Highly Efficient Excitonic Recombination of Non-polar \((11\bar{2}0)\) GaN Nanocrystals for Visible Light Emitter by Hydride Vapour Phase Epitaxy

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While non-polar nanostructured-GaN crystals are considered as a prospective material for the realization of futuristic opto-electronic application, the formation of non-polar GaN nanocrystals (NCs) with highly efficient visible emission characteristics remain unquestionable up to now. Here, we report the oxygen-incorporated a-plane GaN NCs with highly visible illumination excitonic recombination characteristics. Epitaxially aligned a-plane NCs with average diameter of 100 nm were formed on r-plane sapphire substrates by hydride vapor phase epitaxy (HVPE), accompanied by the oxygen supply during the growth. X-ray photoemission spectroscopy measurements proved that the NCs exhibited Ga-O bonding in the materials, suggesting the formation of oxidized states in the bandgap. It was found that the NCs emitted the visible luminescence wavelength of 400–500 nm and 680–720 nm, which is attributed to the transition from oxygen-induced localized states. Furthermore, time-resolved photoluminescence studies revealed the significant suppression of the quantum confined Stark effect and highly efficient exciton recombinations within GaN NCs. Therefore, we believe that the HVPE non-polar GaN NCs can guide the simple and efficient way toward the nitride-based next-generation nano-photonic devices.

III-Nitride-based nanoscale structures have been gained tremendous attention as candidates suitable for opto-electronic applications, owing to their strong carrier confinement characteristics via large band offset between nano materials and matrix, and large exciton binding energy¹⁻³. Among these nitride-based materials, gallium nitride (GaN) nanocrystals (NCs) with a direct wide band gap (3.34 eV) extensively have been studied for the use of next generation devices, such as photovoltaic, solid-state quantum computation, and single-photon sources⁴⁻⁷. To achieve GaN nanostructures on a substrate, various techniques such as self-assembly growth, vapor-liquid-solid (VLS) process using molecular beam epitaxy (MBE), and metal organic chemical vapor deposition (MOCVD) have been widely used so far⁸⁻¹⁰. For example, Zhang et al. reported the formation of GaN NCs via thermal decomposition by MOCVD¹¹. Additionally, GaN nanodots were grown via Ga droplet epitaxy using pretreatment and post-annealing procedure and converted from Ga₂O₃ using combustion process¹²⁻¹⁴. These methods, however, can exhibit the limited introduction of GaN nanostructures into the desirable applications, because of the complicated growth process and low throughput. In addition, polar GaN with wurzite crystal structure experiences a quantum-confined stark effect (QCSE) along c-axis, which is induced by a large spontaneous polarization field¹⁵. This leads to a large spatial separation between electron and hole wavefunctions, resulting in a loss of internal quantum efficiency¹⁶⁻¹⁸. QCSE also causes a long exciton lifetime increasing the time-jitter on

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the emission from a single photon source and large spectral diffusion, thus deteriorating the performance of the polar GaN-based nanostructure devices. Since the growth of GaN along non- and semi-polar orientations has been considered as a solution to circumvent these negative effects by eliminating or reducing the internal electric fields, it has been of significant interest to the community. However, it is inevitable to dope In or Al elements in non-polar GaN crystals to give rise to the visible luminescence with an acceptable intensity. This can impose the declined luminescence properties of the materials and inefficient fabrication process. Even though several studies have attempted to grow nanostructured-GaN with visible luminescence characteristics using various approaches, such as rare earth doping, and defect-related emission, the efficient luminescence characteristics was inappropriate for the practical illumination devices.

In this paper, we reported non-polar (11–20) GaN NCs for the application of a highly efficient visible luminescence source by hydride vapour phase epitaxy (HVPE). HVPE, with its high growth rate, could easily grow nanoscale GaN crystals without complicated processes and growth conditions. Furthermore, the introduction of oxygen elements during HVPE growth enabled the localized states within the bandgap to achieve visible light emission with highly efficient excitonic recombination.

