approach for the growth of GaN on amorphous substances.

1. Introduction

Over the past few decades, III-nitride based optoelectronic devices have been developed to a commercial standard owing to their excellent optical and electrical properties.1) Due to the insufficient supply of gallium nitride (GaN) substrates, current III-nitride devices have been grown on hetero-substrates such as those consisting of sapphire, silicon carbide (SiC), and silicon.2) The most widely used substrate for GaN growth is the sapphire substrate, but it has the fundamental drawbacks of poor thermal conductivity, large lattice mismatch, and insulating property. SiC substrate is also associated with the limitations of a high cost and a small substrate size.3) The wide range of visible light absorption characteristics of Si substrates also restricts the performance of devices.4) To avoid these obstacles and explore novel applications for GaN epitaxy growth, new substrates have been investigated, such as metallic or amorphous substrates.5–8) Specifically, amorphous substrates can be ideal candidates for large-scale manufacturing. However, it is fairly difficult to achieve highly c-oriented GaN on an amorphous substance with strong GaN band edge photoluminescence (PL) emissions due to the absence of a crystal lattice. Thus the development of a pre-orienting layer on amorphous materials is a key factor pertaining to the realization of epitaxial GaN growth on an amorphous substrate. It should provide highly c-oriented GaN regardless of the underlying crystal lattice size or growth direction. Moreover, closely packed pre-orienting layers of a regular size is essential to control the morphology. Chen et al. assessed the epitaxial GaN growth characteristics on amorphous substrates using an oblique-angle-deposited biaxial Mo layer as a pre-orienting layer.9) Zhong et al. also achieved highly c-oriented crystalline GaN films on amorphous substrates with a similar method of Ni deposition.8) Choi et al. was the first to report an LED structure by the application of a Ti pre-orienting layer with a SiO2 mask layer on micro-sized openings via MOCVD.10,11) Recently, Shon et al. reported a planar LED device on an amorphous SiO2 substrate with a graphene buffer layer as a pre-orienting layer via sputtering.12) However, a deep understanding of the growth procedures and the development of growth methods are still required to realize epitaxially grown GaN on an amorphous substrate.

In this work, we investigate the distribution of the grain size and the properties of plasma-assisted molecular beam epitaxy (PA-MBE) and metal–organic chemical vapor (MOCVD) grown GaN on an amorphous layer. In order to achieve high-quality GaN on the amorphous substrate, we applied a combined growth technique: PA-MBE grown GaN (MBE 1st GaN) for a pre-orienting layer on Si3N4/quartz substrate, and following MOCVD grown GaN (MOCVD 2nd GaN) for a high quality layer.

2. Experimental methods

Prior to the epitaxial layer growth step, a 500-nm-thick Si3N4 layer was deposited on a quartz substrate by means of plasma-enhanced chemical vapor deposition (PECVD). Next, pieces of Si3N4/quartz samples (~5 cm²) were mounted onto a molybdenum block and loaded into a preparation chamber of modified PA-MBE (VG V80). After an outgas procedure, a nitridation process and following 1st GaN layer were conducted on the Si3N4 layer in a PA-MBE growth chamber. During the MBE growth process, a reflection high-energy electron diffraction (RHEED; Arios 201) analysis technique was applied for the in-situ monitoring of the quality and orientation of the GaN layer. A 700-nm-thick 1st GaN layer was grown for 1 h at 700 ℃.13) After completing the 1st GaN layer growth process using MBE, the sample was transferred into a MOCVD reactor (Sysnex MO260S) for the 2nd GaN layer growth step. In this step, the 2nd GaN layer was grown not only on the bare surface (planar 2nd GaN) but also on the patterned surface of the 1st GaN layer using the selective area growth method (SAG 2nd GaN). To form the patterned
surface on the 1st GaN surface, a stripe-patterned (window/mask length = 3 µm) SiO2 mask was formed. The growth duration of the 2nd GaN layer was held at 15, 45, and 150 min. Detailed experimental procedures are available in the literature. The surface morphology was investigated by field-emission scanning electron microscopy (FE-SEM; Hitachi S-4700 EMAX). To investigate the structural properties of the GaN layers, transmission electron microscopy (TEM; Tecnai G2 F30 S-Twin) was carried out to obtain bright-field (BF) images. Further optical properties were characterized by temperature-dependent PL (325 nm He:Cd laser power 10 mW) and cathodoluminescence (CL; MONO CL3+) measurements.

