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Photoluminescence characteristics of low indium composition InGaN thin films grown on sapphire by metalorganic chemical vapor deposition

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Abstract

The wavelength shifts in the photoluminescence (PL) from low indium composition (~ 3%) InGaN epitaxial thin films, grown on sapphire substrates by metalorganic chemical vapour deposition, has been studied by a combination of experiment and theory. As temperature increases from 6 K, the PL peak energy red-shifts very slightly first, then blue-shifts to reach a maximum at near 100 K, and red-shifts again till room temperature. This unique PL behaviour, indicating the existence of the phase separation, is interpreted qualitatively from the spatial variation of band structure due to the In-compositional fluctuation. Theoretical calculation, based upon a model involving the band-tail states in the radiative recombination, explains the experimental data successfully.
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1. Introduction

Tremendous progress in the research and development of GaN-based materials and devices for the optoelectronic and electronic applications in the UV–Visible range have been made in recent years. InGaN-based light emitting diodes (LED) and laser diodes (LD) grown on sapphire substrates by metalorganic chemical vapour deposition (MOCVD) are now available commercially [1,2]. Accompanying to these quick developments, a number of questions regarding fundamental material aspects has been left open, for example, the In segregation phenomena in the $In_xGa_{1-x}N$ films [3]. The $In_xGa_{1-x}N$ material system is the likelihood of composition instability, which is easy to lead to phase separation and inhomogeneous properties. This can be seen as both advantageous and detrimental to the desired device performance [4].

InGaN plays a key role as the active layer where the radiative carrier recombination occurs in the InGaN-based LED and LD devices. However, its luminescence mechanism is still an important topic under intense investigation [3–24]. There exists a discrepancy over the emission mechanisms in three-dimensional (3D) InGaN alloy films [3–10] and InGaN-quantum well (QW) structures [11–24].

It has been speculated that the origin of luminescence of InGaN may be due to a number of processes, such as (1) decay of localised excitons at the potential minima originating from the large compositional fluctuation and/or indium phase separation [6,11], (2) piezoelectric or quantum-confined-Stark effect [16], which arises from strain caused by the lattice mismatch between GaN and InGaN, and (3) band-to-band [7] or a donor–acceptor pair (DAP) [5] emission.

Ho and Stringfellow [25] have predicted, based on thermodynamics considerations, that the large difference in interatomic spacing between GaN and InN gives rise to a solid phase miscibility gap for solution of InN up to 6% at

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the InGaN growth temperature of 800 °C. The immiscibility leads to the compositional fluctuation or inhomogeneity in InGaN on the nanometre scale, which has been validated by various experimental observations [9]. Generally, when the InGaN mole fraction is large, a phase separation occurs [26], which means that indium segregation and In-rich/In-poor regions appear. In this case, the so-called self-organised InGaN quantum dots are formed, acting as trap centres for localised excitons. This may not be true when the mole fraction of indium is small.

In this paper, we report on the study of the photoluminescence (PL) mechanism, in the temperature range of 6–300 K, in small-indium-composition InGaN alloy epilayers grown on sapphire substrates. Theoretical calculation and simulation have been made for the radiative recombination using band tail states, which can interpret well the experimental data from our measurements. Our results clarify the PL features and recombination mechanism in InGaN alloys with low indium (below 6%) mole fractions.

2. Experimental

The InGaN alloys used were grown by metalorganic chemical vapor deposition (MOCVD). On (1000) sapphire, a thin, about 30-nm thick, GaN buffer was first grown at low temperature (LT) at 530 °C, followed by approximately 1 μm thick GaN deposited at 1030 °C and finally followed by a nearly 100-nm thick InGaN layer grown at 700 °C. Growth details can be seen from [7,27]. Several InGaN samples with x(In) of about 3%, as determined by high resolution X-ray diffraction, were used in this study. PL was measured at 6–300 K, under the 325 nm laser excitation with a power of about 5 mW focused on the sample surface.

3. Results and discussion

3.1. Experimental results and qualitative analysis

Fig. 1 shows temperature dependent PL spectra from a typical InGaN epilayer with x(In) of 3% at 10–300 K. A well-pronounced emission peak was observed at 3.355 eV with a line width of 28 meV at 10 K, which is due to the InGaN band edge emission. When the excitation power was varied at a fixed temperature, no observable change in the emission energy was found. This rules out the DAP mechanism because that the donor–acceptor pair recombination would have the PL peak energy shifted to high energy side due to the increase of the excitation power level [28].

