

Properties of radio-frequency-sputter-deposited GaN films in a nitrogen/hydrogen mixed gas

Takayuki Miyazaki,^{a)} Kouhei Takada, and Sadao Adachi

Department of Electronic Engineering, Faculty of Engineering, Gunma University, Kiryu-shi, Gunma 376-8515, Japan

Kohji Ohtsuka

Research and Development Division, Sanken Electric Co., Ltd., Niiza-shi, Saitama 352-8666, Japan

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GaN films have been deposited by reactive sputtering in nitrogen gas at pressures from 0.08 to 2.70 Pa with and without the addition of hydrogen gas. X-ray diffraction (XRD), Fourier transform infrared (FTIR), optical absorption, and photoluminescence (PL) spectroscopy have been used to characterize the sputter-deposited GaN films. The XRD pattern reveals that the GaN films deposited in nitrogen gas at pressures lower than 0.53 Pa are polycrystals with the (0001) texture (α -GaN), while those deposited at or above 1.07 Pa display mixed crystalline orientations or an amorphous-like nature. The GaN:H films deposited in nitrogen/hydrogen mixed gas, on the other hand, show an amorphous or amorphous-like nature. The FTIR spectra indicate that the GaN:H films show peaks arising from hydrogen-related bonds at ~ 1000 and ~ 3200 cm^{-1} , in addition to the GaN absorption band at ~ 555 cm^{-1} . The optical absorption spectra at 300 K indicate the fundamental absorption edges at ~ 3.38 and ~ 3.7 eV for the highly oriented α -GaN and amorphous GaN:H films, respectively. PL emission has been observed from sputter-deposited α -GaN films at temperatures below 100 K. The GaN:H films also show strong band-edge and donor-acceptor pair emissions. The PL emission in the GaN:H film may arise from crystalline GaN particles embedded in the amorphous GaN matrix. © 2005 American Institute of Physics. [DOI: 10.1063/1.1888027]

I. INTRODUCTION

The III-N semiconductors are currently attracting much interest for their potential in device applications, such as light-emitting and laser diodes in the blue-ultraviolet spectral region.¹ Unfortunately, bulk GaN of a commercially useful size does not exist. Most single-crystalline GaN crystals are, therefore, prepared in thin film form on a variety of substrate materials, such as sapphire, SiC, Si, MgO, and GaAs. A number of techniques, such as chemical vapor deposition, (CVD) metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy, and plasma-assisted deposition techniques, are used to prepare such GaN thin films.² Among them, the sputtering technique is unquestionably the most convenient and inexpensive.

GaN films are frequently deposited by reactive sputtering of gallium in pure nitrogen or a mixture of nitrogen and argon gases. Most of them are polycrystalline³⁻⁹ or amorphous,¹⁰ although epitaxial GaN films have been reported to be prepared by reactive sputtering.^{11,12} It is important to control the properties of films according to the device application by changing the sputtering conditions. The addition of hydrogen gas may be attractive, but no detailed study has been carried out on its use in GaN deposition to date.

The main objective of this study is to examine the effects of hydrogen addition on the properties of rf-sputtered GaN films. The rf-sputtered films are characterized by x-ray diffraction (XRD), Fourier transform infrared (FTIR), optical

absorption, and photoluminescence (PL) spectroscopy. Relatively strong PL emission is observed from the GaN film sputter deposited in a nitrogen/hydrogen mixed gas.

II. EXPERIMENT

A. Radio-frequency-magnetron sputtering

The GaN films were sputter deposited onto various substrates, such as 4°-off Si(111), Si(100), Corning 7059 glass, and fused quartz. However, no clear substrate dependence has been found in the film properties. Prior to the deposition, the substrates were degreased in organic solvents. The rf-magnetron sputtering system used here was of a planar type modified from the conventional diode sputtering apparatus.¹³ This modification was accomplished merely by setting a circular permanent magnet behind the target electrode (cathode) in the conventional diode sputtering apparatus. The target-to-substrate distance was ~ 5 cm. The sputter target was a 3-in.-diam disk of gallium metal (99.9999% pure).

