

Original Paper

Fluorescence Characteristics of Gallium Nitride Powders Prepared in the Laboratory

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Abstract: Fluorescence characteristics of gallium nitride powder samples prepared in our laboratory were examined. The samples processed at 1100 °C showed band-edge emission and yellow luminescence, but the samples processed at 900 or 1000 °C showed no significant fluorescence. From the results of XRD analysis, it was confirmed that all these samples had wurtzite gallium nitride structure, and the samples processed at 900 or 1000 °C showed the very low crystallinity. It was suggested that a lot of defects were present in the crystals of these powder samples with low crystallinity, so that the recombination of excited electrons and holes was promoted to show no significant fluorescence emission. In addition, the sample processed with coexistence of activated carbon at a high ratio showed blue light emission around 425 nm, and it was concluded that a certain amount of carbon was taken into the crystal lattice.

Key words: Gallium Nitride, Powder, Fluorescence, Crystal Structure, Carbon

1. Introduction

Gallium nitride is III-V compound, and a direct transition type semiconductor with a band gap of about 3.4 eV. The stable crystal structure of gallium nitride is hexagonal wurtzite. And a metastable zincblende structure and a rock salt structure under high pressure have also been reported. All of these structures can be fabricated by changing the synthesis methods and/or the synthesis conditions. Since gallium nitride has a large band gap and is a direct transition type, this material enables to produce a luminescent device emitting blue light with high luminance.

Gallium nitride is a sublimable material, and its melt (liquid phase) has not been confirmed. J. Karpiński et al. studied gallium nitride crystal growth at high pressure^{1,2)}, and concluded that the melting point of gallium nitride at 60 kbar was over 2300 °C. Therefore, crystal synthesis from the liquid phase seems impossible. On the other hand, in crystal formation from gas phase, it is very difficult to control the crystal nuclei generation, crystal orientation and crystal size. As a result, most of the synthesized particles become small or polycrystalline. Due to the crystal grain boundaries in polycrystalline, recombination levels are formed in its band-gap, and the material becomes nonradiative. For use as a effective light emitting device, it is necessary to obtain a single crystal having few crystal defects. At present, it is ordinal to obtain gallium nitride single crystal by using metal-organic vapor phase epitaxy (MOVPE).

As for powder material, it is mainly obtained by high temperature processing of metallic gallium or gallium oxide powder in an ammonia atmosphere. When using gallium oxide as a starting material, the

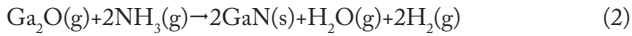
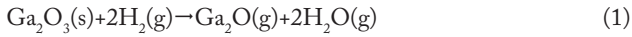
reaction starts at the reduction of gallium oxide by hydrogen, which is formed by thermal decomposition of ammonia, to form gaseous species, Ga₂O, working as a reaction intermediate. Then gaseous Ga₂O reacts with ammonia to produce gallium nitride³⁾. And more, the attempts to fabricate gallium nitride nanoparticles and/or nanorods using gallium oxide⁴⁾ and the synthesis of gallium nitride at low temperature using lithium nitride and gallium oxide⁵⁾ were reported. And many researchs on gallium nitride powder are carried out, such as the studies aiming the use as fluorescent display devices^{6,7)} and visible light responsive photocatalyst by GaN-ZnO solid solution⁸⁾, and the interest in its physical properties has been increased.

In this study, the fluorescence properties of gallium nitride powder samples prepared in the laboratory under various conditions were investigated. Some of these lab-made samples were processed at the coexistence of carbon to promote the nitridation, and a part of coexisting carbon was incorporated into the gallium nitride crystal after processing. These incorporated carbon was suggested to affect various physical properties of the powder crystal. The fluorescence emission characteristics of the samples were discussed with preparing conditions and the effects of incorporated carbon.

2. Experimental

GaN powder sample preparation.

