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Photoluminescence of Neutron-irradiated GaN Films and Nanowires

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Abstract

Photoluminescence (PL) of neutron-irradiated GaN films and nanowires is investigated in this study. The GaN films and nanowires were irradiated by neutron beams in air at room temperature, and the neutron-irradiated films and nanowires were annealed in an atmosphere of NH_3 at temperatures ranging from 500 to 1100 °C. The line-shapes of the PL spectra taken from the neutron-irradiated GaN films and nanowires were changed differently with increasing annealing temperature. In this study, light-emitting centers created in the neutron-irradiated GaN films and nanowires are examined and their origins are discussed. In addition, it is suggested here that the neutron-transmutation-doping is a simple and useful means of homogeneous impurity doping into nanowires with control of the doping concentration.

Key Words : Neutron-transmutation-doping(NTD), GaN, Nanowires, Photoluminescence(PL)

1. INTRODUCTION

Neutron-transmutation-doping (NTD) has been a useful method for the doping into semi-conductors by nuclear reactions [1-3]. When constituent isotope in semiconductors react with thermal neutrons, constituent isotopes become other isotopes by obtaining one neutron. If generated isotopes are unstable, these are transmuted to other atoms by the following beta and gamma recoils[4]. Although impurities can be doped in semiconductors with the reaction of thermal neutrons, fast neutrons give no nuclear reaction because of their very low cross section and give just damages to semiconductors. Therefore, annealing process must be followed to annihilate damages produced by fast neutrons and to remove unwanted effects induced by thermal neutrons.

The NTD method can be utilized to dope impurities more uniformly and to control concentrations of impurities in semiconductors more accurately than conventional *in-situ* or implantation doping methods. This NTD has been applied to a variety of semiconductors including Si, a-Si:H, Ge, GaAs, InSe, GaP, GaS, and GaN[4-10]. Nevertheless, NTD has not been applied for doping impurities to any semiconductor nanowires yet up to now. Semiconductor nanowires including Si, GaN, and InP nanowires have widely been doped in-situ [11-13], but the concentration of impurities in in-situ doped semiconductor nanowires cannot be estimated theoretically and measured experimentally at present. Moreover, the homogeneous concentration profile of impurities in the semiconductor nanowires cannot be confirmed. Compared with the in-situ doping, the NTD is suggested here to be a powerful method for the control of the concentration of impurities in semiconductor nanowires and for the achievement of the homogeneous concentration profile of impurities in semiconductor nanowires.

Photoluminescence (PL) spectra of GaN films and nanowires by neutron-irradiation are investigated in this study. The GaN films and

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nanowires were irradiated by neutron beams in air at room temperature, and their concentrations of transmuted atoms were estimated. The neutron-irradiated films and nanowires were then annealed in an atmosphere of NH_3 at temperatures ranging from 500 to 1100 °C. PL spectra taken from the annealed films are first examined, and PL spectra obtained from the annealed nanowires are then analyzed on the basis of the information attained from the PL spectra taken from the annealed films. Light-emitting centers created in the neutron-irradiated GaN films and nanowires are identified and discussed in this study. In addition, it is suggested here that the neutron-transmutation-doping is a powerful means of homogeneous impurity doping into nanowires.

2. EXPERIMENTAL PROCEDURE

Undoped GaN films with a thickness of 3 μm grown on (0001) sapphire substrates by atmospheric pressure metal organic chemical vapor deposition[14] and undoped GaN nanowires grown on alumina substrates by thermal chemical vapor deposition were irradiated with neutron beams consisting of thermal and fast neutrons. Our synthetic procedure of the GaN nanowires is described below. An alumina substrate (10 mm x 10 mm) coated with nickel (Ni) catalyst nanoparticles was used for the growth of GaN nanowires. A nickel nitrate/ethanol solution (0.01 M) was coated to the surface of the alumina substrate using a spin coater operating at 1200 rpm. Starting GaN powders were ground for 20 h in a mechanical ball-mill system consisting of a steel vial with stainless-steel balls. The catalyzed alumina substrate was placed on the top of a quartz boat loaded with the ball-milled GaN powders. The thermal evaporation of the ball-milled GaN powders was performed at 1000 °C for 1 h under an NH_3 flow of 30 standard cubic centimeters per minute (sccm) at a constant pressure of 0.5 atm. GaN nanowires were synthesized on the alumina substrate after it was cooled.

