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Physical Properties of Gallium Indium Nitride Films Prepared by Photo-Assisted MOVPE

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Abstract. The optical and electrical properties, crystallinity, and photoluminescence of GaInN epitaxial films were remarkably improved by photo-assisted MOVPE using ultraviolet (UV) light from a deuterium (D_2) lamp. The dissociation of NH_3 is promoted by irradiation with a D_2 lamp and indium atoms are effectively incorporated into the crystal lattice of GaInN. Good-quality epitaxial GaInN films were obtained at higher growth temperature of 800°C increasing the flow rate of trimethylindium (TMIn). The photoluminescence peak intensity (band-edge emission) of GaInN films grown at 800°C is 14 times as great as that of 675°C.

1. INTRODUCTION

The pure blue light-emitting diodes (LEDs) and the shorter wavelength laser diodes (LDs) enable us to develop a new full color display system, and very-compact and super-high density optical storage systems, respectively. To realize these new devices, the research and development of wide-bandgap semiconductors should be necessary. There is strong demand for the shorter wavelength light-emitting devices. Recently, there has been great progress in this field. Blue-green laser diodes (LDs) using ZnCdSe/ZnSe quantum well structure were developed by Hasse *et al.* at 3M[1]. Blue light-emitting diodes (LEDs) with a brightness over 1cd using InGaN/AlGaIn double heterostructure were put into practice by Nakamura *et al.* at Nichia Chemical Industries, Ltd[2].

There were two long-term problems in the fabrication of GaN devices. The first problem was that GaN usually comes out as n-type when grown, and producing high-quality p-type material has proved extremely difficult. A technique for forming p-n junctions in GaN by converting magnesium-doped GaN to p-type using low energy electron beam irradiation (LEEBI) treatment by Akasaki *et al.* in 1989[3] and using N_2 ambient thermal annealing was disclosed by Nakamura *et al.* in 1991[4]. The second problem was that no substrate has a crystal lattice well-matched to GaN, sapphire having a high defect density. Progress came with the idea of using polycrystalline aluminum nitride (AlN) as a buffer layer between the sapphire and GaN to cushion lattice mismatch[5-7]. Then, polycrystalline GaN for the AlN was substituted and performance was improved dramatically[8]. This LED has an external quantum efficiency exceeding 2 percent[2].

Ternary III-V and II-VI semiconductor alloys have been investigated intensively as a result of the possibility of controlling the energy bandgap and lattice constant through the alloy composition. Gallium indium nitride (GaInN) is one of the most promising materials for blue LEDs and LDs. It is difficult to obtain good-quality GaInN films, because the growth temperature of InN (about 500°C) is much lower than that of GaN (about 950°C); namely, the value of nitrogen pressure of InN is several orders of magnitude higher than that of GaN. We previously succeeded in growing epitaxial films of GaInN on a sapphire substrate using MOVPE for the first time[9] and observed the electroluminescence of Al/GaInN/GaN diodes at room temperature [10]. In this paper, GaInN epitaxial films are prepared by photo-assisted MOVPE, expecting enhancement and improvement of deposition by photoactivation of the substrate surface. Ultraviolet light irradiation is effective in preparing GaInN epitaxial films that

have good electric properties. This paper describes the optical and electrical properties, crystallinity and photoluminescence of the films grown by photo-assisted MOVPE.

2. FILM GROWTH

Epitaxial films of GaInN were grown on sapphire (0001)-oriented substrates by the MOVPE technique previously used to grow GaN and GaInN [9-11]. The growth system consisted of a vertical water-cooled quartz chamber in which low pressure was achieved through the use of a turbomolecular pump. Trimethylgallium (TMGa) and trimethylindium (TMIn) were introduced into the growth chamber with H_2 carrier gas by flowing H_2 through the vapor of the metalorganic compounds kept at -30°C and 30°C , respectively. Highly pure (5-nine) ammonia (NH_3) was admitted to the chamber through a separate line, to avoid the formation of adducts. The reactor was operated at a pressure of 38 Torr. Sapphire substrates with (0001) orientation were cleaned ultrasonically in organic solvents, and were etched in a hot mixture of phosphoric acid and sulfuric acid. Then the substrates were treated at 1130°C in an H_2 gas flow for about 10 min, to clean the substrate surface, and the initial nitridation of substrate surface was carried out at 1130°C in NH_3 gas flow for about 5min, just before growth[7]. The surface morphology of GaN and GaInN films can be remarkably improved by the preceding growth of AlN as a buffer layer. In our previous paper, we reported that good-quality epitaxial films were obtained when the growth conditions of large V/III ratio (>12000), slow growth rate ($<0.2\mu\text{m/h}$), and growth temperature of 550°C were maintained[10]. The growth temperature was controlled at 550°C to avoid the decomposition of InN. However, the physical properties of epitaxial GaInN films strongly depends on growth parameters, such as the deposition temperature, the molar ratio of NH_3 to metalorganic compounds, and the growth rate. If GaInN films were prepared at the growth temperature higher than 600°C with increasing flow rate of TMIn, furthermore good-quality epitaxial films could be obtained.