The synthesis of gallium nitride powder starting from gallium oxide is supposed to proceed by the following reactions^{9,10)}. Here, (g)



represents a gas phase species and (s) represents a solid phase species. Hydrogen in formula (1) is generated from the thermal decomposition of ammonia and acts as a reducing agent. $\text{Ga}_2\text{O}_3(\text{s})$ is reduced by this hydrogen to form $\text{Ga}_2\text{O}(\text{g})$, which is a necessary intermediate for the formation of GaN. And the generation of $\text{Ga}_2\text{O}(\text{g})$ is the rate-determining step of the overall reaction. The carbothermal reduction process is effective to promote the formation of $\text{Ga}_2\text{O}(\text{g})$. This process is a heat treatment in which metal oxides are reduced by coexistence with carbon sources in a nitrogen or argon atmosphere. For example, the carbothermal reduction process is applied for the reduction of SiO_2 for industrial preparation of AlN^{11} . The reaction formula for forming $\text{Ga}_2\text{O}(\text{g})$ employing the carbothermal reduction is shown as follows.



The commercially available gallium oxide powder (99.99 %, Dowa Electronics) was used as gallium source in this study. Some samples were processed with coexistence of carbon in purpose of promoting nitridation as mentioned above. As carbon source, activated carbon powder (Wako Pure Chemical Co.) or polyvinyl alcohol (Wako Pure Chemical Co., the average molecular weight: 22000) was used. In case of activated carbon was used, gallium oxide powder together with activated carbon powder was ground thoroughly till the mixture became uniform. When the activated carbon was used, however, it was supposed that the direct contact area between GaN particles and the activated carbon particles was very small. Then PVA coating for GaN particles before processing was attempted to increase the direct contact area of gallium oxide and carbon and to promote the reducing reaction by carbon. When PVA was used, gallium oxide powder was dispersed in PVA aqueous solution to prepare a suspension, and then the suspension was freeze-dried to prepare the PVA coated gallium oxide particles. In this paper, the coexistence amount of carbon in the starting material is represented by the element ratio of Ga and C. In case of Ga:C = 1:1, the preparation weight ratio of activated carbon to Ga_2O_3 was 12:93.7.

The prepared starting materials were loaded on mullite boats, and nitriding processing was performed with electric tube furnace (ARF-50KC, Asahi-rika Co.) at the temperature range of 900 °C to 1100 °C. The heating rate was set at 300 °C/h. For almost all sample preparations, both NH_3 gas and N_2 gas were flowed into the system at 200 ccm at room temperature as the nitrogen source, while the nitriding processing was proceeding. And a few samples were processed under only NH_3 gas flow at 200–400 ccm at room temperature. In addition, no nitridation was observed at the processing under only N_2 at every temperature in our experiments.

Measurements.

For fluorescence measurement, the powder samples were fixed on glass plates to be set in spectrofluorometer (FP-6600, JASCO Co.) as the incident angle was 45 degree. The excitation wavelength was

330 nm, and the UV-35 filter was inserted before the detectors. The fluorescence measurements were performed under room temperature. The XRD measurement for crystal structure analysis was performed by the $2\theta/\theta$ method using Rigaku RINT-2500 with Cu target. Also the thermal gravimetric analysis (TGA) was carried out with Discovery TGA (TA instrument Co.) to measure the weight loss of the samples caused by carbon burning.

3. Results and Discussion

Figure 1 shows the fluorescence spectra of the samples processed at different temperatures. The starting material of all samples in Fig. 1 was Ga_2O_3 without carbon. The spectrum of the sample processed at 1100 °C for 3hr showed two emission bands. As shown experimentally by B. Schwenzer et al.¹²⁾, the band around 375 nm could be regarded as the band-edge emission (hereafter referred to as **BE**). The yellow luminescence near 555 nm (hereafter referred to as **YL**) was also observed in the same spectrum. However, neither **BE** nor **YL** were observed at the samples processed both of at 900 °C for 4hr and at 1000 °C for 3hr. The XRD patterns of the same samples are