The flux was 6.73×10^{13} and 1.10×10^{11} $cm^{-2}s^{-1}$ for the thermal and fast neutrons, and the irradiation times were 288 hours. Neutron-irradiated GaN samples were annealed in an atmosphere of NH_3 at temperatures ranging from 500 to 1100 °C for 30 minutes. PL measurements were carried out at 10 K and the light source was the 325-nm line from a He-Cd laser.

3. RESULTS AND DISCUSSION

3.1 Identification of transmuted atoms in GaN

Two isotopes of Ga and two isotopes of N exist in nature; the four isotopes are ^{69}Ga, ^{71}Ga, ^{14}N, and ^{15}N. The natural abundances of four isotopes are listed up in Table 1. Accordingly, since the natural abundance of each isotope existing in the GaN should be the same as in nature, Ga and N constituents of GaN have four isotopes. When irradiated by neutron beams, these isotopes in GaN are transmuted by collisions with thermal neutrons. In the collisions, the probability of transmutation for each isotope is proportional to the cross section of thermal neutron. The cross sections of fourisotopes for thermal neutrons with room temperature energy (25 meV) are summarized in Table 1 for fast neutrons with energies above more than 0.1 MeV, the cross sections of the four isotopes are approximately zero.

Table 1. Natural abundances and cross sections of thermal neutrons for Ga and N isotopes.

	Natural abundance (%)	Cross sections (barn)
^{69}Ga	60.108	1.68
^{71}Ga	39.892	4.7
^{14}N	99.634	0.080
^{15}N	0.366	0.04×10^{-3}

When the isotopes collide with thermal neutrons, nuclear reactions occur and some of the isotopes are transmuted. The nuclear reactions are summarized in Table 2. In Table 2, n, γ, ν and β denote thermal neutron, gamma ray, neutrio, and beta ray, respectively. After the nuclear reactions, ^{69}Ga is transmuted to ^{70}Ge and ^{70}Zn, and ^{71}Ga and ^{15}N are transmuted to ^{72}Ge and ^{16}O, respectively. Therefore, after neutron irradiation, these four different transmuted impurities are doped in GaN.

Table 2. Nuclear reactions for Ga and N isotopes with thermal neutrons.

	1st nuclear reaction 2nd nuclear reaction	Half life Decay energy
^{69}Ga	$^{69}Ga + ^{1}n \rightarrow ^{70}Ga + \gamma$ $^{70}Ga \rightarrow ^{70}Ge + \beta$ (99.59 %)	21.14 m
	$^{69}Ga + ^{1}n \rightarrow ^{70}Ga + \gamma$ $^{70}Ga + ^{1}e \rightarrow ^{70}Zn + \nu$ (0.41 %)	21.14 m
^{71}Ga	$^{71}Ga + ^{1}n \rightarrow ^{72}Ga + \gamma$ $^{72}Ga \rightarrow ^{72}Ge + \beta$	14.1 h
^{14}N	$^{14}N + ^{1}n \rightarrow ^{15}N + \gamma$; ^{15}N:stable	
^{15}N	$^{15}N + ^{1}n \rightarrow ^{16}N + \gamma$ $^{16}N + \rightarrow ^{16}O + \beta$	7.13 s

3.2 Estimation of concentrations of transmuted atoms

Concentrations of atoms transmuted in GaN may be briefly estimated here. The concentration $C(ai)$ of an isotope formed from an existent isotope after the first nuclear reaction may be first obtained from

$$C(ai) = C(c) \times n \times \sigma \times f \times p \quad (1)$$

where $C(c)$, n, σ, f and p are concentration of the constituent atom, natural abundance, capture cross section of thermal neutron, fluence of thermal neutron, and probability of nuclear reaction respectively. The concentration of ^{70}Ga isotopes transmuted from ^{69}Ga isotopes existing in GaN may be estimated. The concentration $C(c)$ of the constituent atom may be obtained from

$$C(c) = \frac{GaN\,density \times Avogadro\,number}{molecular\ weight\ of\ GaN} \quad (2)$$
$$= \frac{6.1g/cm^3 \times 6.022 \times 10^{23}}{83.73g} = 4.39 \times 10^{22}/cm^3$$