Experimental Formation of NCs. A-plane GaN NCs were grown on 2-inch (1–102) r-plane Al2O3 substrates (Hi-solar Co., Ltd.), using a vertical-type home-built hot wall HVPE reactor under atmospheric pressure. Firstly, HCl of 20 sccm, and NH3 of 300 sccm were supplied into r-plane Al2O3 substrates in the temperature of 920 °C, respectively. HCl acid gas etched Al2O3 surface, thus causing oxygen-terminated surface. This facilitated the nucleation of GaN NCs. Simultaneously, to form a-plane GaN nanocrystals with visible luminescence wavelength, O2, GaCl, and NH3 elements were incorporated into the oxygen-terminated Al2O3 surface. The gas flow rates of O2, HCl,
and NH₃ were 5 sccm, 15 sccm, and 100 sccm, respectively. HCl gas was delivered into Ga metal source zone where HCl and Ga metal reacted, thus forming GaCl. Consequently, this produced oxidized non-polar GaN NCs on r-plane Al₂O₃ substrate. The sequence and procedure on the growth of non-polar GaN NCs are detailed in Fig. 1(a,b). This process is similar to other literature except for the intentional oxygen supply²¹–²³. The average size and spatial density of the a-plane GaN islands on r-plane sapphire were 100 nm, and 1.5 × 10⁹ cm⁻², respectively, confirmed by AFM (See Fig. 1(c)). To compare the optical characteristics of non-polar a-plane GaN NCs, oxygen-introduced c-plane GaN NCs with average size of 100 nm were formed on c-plane sapphire substrate.

Figure 2. (a) Cross-sectional HRTEM image of the non-polar a-plane GaN NCs. The fast Fourier transformation of NC area in the HRTEM image indicates the NC was grown to the direction¹¹–²⁰. (b) EDS mapping analysis of the corresponding area. EDS elemental analysis of the NCs for (c) Ga, (d) N, (e) Al, and (f) O elements did not found any meaningful spectrum related to AlN supposedly to be created by the nitridation on the sapphire substrate²⁵.
Characterization. The size and density of non-polar a-plane NCs were evaluated by atomic force microscopy (AFM, Innova-LabRAM HR800, Horiba Jobin & Bruker). High resolution transmission electron microscopy (HRTEM) analysis was carried out to investigate the structural properties of the NCs using a FEI double Cs corrected Titan3 G2 60–300 S. The elemental mapping of the NCs was obtained using a Super-X detector with an XFEG higher efficiency detection system, which integrates four FEI-designed silicon drift detectors close to the specimen. Moreover, high resolution X-ray diffraction (XRD, MP-XRD Malvern Panalytical) analysis was conducted to estimate the crystal quality of the non-polar nanomaterials. X-ray photoelectron spectroscopy (XPS, Sigma Probe, Thermo VG Scientific) measurements were employed to confirm the material chemistry after the entire structure formation. The optical properties were determined by photoluminescence (PL) at room temperature using excitation by a He–Cd laser of 325 nm wavelength. In addition, time-resolved PL (TRPL, XperRam S, Nanobase Co., Ltd) measurements were taken at 10 K, using the corresponding monochromater.

Results and Discussion

The TEM analysis shows the non-polar GaN NCs of 100 nm and 60 nm in the average diameter and height, respectively, on the sapphire substrate, as seen in Fig. 2(a). The growth direction of NCs are toward 11–20 from the fast Fourier transform (FFT) analysis of the high-resolution TEM (HRTEM) image, as shown in the inset of Fig. 2(a). It can be seen that the stacking faults (SFs) are present in the NCs. SF is known as the most typical intrinsic defect in the heteroepitaxial non-polar GaN materials24. Notably, an STEM-EDS map confirms that the non-polar GaN NCs consist of the elements of Ga, N, as shown in Fig. 2(b–f). N. Grandjean et al. reported the formation of AlN nucleation layer via nitridation of an Al2O3 substrate. According to the literature, an AlN layer was formed on an Al2O3 surface by exposing the Al2O3 surface to an NH3 gas of 20 sccm at temperature of 850 °C, which was confirmed by in situ reflection high-energy electron diffraction25. However, almost negligible Al spectrum on the sapphire substrate by the high temperature surface treatment was observed, suggesting that the NCs were directly deposited on the substrate material. Furthermore, we were not able to detect oxygen elements in the NCs from STEM-EDS map mainly due to the detection limit and oxygen detectability of the EDS equipment, not the absence of the elements in the materials.