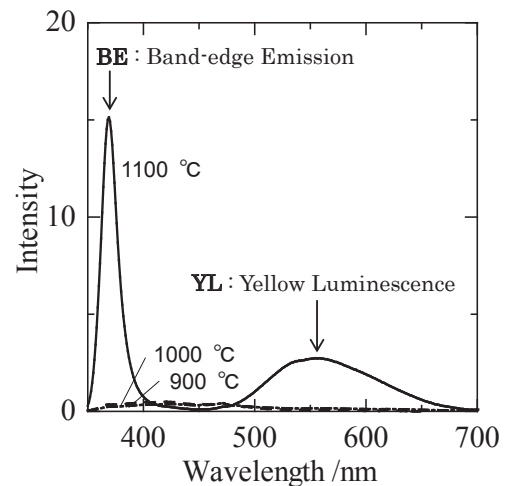


Fig. 1 Fluorescence spectra of the samples processed without coexistence of carbon at various temperatures.

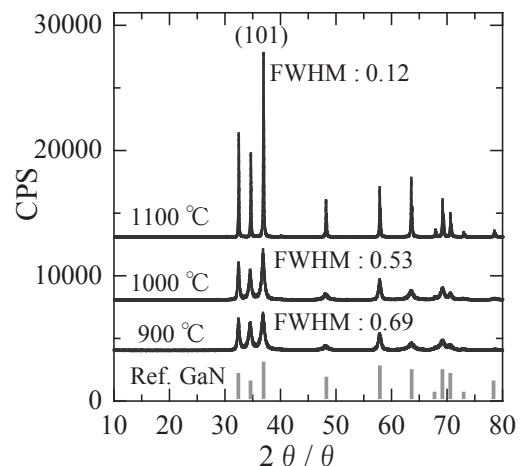


Fig. 2 XRD patterns of the samples same as shown in Fig. 1. The FWHM (full width at half maximum) values, measured with (101) peaks around 37 degree, are shown on the right of the peaks.

shown in Fig. 2. The FWHM (full width at half maximum) values, measured with (101) peaks around 37 degree, are shown on the right of the peaks. The FWHM value of the sample processed at 1100 °C was extremely small, and it was supposed to have high crystallinity.

Other samples prepared under various conditions, including the samples processed with coexistence of carbon, were evaluated at the same fluorescence and XRD measurements. As the samples processed with coexistence of carbon might have remaining carbon after nitridation, high temperature post-treatment at 600 °C for 3 hours in the air were performed to remove it.

Figure 3 shows the relation between **BE**, **YL** emission intensities and FWHM values. The processing temperatures and starting materials of each sample are indicated in the inner box. The samples A to D, processed at 900 or 1100 °C, showed relatively large FWHM values, 0.4 to 0.7. In contrast, the samples E to J, processed at 1100 °C, showed very small FWHM values, less than 0.2, meaning to have high crystallinity. And the samples with larger FWHM values showed neither **BE** nor **YL** at all. The samples with low crystallinity was considered to have a lot of defects in their crystals, and these defects worked as recombination centers for photo-generated electron-hole pair, and then deactivated the excited electrons. These results suggested that high crystallinity is essential for fluorescence emission. However, the emission intensities of the samples with high crystallinity varied much. Even the samples at the same preparing condition showed various FWHM and emission intensities. So,

to understand the relation between their fluorescence properties and crystallinity, other factors such as the influences of the particle size on FWHM values should be considered.

The fluorescence spectra of the samples processed with coexistence of activated carbon are shown in Fig. 4. The processing condition of these samples was at 1000 °C + 1100 °C. The samples processed at high carbon coexistence ratios, i.e. Ga (in Ga₂O₃):C = 1:5, 1:10, showed blue luminescence (hereafter referred to as **BL**) around 430 nm. At the same time, it was observed that **BE** decreased as the

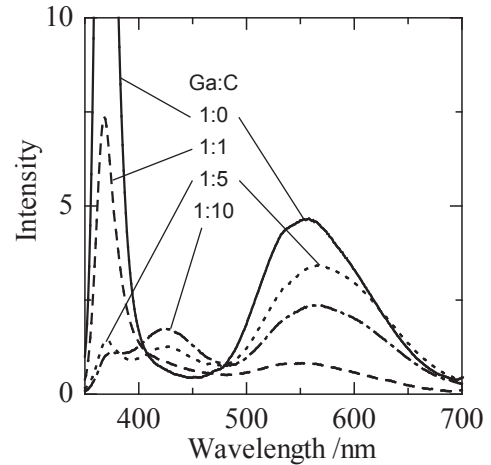


Fig. 4 Fluorescence spectra of the samples processed with coexistence of activated carbon at 1000 °C for 2hr followed by at 1100 °C for 1hr.