Then, the concentration $C(^{70}Ga)$ of the ^{70}Ga isotopes formed from ^{69}Ga isotopes may be obtained from

$$C(^{70}Ga) = C(c) \times n \times \sigma \times f \times p \quad (3)$$
$$= C(^{69}Ga) \times \sigma \times f \times p$$
$$= (4.39 \times 10^{22}/cm^3 \times 0.601) \times 1.68 \times 10^{-24} cm^2 \times 6.98 \times 10^{19}/cm^2 \times 0.9959$$
$$= 3.08 \times 10^{18}/cm^3$$

Note that the concentration of ^{70}Ge is estimated to be that of ^{70}Ga considering its small half time of decay as shown in Table II. If the same estimation procedures as above are performed, the concentrations of ^{70}Zn, ^{72}Ge, and ^{16}Oisotopes transmuted from ^{69}Ga, ^{71}Ga, and ^{15}N isotopes present in GaN may be also estimated. The concentrations in each sample are summarized in Table 3.

The concentration of the transmuted Ge ions ($1.18 \times 10^{19}/cm^3$) is much higher than those of the transmuted Zn and O ions, so the optical and electrical properties of the neutron-irradiated GaN are dependent on the transmuted Ge ions rather than the transmuted Zn or O ions. The neutron-irradiated GaN is expected to be n-type, since the transmuted Ge ions are n-type dopants; the transmuted Zn ions are p-type dopants, and the transmuted O ions are n-type dopants.

Table 3. Thermal neutron fluence and concentrations of transmuted atoms.

Thermal neutron fluence	Concentration of ^{70}Ge	Concentration of ^{70}Zn	Concentration of ^{72}Ge	Concentration of ^{16}O
6.89×10^{19} cm^{-2}	3.08×10^{18}/cm^3	1.27×10^{16}/cm^3	8.67×10^{18}/cm^3	4.49×10^{11}/cm^3

3.3 Photoluminescence

The PL spectra taken for unirradiated and as-neutron-irradiated GaN films are compared in the wavelength range of 340~680 nm in Fig. 1.

