Synthesis of gallium nitride powder and improved UV emission of gallium nitride in pulse-modulated ICP

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Abstract: Gallium nitride (GaN) powders were synthesized in thermal plasma from an aqueous liquid precursor. The powders contained some lattice defects in the crystal. Pulse-modulated plasma irradiation technique was applied to improve the UV emission at 380 nm of commercial GaN powder. When treated in the tail plasma flame, where the hydrogen radical concentration reaches to the largest one, the specimens showed the relatively intense UV emission.

Keywords: RF thermal plasma; pulse-modulation; gallium nitride

1. Introduction

Gallium nitride (GaN) has a wurtzite structure with a wide direct bandgap of 3.4 eV at 300 K. GaN-based material is suitable for the optoelectronic devices due to its band edge luminescence in the blue and near-ultraviolet region and its high thermal conductivity. A number of optoelectronic devices, such as blue, near ultraviolet, violet light emitting diodes and laser diodes, are currently being made out of this.

Many technological and scientific activities have been focused on the GaN fine particles, because it exhibits many properties that cannot be found in their bulk counterparts. Recently, photocatalysis on the splitting of water under visible light was investigated [1]. The particulate catalyst was composed of gallium and zinc oxynitride in nanometer-size. Spherical nanoparticles were expected to have high photocatalytic activity by reason of large specific surface area and high dispersion property in optical devices.

However, synthesis of high quality GaN is still difficult. GaN usually contains many structural and lattice defects. Because these defects affect the optical properties, the major luminescence emissions appear at different wavelength, ultraviolet, blue, green, yellow and red bands. The broad yellow luminescence band centered around 540-560 nm result from Ga vacancy. The red luminescence band in the range of 620–830 nm was derived from several defects in Ga-rich GaN [2-4].

The purpose of this work is to synthesize high purity GaN fine particles from liquid precursor including gallium sources using RF thermal plasma. Thermal plasma pyrolysis usually yields high purity spherical fine particles because of its extremely high temperature and high quenching rate.

Secondly, newly developed pulse-modulated high-power inductively coupled plasma (PM-ICP) is used for the improvement of luminescence properties. It is expected to offer the unique physico-chemical condition for materials processing because of the increased concentration of chemically reactive species, as well as the appropriate heat flux. When operating the plasma in PM mode, the electron and heavy species temperatures respond to the changes in input power at different time scales. The degree of deviation from equilibrium can be enhanced in such plasma, which in turn affects the behavior of the plasma. The temporal-spatial behavior of thermal and chemical non-equilibrium in an Ar-H_2 PM-ICP for hydrogen doping was investigated by means of numerical modeling. A peak hydrogen radical density was observed in 75–80 mm length from the bottom of coil to the specimens, a region that has been experimentally demonstrated to have optimal efficiency of hydrogen doping into functional materials [5]. Numerical analysis also indicated that the hydrogen atom density was maintained at high levels between 2.1×10^{22} and 4.5×10^{22} m^{-3}, throughout a pulse cycle [6, 7].

In the case of zinc oxide, the UV emission efficiency was improved by the irradiation of Ar-H_2 PM induction plasma [8, 9]. By the optical emission spectroscopy, the pulse-modulated RF plasma could produce intentionally a non-equilibrium state of particle temperatures and the high flux density of radical species [10]. It was also suggested that the optical properties of GaN might be controlled by hydrogen [11].

In this work, Ar-H_2 or Ar-H_2-N_2 plasma irradiation was performed to get the appropriate luminescence property. The relationship between the treatment conditions and the emission properties were examined.

2. Experimental

The synthesis of GaN particle was carried out by mist-pyrolysis using thermal plasma. Liquid precursor was gallium chloride ($GaCl_3$) aqueous solution of relatively high concentration (2.1 mol/l). The liquid is sprayed into a hot zone of plasma with 10^4K and immediately evaporated, and the vapor forms particle by condensation in the tail flame zone.