The sputtering system was evacuated to a base pressure of $\sim 10^{-5}$ Pa using a turbo-molecular pump. Pre-sputtering was carried out prior to film deposition, with the inserted shutter, to obtain a clean and chemically stable gallium target surface. The sputtering gas was nitrogen of 99.9997% purity. The sputtering pressures and rf power were 0.08–2.70 Pa and 50 W (13.56 MHz), respectively. GaN:H films were also deposited by rf-magnetron sputtering in a mixture of nitrogen and hydrogen gases. The purity of hydrogen gas was 99.999 99%. All films were deposited without intentional heating of the substrates. The equilibrium substrate tempera-

^{a)}Author to whom correspondence should be addressed; electronic mail: miyazaki@gunma-u.ac.jp

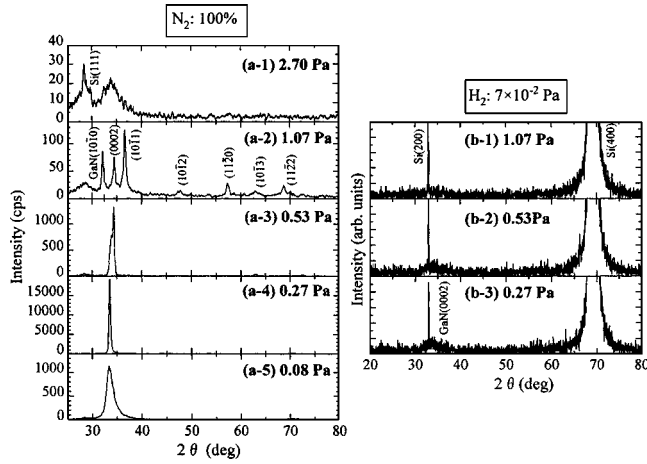


FIG. 1. XRD patterns for GaN films sputter deposited in nitrogen gas (a) without and (b) with hydrogen gas at a partial pressure of 7×10^{-2} Pa. The substrates used were 4° -off Si(111) and Si(100), respectively.

ture was estimated to be $\sim 60^\circ\text{C}$ at a rf power of 50 W. The thickness of the sputter-deposited GaN films was typically $0.5\ \mu\text{m}$.

B. Measurements

The crystallinity of the sputter-deposited GaN and GaN:H films was evaluated by XRD analysis, using a RAD-IIC x-ray diffractometer (Rigaku Co., Ltd.) with Cu $K\alpha$ radiation. The XRD patterns were obtained in the θ - 2θ scanning mode.

FTIR measurements were carried out at normal incidence using a Nicolet Magna 560 spectrometer in the 400 – $4000\ \text{cm}^{-1}$ wavelength region at room temperature. The optical absorption spectra in the fundamental-absorption-edge region of the sputter-deposited GaN materials were also measured using a JASCO V-570 spectrometer at room temperature.

The $325\ \text{nm}$ line of a He–Cd laser (KIMMON IK3302R-E) chopped at 320 Hz was used as the excitation light source for PL measurements. The PL spectra were obtained in the 2.0 – $3.6\ \text{eV}$ photon-energy range using a grating spectrometer (JASCO CT-25C) and a Peltier-device-cooled photomultiplier tube (HAMAMATSU R375). The measurements were performed using a closed-cycle refrigerator cryostat (IWATANI CRT105PL) between 14 and 300 K.

III. RESULTS AND DISCUSSION

A. X-ray diffraction results

Figures 1(a) and 1(b) show the XRD patterns obtained in the θ - 2θ scan mode for the sputter-deposited GaN films on silicon substrates without and with the addition of hydrogen gas, respectively. The sputtering pressure was varied from 2.70 to 0.08 Pa in the case of Fig. 1(a) and from 1.07 to 0.27 Pa in the case of Fig. 1(b). The samples corresponding to the spectra in Fig. 1(b) were deposited under a hydrogen partial pressure of $\sim 7 \times 10^{-2}$ Pa. The peaks observed at the lowest position, $2\theta=28.4^\circ$, in Fig. 1(a) and those at $2\theta=33.0^\circ$ and 69.1° in Fig. 1(b) originate from the 4° -off Si(111) and Si(100) substrates, respectively.

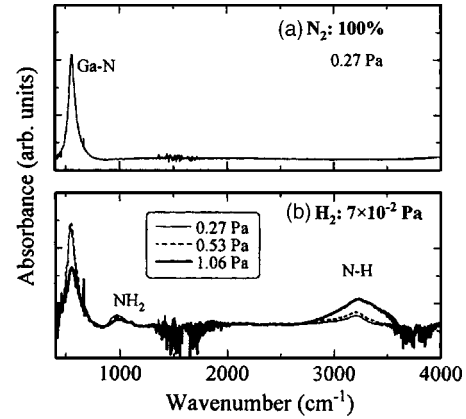


FIG. 2. FTIR absorption spectra for (a) α -GaN and (b) GaN:H films sputter deposited on Si(100) substrates at 0.27 Pa in 100% nitrogen gas and at 0.27–1.06 Pa in nitrogen/hydrogen mixed gas, respectively.

