Luminescence characteristics of amorphous GaN quantum dots prepared by laser ablation at room temperature

Seung Hwan Shim*, Jong-Won Yoon**, Naoto Koshizaki**, Kwang Bo Shim*

*Department of Ceramic Engineering, Ceramic Processing Research Center (CPRC), Hanyang University, 17 Haengdang-Dong, Seongdong-Ku, Seoul 133-791, South Korea

** Nanoarchitectonics Research Center (NARC), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

Abstract

Amorphous GaN quantum dots(a-GaN QDs) with particle diameters less than bohr radius(~11nm) were successfully fabricated at room temperature by a laser ablation of high densified GaN target. Transmission electron microscopy, SAED diffraction pattern and X-ray photoelectron spectroscopy confirmed the presence of a-GaN QDs with particle size of 7.9, 6.9, 4.4nm under the Ar gas pressures of 50, 100 and 200 Pa, respectively. The room temperature PL and absorbance spectra showed a strong band emission centered at 3.9 eV in a-GaN QDs made under the gas pressures of 100 and 200 Pa, which is nearly 0.5eV blueshifted with respect to the bulk crystal band gap.

1. Introduction

As nano-scaled semiconductors have currently gained great interest, study of novel properties that generated from these materials controlled by nano-scale has been reported, and also it is expected that this approach result in the application to new nanostructured devices which has various properties by band gap designing[1,2].

Recently, many researchers have reported the method, such as aerogel cavities[3], polymer matrices[4], metalorganic chemical vapor deposition[5] and laser ablation[6] to fabricate the GaN nanocrystals and in particular ultra fine nanocrystals scaled below bohr radius showed a lager blueshift due to the quantum confinement effect compared with the bandgap emission of bulks(3.4eV) in PL spectra[7-10]. But high quality GaN nanocrystals have been hindered by the difficulties in developing the synthesis process, due to the very low reactivity between Ga and N, a low decomposition temperature, the nitrogen stoichiometry issue[11-13] and the grain growth by the heat treatment. A-GaN has a number of potential advantages of low cost process and the independent stability for deposition

on arbitrary substrates, so many work on GaN has been remarkably concentrated on the amorphous materials. Instead of this advantages, a-GaN has a low density of midgap defect and the open structure suitable to incorporate the great concentration of the doping atoms. Consequently, a-GaN has been expected as the independent materials of its crystalline counterpart, indicating that optical and electrical properties may be far superior to typical amorphous materials, a-Si and a-Ge[14,15].

In fact, it was reported that a-GaN thin films and nanoparticls were fabricated by the reactive sputtering method[16] and in the polymer matrix[17], respectively and the blue light emitting characteristics observed from them were similar to it of crystalline GaN. But up to now it has been no report of blueshift due to the confinement effect in nano scaled a-GaN.

In this work, a-GaN nanoparticles were fabricated by pulsed laser ablation of high densified target. The process condition to control their size to below bohr radius were established and their structural and optical characteristics were investigated.

2. Experimental procedure

In this work, the high density of the sintered GaN pellet was used as the target to reduce defects such as debris due to the low density of target during the process of laser ablation. GaN specimens were fabricated at room temperature without heat-treatment under Ar gas pressure ranged from 1 to 200Pa and an off-axis configuration, on a quartz substrate placed perpendicular to target for an uniform size distribution[18].

ArF excimer laser(Lambda Physik, LPX110i, λ =193nm) was used as a laser source, operated at a repetition rate of 10Hz. Pulse energies were typically 34mJ/pulse and laser beam was focused to a laser focal spot size of ~4× 1 ㎟ on the target suface through an UV grade quartz window. The crystallinity of the deposited GaN specimen were examined by X-ray diffraction(Rigaku, RAD-C) using Cu Kα radiation. The surface composition and chemical state of Ga, N, O in the deposited specimens were evaluated by X-ray photoelectron spectroscopy (XPS; PHI, 5600ci) using the monochromated Al Kα source. The structure, particle shape and size distribution of the specimens were analyzed using transmission electron microscopy(TEM; JEM2000-FXⅡ, 200kV) and Image analyzer software(Image-Pro Plus 4.1 Mediacybernetics). The optical absorption was measured by a spectrometer (Shimadzu, UV-2100PC) and the room temperature photoluminescence spectra was performed with a spectrometer having a 0.1nm resolution and 500 W Xenon lamp as optical exitation source.