GaInN epitaxial films were prepared by photo-assisted MOVPE, expecting enhancement and improvement of deposition by the effective dissociation of NH_3 due to UV light irradiation around the substrate surface. The quartz chamber has two window ports to irradiate the substrate by the light beam. A deuterium (D_2) lamp was used as a light source for irradiation during crystal growth. The wavelength region of the ultraviolet (UV) light was from 160 to 400 nm. The dissociation of NH_3 is promoted by irradiation with a D_2 lamp, as four absorption peaks of NH_3 exist in the wavelength region from 190 to 210 nm. The irradiation intensity on the substrate surface was 14.8 mW/cm^2 measured by the thermopile. The growth temperatures during the deposition were set at 500, 675 and 800°C . The flow rate of TMGa was $6.54\mu\text{mol/min}$. The flow rates of TMIn changed to 0.298, 2.38 and $15.6\mu\text{mol/min}$ corresponding to the growth temperature. The flow rate of NH_3 was 0.0799 mol/min . The molar ratio of NH_3 to metalorganic compounds (TMGa and TMIn) varies from 11680 to 3600. The film growth conditions are summarized in Table 1.

Table 1 Film growth conditions.

growth temperature ($^\circ\text{C}$)	500,	675,	800
deposition pressure (Torr)		38	
Flow rate of TMGa ($\mu\text{mol/min}$)		6.54	
Flow rate of TMIn ($\mu\text{mol/min}$)	0.298-	15.6	
Flow rate of NH_3 (mol/min)		0.080	
Carrier gas: MO line (SLM)		0.25	

3. RESULTS AND DISCUSSION

The variations of the absorption coefficient of the GaInN films with photon energy are shown in Fig.1, with growth rate as a parameter. These films were prepared at a V/III ratio of 16000. The curve near the fundamental absorption edge creates a notable tail along the low energy side with increasing growth rate. When the growth rate is slow, the imperfections in the GaInN films remarkably decrease.

Fig.1 Variations of absorption coefficient of GaInN films with photon energy.

Fig.2 Composition dependence of the optical bandgap of GaInN films as a function of growth rate.

Consequently, the squared absorption coefficients rise up abruptly. It is necessary that the growth rates of GaInN films are below 0.2 μm/h to obtain good-quality epitaxial GaInN films, as shown Fig. 1. The composition of the films was examined by X-ray fluorescence.

The composition (In mole fraction) dependence of the optical bandgap of Ga₁₋ₓInₓN alloy films is shown in Fig. 2. These alloy films were prepared at a slow growth rate below 0.2 μm/h. The values of bandgap were given by the extrapolation of the linear part of the curves of the squared absorption coefficient with photon energy. The bandgaps of the films varied with the composition (to X=0.3) from 3.39 eV (GaN) to 2.70 eV at room temperature[10]. It has been demonstrated that the energy bandgap (E_g) of ternary alloys Ga₁₋ₓInₓN in our study obeys parabolic forms on the mole fraction X:

$$E_g(X) = (1-X) E_g(\text{GaN}) + X E_g(\text{InN}) - bX(1-X), \quad (1)$$

where $E_g(X)$ is the energy bandgap of Ga₁₋ₓInₓN, $E_g(\text{GaN})$ and $E_g(\text{InN})$ are the energy bandgap of GaN and InN, respectively, and b is the bowing parameter. The bowing parameter of Ga₁₋ₓInₓN was estimated at 0.8 eV until the composition X=0.3 from the curve fitting with the composition dependence of energy bandgap of GaInN prepared at a slow growth rate below 0.2 μm/h as shown in Fig. 2. The optical bandgap (Fig.3) of the films prepared at 500°C did not vary with and without UV light irradiation. While, in the films prepared at 675 and 800°C, the optical bandgap of the films grown under the UV light irradiation is smaller than that of the films prepared without irradiation. This shows that the content of indium incorporated into the crystal lattice depends on the deposition temperature and UV light irradiation. These results indicate that the decomposition of InN occurs at the temperatures around 600°C. In the GaInN films prepared under UV light irradiation, the optical bandgap tends to decrease by 0.079 eV at 675°C and 0.157 eV at 800°C, in comparison with non-irradiated samples as shown in Fig.3, as a function of growth

Fig.3 The growth temperature dependence of the optical bandgap of GaInN films.

temperature. This indicates that the dissociation of NH_3 is promoted by irradiation with a D_2 lamp and indium atoms are effectively incorporated into the GaInN crystal lattice due to an increase in the radical nitrogen. The full width at half maximum (FWHM) of the X-ray diffraction peak of the (0002) plane of the GaInN film is shown in Fig.4, as a function of growth temperature with and without irradiation of UV light. Without UV light irradiation, the GaInN films were grown epitaxially and had a mirror-like surface until the growth temperature of 675°C . However, GaInN films were mixtures of the (0002) plane and others, and the surface morphology of the films was an uneven surface, above 700°C . While, GaInN films prepared under UV light irradiation were epitaxial films and exhibited a mirror-like surface[11]. The FWHM of the X-ray diffraction peak of the (0002) plane for the GaInN films grown under UV light irradiation decreased in comparison with non-irradiated films. The crystallinity of GaInN film is remarkably improved by irradiation with UV light.