To shed light on the crystal orientation and the structure of the GaN NCs, we employed the X-ray diffraction (XRD) analysis, as shown in Fig. 3. We can clearly observe the reflections of r-plane sapphire (1–102), (2,2–204) and GaN (11–20), respectively, as shown in Fig. 3(a)26. The sharp and narrow peak for (11–20) reflection in GaN NCs supports that the materials exhibit high crystalline. It is noticeable that any additional crystal phases were not detectable except for the original material reflections. This corresponds to STEM-EDP, which also supports that highly aligned pure single crystalline a-plane GaN NCs were successfully grown on r-plane sapphire substrate. Furthermore, 2 axis-scan revealed that the non-polar GaN NCs were deposited on r-plane sapphire with the off-axis of 1.85° along a-axis, as shown in Fig. 3(b).

To determine the chemical states of the elements in the NC materials, XPS analysis were conducted, as shown in Fig. 4. Figure 4(a) shows XPS survey analysis after the formation of non-polar GaN NCs. Substrate-related Al 2p and O 1 s peaks are apparently positioned at 72.28 eV and 528.21 eV, respectively. Ga-related XPS peaks including Ga Auger peaks, and N 1 s are visible in XPS spectra, confirming the formation of HVPE a-plane GaN NCs on the substrate. This corresponds with the results of STEM-HAADF and XRD. Furthermore, XPS core level spectra investigations for Ga 3d, and O 1 s signals were employed, respectively, as illustrated in Fig. 4(b,c). The deconvoluted Ga 3d core level signals clearly ensure the presence of Ga-N, and Ga-O bonding in the materials, as shown in Fig. 4(b). The signal of Ga-O bonding at 20.9 eV suggests the formation of GaOxNy, or substitutional oxygen (Ox) complex defects in the nano-architectures27. Since we could not detect the oxide signals in STEM and XRD, we speculate that Ga-O spectrum is associated with the presence of Ox-related point defect complex. In addition, Ga-O bond peak centered at 530.5 eV in O1s core level spectra further provided that the nature of GaN NCs involved oxygen elements, as illustrated in Fig. 4(c)28.

To investigate the optical characteristics of HVPE a-plane GaN NCs, we performed PL measurements, as presented in Fig. 5(a). Typically PL spectrum of c-plane GaN layers on sapphire substrates shows band edge
emission at 365 nm and yellow luminescence band. However, c-plane NCs exhibits dominant wavelength at 366 nm and 388 nm, accompanied with broad plateau in the wavelength range from 400–800 nm. We consider that carbon- and oxygen-related defect complex imposes the broad red luminescence in c-plane GaN nanodots. The 366 nm peak close to the bandgap energy of GaN can be assigned to exciton recombination. It is well known that 388 nm wavelength in GaN materials is related to structural defects, such as stacking faults and screw dislocation along c-axis. On the sharp contrary, we can clearly observe that the dominant peaks of a-plane GaN NCs appeared around blue and red emission spectra of 400–500 nm and ~680 nm. The peak positions of the NCs were centered at wavelength of 442 nm and 680 nm. The broad shape of PL peaks may be related to the size distribution of GaN NCs and defect-related states. One can observe that near band edge (NBE) emission around 366 nm in a-plane GaN NCs is present but very weak. It is noticeable that structural defect-related emission at the wavelength of 388 nm is also declined in PL spectrum of non-polar GaN NCs, compared to that of c-plane ones. Since it is well established that the densities of extended defects in non-polar GaN crystals are much higher than those of c-plane ones, we consider that this is not attributed to the extended structural defects in non-polar nanomaterials. Rather, we assign that this nature originated visible luminescence transition.