3. Result and discussion

The different phenomena among Ar gas pressure (1~200Pa) were observed in a laser ablation process. At a pressure of below 50Pa, continuous films were formed through the process that the ejected species are immediately deposited on the substrate without any collision due to a low pressure and then their nucleation and growth occurred. However, at

a higher pressure of above 50Pa, nanometer sized particulates were formed from the gas-condensation process related to collisions of the ejected species by the background gas pressure. In particular, a large number of snowflake-like aggregates were observed in the sample fabricated at 200Pa of gas pressure and mainly consisted of nanoparticles.

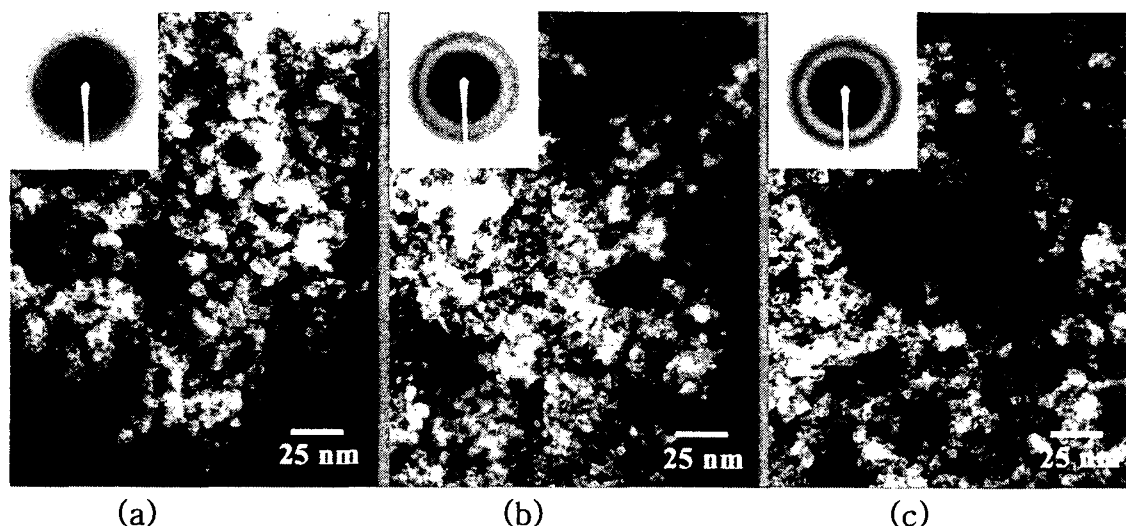

Fig. 1. Dark-field TEM images of a GaN QDs fabricated by laser ablation under Ar pressure of (a) 50 Pa (b) 100 Pa (c) 200 Pa.
The SAED patterns (inset) point to a significant amount of amorphous phase.

Fig. 1 shows dark field TEM images and SAED patterns of the GaN specimens deposited at room temperature according to the gas pressure of 50, 100 and 200 Pa. The majority of the deposited specimens were spherically shaped QDs with a size below 10nm and the size of GaN QDs decreased as the background gas pressure increased.

The selected area electron diffraction(SAED) pattern from this specimens show broad diffraction rings and diffusing background scattering indicating that this GaN QDs are mainly amorphous phase. This fact was strongly supported from XRD results that these specimens were typically amorphous structure without any X-ray diffraction peak. The size distribution variation of a-GaN QDs as a function of the ambient gas pressure is represented as the particle size histogram in Fig. 2. Here, a total of above 250 GaN QDs were analyzed using the image analyzer software and a-GaN QDs fabricated at 50, 100 and 200 Pa were found to have a mean diameter of 7.9, 6.9 and 4.4 nm, respectively showing that the higher Ar pressure, the smaller particle size. This effect of Ar gas pressure was prominently shown in the size distribution more than in the particle size, which most of a-GaN QDs fabricated at 50 Pa have relatively wider size distribution than that at 100, 200 Pa, respectively.