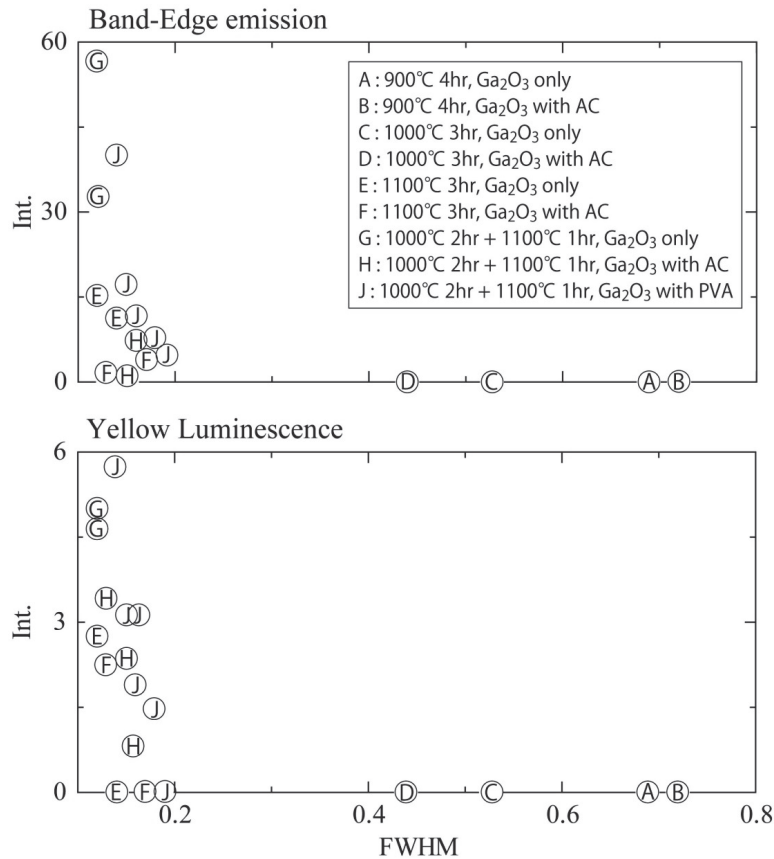


Fig. 3 The relation between FWHM values and emission intensities of **BE** (top), **YL** (bottom) shown by the results of 9 different samples. Nitridation conditions and the starting materials of each sample are indicated in the inner box, and AC in the conditions means activated carbon.

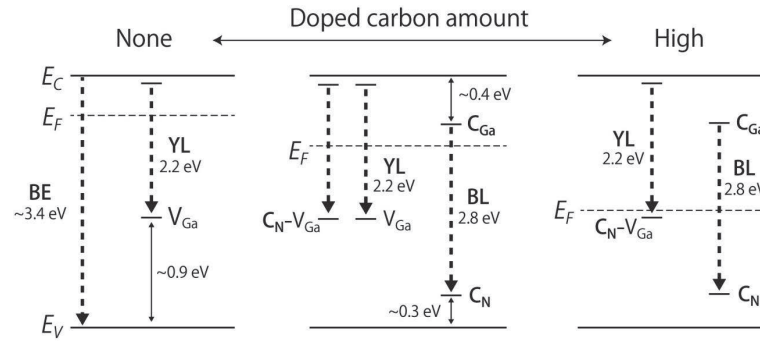


Fig. 5 The energy diagrams for carbon incorporated gallium nitride crystals, proposed by D. Zhou et al.¹⁴⁾. E_C : the lowest level of the conduction band, E_V : the highest level of the valence band, and E_F : the Fermi level. About other signs representing the various energy levels, such as V_{Ga} , see the text.