The XRD pattern in Fig. 1(a-1) shows no strong GaN peak. This indicates that the film deposited at 2.70 Pa is amorphous or amorphous-like in nature. The GaN film deposited at 1.07 Pa [Fig. 1(a-1)], on the other hand, shows XRD pattern consisting of many peaks originating from various crystal planes of hexagonal (α -) GaN, such as $(10\bar{1}0)$, (0002) , and $(11\bar{2}0)$. These peak positions agree with those reported on the Joint Committee on Powder Diffraction Standards (JCPDS) card of α -GaN (Ref. 14). This indicates that the film deposited at 1.07 Pa is polycrystalline with mixed orientations of the crystalline planes. For the GaN films deposited at 0.27–0.08 Pa [Figs. 1(a-4) and 1(a-5)], only the strong peak related to the α -GaN(0002) plane is observed at around $2\theta=33^\circ$. These results suggest that the films deposited at low pressures have a highly preferred orientation (c plane). Note that the XRD intensity observed in Fig. 1(a-4) is much stronger than the others.

The XRD pattern shown in Fig. 1(b) suggests that the GaN:H films are amorphous or amorphous-like. A very weak crystalline peak can be recognized in the low-angle region of the XRD pattern ($2\theta\sim 33.5^\circ$). This peak is due to GaN(0002) and becomes stronger with lower deposition pressures.

In order to examine whether the GaN films deposited in 100% nitrogen gas at low pressures are epilayers (i.e., single-crystalline layers), we performed reflection high-energy electron diffraction (RHEED) observations of the film deposited at 0.27 Pa [Fig. 1(a-4)]. The RHEED pattern shows a streaky spot pattern, suggesting that the film is oriented along the c direction and that its surface is very smooth. However, no change in the RHEED pattern was observed after the rotation of the film around the c axis. This indicates that the GaN film is not single crystalline, but is highly oriented to the c axis.

B. Fourier transform infrared spectroscopy

Figure 2 shows the FTIR spectra obtained from (a) α -GaN and (b) GaN:H films sputter deposited on Si(100) substrates at 0.27 and 0.27–1.06 Pa, respectively. Only a vibrational mode at around $555\ \text{cm}^{-1}$ is observed in Fig. 2(a). This mode is caused by the GaN lattice absorption band and is observed in single-crystalline α -GaN at around $533\ \text{cm}^{-1}$

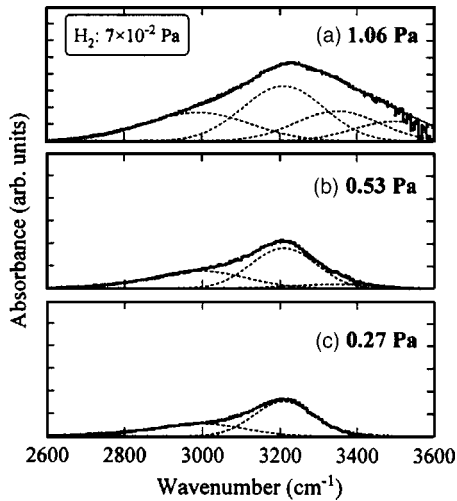


FIG. 3. FTIR absorption spectra in the $\sim 3200\text{ cm}^{-1}$ region of GaN:H films sputter deposited on Si(100) substrates at (a) 0.27, (b) 0.53, and (c) 1.06 Pa in nitrogen gas mixed with hydrogen gas at a partial pressure of $7 \times 10^{-2}\text{ Pa}$. The dashed lines represent the deconvolution of each spectrum into several hydrogen-related peaks.

$[\mathbf{E} \perp c; A_1(\text{TO})]$ and 560 cm^{-1} $[\mathbf{E} \parallel c; E_1(\text{TO})]$.¹⁵ The spectra shown in Fig. 2(b) show not only the GaN absorption band at $\sim 555\text{ cm}^{-1}$, but also new peaks at ~ 1000 and $\sim 3200\text{ cm}^{-1}$. It is clear that the hydrogen atoms introduced into GaN form hydrogen-related bonds with the host lattice atoms.