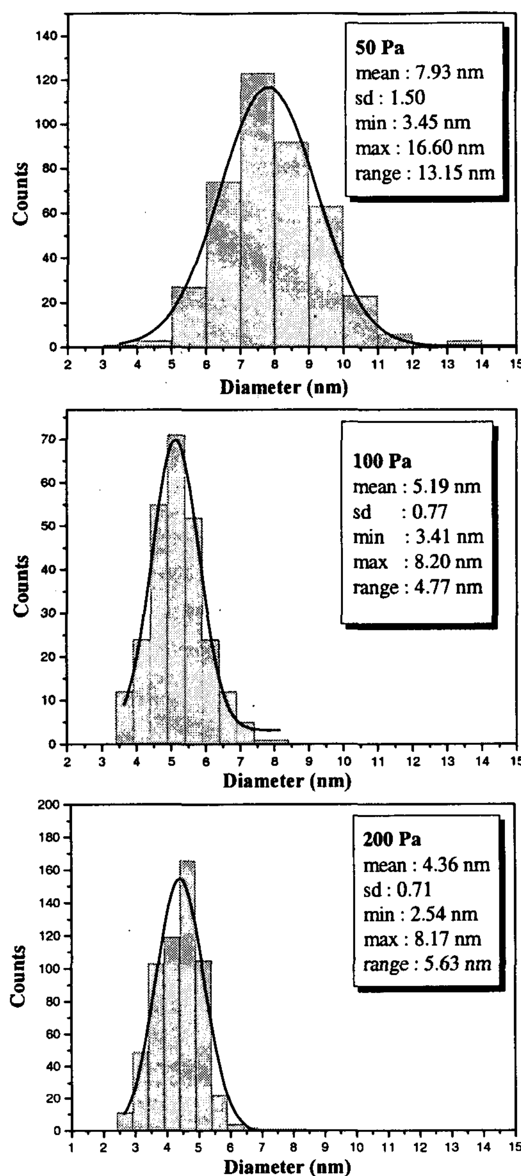

Fig. 2. Particle size distributions of GaN QDs showing that the increase of Ar pressure results in a decrease in size and a narrower size distribution.

The XPS data of a-GaN QDs in Fig. 3 reveals the binding energy of Ga $2p_{3/2}$ and N 1s were calibrated by C 1s peak of 285.2 eV. The positions of these peaks were a Ga $2p_{3/2}$ at 1118.1 and a N 1s at 397.5 eV, indicating little change among the gas pressure. This values confirm the existence of GaN[19]. A calculation of Ga/N ratio from the XPS result of 50, 100, 200 Pa gave a value of 1.23, 1.19 and 1.17, reflecting a part of the formation of Ga_2O_3 on the GaN surface.