Figure 4. (a) XPS survey spectrum of HVPE a-plane GaN NCs. Deconvoluted XPS spectrum of the (b) Ga 3d, (c) O 1s signal obtained from the non-polar NCs.
Figure 5. (a) PL spectra of c- (red), and a-plane (blue) GaN NCs with 100 nm-diameter at room temperature. (b) Schematic illustration of bleached photoluminescence of HVPE a-plane GaN NCs.

Figure 6. Time-resolved PL spectra of oxygen-induced a- and c-plane HVPE GaN NCs with different sizes at 10 K. The blue and red line represent the PL decay curves of a-plane GaN NCs and c-plane GaN NCs, respectively.

|          | $\tau_{\text{fast}}$ (ns) | $\tau_{\text{slow}}$ (ns) |
|----------|--------------------------|---------------------------|
| a-plane NCs | 0.44                     | 5.7                       |
| c-plane NCs | 5.38                     | 10.81                     |

Table 1. TRPL parameters extracted from fitting of the double exponential function for a-plane GaN NCs, and c-plane GaN NCs.
produced from defect-induced deep level states in the bandgap of the NCs due to the oxygen influx during the HVPE growth. Note that the emission energy is smaller than the energy of GaN band edge recombination, associated with the presence of the quantum confinement Stark effect, inherited from the internal electric field in the structure. Since non-polar materials exhibit the negligible piezoelectric field, we speculate that this can be related to the electronic deep trap states in the NCs, such as donor and acceptor pair (DAP), Mg-, carbon-, and intrinsic-related defects. Reshchikov et al. reported that the subsequent oxidation of GaN materials would evolve the blue band in the GaN, which originated from a transition from the shallow donors in the near surface region to band-bended surface states. In other words, luminescence between the electrons captured in shallow donors and the holes localized by the oxidized surface states can emit the blue emission of GaN materials. Additionally, it has been reported that red luminescence of GaN reflects the transition from a shallow/deep donor or from the conduction band to an unknown deep acceptor, inherited from the presence of $V_{\text{Ga}}$ or $V_{\text{Ga}O_N}$.$^{30-32}$ Note that HVPE growth of GaN NCs was performed with O$_2$ supply, implying the introduction of oxidized states in the materials. Indeed, even if the flow rate of O$_2$ during a-plane GaN NC growth is very low, typical HVPE GaN epitaxial layers exhibits more than oxygen concentration of $10^{16}/$cm$^3$, which can also help the formation of the defect-related states in GaN materials.$^{43,44}$ Since impurities like C, or Mg were not used in this case, consequently, we consider that the significant incorporation of oxygen in the NCs take part in the reformation of the visible blue and red luminescence of a-plane GaN NCs, as shown in Fig. 5b. The presence of the oxygen peak in XPS result of Fig. 3 further support this statement. V. Findal et al. computed the surface energies as a function of crystallographic orientations of GaN.$^{45}$ They addressed that the surface energies of a-plane GaN, and Ga-face c-plane GaN were estimated to be 159 meV/Å$^2$, and 129 meV/Å$^2$, respectively. We assure that this is attributed to higher surface energy of a-plane GaN. It is well established that the higher surface energy, the higher surface instability, thus encouraging the growth of such higher reaction with other materials.$^{46}$ This result suggests that the reaction between O$_2$ elements could be much activated in a-plane GaN with higher surface energy, compared to Ga-face c-plane GaN, thus making higher oxidized states of a-plane GaN NCs. Consequently, we speculate that this results in the nature of broad visible luminescence range in a-plane GaN NCs. To achieve visible luminescence in GaN-based devices, it is essential to incorporate dopant materials, such as indium (In) elements in GaN crystals. This can cause the piezoelectric fields in the materials, thus reducing the efficiency of device by the separation of hole and electron wave-functions.$^{47}$ However, we believe that oxygen-mediated a-plane GaN nanocrystal materials on n-GaN layer/sapphire substrates can be easily utilized as visible luminescence photonic devices only by inserting p-GaN layer. The device is under study. One can found the co-existence of 679 nm and 695 nm peak position in c- and a-plane GaN. It is well established that that luminescence of 679 nm is related to high concentrations of C and O, and the overlap of the donor acceptor pair (DAP) band and the electron-to-acceptor (e,A0) transition band. Furthermore, emission at 695 nm is attributed to DAP transition.$^{45,46}$