The plasma was generated by a PL-50 induction plasma torch (model PL-50, TEKNA Plasma Inc., Canada) connected to a 2 MHz RF power-supply system operated at 40 kW. The liquid precursor was fed through a water-cooled atomizer probe into the plasma. Argon gas was used to atomize the liquid leaving the probe [12]. Argon was injected as the central gas, and a mixture of Ar-H_2 (90 l/min) was injected as the sheath gas. NH_3 is normally preferred as the source of active nitrogen atoms. The NH_3 gas was injected for nitridation into the region of particle generation. During particle synthesis, the H_2 was added to Ar as the sheath gas to increase the content of reactive Ga metal.

Secondly, isostatic pressed pellets were irradiated in Ar-H_2-N_2 pulse-modulated RF induction plasma. The torch used in the present work has the same structure as that was used in the original continuous generation and a configuration of two coaxial tubes of 160 mm length. The torch is surrounded by the water-cooled rf coil. The inner diameter of the quartz tube and the outer radius of the tube are 55 and 70 mm, respectively. The induction coil consists of 13 turns. Sheath gas was injected through the sheath channel with swirl from outer slots of the gas distributor. A solid-state amplifier (MP-22CDY, Denki Kogyo Co., Ltd., Japan) was employed for the pulse-modulated plasma generation. The inverter-type power source is capable of supplying up to 22 kW with a nominal frequency of 1 MHz and has a high matching efficiency of up to 90%. The rf power is pulse modulated by imposing an external pulsed signal which switches a static induction transistor.

Hydrogen irradiation was carried out in PM mode operations of ICP. We used a PM with 10 ms 'on' and 5 ms 'off'. That is, the waveform was a 66.7-Hz rectangular wave with a pulse duty factor of 66.7%. The input rf powers for the 'on' and 'off' levels were 13 kW and 4 kW, respectively. Hydrogen gas diluted with Ar gas continuously flowed in the ICP reaction chamber. The flow rate was 3 l/min for H_2, 3l/min for N_2 gas and 98 l/min for Ar gas. The total gas pressure in chamber kept at 26 kPa, and the total irradiation times were 5, 10 and 15 minutes, respectively. The samples were placed at 80 mm distance on a sample holder of molybdenum metal cooled with a water circulator.

Green compacts were irradiated in plasma. The green compacts of ~ 1 mm thickness were prepared by the isostatic pressing of GaN powder. The powder was purchased from commercial suppliers (4N, Aldrich, USA).

Luminescence properties of the samples were characterized by photoluminescence (PL). The PL spectroscopy under 325 nm He-Cd laser excitation was performed on a Renishaw spectrophotometer (Renishaw plc, U.K.). The Raman spectroscopy was made using Ar^+ laser excitation (514.5 nm) with source power of 50 mW (model NR-1800, Jasco Co., Japan).

3. Result

3.1. Synthesis of gallium nitride powder in thermal plasma

In the case of $GaCl_3$ aqueous solution as a liquid precursor, no Ga-N could be detected in the XRD of the as-synthesized powders because of the low content of GaN in the powder mixture of GaN and much by-product NH_4Cl.

Figure 1 shows the various PL spectra of the powders obtained at 5, 10 and 15 L/min of hydrogen flow rates, respectively. It showed the broad three emission bands at 380, 500-700 and 760 nm. The 760 nm emission was excluded because of the second-order spectrum of 380 nm. The GaN was evidenced by the weak peaks, at 380 nm, near the band edge emission.