3. Results and discussion

Figure 1 shows a schematic illustration of the MBE 1st GaN, the MOCVD planar 2nd GaN and the SAG 2nd GaN results. In Fig. 1(a), coalesced GaN nanocolumns were grown on an amorphous Si3N4/quartz substrate in the Volmer–Weber (VW) growth mode. Each nanocolumn has a diameter of approximately 100 nm with the c-plane growth direction which is perpendicular to the wafer surface. In the SEM image, several cracks were observed on the 1st GaN surface due to the large thermal expansion coefficient difference between the GaN and the quartz substrate. The inset of Fig. 1(a) shows the in-situ RHEED pattern during the PA-MBE growth process, where the polycrystalline orientations of (002), (004), (101), and (103) are shown.

Figures 2(a) and 2(d) show two schematic representations of the MOCVD planar and SAG 2nd GaN as grown on the 1st GaN layer. Figure 2(a) shows the planar 2nd GaN procedures grown for 15, 45, and 150 min. As compared with Fig. 2(a), laterally grown GaN grains are shown with the bending of dislocations. As the growth time increases, the grains also coalesced and dislocations (orange arrow) are terminated at the surfaces of the voids with bending. Dislocations were clearly reduced in the SAG 2nd GaN grains, whereas other defects of SFs (blue arrow) were increased apart from threading dislocations (TDs) (orange arrow) with bunch of dislocations (yellow arrow). As an additional defect, those related to stacking faults (SFs) (blue arrow) were clearly shown in Fig. 2(b). Voids (red arrow) were also found, which were caused by irregular coalescence with neighboring grains. After 150 min of growth of the planar 2nd GaN, all grains mostly coalesced without voids, as shown in Fig. 2(c). The SAG 2nd GaN was also grown on the 1st GaN via the same growth mechanisms used in the SK growth mode, but showing different growth behaviors. Figure 2(d) shows the schematics of the SAG 2nd GaN growth procedures after growth for 15, 45, and 150 min. As compared with Fig. 2(a), laterally grown GaN grains are shown with the bending of dislocations. As the growth time increases, the grains also coalesced and dislocations (orange arrow) are terminated at the surfaces of the voids with bending. As shown in Fig. 2(e), dislocations were clearly reduced in the SAG 2nd GaN grains, whereas other defects of SFs (blue arrow) were increased apart from threading dislocations. The grains coalesced after 150 min of growth of the SAG 2nd GaN, but several voids (red arrow) also arose, as shown in Fig. 2(f).

The optical properties of each planar and SAG 2nd GaN grains were analyzed by both CL and PL. Figures 3(a) and
3(b) show cross-sectional SEM images of the planar 2nd GaN and the corresponding panchromatic CL emission image, respectively. Dark regions dominated in the planar 2nd GaN grain, indicating that the dislocation density is fairly high. Figure 3(c) shows the spot-mode CL spectra of P1 to P7 in (a). No emission was measured at the crystallized Si₃N₄ (P1) or MBE 1st GaN (P2). In addition, no emission was observed around the area adjacent to the interface between the 1st and 2nd GaN (P3). On the one hand, emission peaks were observed within the 2nd GaN grain (P4 to P7) with broadened spectra. The peak broadening is typically attributed to the mixed emission from SFs and a near band edge. Hence, the observed broadening can be corresponded to the emission from a near band edge peak of 3.44 eV to prismatic stacking fault (PSF) peaks in the range of 3.35 to 3.37 eV. The monochromatic CL image in the inset of Fig. 3(c) shows another emission component from a BSF of 3.42 eV. Figures 3(d) and 3(e) show an image of the cross-sectional SAG 2nd GaN and the corresponding panchromatic CL emission image, respectively. Dark regions were reduced much more due to the lateral growth mechanism of the SAG 2nd GaN. Moreover, the spreading out grains...
growth is observed with bending. This bending behavior of dislocations was clearly observed in the spot-mode CL spectra shown in Fig. 3(f). Emissive regions were observed (S2 to S7) at the edge of the SAG 2nd GaN grain. Each peak was well organized with a PSF emission peak of 3.35 eV, the most dominant BSF emission peak of 3.42 eV [inset of Fig. 3(f)], and a band edge peak around 3.44 eV. However, no CL emission was detected at the 2nd GaN near the interface (S1) due to the poor crystal quality. Moreover, the high dislocation density area of dark region (S8 to S10) was not emissive.

The CL emissive characteristics on the grain surface of the SAG 2nd GaN were also investigated, as shown in Figs. 3(g)–3(i). At the outside grains of S11 and S16, a broad defect peak around ∼3.35 eV was observed only. It caused by the MBE 1st GaN layer underneath the mask region, which included the high dislocation density of the nanocolumn structures. At the grain surface (S12 to S15), a PSF emission peak of 3.35 eV with a BSF emission peak of 3.42 eV were noted, as shown in Fig. 3(i).