Chichibu et al. [6] have reported a PL study on InGaN alloys with 6% In, and found that the InGaN PL peak energy, $E_0(T)$, is monotonically decreased with an increase

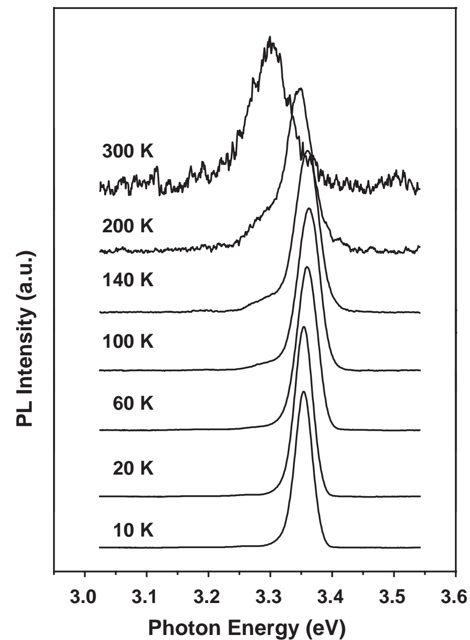

Fig. 1. Photoluminescence spectra, at various temperatures, of an InGaN alloy epilayer with x(In) of 3%.

of temperature in the range of 10–300 K and can be well described by the Varshni equation:

$$E_0(T) = E_0(0) - \alpha T^2/(T + \beta), \quad (1)$$

where α and β are the Varshni's parameters, respectively. They assigned the peak to the recombination of excitons localized at the potential minima originating from the large compositional fluctuation.

The temperature dependence of the PL peak energy for our sample is plotted in Fig. 2, which is different from that observed by Chichibu et al. [6]. From the results, we ruled out, in our case, the possibility of excitons localized at the potential minima originating from the large compositional fluctuation. For the same reason, the possibility of the band-to-band recombination, which obeys the Varshni equation, can also be ruled out.

It has been reported that the compositional inhomogeneity or fluctuation in InGaN leads to anomalous temperature dependence of PL [8,10,15–17,19] and electroluminescence (EL) [12] emission, i.e. the so-called "S-shaped" [14] temperature dependent emission wavelength shift behaviour. This type of red/blue/red emission shifts of the band edge-related peak energy has been observed from InGaN/Gann quantum well (QW) structures [12,15–17,19], and InGaN films [8,10] mainly with high In-composition. However, in InGaN film with low In mole fraction, this S-shaped wavelength versus temperature characteristics was not widely reported in the literature [8].

As shown in Figs. 1 and 2, we have observed a unique PL characteristics from low x(In) InGaN films. As the temperature increases from 6 K, the PL peak energy red-shifts very slightly first (for some samples, the PL peak

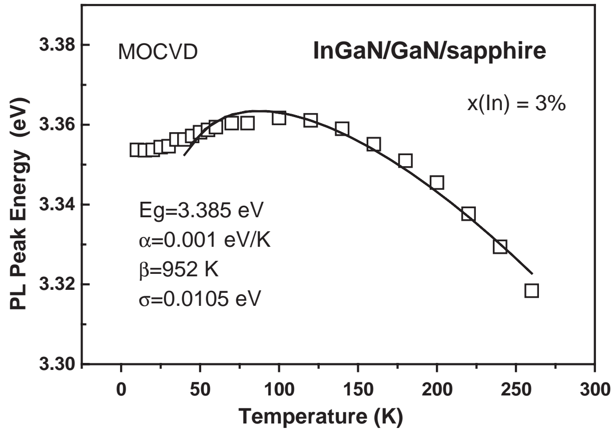

Fig. 2. The temperature dependence of the PL emission peak energy of InGaN alloy epilayers.

stays in the same energy), then blue-shifts to reach a maximum at near 100 K, and again red-shifts till room temperature is reached. This has been observed in several MOCVD-grown InGaN films with x(In) of approximately 3%, which is different from most cases reported so far in the literature. This unique blue-red shift PL behaviour was observed in InGaN MQW with high In-composition (20%) InGaN well [15], but scarcely seen in low x(In) InGaN films. It is also a clear indication of the existence of In-compositional fluctuation or phase separation in our InGaN films with small In-composition less than the critical value of 6% [25].

The indium-inhomogeneity provides a basis for a qualitative explanation of the unique blue/red shift in the temperature dependence of the PL spectra from our low x(In) InGaN alloys. Referring to Fig. 8 of Ref. [7], due to the spatial variation of the In-composition, there exists spatially separated conduction-band minima. In the very low temperature range, the carrier lifetime is long enough for electrons to diffuse to the nearby minima before recombining with holes. However, the carrier lifetime decreases very rapidly with increasing temperature. As the temperature increases (beyond 20 K from Fig. 2), the PL lifetime as well as the diffusion length of photoexcited carriers are reduced. Thus more electrons are unable to diffuse to the local minima before recombining with holes, emitting light with energy higher than the average energy gap of InGaN. This leads towards a shift to higher energy of the PL spectrum. But at much higher temperature, this blue-shift is compensated by the normal downward shift of the band gap, described by the Varshni equation (1), which is dominant at high temperature range, leading to the red-shift beyond 100 K.