To evaluate the quality of the GaInN films, the PL spectra were measured at a temperature of 77K. A He-Cd laser ($\lambda=325\text{nm}$) was used as an excitation source. The PL spectra of GaInN films prepared under irradiation at the growth temperatures of 675°C and 800°C are shown in Fig.5. In the GaInN films grown under irradiation of UV light, a PL peak that corresponds to the band-edge emission of GaInN was clearly observed. The indium mole fractions X were 0.23 and 0.31 for $\text{Ga}_{1-X}\text{In}_X\text{N}$ films prepared at 675°C and 800°C , respectively. These GaInN films were prepared at 675°C and 800°C increasing the flow rate of TMIn. The PL peak intensity of GaInN films grown at 800°C is 14 times as great as that of 675°C , and the FWHMs of PL peak of GaInN films prepared at 675°C and 800°C were about 40nm (peaking at 430nm) and about 25nm (peaking at 455nm), respectively. The temperature dependence of PL intensity was measured to investigate models for blue-

Fig.4 Change of FWHM of the (0002) reflection of GaInN films with the growth temperature.

Fig.5 Dependence of photoluminescence spectra of GaInN films on the growth temperature.

Fig.6 Activation energy for photoluminescence of GaInN films prepared at 675 and 800°C .

light emission mechanism, as shown in Fig.6. The activation energy for PL was 17 meV and 56 meV for the films prepared at a temperature of 675°C, and 85 meV for the films prepared at 800°C. These results suggest different models for the mechanism of PL of a deep emission peaking at 430nm.

The resistivities, electron densities, and Hall mobilities of GaInN films prepared at various growth temperatures were measured at room temperature. These data are listed in Table 1. These GaInN films were prepared under a pressure of 38 Torr. The Hall mobilities were larger than that of GaInN films grown without UV light irradiation. These results indicate that the dissociation of NH_3 is promoted by irradiation with a D_2 lamp and indium atoms are effectively incorporated into the GaInN crystal lattice due to an increase in the radical nitrogen atoms. The crystallinity of GaInN films is markedly improved by irradiation with UV light. However, an increase in the radical nitrogen atoms due to irradiation with UV light did not contribute to a decrease in nitrogen vacancies in the GaInN films as shown in Table 2. Typically undoped GaInN films were n-type with an electron density on the order of 10^{19}cm^{-3} at room temperature. The electron density scarcely varied with UV light irradiation. Nitrogen vacancies, which are characterized in the GaN and GaInN films, did not vary by UV light irradiation. To obtain good-quality epitaxial GaInN films with a low electron density in the order of $10^{15}\sim 10^{16}/\text{cm}^3$, it is necessary that GaInN growth is carried out at an atmospheric pressure.

Table 2 Electrical properties of GaInN films prepared at various temperatures.

Growth temperature (°C)	500		675		800	
D_2 lamp irradiation	Yes	No	Yes	No	Yes	No
Resistivity($\Omega\text{ cm}$)	2.43×10^7	2.42×10^7	7.81×10^{-3}	1.06×10^{-2}	1.32×10^{-2}	2.62×10^{-3}
Hall Mobility(cm^2/Vs)	—	—	47.3	31.5	32.8	23.2
Electron Density(cm^{-3})	—	—	3.27×10^{19}	3.63×10^{19}	2.78×10^{19}	1.99×10^{19}

4. CONCLUSIONS

The optical and electrical properties, photoluminescence, and crystallinity of GaInN films grown by an ordinary and photo-assisted MOVPE, were discussed in this paper. These GaInN films were prepared under a pressure of 38 Torr. As GaInN is one important candidate as the active layer for the GaN-based blue LEDs and LDs, it is necessary that furthermore good-quality GaInN films are prepared by the development of the various techniques. These results can be summarized as follows.

- (1) The bowing parameter of $\text{Ga}_{1-x}\text{In}_x\text{N}$ alloy films was estimated at 0.8 eV until the indium mole fraction $X=0.3$.
- (2) The crystallinity and electron mobility of a GaInN epitaxial film were remarkably improved by photo-assisted MOVPE using UV light irradiation from a D_2 lamp. The dissociation of NH_3 is promoted by irradiation with a D_2 lamp and indium is effectively incorporated into the crystal lattice.
- (3) Good-quality epitaxial GaInN films were obtained by the fabrication at higher growth temperature of 800°C increasing the flow rate of trimethylindium (TMIn). The photoluminescence peak intensity of GaInN films grown at 800°C is 14 times as great as that of 675°C.
- (4) To obtain good-quality epitaxial GaInN films with a low electron density in the order of $10^{15}\sim 10^{16}/\text{cm}^3$, it is necessary that GaInN growth is carried out at an atmospheric pressure.

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