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Exciton localization effect in Mn-implanted GaN by photoluminescence measurements

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ABSTRACT

We investigated the temperature-dependent and excitation power-dependent photoluminescence spectra of Mn-implanted (Ga,Mn)N samples with five Mn-implantation doses. The near-band-energy emission was observed and was attributed to the Mn-related exciton transition, which exhibits localized exciton behaviour resulting from alloy potential fluctuations and demonstrates a special temperature-dependence characteristic of alloy disorder. In terms of the integrated photoluminescence intensity as a function of temperature, the activation energy of the localized exciton was obtained. All these results show strong dependence on the Mn concentration of (Ga,Mn)N epilayers.

1. Introduction

During the past several years, more and more efforts have been devoted to (Ga,Mn)N-diluted magnetic semiconductors (DMS) for exploiting the charge and the spin of electrons [1] because of the following two important reasons. Firstly, GaN-based III–V semiconductors have potential applications in electronic and optoelectronic devices, such as blue-ultraviolet light-emitting diodes and laser diodes [1–3]. Secondly, it has been predicted theoretically [4] and experimentally [5,6] that the Curie temperature exceeds room temperature. Although a great deal of emphasis has been placed on the origin of the ferromagnetic behaviour in (Ga,Mn)N, there are many fundamental properties, especially the magnetic ion-related properties, about (Ga,Mn)N that are still not clear and need to be investigated.

Photoluminescence (PL) measurement is a standard optical characterization technique for studying various fundamental aspects of solids such as the nature of electronic states, the exciton effects and the light emission mechanisms, which is especially important and essential for optoelectronic device applications. In the past, most of the research on PL measurement concentrates on the origin of PL peaks of (Ga,Mn)N material with low Mn concentrations [7–9]. In fact, study on the (Ga,Mn)N system with a set of high Mn concentrations is more interesting and preferred, because the high magnetic ion concentration is desired in DMS materials. But detailed magnetic Mn ion-related PL studies of the (Ga,Mn)N system with high Mn concentrations are seldom available unless in Ref. [10] and in this paper.

It is well known that (Ga,Mn)N is a kind of material with multi-compositions, and statistical fluctuations in the composition of a random alloy may lead to potential fluctuations, resulting in spatially localized excitons. It is reported that exciton localization is the key to the high luminescence efficiencies observed in some multi-composition semiconductor devices, such as InGaN-based laser diodes [11]. As an important candidate of spintronic semiconductor device material, it is naturally necessary to investigate whether there also exists exciton localization effect in (Ga,Mn)N material and what its detailed behaviour is from the viewpoint of further potential device application. PL measurement is one of the best survey tools for probing the exciton effects, especially exciton localization due to alloy disorder [12]. However, nearly no systematic investigation about exciton localization

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behaviour of (Ga,Mn)N has been studied yet. In this paper, the temperature- and power-dependent PL spectra of Mn-implanted (Ga,Mn)N samples with both low and high Mn concentrations were investigated. The Mn-related band-edge exciton transitions were observed and analyzed in detail. The phenomena of potential fluctuations and exciton localization effect were studied.

2. Experiment

The Si-doped GaN film was grown on (0 0 0 1) sapphire substrates by hydride vapor phase epitaxy (HVPE). The GaN epilayer shows n-type conductivity and the thickness is 3.8 μm. The as-grown sample was then cut into 10 equivalent pieces. Every two pieces were uniformly implanted with the same Mn dose at a constant energy of 190 keV. Totally, we get 10 pieces of (Ga,Mn)N samples with five Mn-implantation doses of 1×10^{16}, 3×10^{16}, 5×10^{16}, 7×10^{16} and $9\times10^{16}\,cm^{-2}$, respectively, corresponding to approximately 1%, 3%, 5%, 7% and 9% Mn concentrations at the peak of the implant profile. To avoid amorphization, the samples were held at a temperature of 350 °C during the implantation step. After implantation, one piece of each implantation dose was selected to deal with rapid thermal anneal (RTA) at 900 °C for 1 min in a flowing N_2 gas with the implanted area face down. Detailed structural analyses were reported in Ref. [13]. The photoluminescence spectra were measured in a wide temperature range (83–303 K) using He–Cd laser ($\lambda_L = 325$ nm) excitation. The laser beam was focused yielding a spot size of 1 μm. The PL was analyzed in backscattering geometry using the Jobin Yvon LabRaman HR 800 UV micro-Raman spectrometer.