Note that the $\sim 3200\text{ cm}^{-1}$ absorption peak seen in Fig. 2(b) is composed of many hydrogen-related bonds, as demonstrated in Fig. 3. The primary N–H bonds peaking at 3210 and 3500 cm^{-1} may represent the N–H bond in GaNH_3^+ or NH_4^+ molecules.¹⁶ The secondary peaks at 2990 and 3350 cm^{-1} represent the N–H bond in GaNH_2 or NH_3 molecules. The higher wave number peaks at 3500 and 3350 cm^{-1} can be considered to be due to N–H bonds that are not bound to water molecules, while those at the lower wave numbers of 2990 and 3210 cm^{-1} may be bound with water molecules. The latter peaks may, thus, be observed at lower wave numbers than the former.

In order to elucidate the effects of added hydrogen on the lattice absorption properties, we have prepared GaN:H films deposited with different amounts of hydrogen ($1\text{--}7 \times 10^{-2}\text{ Pa}$) in the reactive gas at a constant sputtering pressure (0.53, 0.80, or 1.06 Pa). Examples of FTIR absorption spectra obtained from these films are shown in Fig. 4 for

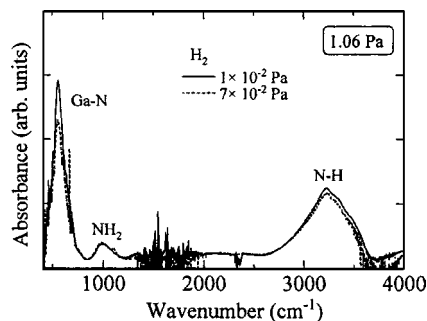


FIG. 4. FTIR absorption spectra for GaN:H films sputter deposited at 0.27 Pa on Si(100) substrates in nitrogen gas mixed with hydrogen gas at a partial pressure of 1×10^{-2} or $7 \times 10^{-2}\text{ Pa}$.

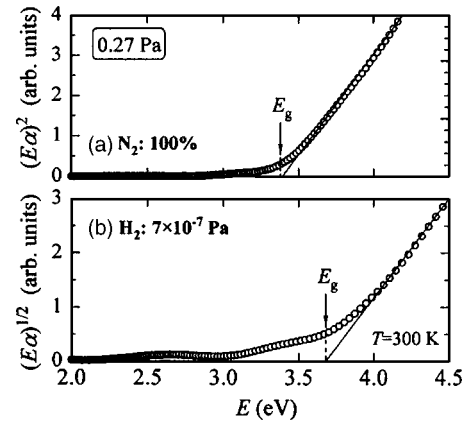


FIG. 5. (a) Plots of $(\alpha E)^2$ vs photon energy E for α -GaN film at 300 K and (b) those of $(\alpha E)^{1/2}$ vs E for GaN:H film at 300 K. The α -GaN and GaN:H films were sputter deposited at 0.27 Pa on Corning 7059 glass in 100% nitrogen gas and in nitrogen/hydrogen mixed gas, respectively.

1.06 Pa. On the basis of these spectra and those shown in Fig. 2(b), we conclude that the hydrogen bond density is strongly dependent on the total sputtering pressure, but not on the hydrogen partial pressure.

C. Optical absorption

One of the most important parameters characterizing semiconductor properties is the band-gap energy E_g . In order to determine the fundamental absorption edges of the sputter-deposited GaN and GaN:H films, we have measured optical absorption spectra of these films deposited on Corning 7059 glass.

The experimental absorption spectra $\alpha(E)$ measured at $T=300\text{ K}$ for α -GaN and GaN:H films are shown in Figs. 5(a) and 5(b), respectively. The dependence of α on photon energy E can be written as

$$\alpha(E) = A(E - E_g)^n \quad (1)$$

or, equivalently,

$$\alpha(E)^{1/n} = A^{1/n}(E - E_g), \quad (2)$$

where $n=1/2$ and 2 correspond to the direct and indirect band gaps, respectively. It is known that crystalline GaN is a direct-band-gap semiconductor having a band-gap energy of $E_g \sim 3.4\text{ eV}$ for α -GaN or $\sim 3.2\text{ eV}$ for cubic (β -) GaN at room temperature.¹⁵ The plot shown in Fig. 5(a) gives the intercept at $E_g=3.38\text{ eV}$ on the energy axis. This value is nearly equal to that for single-crystalline α -GaN ($\sim 3.4\text{ eV}$). Kubota, Kobayashi, and Fujimoto¹¹ succeeded in the epitaxial growth of hexagonal GaN films on sapphire substrates by rf-magnetron sputtering and measured their absorption spectra. The E_g value obtained by those authors was 3.21 eV , which is considerably smaller than any previously reported α -GaN value.