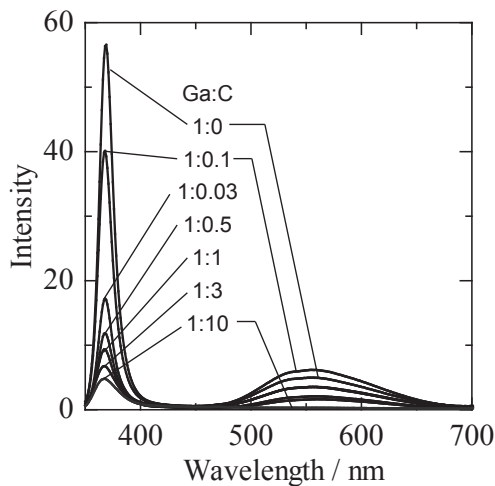


Fig. 6 Fluorescence spectra of the samples prepared with PVA coated Ga_2O_3 as starting material at various carbon coexistence ratios, nitridation condition was at $1000^\circ C$ for 2hr followed by at $1100^\circ C$ for 1hr.

carbon coexistence ratio increased. J. L. Lyons et al.¹³⁾ reported that carbon atoms replaced the N positions under N-rich conditions, it caused lowering the Fermi level, then they replaced the Ga positions. In the particles of the samples with relatively large amount of carbon, such as processed at Ga:C = 1:5 and 1:10, carbon atoms were considered to replace both N and Ga positions. D. Zhou et al.¹⁴⁾ proposed the mechanism for YL and BL emissions, and Fig. 5 is the illustration diagram from their paper. They attributed YL to the electron transition from impurities levels, which were created just below of conduction band, to Ga vacancies levels, V_{Ga} , and the transition energy they showed was 2.2 eV, equivalent to the energy of 564 nm light, and BL to the electron transition from C_{Ga} levels to C_N levels, and the value was 2.8 eV, equivalent to 443 nm light. Here, C_{Ga} represents the carbon replaced the gallium position; C_N represents the carbon replaced the nitrogen position; C_N-V_{Ga} represents the complex of C_N and V_{Ga} , whose energy level is almost the same as V_{Ga} . As the coexisting carbon concentration becomes larger, C_N is created first and followed by C_{Ga} creation. Our results that BL was observed at the samples of high carbon coexistence ratios were consistent with D. Zhou's mechanism. Carbon behaves as an amphoteric impurity in gallium nitride crystal, and it becomes a donor or an acceptor depending on whether it substitutes for Ga or N

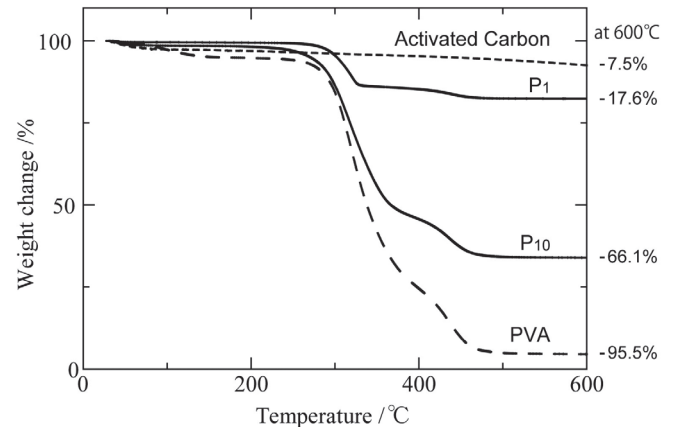


Fig. 7 TGA analysis of activated carbon, PVA, and two starting materials, P1 and P10. The Ga:C (in PVA) ratios of P1 and P10 were 1:1 and 1:10, respectively.

atom. Therefore, when a large amount of carbon was incorporated in gallium nitride crystal, light emission via impurity levels, such as C_{Ga} and C_N , became considerable, so that BL was observed and BE became less.

