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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 $9\times10^{16}\,\mathrm{cm}^{-2}$, 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 struct[illegible] The photoluminescenc[illegible] temperature range (83[illegible]03[illegible] excitation. The laser b[illegible]m [illegible] 1 μm. The PL was ana[illegible]ed i[illegible] Jobin Yvon LabRama[illegible] 80[illegible]

3. Results and dis[illegible]

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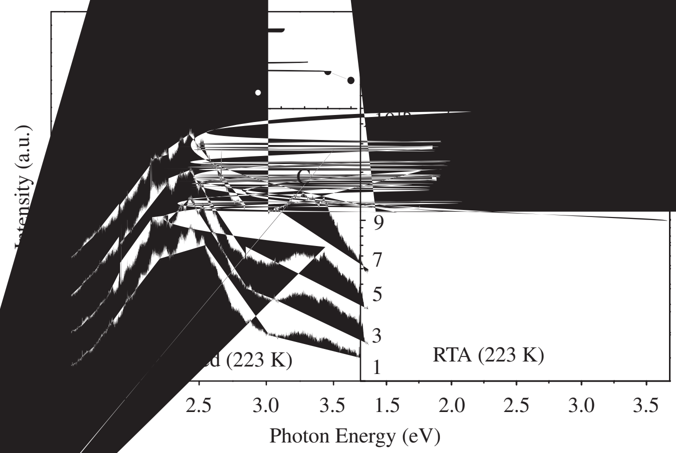

[illegible] ^{16} cm[illegible]. The inset shows dependence of energy position of peak C on the Mn-implantation dose.

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 $3\times10^{16}\,\mathrm{cm}^{-2}$, 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 [illegible] band-edge excitons transition. In terms of [illegible] 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

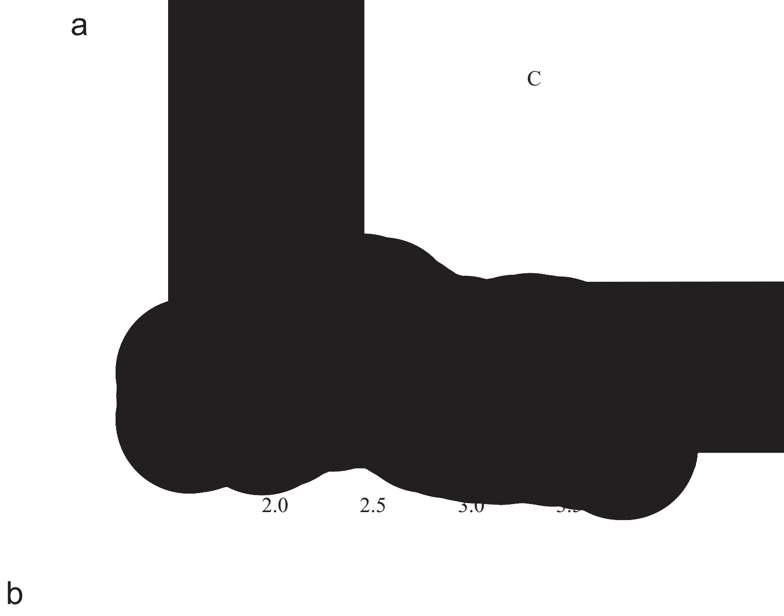

Fig. 3. (a) Temperature-dependent PL spectra of the as-implanted (Ga,Mn)N (Mn: $9\times10^{16}\,\mathrm{cm}^{-2}$), (b) dependence of the position of peak C on temperature of as-implanted (Ga,Mn)N (solid symbol) with different Mn doses and RTA (Ga,Mn)N (open symbol) with Mn doses of 7 and $9\times10^{16}\,\mathrm{cm}^{-2}$,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

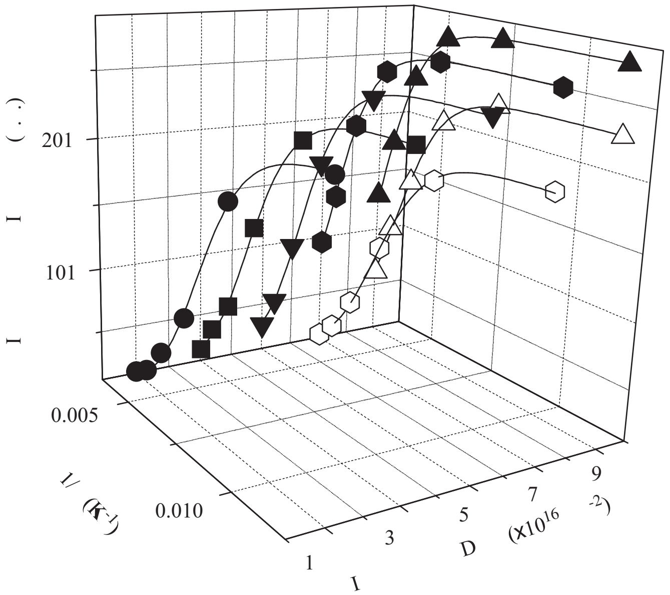

Fig. 4. The dependence of integrated PL intensity of peak C on the temperature of as-implanted (Ga,Mn)N samples (solid symbol) with different Mn doses and RTA (Ga,Mn)N samples (open symbol) with Mn doses of 7, $9\times10^{16}\,\mathrm{cm}^{-2}$, together with the fitting of Eq. (2) (solid curves).

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 $9\times10^{16}\,\mathrm{cm}^{-2}$ are 9.6, 11.4, 14.8, 17.1 and 22.0 meV, respectively. For RTA samples with Mn doses 7 and $9\times10^{16}\,\mathrm{cm}^{-2}$, 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]:

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

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 $9\times10^{16}\,\mathrm{cm}^{-2}$, respectively, in as-implanted samples, and are 86 and 98 meV for RTA samples (7 and $9\times10^{16}\,\mathrm{cm}^{-2}$), 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 $(\mathrm{Ga}_{0.991}\mathrm{Mn}_{0.009})\mathrm{N}$ 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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