As mentioned before, the GaN:H films sputter deposited in a mixture of nitrogen and hydrogen gases are amorphous or amorphous-like. The optical transitions in amorphous semiconductors can be described, to a first approximation, by the “*nondirect*” transition model in which the conservation of energy, but not of the wavevector, is significant.¹⁷ The ab-

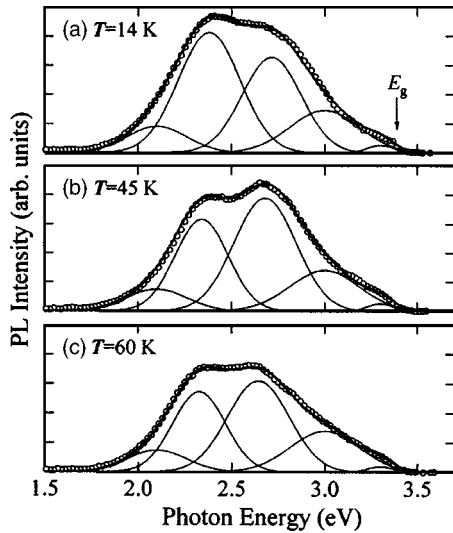


FIG. 6. PL spectra for α -GaN film sputter deposited on the Si(100) substrate at 0.27 Pa in 100% nitrogen gas, measured at (a) 14, (b) 45, and (c) 60 K. The light solid lines represent the deconvolution of each spectrum into several Gaussian emission peaks. Note that the intensity scales in (a)-(c) are all the same units; then, the relative intensity of the three PL can be directly compared.

sorption coefficient in this case can be given by almost the same expression as that for the indirect transitions in crystalline semiconductors, i.e., Eq. (1) with $n=2$. The optical absorption data obtained from the GaN:H film are plotted in Fig. 5(b) as $\alpha^{1/2}$ vs E . From this plot, we obtain $E_g \sim 3.7$ eV. This value is much larger than those for crystalline GaN (~ 3.4 eV for α -GaN or ~ 3.2 eV for β -GaN). Indeed, we can clearly see the oscillations in the $\alpha(E)$ spectra for E up to 3.7 eV. Note that these oscillations originate from the multiple internal reflections of light in the sputter-deposited GaN films where the films are effectively transparent.

D. Photoluminescence

1. GaN film

Figure 6 shows the PL spectra measured at $T=14$, 45, and 60 K for a GaN film sputter deposited on Si(100) substrates in a pure nitrogen atmosphere of 0.27 Pa. These spectra can be resolved into five peaks centered at ~ 2.1 , ~ 2.3 , ~ 2.7 , ~ 3.0 , and ~ 3.3 eV, as determined from a Gaussian line shape fit. The ~ 3.3 eV peak may correspond to the edge or donor-acceptor pair emission, but is not sharp even at low temperature. The yellow emission band at ~ 2.3 eV is often observed in α -GaN. A description of the luminescent properties of GaN has been given by Akasaki and Amano¹⁸ and Leroux and Gil¹⁹ who reviewed some of the work done on undoped and doped GaN crystals.

We have observed PL emission only at temperatures lower than ~ 100 K. Some authors have observed PL,²⁰⁻²² cathodoluminescence,²⁰ and electroluminescence^{23,24} from "rare-earth-activated" GaN films deposited by sputtering. Note that rare-earth elements, such as Er and Tm, may be incorporated into semiconductors as an optically active inclusion, not strictly as dopants.

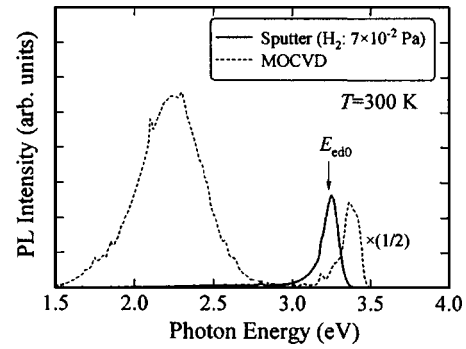


FIG. 7. Room-temperature PL spectrum for GaN:H film deposited on the Si(100) substrate at 0.27 Pa in nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. For comparison, the PL spectrum for a single-crystalline α -GaN film grown on a (0001) sapphire substrate by MOCVD is shown by the dashed line in reduced scale of $\times(1/2)$.