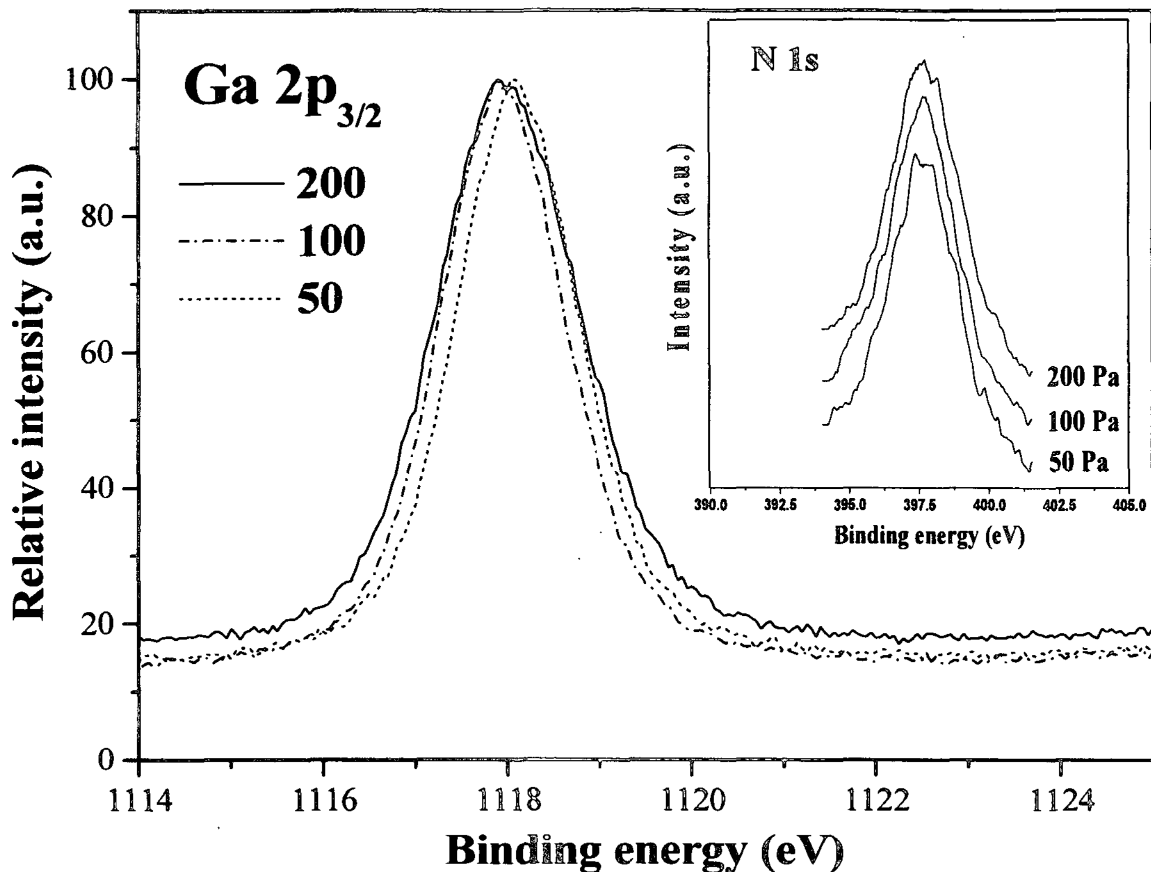

Fig. 3. XPS spectrums of Ga 2p and N 1s spectra (inset) showing little shift of the peak center according to the Ar pressure.

Room temperature photoluminescence and absorption characteristics of a-GaN QDs deposited at Ar pressures of 50, 100 and 200 Pa were collected and represented in Fig. 4. From photoluminescence results, two broad emission peaks centered at 3.3 and 3.9 eV were observed in all the specimens, in particular, the stronger emission peaks at 3.9 eV means a large shift to higher energies of a bandgap emission compared with the bulk crystal(3.4 eV) and amorphous GaN (2.8eV)[17, 20] and such blueshift in PL spectra is more predominant in the cases of 100, 200 Pa. Rough estimate of the band gaps obtained from a plot of α^2 vs $h\nu$ were found to be 3.5, 3.8 and 4.0 eV for QDs fabricated at 50, 100 and 200 Pa, respectively showing a gradual increase in absorption at the band edge due to the band tailing which occurs in amorphous materials. This values in absorption spectra means the shift of theses optical gap to higher energy and agree reasonably well with PL results. The large blueshift in the bandgap of QDs fabricated at 100, 200 Pa might be attributed to