3. Results and discussion

Fig. 1 shows PL spectra of (a) as-implanted and (b) RTA (Ga,Mn)N samples with five different implantation doses at 223 K. The sharp bound exciton peak (3.4 eV), which appears in GaN, cannot be found both in as-implanted and RTA (Ga,Mn)N PL spectra, whereas three new broad peaks were observed. To determine the definite energy position of each peak, we decomposed each PL spectrum with three Lorentz peaks A, B and C. Peak A at 2.2 eV is the typical yellow luminescence band, which is ascribed to a shallow donor–deep acceptor transition that does not have obvious relationship with the Mn-implantation dose. It is

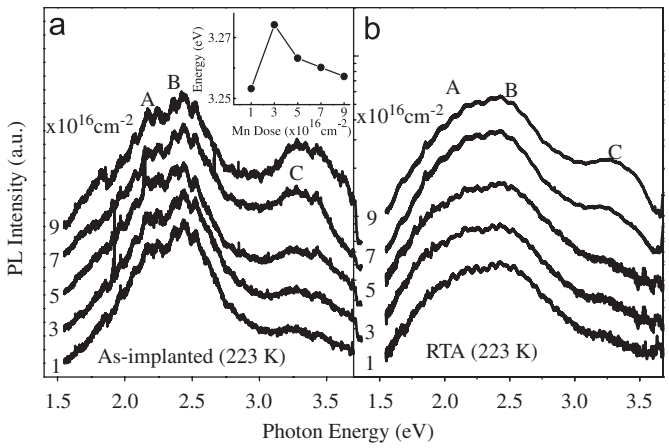

Fig. 1. PL spectra of (a) as-implanted and (b) RTA (Ga,Mn)N samples with different Mn doses at 223 K, and the axis of Fig. 1(b) is displayed in logarithmic scale. The ion-implantation dose from top to the bottom is 1, 3, 5, 7 and $9\times10^{16}\,cm^{-2}$. The inset shows dependence of energy position of peak C on the Mn-implantation dose.

proposed that the most probable candidate of shallow donor is V_N and deep acceptor is V_{Ga} for n-type (Ga,Mn)N [14]. Peak B at 2.5 eV has been clearly identified at this moment. It is suggested that it originates from the donor–Mn acceptor pair transition [15], which obviously depends on Mn-implantation dose. Peak C near 3.28 eV was seldom reported in the literature up to now. From Fig. 1, we can see that the energy position of peak C varies with the increasing Mn concentration and the intensity of peak C enhanced significantly. In order to demonstrate the dependence of energy position of peak C on Mn concentration clearly, we read out the energy of peak C at each Mn concentration as shown in the inset. The energy of peak C increases with the Mn-implantation dose at first, and then decreases as the Mn-implantation dose exceeds $3\times10^{16}\,cm^{-2}$, which is consistent with the dependence of band gap of (Ga,Mn)N on the Mn-implantation dose [13]. At different Mn concentrations (1%, 3%, 5%, 7% and 9%), the energy of peak C is close to the band gap of (Ga,Mn)N (about 3.4 eV [13]) and far larger than donor–acceptor transition [14–16]. So we consider that the PL signal of peak C is most likely associated with the band-edge exciton. Using the effective mass theory of the hydrogen model [17], the binding energy about 84 meV for the free exciton of (Ga,Mn)N was obtained, which was smaller than the difference between energy gap and energy of peak C. Therefore, we thought that peak C should have been resulted from the impurity-bound band-edge excitons transition. In terms of energy of peak C and the fact that the position and intensity of peak C varied with the increase of Mn-implantation dose, as shown in Fig. 1, we conclude that peak C came from Mn-related band-edge exciton transition. Through the binding energy of free exciton E_b and energy gap of (Ga,Mn)N, the binding energy of the Mn impurity-bound exciton was calculated to be $E_{BX} = 63$ meV, using equation $\hbar w = E_g - E_b - E_{BX}$ [18]. Jeon et al. [7] have also observed a peak near 3.28 eV at 15 K for (Ga,Mn)N with Mn concentration of 0.5%, which they thought to be associated with the band-edge bound exciton transition. Considering the different Mn concentrations and the measuring temperature, the energy position of peak C is close to our results. Therefore, we thought that peak C has resulted from the Mn-related band-edge exciton. Compared to the case of the as-implanted samples, the relative-intensity ratio of peak C to peak A decreases greatly after annealing because nonradiative recombination centers were annealed out by RTA treatment, resulting in the relative intensity of peak A increasing drastically and the difficulty in detecting peak C at low implantation dose. To demonstrate peak C more clearly, the axis of Fig. 1(b) is displayed in logarithmic scale.