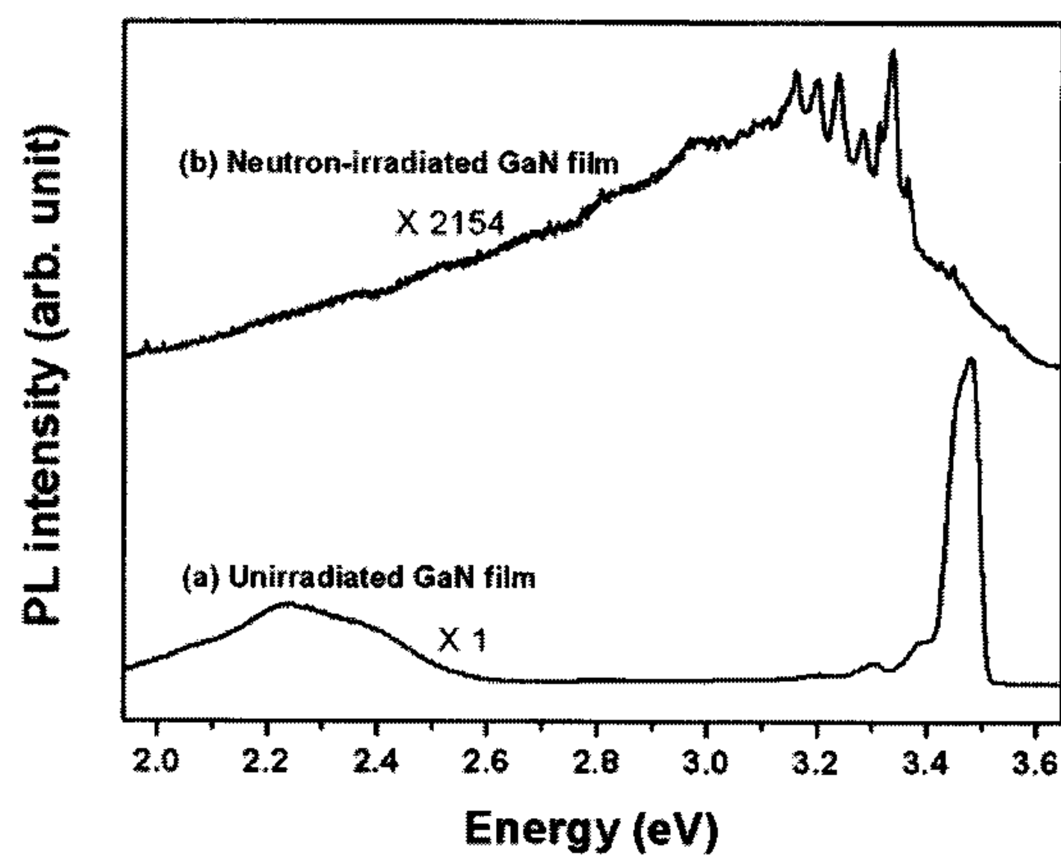

Fig. 1. PL spectra taken at10 K for (a) unirradiated and (b) as-neutron-irradiated GaN films.

A bound exciton peak and a yellow band are present at 3.48 and 2.2 eV, respectively, in the spectrum of the unirradiated GaN film the bound exciton peak corresponds to the recombination of excitons bound to neutral donors. In the PL spectrum of the as-neutron-irradiated GaN film, a broad PL band is seen in the wide wavelength from 340 to 680 nm and this band peaks at 3.15 eV; the bound exciton peak and the yellow band are absent in this PL spectrum. The broad PL band is composed of damage-induced bands including a 2.84 eV emission associated with the Ga interstitials[9]. The integrated PL intensity is quenched significantly for the as-neutron-irradiated GaN film, compared with the unirradiated GaN film. The absence of the exciton peak and the PL quenching in intensity indicate that the neutron-irradiation gives a serious damage to the crystality of the GaN film.