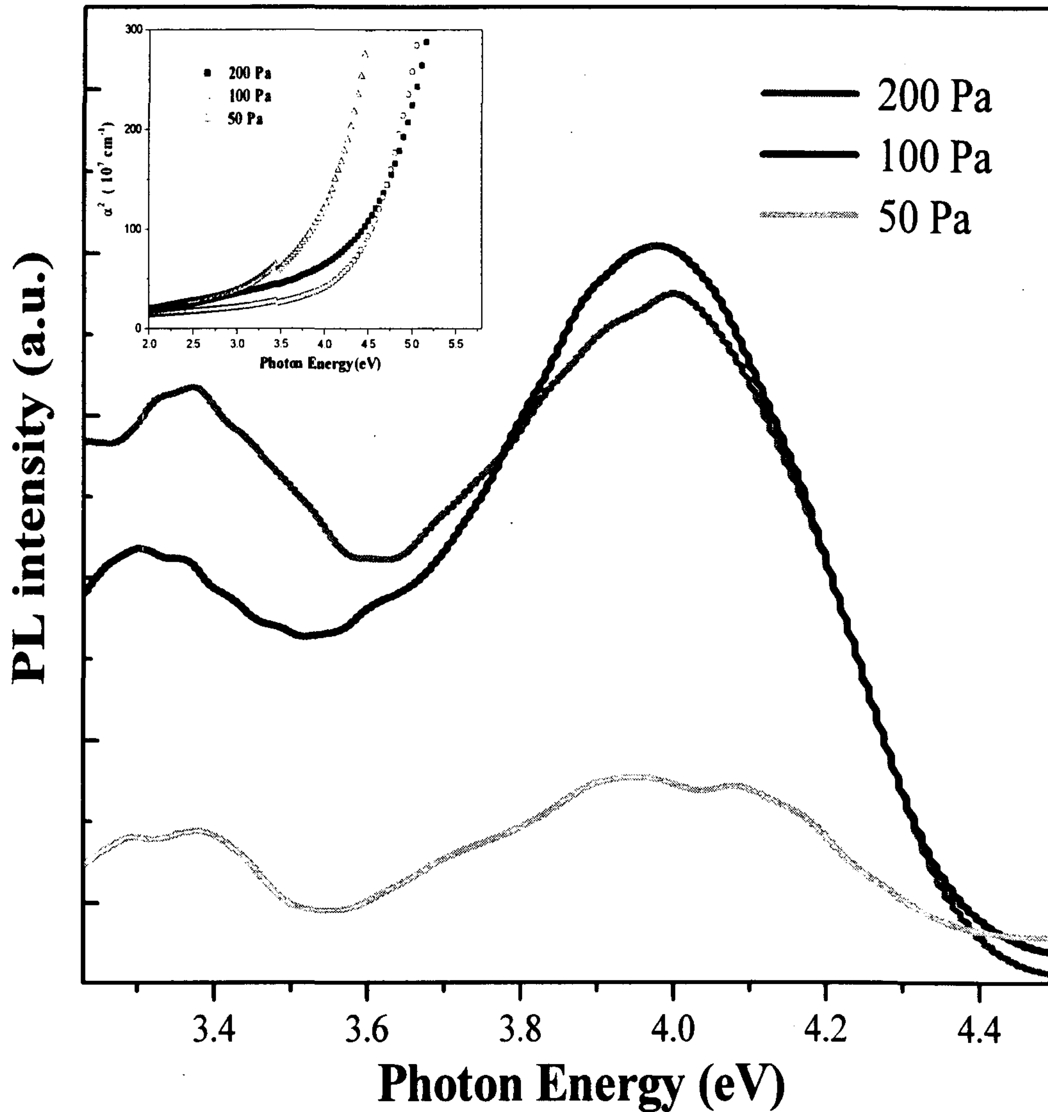

Fig. 4. Room-temperature photoluminescence spectra from a-GaN QDs, showing large blueshift of band-gap emission. Inset shows plot of absorption coefficient against photon energy.

strong confinement effect from a size reduction of a-GaN QDs with smaller size of about 7 nm as the exciton Bohr radius for GaN is reported to be ~11nm.