It is well known that statistical fluctuations in the composition of a random alloy lead to potential fluctuations, which may result in spatial excitons localized, which is important to the luminescence efficiencies in multi-composition semiconductor devices. To investigate whether the band-edge exciton is localized due to the alloy potential fluctuations of the (Ga,Mn)N material, the PL spectra with different excitation power at low temperature were measured and displayed in Fig. 2(a). The band-edge exciton transition line of peak C at different excitation powers is shown in the inset of Fig. 2(a). It is known that three typical characteristics should be satisfied for exciton localization: (1) line narrowing, (2) redshift of peak energy and (3) an asymmetric change of the line shape with the decrease in excitation intensity [19]. Our results of the (Ga,Mn)N material can demonstrate the exciton localization characteristic of peak narrowing and peak shifting. However, due to the fact that peak C is obtained by a Lorentz fitting, the line shape is always symmetric. The asymmetric change of the line shape with the decrease of excitation intensity cannot be observed. Fig. 2(b) demonstrates the effect of excitation power on the integrated intensity of peak C at different temperatures. The integrated intensity increases with the increase in excitation

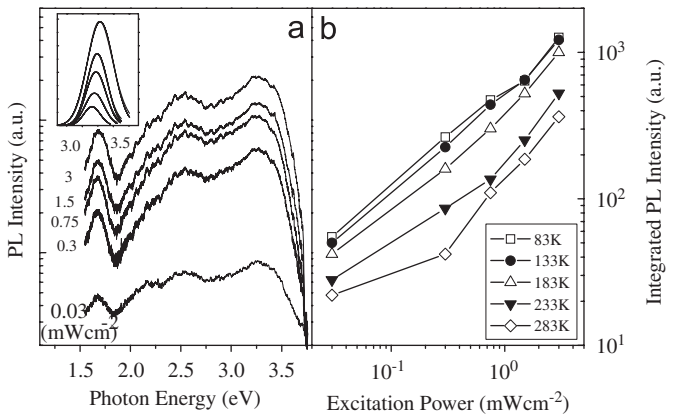

Fig. 2. (a) Power-dependent PL spectra of the as-implanted (Ga,Mn)N (Mn: $9\times10^{16}\,cm^{-2}$) at 83 K. The inset shows the theoretically calculated PL spectrum of peak C, and the excitation power from the top to the bottom is 3, 1.5, 0.75, 0.3 and 0.03 mW cm^{-2}. (b) Dependence of the integrated intensity of peak C on excitation power at different temperatures.

power. Linear dependence is observed at lower temperature and disappears with the increase of temperature. Such phenomena show another piece of evidence to support the existence of localized exciton transition in alloy semiconductors (Ga,Mn)N at low temperature and can be understood in terms of the localized states due to alloy fluctuations [12,20].

In order to obtain a detailed quantitative description of the potential fluctuations and excitons localization, the PL spectra at different temperatures were measured. All samples follow a similar temperature-dependent behaviour. For simplicity, Fig. 3(a) presents only the temperature-dependent PL spectra of one as-implanted (Ga,Mn)N (Mn: $9\times10^{16}\,cm^{-2}$) sample for demonstration. The intensity of peak C decreases as temperature increases, and disappears at high temperatures. The position of peak C of the as-implanted samples (solid symbols) with five different implantation doses and two RTA (Ga,Mn)N (open symbols) with Mn doses 7 and $9\times10^{16}\,cm^{-2}$ in the range from 83 to 303 K are illustrated in Fig. 3(b). Due to the weak signal of peak C after RTA, only the results with high implantation dose (Mn: 7 and $9\times10^{16}\,cm^{-2}$) are presented in the following discussion. From Fig. 3(b) we can see that at each temperature the position of peak C follows similar dependence on Mn concentration as shown in the inset of Fig. 1, i.e. the position of peak C increases with the Mn-implantation dose at first, then decreases as the Mn-implantation dose exceeds $3\times10^{16}\,cm^{-2}$, and the energy of peak C in RTA samples is higher in contrast to that of the as-implanted samples. These results are all consistent with the dependence of lattice constant and band gap on the Mn-implantation dose and rapid thermal annealing effect [13], which also verifies that peak C results from band-edge exciton transition. It is also noted that all the samples follow similar temperature-dependent behaviour. With temperature increasing, energy of peak C with different implantation doses increases at first and then decreases. This can be explained by a simple model based on the Varshni formula in the case of nondegenerate occupation (at low excitation and/or at temperatures higher than 50–80 K) [21]

$$E_{peak}(T) = E_g(0) - \frac{\alpha T^2}{\beta + T} - \frac{\sigma^2}{k_B T} \quad (1)$$

where $E_g(0)$ is the band gap at $T = 0$ K, α and β are Varshni thermal coefficients describing band gap reduction with temperature and σ is a standard deviation in the case of the most probable Gaussian distribution of potential fluctuations and results in broadening of the emission line [22]. Through this model some