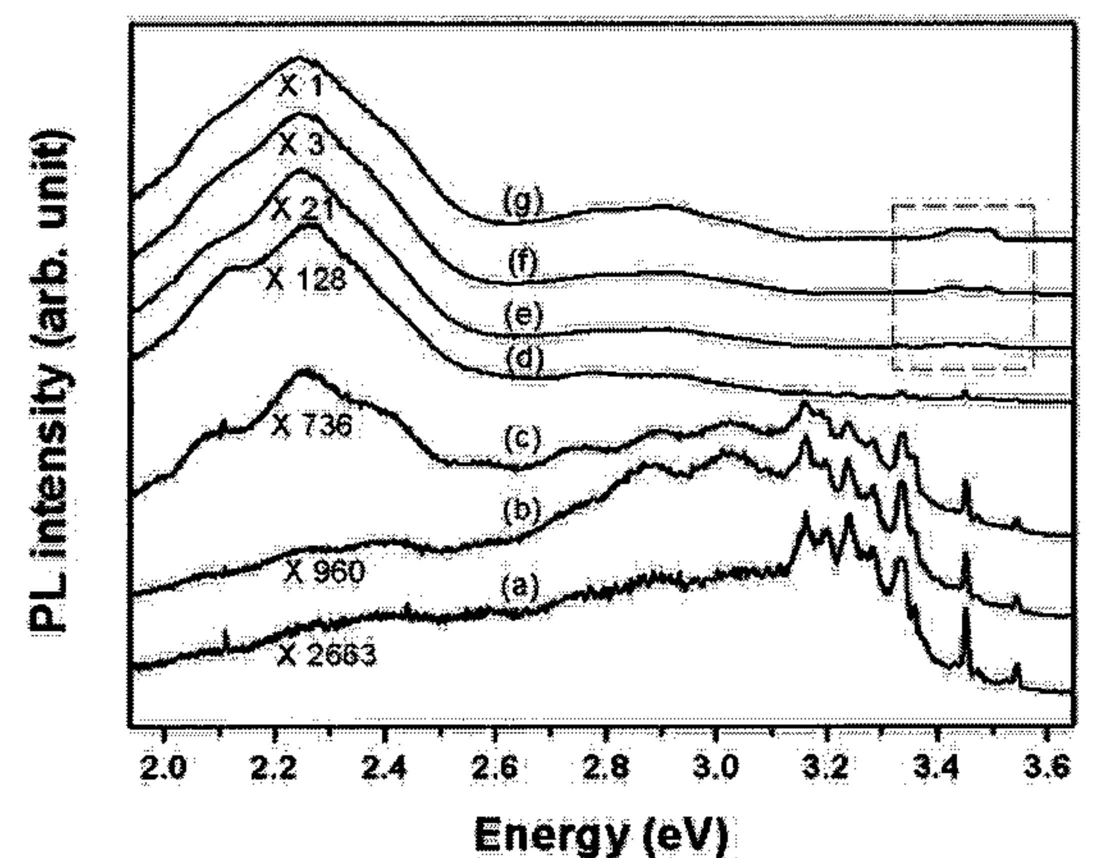

Fig. 2. PL spectra taken at 10 K for neutron-irradiated GaN films annealed in a NH_3 atmosphere at the following selected temperatures; (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, (f) 1000 °C, and (g) 1100 °C.

The PL spectra of the GaN film annealed at selected temperatures after the neutron-irradiation are shown in Fig. 2. Some PL bands with their different origins are overlapped in these PL spectra. The PL lineshape is changed dramatically with increasing annealing temperature due to different formation mechanism of light-emitting centers associated with the PL bands. Broad PL bands present in the energy range from 2.5 to 3.1 eV are responsible mainly for the Ga interstitials or negatively charged DX-like center of Ge at Ga site[9]; the broad

PL bands seen in the PL spectra of the GaN films annealed at temperatures of 500, 600, and 700 °C are related to the Ga interstitials, and the broad PL bands seen in the PL spectra of the GaN films annealed at temperatures of 800, 900, 1000 and 1100 °C are associated with negatively charged DX-like centers of Ge at Ga site[9]. For the PL spectra of all the annealed GaN films, the 2.25 eV PL band present in the energy range from 1.9 to 2.5 eV are attributed to complex defects attributed to Ge at Ga site and Ga vacancies[9]. The 2.25 eV PL band isenhanced dramatically in intensity with increasing annealing temperature. In the PL spectra of the GaN films annealed at temperatures of 900, 1000 and 1100 °C, two different bound exciton peaks are seen at 3.48 and 3.43 eV, as shown in Fig. 3; a box drawn by dashed lines in Fig. 2 is magnified in Fig. 3. The bound exciton peak at 3.48 eV corresponds to the recombination of excitons bound to neutral donors already seen in the PL spectrum taken for the unirradiated GaN film, and the bound exciton peak at 3.43 eV is associated with the recombination of excitons bound to transmuted Ge ions on Ga sites; the peak position of the Ge-related exciton peak is consistent with that reported in Ref. 10. The observation of the bound exciton peaks indicates the recovery of the damage caused by neutron-irradiation. In addition, the PL bands associated with transmuted Zn and O ions may not be observed in the PL spectra of the neutron-irradiated GaN film and nanowires due to either their low concentration or non-radiative recombination in the Zn- or O-related centers.

The PL spectra taken for unirradiated and as-neutron-irradiated GaN nanowires are presented in Fig. 4. In the spectrum of the unirradiated GaN nanowires, a broad donor-accept pair emission and some PL peaks overlapped on the band are present. The bound exciton peak associated with neutral donors and the 2.2 eV yellow band are absent in this PL spectrum, although the GaN nanowires are single-crystalline (revealed by our study on transmission electron microscopy images of these nanowires). The absence of the bound exciton peak reveals that excitons are dissociated by the electrical field due to unintentionally doped defects present in the GaN nanowires[15]. The absence of the yellow emission is due to that dislocations are free in the unirradiated GaN nanowires; the yellow emission is related to point defects that can be either accumulated or depleted near dislocations and other such imperfections[16].