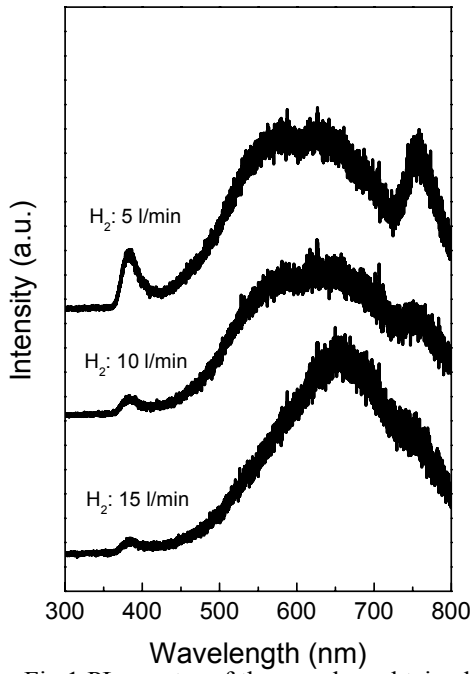

Fig.1 PL spectra of the powders obtained at 5, 10 and 15 L/min of hydrogen flow rates.

When hydrogen flow rates decreased, the peak wavelength shifted from 650 to 560 nm. The emission shifts were due to a kind of lattice defects in crystal, depending on the content of reactive Ga vapor through particle formation process. When hydrogen flow rate decreased, the particles were condensed and reacted in relatively low concentration Ga condition to form GaN with Ga vacancy.

3.2. Improved bandgap-related emission of gallium nitride in pulse-modulated hydrogen-containing plasma

Figure 2 shows the normalized PL spectra of the specimens at the distance between the bottom of RF coil and the holder at 75, 80 and 85 mm, respectively. Only a

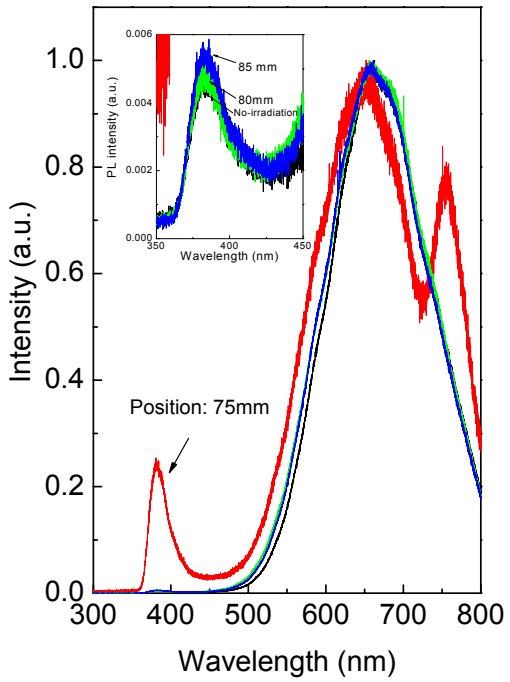

Fig. 2 Variation of PL spectra of the distance between RF coil bottom and specimens at 75, 80 and 85 mm, and no-irradiation specimen.

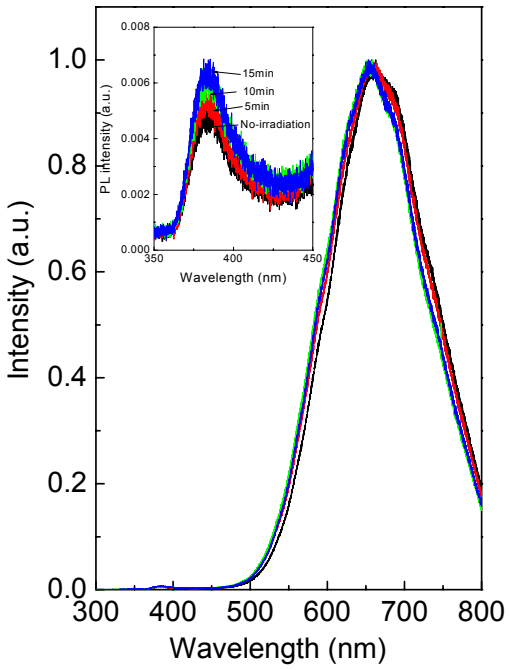

Fig. 3 Variation of PL spectra of the pellets at different plasma irradiation time for 5, 10 and 15 minutes, and no-irradiation specimen, Ar-H_2-N_2 plasma irradiation at the position of 80 mm.

specimen irradiated at a highest position, 75 mm, showed the coloration, although no change of crystal structure was identified by X-ray diffraction measurement. The coloration implies the formation of lattice defects in GaN through plasma heating. In all plasma-irradiated specimens, the UV emission intensity at 380 nm became higher than raw materials. Especially, the specimen set at the highest position, 75 mm, in tail of plasma flame, has the highest UV emission.