2. GaN:H film

As mentioned above, PL emission from the sputter-deposited crystalline GaN film is very weak and observed only at low temperatures ($T < 100$ K). On the other hand, we have observed relatively strong PL emission from GaN:H film even at high temperatures. In Fig. 7, we show, as an example, the PL spectrum for GaN:H film measured at $T=300$ K. The film was sputter deposited onto a Si(100) substrate at 0.27 Pa of nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. For comparison, the PL spectrum taken from a single-crystalline α -GaN film is shown in Fig. 7 by the dashed line. This film was grown epitaxially using trimethylgallium and ammonium in a vertical MOCVD reactor on a (0001) sapphire substrate at 1040 °C after depositing a GaN nucleation layer at 600 °C for 60 s.

The PL emission from the sputter-deposited GaN:H film shows a single emission peak, E_{ed0} , at ~ 3.25 eV. On the other hand, the MOCVD-grown α -GaN film exhibits an emission at ~ 3.4 eV and a deep yellow emission at ~ 2.3 eV. Note that the GaN:H film is evaluated to be predominantly amorphous [Fig. 1(b)] and has the relatively large band-gap energy of ~ 3.7 eV [Fig. 5(b)]. Furthermore, the ~ 3.25 eV (E_{ed0}) emission shown in Fig. 7 is relatively intense, about half that of the ~ 3.4 eV emission in the MOCVD-grown α -GaN film, and sharp. It is, thus, very difficult to consider that the ~ 3.25 eV peak observed in the GaN:H film originates from the amorphous GaN matrix. The peak is, therefore, considered to be due to crystalline GaN particles embedded in the amorphous GaN matrix. An emission from nanoscale ZnSe particles embedded in amorphous ZnSe has also been reported by Lee *et al.*²⁵

Figure 8 shows the PL spectra for GaN:H film taken at 14–300 K. It is seen that the GaN:H film exhibits very complex luminescent properties, i.e., its spectra are strongly dependent on temperature T . This is particularly obvious around $T \sim 180$ K, as shown in the enlargement in the inset of Fig. 8. A single peak is observed for T from 300 K down to ~ 220 K, below which new peaks appear in the band-edge region and in the donor-acceptor (DA) pair and deep-emission regions. The PL intensity is also found to increase with decreasing T .

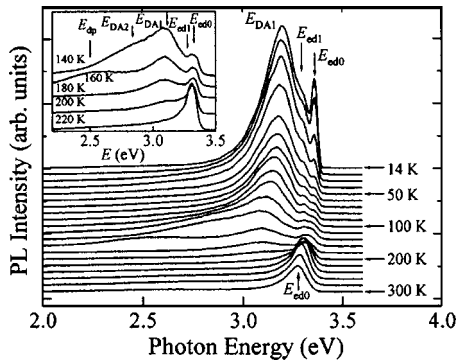


FIG. 8. PL spectra for GaN:H film measured at T from 14 to 300 K. The GaN:H film was sputter deposited at 0.27 Pa on the Si(100) substrate in nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. The inset shows the PL spectra between $T=140$ and 220 K.

By performing Gaussian line shape analysis, our measured PL spectra can be resolved into several peaks. We show in Fig. 9 the results of such analysis. For $T=14$ K, the analysis reveals two edge-emission peaks at 3.363 eV (E_{ed0}) and 3.315 eV (E_{ed1}), a DA-pair emission at 3.199 eV (E_{DA1}), and a very weak deep emission at ~ 2.5 eV (E_{dp}). The individual contributions of each emission peak or band to the PL spectra are indicated in Figs. 9(a)–9(c) by the light solid lines. Here, we assumed that the DA-pair emission intensity can be simply written, using a Gaussian function, as²⁶

$$I_{DA1}(E) = \sum_{n=0}^{\infty} S_{DA1}^n \exp\left[-\frac{[E - (E_{DA1}^0 - n\hbar\omega_{LO})]^2}{\Gamma^2}\right], \quad (3)$$

where E_{DA1}^0 is the zero-phonon ($n=0$) emission energy, S_{DA1}^n is the strength of the n th phonon emission line, $\hbar\omega_{LO}$ is the longitudinal optical (LO) phonon energy (92 meV; Ref. 15), and Γ is the broadening parameter. As the impurity (donor or acceptor) energy increases, the interaction of the electron with lattice vibrations or the electron-phonon coupling be-