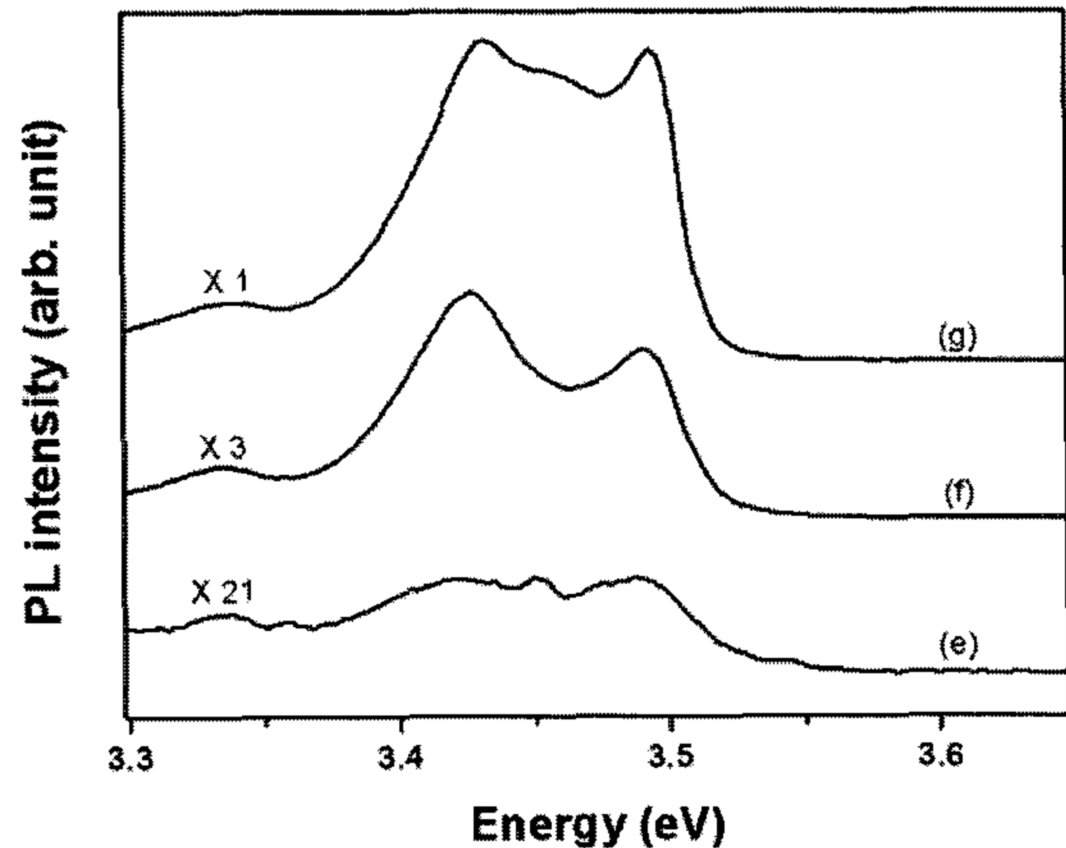

Fig. 3. Magnification of a box drawn by a dashed line in the PL spectrum shown in Fig. 2.