3.2. Theory and calculation results

Further, we explore a theoretical model to give a consistent interpretation of the InGaN PL recombination mechanism. In InGaN alloy epilayers, there are mainly two mechanisms, which may cause band gap fluctuations. They are randomly distributed In-composition and dislocations due to the misfit between the InGaN epilayer and the layers beneath. The band gap fluctuations may be represented by the band tail states theoretically.

We assume the density of states of the band-tail states to be described by a Gaussian line shape

$$\rho_{\mathrm{e,h}}(E) = \rho_{0\mathrm{e,h}}\exp\left[-\left(E-E_{0\mathrm{e,h}}\right)^2/2\sigma_{0\mathrm{e,h}}^2\right] \quad (2)$$

where ρ_e, ρ_h, $\rho_{0\mathrm{e}}$, $\rho_{0\mathrm{h}}$, $E_{0\mathrm{e}}$, $E_{0\mathrm{h}}$, $\sigma_{0\mathrm{e}}$, and $\sigma_{0\mathrm{h}}$ are fixed parameters for band-tails of electron and hole states, respectively. Assuming that the optical transitions between the band tail states with no momentum conservation, the spontaneous emission spectrum can be represented in the form of an integral convolution:

$$I_{\mathrm{sp}}(hv) = B(hv)\int \rho_\mathrm{e}(E+hv)f_\mathrm{e}(E+hv)\rho_\mathrm{h}(E)f_\mathrm{h}(E)\mathrm{d}E \quad (3)$$

where $B(hv)$ is the recombination coefficient, and $f_\mathrm{e}(E+hv)$ and $f_\mathrm{h}(E)$ are occupation functions for electron and hole tails, respectively. We also assume that the occupation functions are Fermi-Dirac distributions with a quasi-Fermi level for each tail (the quasi-equilibrium approximation). In this consideration, we do not include the spectral dependence of $B(hv)$.

For the case of non-degenerate occupation, which is true in our experiments, Fermi-Dirac distribution can be replaced by Boltzmann's tails of the occupation functions,

$$f_\mathrm{e}(E+hv) \approx \exp[(F_\mathrm{e}-E)/k_\mathrm{B}T] \quad (4)$$

and

$$f_\mathrm{h}(E) \approx \exp[(E-F_\mathrm{h})/k_\mathrm{B}T], \quad (5)$$

where F_e and F_h are the quasi-Fermi-levels of electrons and holes, respectively.

Carrier distributions for electrons and holes, $N(E)$ and $P(E)$, are then given by

$$\begin{aligned} N(E) &= \rho_\mathrm{e}(E)f_\mathrm{e}(E,T,F_\mathrm{e}) \\ &= \rho_{0\mathrm{e}}\exp[(F_\mathrm{e}-E_{0\mathrm{e}}{*}/K_\mathrm{B}T)] \\ &\quad \times \exp\left[-\sigma_\mathrm{e}^2/\left(2k_\mathrm{B}^2T^2\right)\right] \\ &\quad \times \exp\left[-(E-E_{0\mathrm{e}}{*})^2/\left(2\sigma_\mathrm{e}^2\right)\right] \end{aligned} \quad (6)$$

and

$$\begin{aligned} P(E) &= \rho_\mathrm{h}(E)f_\mathrm{h}(E,T,F_\mathrm{h}) \\ &= \rho_{0\mathrm{h}}\exp[(E_{0\mathrm{h}}{*}-F_\mathrm{h})/k_\mathrm{B}T] \\ &\quad \times \exp\left[-\sigma_\mathrm{h}^2/\left(2k_\mathrm{B}^2T^2\right)\right] \\ &\quad \times \exp\left[-(E-E_{0\mathrm{h}}{*})^2/\left(2\sigma_\mathrm{h}^2\right)\right] \end{aligned} \quad (7)$$

where $\rho_{e,h}(E)$ is the electron (hole) tail density of states, $f_{e,h}(E, T, F_{e,h})$ is the electron (hole) occupation function, $\rho_{0e,h}$ is constant, $\sigma^2_{e,h}$ is the dispersion of the Gaussian tail for electron (hole), respectively. E_{0e}* and E_{0h}* are related to the center energies E_{0e} and E_{0h} of the corresponding tail via:

$$E_{0e}{*} = E_{0e} - \sigma_e^2/(k_B T) \quad (8)$$

and

$$E_{0h}{*} = E_{0h} - \sigma_e^2/(k_B T), \quad (9)$$

respectively. Note that both carrier distributions in Eqs. (8), (9) are Gaussian with the same values of dispersion as in the density of state functions.