In order to change the heating condition, nitrogen gas was mixed to argon-hydrogen plasma with the intention of decreasing the thermal conductivity of plasma [10]. Figure 3 shows the variation of normalized PL spectra of the pellets at different plasma irradiation time for 5, 10 and 15 minutes, respectively. The small figure in figure 3 indicated the change of UV emission intensity at 380 nm for plasma irradiation time. In all specimens, the intensity of the 380 nm bandgap-related emission from GaN was increased slightly by Ar-H_2-N_2 plasma irradiation. Specimens irradiated at the longer time showed the higher emission. It indicates that Ar-H_2 plasma irradiation also increase the UV emission intensity by increase of irradiation time.

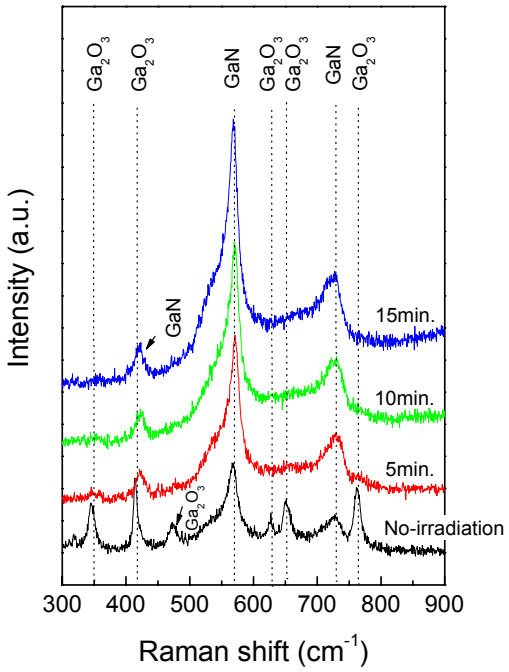

Fig. 4 Raman spectra of pellets at different plasma irradiation time for 5, 10 and 15 minutes, and no-irradiation specimen Ar-H_2-N_2 plasma irradiation at the position of 80 mm.

Figure 4 shows the Raman spectra of the specimens at different irradiation time for 5, 10 and 15 minutes, and no-irradiation in Ar-H_2-N_2 plasma at the position of 80 mm. Raman bands corresponding to both GaN and Ga_2O_3 were

identified. For example, in the case of the GaN, Raman band at 317, 420, 530, 567 and 727 cm^{-1}. And 344, 414, 471, 627, 651 and 762 cm^{-1} corresponding respectively to Ga_2O_3, were observed. It was indicated that the raw material was covered with thin oxide layer on the powder surface. In all plasma-irradiation specimens, the Ga_2O_3 spectra were decreased, while the GaN spectra became higher. The surface gallium oxide layer was removed by plasma-irradiation, and the GaN surface was exposed. After removal oxidation layer, hydrogen have effect on the compensation of lattice defects in GaN crystal.

4. Conclusion

Gallium nitride particle were synthesized in RF thermal plasma from $GaCl_3$ aqueous solution. Room temperature photoluminescence exhibited the band-edge emission of GaN at 380 nm and defect emission peak around 560-650 nm.

The treatment of a green compact of GaN powder in the tail flame of Ar-H_2 PM-ICP at the position of 75 mm gave the increase of band-edge emission of GaN. In this region, the temperature of heavy species and the hydrogen atom density are suited for hydrogen doping. The PM mode operation of hydrogen plasma irradiation is useful for the improvement of luminescence efficiency in GaN.

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