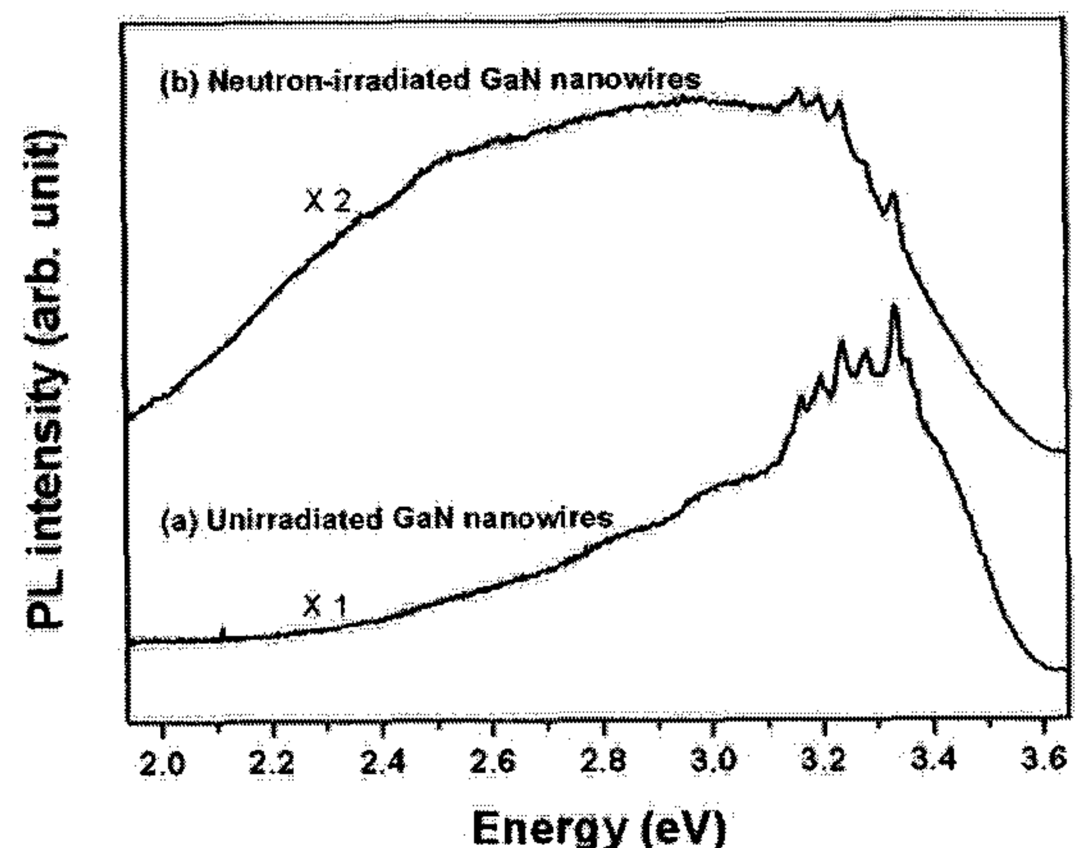

Fig. 4. PL spectra taken at 10 K for (a) unirradiated and (b) as-neutron-irradiated GaN nanowires.

Note that any dislocations were not observed in many transmission electron microscopy images taken for our GaN nanowires under study. In the spectrum of the as-neutron-irradiated GaN nanowires, the broad donor-accept pair emission and the PL peaks overlapped on the band are still present. In this PL spectrum, a broad emission band in the energy range from 1.9 to 3.1 eV is overlapped with the broad donor-accept pair emission; this broad emission is attributed to Ga interstitials[9].