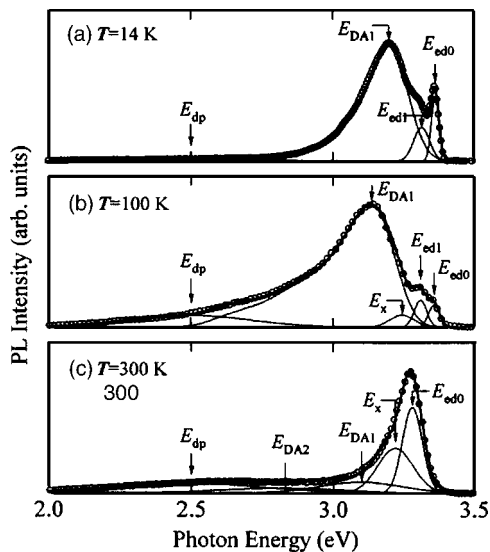


FIG. 9. PL spectra for GaN:H film measured at (a) 14, (b) 100, and (c) 300 K. The GaN:H film was sputter deposited at 0.27 Pa on the Si(100) substrate in nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. Individual contributions to the PL intensity from each emission peak or band are shown by the light solid lines.

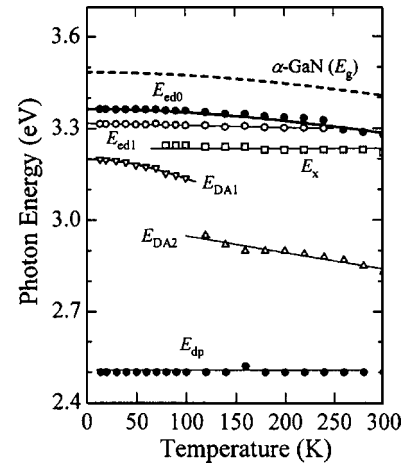


FIG. 10. PL peak energies plotted as a function of temperature T for GaN:H film sputter deposited at 0.27 Pa on the Si(100) substrate in nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. For comparison, the temperature dependence of the excitonic energy gap E_g in single-crystalline α -GaN, taken from Ref. 15, is shown by the heavy dashed line. The heavy solid line represents the fitted result of Eq. (5) to the experimental $E_{ed0}(T)$.

comes stronger. In this particular case, LO phonon coupling is by far the strongest because of the polarization field associated with it. For the shallow hydrogenic impurity centers, phonon coupling is weak and often only one LO phonon replica ($n=1$) can be observed. For deeper centers, phonon coupling is much stronger, and three or more LO phonon replicas can often be recognized. Theoretically, the intensity I_{DA1} in Eq. (3) is given by a Poisson distribution function²⁶

$$S_{DA1}^n \propto \exp(-\bar{N}) \frac{\bar{N}^n}{n!}, \quad n = 0, 1, 2, \dots, \quad (4)$$

where \bar{N} is the mean number of emitted phonons.

At higher temperatures, the edge-emission peaks become considerably broader and new emission peaks, labeled E_x and E_{DA2} , appear at ~ 3.2 and ~ 2.9 eV, respectively. As expected, the line shape of I_{DA1} (E_{DA1}) expressed by Eq. (3) is strongly asymmetric and has a tail on the low-photon-energy side [see Figs. 9(a) and 9(b)].

We show, in Fig. 10, the temperature variation of each peak energy in the PL emission spectra of GaN:H film. For comparison, the temperature dependence of the excitonic energy gap E_g in single-crystalline α -GaN, taken from Ref. 15, is plotted by the heavy dashed line.

Conventionally, the temperature variation of the band-gap energy is expressed by Varshni's formula²⁷

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta}, \quad (5)$$

where $E_g(0)$ is the band-gap energy at $T=0$ K, α is in electron volts per Kelvin, and β is closely related to the Debye temperature θ_D of the material (in Kelvin). The heavy solid line in Fig. 10 represents the fitted result of Eq. (5) to the experimental data of $E_{ed0}(T)$. The fit-determined parameters are $E_{ed0}(0)=3.363$ eV, $\alpha=10.0 \times 10^{-4}$ eV/deg, and $\beta=850$ K.