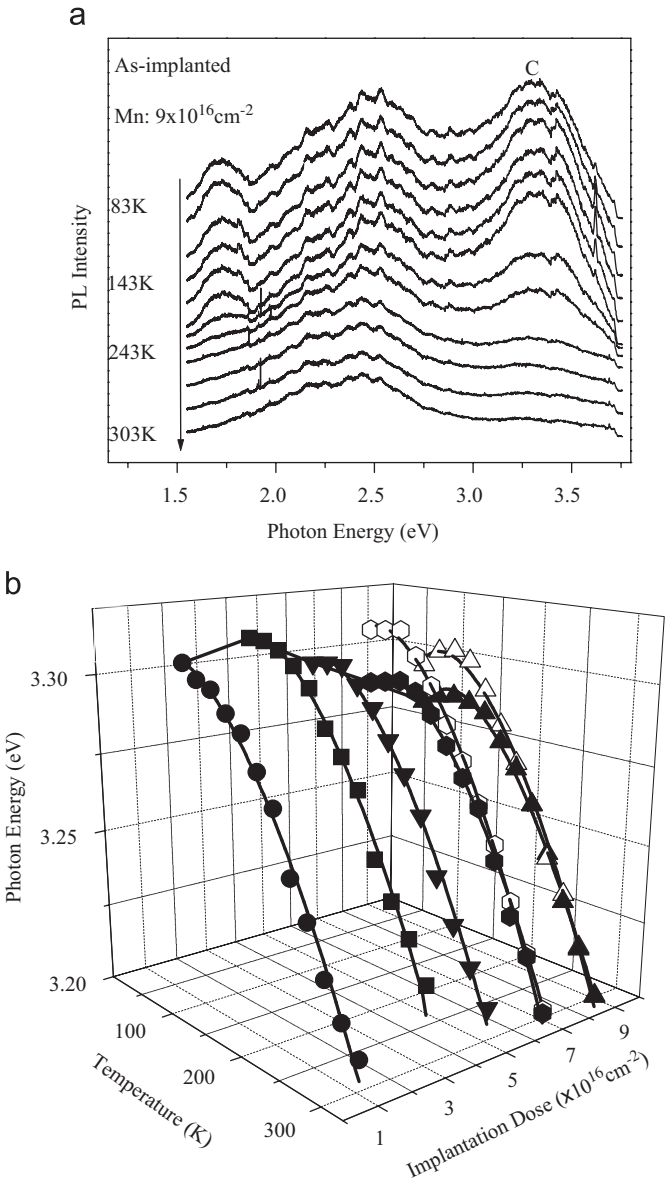

Fig. 3. (a) Temperature-dependent PL spectra of the as-implanted (Ga,Mn)N (Mn: $9\times10^{16}\,cm^{-2}$), (b) dependence of the position of peak C on temperature of as-implanted (Ga,Mn)N (solid symbol) with different Mn doses and RTA (Ga,Mn)N (open symbol) with Mn doses of 7 and $9\times10^{16}\,cm^{-2}$, together with the fitting of Eq. (1) (solid curves).

quantitative parameters can be extracted, depicting the potential fluctuations in (Ga,Mn)N compounds. However, at sufficiently low temperatures when k_BT is smaller than the local potential fluctuation amplitudes, the excitons do not have enough thermal energy to overcome the potential barrier and are trapped in the local potential minima, leading to the relaxation being impossible [11], which is called exciton freeze-out. When exciton freeze-out occurs, the luminescence peak position $E_{peak}(T)$ no longer follows Eq. (1), instead $E_{peak}(T)$ will decrease with increasing temperature. It indicates $E_{peak}(T)$ follows a nonmonotonic S-shaped dependence in a wider range. That is to say, with the increase in temperature, it decreases to an energy minima at first and then increases to a maximum point. After that, it shows a continuous decrease with further increasing temperature. We temporarily name the temperature at energy minima of S-shaped $E_{peak}(T)$ as the freeze-out temperature. However, due to the limited temperature range of our PL experiment (83–303 K), we can only observe the S-shaped