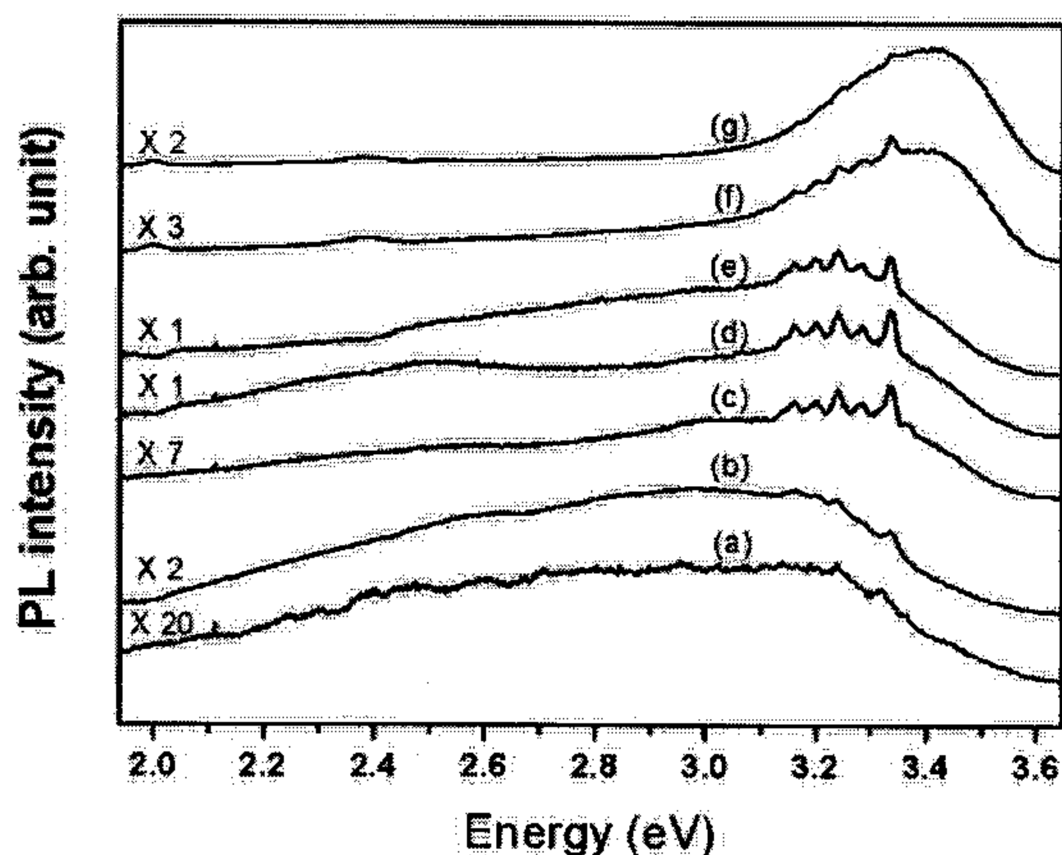

Fig. 5. PL spectra taken at10 K for neutron-irradiated GaN nanowires annealed in a NH_3 atmosphere at the following selected temperatures; (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C, (e) 900 °C, (f) 1000 °C, and (g) 1100 °C.

The PL spectra of the GaN nanowires annealed at selected temperatures after the neutron-irradiation are shown in Fig. 5. The exciton band associated with the transmuted Ge ions on Ga sites increases in intensity with increasing annealing temperature, compared with the broad donor-accept pair emission and the broad emission attributed to Ga interstitials observed in the spectrum of the unirradiated GaN nanowires. The energy position of the exciton band is at 3.41 eV and its linewidth is 325 meV. The band position is lower in energy and the linewidth of the exciton band is broader, compared with the neutron-irradiated GaN films. The lowering of the band position and the linewidth broadening of the exciton band are caused by the internal biaxial stress existed in the nanowires[17]. The broad 2.9 eV PL bands associated with negatively charged DX-like centers of Ge at Ga site and the 2.25 eV PL bands associated with complex defects attributed to Ge at Ga site and Ga vacancies seen in the PL spectra of the neutron-irradiated GaN films are absent in the PL spectra of the neutron-irradiated GaN nanowires annealed at temperatures of 800, 900, 1000 and 1100 °C. The absence of the 2.25 eV and 2.9 eV PL bands reveals that defects associated with these bands including Ga vacancies are free in the GaN nanowires.

4. CONCLUSION

PL spectra of neutron-irradiated GaN films and nanowires doped by neutron-irradiation are investigated in this study. The GaN films and nanowires were irradiated for 288 hours by a neutron beam containing thermal neutrons with a flux of 6.73×10^{13} $cm^{-2}s^{-1}$. The estimated concentration of the transmuted Ge ions created in GaN is $1.18\times10^{19}/cm^3$. In the PL spectra of the annealed GaN film and nanowires, the bound exciton band associated with transmuted Ge ionson Ga sites were observed. For the GaN nanowires, the band position is lower in energy and the linewidth of the exciton band is broader, compared with the neutron-irradiated GaN films. The lowering of the band position and the linewidth broadening of the exciton band are caused by the internal biaxial stress existed in the nanowires. The observation of the Ge-related bound exciton peaks indicates the recovery of the damage caused by neutron-irradiation and the activation of the doped Ge ions. Finally, it is suggested in this paper that the neutron-transmutation-doping is a simple and useful means of homogeneous impurity doping into nanowires with control of the doping concentration.

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