For the further analysis of the band transition behavior and the defect peak analysis, planar 2nd GaN and SAG 2nd GaN were investigated by temperature-dependent PL measurements. Figure 4(a) shows the near band edge PL spectra of the planar 2nd GaN after 15 min of growth in a temperature range of 12–300 K. At a low temperature, the dominant PL spectra of the neutral donor bound exciton (D*X) line were observed. It is noteworthy that the D*X peak position of 3.488 eV (at 12 K) is related to the degree of strain in the planar 2nd GaN. This value is in good agreement with earlier results of compressive strain induced thin GaN layer on sapphire (<4 µm). Other transition lines of donor acceptor pair (DAP) recombination near 3.275 eV and their longitudinal phonon replicas (DAP-LO) at 3.19 eV were also found to be related to unusual acceptors in the planar 2nd GaN.

Figure 4(b) also shows the temperature-dependent PL spectra of the SAG 2nd GaN grown for 15 min. The D*X line was no longer visible, but new peaks at 3.42 and 3.37 eV, labeled as SF1 and SF2, respectively, can be observed. These peaks were also shown in the CL measurement results in Fig. 3. The SF1 luminescence peak is well known as the BSF emission peak and is commonly observed in GaN. It has been reported that the presence of SFs during c-plane GaN growth results in a luminescence range of 3.40 to 3.42 eV. On the other hand, SF2 peaks have also been assigned to PSF, but there is no clear understanding of the recombination mechanism. The emission lines of DAP and their LO phonon replicas were also observed. According to the peak of DAP at 3.27 eV, DAP-LO (at 3.18 eV) and DAP-2LO (at 3.09 eV) were separated by 90 meV.

Figure 5 shows the temperature-dependence of the PL energies originating from PL spectra of Figs. 4(a) and 4(b). Other samples of planar and SAG 2nd GaN grown for 45 and 150 min were also shown in Fig. 5. All of the sample positions were obtained by Gaussian line fitting with a multi-peak analysis. In Fig. 5(a), planar 2nd GaN samples grown for 15, 45, and 150 min are shown. The D*X peaks (filled star symbols) follow in the temperature range of 12–200 K, and its peaks decreased with an increase of the temperature. The thermal behavior can be described by the Varshini’s equation, resulting in

$$E(T) = E(0) - \frac{\alpha T^2}{T + \beta},$$

where $E_0$ is the energy gap at 0 K and $\alpha$ and $\beta$ are constants. The best fit shows that the constants $\alpha$ and $\beta$ were 0.44 meV/K and 470 K, respectively. The second fitting for DAP (filled symbols) and their replicas (half-filled and open symbols) are also well matched with the relationship of the optical depth of 222–225 meV. In the sample of planar 2nd GaN grown for 150 min, the BSF emission peak line of SF1 (asterisk symbol) and the PSF emission peaks of SF2 (∗ symbol) newly appeared. We speculate that during the growth time of 120 min, the grains become enlarged and had more opportunities to come into contact with each other. Thus, the coalesced planar 2nd GaN included more defects related to stacking faults than the samples grown for 15 and 45 min.

In a similar manner, the temperature-dependent PL peak energies of the SAG 2nd GaN grown for 15, 45, and 150 min are investigated, as shown in Fig. 5(b). In contrast to the
The integrated PL intensities are shown as Arrhenius plots for (a) the planar 2nd GaN and (b) the SAG 2nd GaN.

The planar 2nd GaN, BSF emission peaks around ~3.42 eV were observed. With a result identical to that shown in Fig. 3(i), the high density of the SFs suppressed the D'X emission.

The reason for the dominant BSF emission peak of SF1 stems from the enhanced lateral overgrowth behavior of the SAG 2nd GaN. Grains from window regions have more opportunities to come into contact with the SiO₂ mask layer along the lateral growth direction. Despite the reduction of the TDs, elongated lateral defects are formed parallel to the substrate, causing stacking fault emissions to dominate. In the SAG 2nd GaN samples, DAP and their replicas were also found.

Figure 6 shows the Arrhenius fittings for the nonradiative recombination centers of the planar and SAG 2nd GaN. The integrated PL intensity can be fitted by the following equation:

\[ I(T) = \frac{I_0}{1 + \sum A_i \exp(-E_i/k_B T)} \]

where, \( I_0 \) is the peak intensity at the temperature of 0 K, \( A_i \) is a constant parameter, and \( E_i \) denotes the activation energies of the corresponding nonradiative recombinations. From the equations, the D'X intensities are well described using the single activation energy shown in Fig. 6(a).

Acknowledgment

This research was supported by the Core Technology Development Program for Next-generation Energy of Research Institute for Solar and Sustainable Energies (RISE).

References