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Clarification of difference for transition between photoluminescence and cathode-luminescence based on GaMnN

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ABSTRACT

GaN:Mn epilayers were grown on Al_2O_3 substrate uisng molecular beam epitaxy (MBE) and were subsequently implanted with Mn^+ ions (1% and 10%). Photoluminescence (PL) with 1% of Mn showed that optical transitions related to Mn revealed the donor-Mn pair (D, Mn) at 2.5 eV and the electron-Mn pair (e, Mn) around 3.1 eV, and yellow luminescence (YL) around 2.20–2.25 eV. Photoluminescence (PL) with 10% of Mn showed the same but enhanced optical transitions as above. However, the new transitions around 1.65 eV for the sample with 10% which did not appeared with Mn of 1% were very weakly produced. The results of cathode-luminescence (CL) with 10% of Mn showed transitions related to Mn in PL together with new transitions around 1.72 eV. However, the new transitions around 1.72 eV for the sample with 10% according to high accelerating voltage were very remarkably activated in contrast with PL transitions which appeared were very weakly produced in samples with Mn of 10%. Transitions around 1.72 eV in CL correspond to though around 1.65 eV in PL. This result means that deep donor (probably, V_N) is detected with increasing accelerating voltage and Mn–V_N complex is formed. This is supported by strong electron beam sensitivity of the IR emission bands. It is well known that heavy Mn doping ($>\sim 10^{19}$ C m^{-3}) leads to a downshift of the Fermi level and promotes the formation of defect complexes of Mn–V_N. In our case, Mn doping concentration is $>\sim 10^{21}$ C m^{-3}. Therefore, it is conjectured that the CL transition around 1.72 eV corresponds to Mn–V_N complex.

1. Introduction

GaN is a promising candidate for high-power, high-temperature optoelectronic devices such as blue diodes and lasers [1,2] and has been still investigated by many research groups. And also, incorporation of transition metals such as Mn into III–V semiconductor compounds including GaN, InP, GaAs… etc. exhibits ferromagnetism in addition to conventional semiconductor properties [3,4]. Itinerant carriers are known to be responsible for the ferromagnetism in these semiconductors. Finding of a ferromagnetic semiconductor (FMS) opened a new research area of spintronics for which electronic charge and spin can be controlled by changing external conditions. GaN is a direct wide-gap (~3.44 eV at room temperature) compound semiconductor with a heavy effective carrier mass ($m_e^* \sim 0.2m_0$). Theoretically, according to a recent RKKY (Ruderman–Kittel–Kasuya–Yosida) theory based on the Zener model with a Mn concentration of 5% per cation in 2^+ charge state and 3.5×10^{20} holes/cm^3 [5], Mn-doped GaN and ZnO have high Curei temperature (T_C) above 300 K and many experimental studies have been actively carried out [6–17]. Meanwhile, according to another double exchange model [18], the total energy (TE) within the local spin density approximation was calculated for both $(Ga_{1-x}TM_x^{\uparrow})N$ and $(Ga_{1-x}TM_{x/2}^{\uparrow}TM_{x/2}^{\downarrow})N$ as a function of x. TM indicates transition metal. Then $\Delta E = $ TE (spin glass state) − TE (ferromagnetic state). For x=5%, 10%, 15%, 20%, and 25%, the ferromagnetic states were also stable in GaNMn, GaNV, and GaNCr. Therefore, both the modified RKKY model based on Zener model and double exchange model explained the ferromagnetism based on GaMnN. Based on contents above, the studies of PL and CL transitions related to Mn-activation are necessary and important.

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In this paper, we report the results of PL and CL emission characteristics of a series of Mn^{+}-ion implanted GaN epitaxial layers.