In order to clarify the carrier characteristics in a-plane GaN NCs, TRPL measurements were carried out at 442 nm emission peak and 10 K by estimating the lifetime of excitons in a-plane and c-plane HVPE GaN NCs with the corresponding NC sizes of 100 nm, as seen in Fig. 6. The PL lifetime curves are well fitted with double exponential functions as follows:

$$I(t) = A_{\text{fast}} \exp(-t/\tau_{\text{fast}}) + A_{\text{slow}} \exp(-t/\tau_{\text{slow}})$$

where $A_{\text{fast}}$ and $A_{\text{slow}}$ are the normalization constants, $t$ is time, $\tau$ is the photo-excited carrier lifetime, and $I(t)$ is the time-dependent PL intensity. All the parameters in the double exponential function are presented in Table 1.

It is noticeable that the all measured decay time for the c-plane GaN NCs shows much longer lifetimes than that for a-plane GaN ones. The fast decay regions implies the fast exciton recombination process. On the other hand, the localized carrier recombination process dominates the slow decay components.$^{46}$ Since TRPL measurements were conducted at low temperature, non-radiative recombination in NCs is negligible. Therefore, we consider that the shorter exciton recombination time of a-plane HVPE GaN NCs is attributed to a significantly increased overlap of electron and hole wavefunctions and reduction of the internal electric filed in HVPE a-plane GaN NCs, indicative of highly enhanced excitonic recombination.$^{46}$ This is in excellent agreement with previous results reported elsewhere.$^{46-48}$ We believe that these remarkably improved optical properties and simple formation of HVPE non-polar a-plane GaN NCs prove to be a viable matrix for a direct visible emission source.

Conclusions

It was demonstrated that HVPE non-polar a-plane GaN NCs with oxygen-mediated localized states were grown on r-plane sapphire substrates for direct visible light emission. TEM, XRD analysis showed that the formation of the NCs were epitaxially deposited along a-axis of 1.85° on r-plane Al$_2$O$_3$ structures. XPS analysis proved that the nature a-plane GaN NCs is comprised of Ga-N bonding and O$_2$ point defect complex, indicative of the presence of oxygen-induced localized states in the bandgap. Photoluminescence studies also confirmed the blue- and red-light emission of the NCs around wavelength of 400–500 nm, and 680–720 nm with the reduced NBE and structural defect-related spectrum, compared to those of c-plane ones. These visible emission bands are attributed to the localized states of GaN NCs, inherited from their oxidized phases. Furthermore, the relatively shorter lifetime of the NCs in TRPL analysis suggested the suppression of the internal electric field and enhanced efficient excitonic recombination. Therefore, this study could offer a new feasible approach to achieve GaN NCs for direct visible luminescence application.

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Author contributions

M. Lee conceived the idea, performed the GaN nanocrystal growth and decipher the PL and XPS measurement. D. Lee performed PL measurements. H.S. Baik conducted TEM analysis. H. Kim performed XRD measurements and interpreted the data. H.U. Lee conducted AFM characterization and its interpretation. Y. Jung measured and interpreted PL spectra. M. Yang deciphered STEM analysis. M.G. Hahm and J. Kim designed the experimental and supervised the project. All authors discussed and reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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