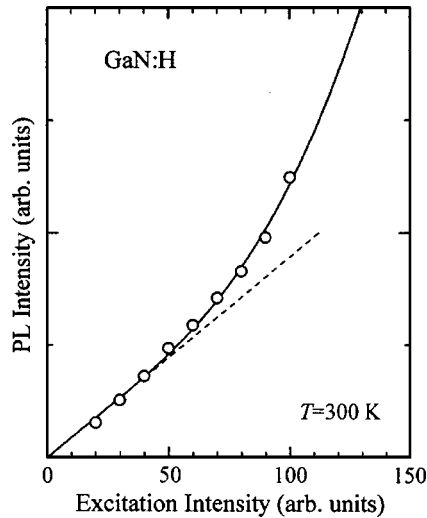


FIG. 11. Excitation laser-power dependence of the PL intensity for GaN:H at $T=300$ K. The GaN:H film was sputter deposited at 0.27 Pa on the Si(100) substrate in nitrogen gas mixed with hydrogen gas at a partial pressure of 7×10^{-2} Pa. The open circles represent the experimental data, while the solid line is drawn through the data as a guide to the eye. The dashed line indicates the relation of $I \propto (I_{\text{ex}})^{\gamma}$ with $\gamma=1$.

The characteristic temperature of $\beta=850$ K determined here is equal to the Debye temperature $\theta_D \sim 820\text{--}874$ K at $T=300\text{--}2000$ K for α -GaN.¹⁵ It is also found that β is roughly equal to the effective LO phonon temperature of $\theta \sim 1070$ K obtained from $k\theta = \hbar\omega_{\text{LO}}$ (~ 92 meV). This suggests that the major contribution to the temperature variation of $E_{\text{ed}0}$ is from the optical phonons. The temperature variation, -5×10^{-4} eV/deg, for $E_{\text{DA}2}$ in Fig. 10 is equal to that of the excitonic energy gap, $-(3.6\text{--}5.3) \times 10^{-4}$ eV/deg, observed for single-crystalline α -GaN (Ref. 15). It should be noted, however, that $E_{\text{ed}1}$ and E_x show no strong dependence on T . As a result, $E_{\text{ed}0}$ and $E_{\text{ed}1}$ cross at $T \sim 250$ K. Above 250 K, these two peaks are observed as a single broad peak [Fig. 9(c)]. Unfortunately, the origins of $E_{\text{ed}1}$ and E_x are not clear at present.

Finally, we show, in Fig. 11, the laser-power dependence of the PL emission intensity for $E_{\text{ed}0}$ measured at $T=300$ K. The integrated PL intensity I versus laser power I_{ex} can be simply written as $I \propto (I_{\text{ex}})^{\gamma}$, where the dimensionless exponent γ is known to be $1 < \gamma < 2$ for free-exciton or bound-exciton emission and $\gamma \leq 1$ for free-to-bound or DA-pair emission.²⁸ Our experimental data indicate that at low excitation levels, the exponential parameter γ is unity, but at higher levels, the emission intensity I increases superlinearly with I_{ex} . The observed superlinearity may arise from the effects of fine GaN particles embedded in the amorphous GaN matrix.

IV. CONCLUSIONS

We deposited GaN films by reactive rf-magnetron sputtering in a nitrogen gas without and with the addition of hydrogen gas. The XRD patterns suggested that the GaN films sputter deposited in nitrogen gas at pressures lower than 0.53 Pa without hydrogen gas are polycrystalline films with the (0001) texture, while those deposited at or above

1.07 Pa display mixed crystalline orientations or an amorphous-like nature. On the other hand, the GaN:H films deposited with the addition of hydrogen gas showed an amorphous or amorphous-like nature. The FTIR spectra suggested that the GaN:H films show not only the GaN lattice absorption at ~ 555 cm^{-1} , but also new peaks at ~ 1000 and ~ 3200 cm^{-1} originating from the hydrogen-related bonds with the host lattice atoms. The room-temperature optical absorption spectra indicated the fundamental absorption edges at ~ 3.38 and ~ 3.7 eV for the highly oriented α -GaN and amorphous GaN:H films, respectively. The PL emission was observed from the sputter-deposited α -GaN film at $T < 100$ K and found to show five emission bands centered in the $\sim 2.1\text{--}3.3$ eV spectral region. The amorphous GaN:H film showed a relatively strong PL emission even at room temperature. The $T=14$ K spectrum exhibited two edge emissions at 3.363 and 3.315 eV, a DA-pair emission at 3.199 eV, and a very weak deep emission at ~ 2.5 eV. The PL emission observed in the GaN:H film may originate from crystalline GaN particles embedded in the amorphous GaN matrix.

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