The fluorescence spectra of the samples processed in coexistence with carbon by coating of PVA are shown in Fig. 6. The processing condition was same as in Fig. 4. In the case of PVA coating, BL was not observed even when the carbon coexistence ratio was high. On the other hand, similar to the case of activated carbon, BE became less as the coexistence amount of carbon at nitridation processing increased.

The weight change of the samples at high temperature post-treatment in the air was measured to confirm the carbon remaining after nitridation. The samples without carbon or with small amount of activated carbon showed no weight change. However, the samples processed at high carbon coexistence ratios, i.e. Ga:C = 1:5, 1:10, using activated carbon, showed a certain weight loss caused by burning of remaining carbon. In contrast, in case of PVA coating, all samples, including the samples processed at high carbon coexistence ratios, showed no weight loss. This result suggested that PVA was lost while nitridation processing.

Figure 7 shows the results of TGA in nitrogen flow of activated carbon and PVA and two starting materials for P1 and P10. The Ga:C (in PVA) ratios of P1 and P10 were 1:1 and 1:10, respectively.

Except for activated carbon, the other three showed the similar TG profiles, showing weight losses at around 280 and 400 °C. The total weight losses after 600 °C heating in nitrogen were 17.6% for P₁, 66.1 % for P₁₀, 7.5% for activated carbon, and 95.5% for PVA. The value of 17.6% for P₁ was close to the weight proportion of PVA in P₁ before TGA measurement, 19%. Also the value of 66.1% for P₁₀ was close to the weight proportion of PVA in P₁₀, 70.1%. The 7.5% weight loss for activated carbon could be due to the detachment of adsorbed water. These results suggested that PVA was decomposed and almost removed at 600 °C in a nitrogen atmosphere, and the most of residues of P₁ and P₁₀ were Ga₂O₃ contained in each starting material and remaining PVA was a little bit. Yamaguchi et al.¹⁵⁻¹⁷⁾ reported that PVA decomposed thermally at 230 °C in a nitrogen atmosphere, and the decomposition products obtained were water, acetaldehyde, crotonaldehyde, benzaldehyde, acetophenone, etc.

As mentioned above, PVA did not work well as a carbon source to express **BL**, but created crystal defects, which worked to deactivate the photo-generated electrons, and depressed **BE** and **YL** as a result. This crystal defects formation by incorporated carbon, from both of PVA and activated carbon, is also suggested in Fig. 3. The FWHM values of samples H, prepared with coexistence of activated carbon, and samples J, prepared with coexistence of PVA, were somewhat larger than those of samples G, without carbon. This means that the crystallinity of samples H and J were lower than that of samples G. The crystal defects related to incorporated carbon seemed to work as nonradiative recombination centers.

4. Summary

The gallium nitride powder prepared at 900 or 1000 °C had low crystallinity, and showed neither band-edge emission nor yellow luminescence. It was suggested that many defects existed in the low crystallinity powder crystals and these defects acted as nonradiative recombination centers and that the excited electrons were deactivated. And high crystallinity seemed necessary for fluorescence emission. In case of the coexistence of activated carbon at nitridation processing, the gallium nitride powder prepared with relatively large amount of carbon showed blue luminescence. Therefore, it was assumed that carbon was taken into the gallium nitride crystal. However, band-edge emission became less as the coexistence amount of carbon at nitridation process increased.

In this study, the relationship between fluorescent luminescence and crystal properties were investigated. PVA was confirmed to decompose easily at 600 °C in a nitrogen atmosphere, and it did not

work well as a carbon source to express blue luminescence, **BL**. In using activated carbon, the optimization of Ga:C ratios and nitridation conditions are desired to express **BL** efficiently. Also the other carbon sources, such as graphite, would be tried for the efficient incorporation of carbon to GaN crystals to express **BL**. On the other hand, the relationship between yellow luminescence and gallium nitride crystal structure was not clear yet, further investigations were needed. In the future, GaN materials showing various colors luminescence will be developed by optimizing the incorporation of carbon and controlling blue luminescence and yellow luminescence.

Acknowledgment

The authors express special thanks to Sakai Chemical Industry Co. Ltd. for providing the sample materials and also important information on gallium nitride powder preparation.

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