4. Conclusion

In summary, amorphous GaN QDs with particle diameters from 4 nm to 8nm were fabricated at room temperature through a laser ablation of the highly densified GaN target. In particular, amorphous QDs at 100 and 200 Pa had not only the mean diameter less than the exciton Bohr radius for GaN 11nm but also the narrow size distribution, suggesting that

these size is small enough to show quantum confinement effect. The PL and absorbance results indicate a characteristic band-edge blueshift in the optical band gap and these observation of blueshifed emissions from a-GaN QDs suggest that amorphous GaN can have independent promise as an optical material compared to the crystalline counterpart.

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[1]. T. Yoshida, S. Takeyama, Y. Yamada and K. Mutoh, Appl. Phys. Lett. 68, 1772 (1996).

[2]. K.M. Hassan, A.K. Sharma, J. Narayan, J.F. Muth, C.W. Teng and R.M. Kolbas, Appl. Phys. Lett. 75, 1222 (1999).

[3]. T.J. Goodwin, V.J. Leppert, C.A. Smith, S.H. Risbud, M. Niemeyer, P.P. Power, H.W.H. Lee and L.W. Hrubesh, Appl. Phys. Lett. 69, 3230 (1996).

[4]. J.L. Coffer, M.A. Johnson, L. Zhang, R.L. Wells and J.F. Janik, Chem. Mater. 9, 2671 (1997).

[5]. M. Miyamura, K. Tachibana, Y. Arakawa, Appl. Phys. Lett. 80, 3937 (2002).

[6]. T.J. Goodwin, V.J. Leppert, S.H. Risbud, I.M. Kennedy, H.W.H. Lee, Appl. Phys. Lett. 70, 3122 (1997).

[7]. Y.G. Cao, X.L. Chen, J.Y. Li, Y.C. Lan, J.K. Liang, Appl. Phys. A 71, 229 (2000).

[8]. N. Preschilla A, S. Major, N. Kumar, I. Samajdar, R.S. Srinivasa, Appl. Phys. Lett., 77, 1861 (2000).

[9]. P. Ramvall, S. Tanaka, S. Nomura, P. Riblet and Y. Aoyagi, Appl. Phys. Lett., 73, 1104 (1998).

[10]. B. Daudin, F. Widmann, G. Feuillet, Y. Samson, J.L. Rouviere, N. Pelekanos, Mater. Sci. Eng. B59, 330 (1999).

[11]. C.M. Balkas, R.E. Davis, J. Am. Ceram. Soc. 79, 2309 (1996).

[12]. Jen-Wei Hwang, J.P. Cambell, J. Kozubowski, S.A. Hanson, J.F. Evans, W.L. Gladfelter, Chem. Mater. 7, 517 (1995).

[13]. N. Newman, J. Ross, M. Rubin, Appl. Phys. Lett. 62, 1242 (1993).

[14]. P. Stumm, D.A. Drabold, Phys. Rev. Lett. 79, 677 (1997).

[15]. S.B. Aldabergenova, M. Albrecht, A.A. Andreev, C. Inglefield, J. Viner, V.Yu. Davydov, P.C. Taylor, H.P. Strunk, J. Non-Cryst. Solids, 283, 173 (2001).

[16]. S. Nonomura, S. Kobayashi, T. Gotoh, S. Hirata, T. Ohmori, T. Itoh, S. Nitta, K. Morigaki, J. Non-Cryst. Solids 200, 174 (1996).

[17]. Y. Yang, V.J. Leppert, S.H. Risbud, B. Twamley, P.P. Power, H.W.H. Lee, Appl. Phys. Lett. 74, 2262 (1999).

[18]. J.F.M. Cillessen, M.J.M. de Jong, X. Croizē, Rev. Sci. Instrum. 67, 3229 (1996).
[19]. J.Q. Hu, B. Deng, W.X. Zhang, K.B. Tang, Y.T. Qian, Chem. Phys. Mater. 351, 229 (2002).
[20]. A. Bittar, A. Markwitz, Appl. Phys. Lett. 78, 619 (2001).