The convolution of two Gaussians in Eq. (3) gives again a Gaussian with a sum of partial dispersions:

$$\begin{aligned} I_{sp}(hv) &= B\int N(E+hv)P(E)\mathrm{d}E \\ &= B{*}\rho_{e0}\exp\left[-(hv-hv_0)^2/2\sigma^2\right], \end{aligned} \quad (10)$$

where $hv_0 = E_{0e} - E_{0h}$, $\sigma^2 = \sigma_e^2 + \sigma_h^2$, and $B{*} = B\exp[-(hv - hv_0)^2/2\sigma^2]\exp[(\Delta F - hv_0)/k_B T]$, in which $\Delta F = F_e - F_h$, respectively.

The resulting spectrum has a T-dependent peak at the energy hv_0 given by

$$\begin{aligned} hv_0 &= E_{0e} - \sigma_e^2/(k_B T) - E_{0h} - \sigma_h^2/(k_B T) \\ &= E_0 - \sigma^2/(k_B T) \end{aligned} \quad (11)$$

where $E_0 = E_{0e} - E_{0h}$ is the energy separation between the centres of both densities of state (Gaussians), and $\sigma^2/(k_B T)$ is the Stokes-type red shift. From Eq. (11), it can be seen that the PL peak energy due to the recombination of carriers localized at the band-tail states is determined by two factors: one is the quantity E_0, and the other is $\sigma^2/(k_B T)$. The quantity E_0 is related to the band gap E_g. Therefore, it depends on the temperature in the same manner as E_g, namely, following the temperature dependence given in Eq. (1), $E_0(T) = E_0(0) - \alpha T^2/(T+\beta)$, which possesses the following characteristics: at $T<100$ K, the energy is almost independent of T, while beyond 100 K the energy begins to shift towards the lower energy.

Therefore, the InGaN PL peak energy due to the recombination between the band-tail states will blue-shift as the temperature increases to about 100 K since it is dominated by $\sigma^2/(k_B T)$. At $T>100$ K the quantity E_0 starts to act, and causes the whole spectrum to shift to lower energy. So, this temperature behaviour can be interpreted qualitatively. The calculation based on the band-tail state model is plotted as a solid line in Fig. 2 and fits well with our experimental data in the temperature range of 50–300 K. So, we may conclude that the recombination mechanism in InGaN alloy epilayers with small indium compositions is due to the transitions between the carriers localized at the band-tail states.

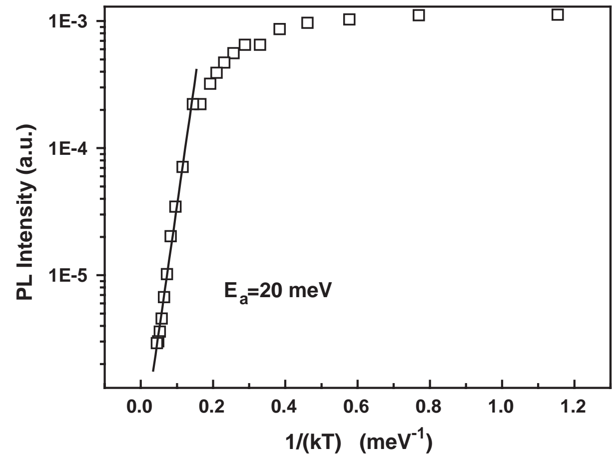

Fig. 3. The temperature-dependence of the integrated intensity of the emission peak in InGaN alloy epilayers. The solid line is the Arrhenius analysis.

3.3. Activation energy

We also monitored the change of the emission peak intensity in InGaN alloy epilayers as a function of temperature. The result is shown in Fig. 3. It can be seen that the integrated intensity remains nearly constant at low temperatures (for larger 1/kT) and decreases dramatically when the temperature goes beyond 70 K (1/kT= 0.17). Obviously, a luminescence decay channel was activated at higher temperatures. The activation energy is found to be 20 meV by the Arrhenius analysis from Fig. 3. Since no other radiative emission mechanisms were involved in the recombination in InGaN alloy epilayers, according to our analysis we believe that a non-radiative recombination channel is responsible for the decay of the emission intensity.

4. Conclusion

In summary, a unique wavelength-shift, blue and then red shifts with temperature in the PL characteristic has been observed experimentally for low indium-composition (~ 3%) InGaN thin films grown by MOCVD. It indicates the existence of composition fluctuation or phase separation in low x(In) InGaN below the critical value of 6%. Our T-dependent PL measurements and theoretical analysis have concluded that the recombination mechanism in InGaN alloy epilayers with low indium compositions is due to the transitions between the carriers localized at the band-tail states, which can be modelled by the radiative transitions between the carriers localized at the Gaussian-distributed band-tail states.

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