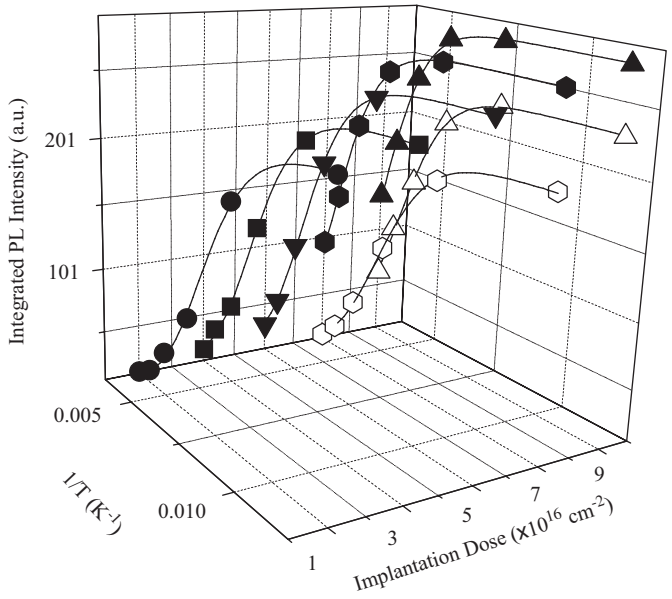

Fig. 4. The dependence of integrated PL intensity of peak C on the temperature of as-implanted (Ga,Mn)N samples (solid symbol) with different Mn doses and RTA (Ga,Mn)N samples (open symbol) with Mn doses of 7, $9\times10^{16}\,cm^{-2}$, together with the fitting of Eq. (2) (solid curves).

trend of temperature dependence at high implantation dose, which may also prove the existence of the alloy potential fluctuations and localized exciton transition [20], and the freeze-out temperature cannot be measured directly. But from the temperature where $E_{peak}(T)$ gets to the maximum point in Fig. 3(b), we can roughly estimate the trend of the freeze-out temperature, which increases with increasing Mn-implantation dose. It is easy to understand that the lower the freeze-out temperature, the smaller the potential fluctuation barrier. Therefore, we conclude that the potential fluctuation barrier also increases with increasing Mn-implantation dose.

By fitting the results of Fig. 3(b) with Eq. (1), we can obtain the standard deviation σ of all the samples. σ of the as-implanted samples with Mn-implantation dose ranging from 1 to 9×10^{16} cm^{-2} are 9.6, 11.4, 14.8, 17.1 and 22.0 meV, respectively. For RTA samples with Mn doses 7 and $9\times10^{16}\,cm^{-2}$, the standard deviations σ are 15.2 and 18.1 meV, respectively. It is known that σ gives a measure of the magnitude of the potential fluctuations, so it is easy to understand that σ increases with increasing Mn-implantation dose and decreases after annealing, which also agrees well with the results of freeze-out temperature.

To determine the activation energy of the band-edge exciton of peak C, we analyzed the temperature dependence of integrated PL intensity with different Mn doses in Fig. 4, using the following equation [23]:

$$I(T) = I_0/[1 + C\,\exp(-E_A/kT)] \quad (2)$$

where E_A is the activation energy of the exciton and C is a temperature-independent constant. The resulting activation energies are 76, 84, 94, 105 and 112 meV for Mn doses ranging from 1 to $9\times10^{16}\,cm^{-2}$, respectively, in as-implanted samples, and are 86 and 98 meV for RTA samples (7 and $9\times10^{16}\,cm^{-2}$), respectively, corresponding to the magnitude of effective potential fluctuations [24] and reflecting more effective confinement with increasing Mn-implantation dose. At the same Mn-implantation dose, the activation energy reduces after annealing, which is in agreement with the standard deviation measurement, indicating that RTA treatment depresses the potential fluctuations. Our experimental result of 76 meV for the 1% Mn concentration (Ga,Mn)N sample is much larger than the experimental activation energy of 17 meV for $(Ga_{0.991}Mn_{0.009})N$ obtained by Jeon et al. [8]. This may be because our result corresponds to the as-implanted sample, but not the RTA sample. We note that the increase in thermal activation energy with Mn-implantation dose is in reasonably good agreement with the dependence of the potential fluctuations barrier on Mn dose, indicating deeper excition localization under higher Mn dose.

4. Conclusions

In summary, we investigate the Mn-related band-edge excitonic transitions of (Ga,Mn)N alloy with five different Mn-implantation doses by temperature-dependent and excitation power-dependent PL measurements. It is shown that the PL peak near 3.28 eV originates from band-edge exciton, which exhibits localized behaviour. The freeze-out temperature, the standard deviation of the potential fluctuations fitted from the characteristic S-shapes temperature dependence on Mn-implantation dose, as well as the activation energy increase with increasing Mn-implantation dose, indicating more effective confinement with increasing Mn dose.

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