2. Experimental details

The undoped GaN epilayers studied in this work were grown on (0 0 0 1) sapphire substrates using a plasma assisted molecular beam epitaxy (PAMBE) system. The thickness of the GaN epilayers is 1300 nm. While growing undoped GaN epilayers, the growth conditions have been maintained especially under Ga-rich atmosphere. After growing GaN epilayer, the Hall measurement shows n-type carrier concentration (2×10^{18} cm^{-3}) at room temperature. Point defects such as nitrogen vacancies (V_N) and gallium interstitials (Ga_i) have been known to be responsible for the high residual (10^{17}–10^{20} cm^{-3}) n-type character of the undoped GaN [19]. An as-grown, undoped GaN epilayer has been uniformly implanted with Mn^{+} ions with an energy of 200 keV and a dose of 1×10^{16} Mn^{+}/cm^2 (1%) and 5×10^{16} Mn^{+}/cm^2 (10%). The estimated depth of the implanted layer is about $\geq$400 nm from the surface which was calculated using transport and recoil of ion in materials (TRIM) code. After the implantation of Mn^{+} ions, rapid thermal annealing (RTA) has been performed in a flowing nitrogen atmosphere and the annealing temperature and times were varied between 700 and 900 °C for 10–20 s, respectively. Samples are covered with undoped GaN during the RTA process. An energy dispersive X-ray (EDX) spectrometry was taken in order to confirm the concentration of injected Mn. The PL (Photoluminescence) measurements were performed using a 0.75 m spectrometer equipped with an ultraviolet-sensitive photomultiplier tube. The excitation source was the 325 nm line of a He–Cd laser with the total power of 50 mW. A He–Cd laser with the total power of 50 mW is important thing because it is hard to obtain PL transitions with the lower power ~10 mW due to higher implanting energy. The samples were mounted on a cold finger in a closed cycle He-cryostat to control the temperature between 14 and 300 K. The CL measurements were carried out using a Philips XL-30S field emission scanning electron microscope equipped with an Oxford Instrument Mono CL2. CL spectra of samples were measured at 77 K, 300 K and various accelerating voltage.

3. Result and discussions

We first discuss XRD, PL results and next CL results, and then analysis the relevant and different relations between PL and CL results. EDX spectrometry was taken in order to confirm the concentration of injected Mn. The concentration of injected Mn with approximately 1% and 10% was verified (not shown because of much data). The XRD patterns were measured so as to confirm the incorporation of Mn and GaMnN. As shown in the inset of Fig. 3, the GaN:Mn samples with Mn^{+} concentrations of 10% show additional peaks related to Mn. The peaks at 31.2° and 33.7° correspond to Mn (211) and GaMnN. Fig. 1 shows PL spectra measured at 14 K for the as-grown GaN epilayer (inset) and the GaN:Mn epilayers with Mn concentrations of 1%. For the as-grown GaN epilayer, the peak at 3.47 eV belongs to the donor-bound exciton (D°, X). After implantation with Mn^{+} concentration of 1%, the PL peak (D°, X) which appeared in the as-grown sample almost disappeared because the crystallinity was damaged due to the high implanting energy and heavy dose. A concentration of defects such as Ga vacancies (V_{Ga}), N vacancies (V_N), and Ga interstitials (Ga_i) were generated [16]. The GaN:Mn epilayers annealed at 700–850 °C for 10 s with Mn^{+} concentration of 1% displayed new features along with the disappearance of (D°, X). The new distinct peaks of YL around 2.20–2.25 eV, (D, Mn) at 2.5 eV, and (e, Mn) around 3.1 eV were produced in all samples annealed at 700–850 °C for 10 s. Broad and closely separated transitions of YL around 2.20–2.25 eV are caused by several closely spaced deep acceptor states. A few models (for example, shallow donor V_N–acceptor V_{Ga} etc.) of YL were proposed but the exact model was not clarified until now. But, in our case, in view of the EDX result, the possible candidate for donor is the nitrogen vacancy because the molar concentration of N is slightly lower than that of Ga. However, our interesting transitions are (D, Mn) at 2.5 eV and (e, Mn) around 3.1 eV related to activation of Mn. We exclude the possibility of a YL band at 2.5 eV because the apparent coexistence of the transition at 2.25 eV which is typical YL and 2.5 eV band has not been reported to date even though many researchers have studied GaN using various impurities [20]. (D, Mn) and (e, Mn) based on type II discussed below, transitions started to appear in sample annealed at 700 °C for 10 s, but the intensities were weak. With an increase of annealing temperature of 800 and 850 °C for 10 s, the (D, Mn) and (e, Mn) were gradually activated compared with sample annealed at 700 °C for 10 s. The YL peaks of sample annealed at 800 °C for 10 s are separated compared with sample annealed at 700 °C for 10 s. With increasing annealing temperature, clear YL and (D, Mn) appeared. The intensity of (D, Mn) and (e, Mn) for the sample annealed at 700 °C for 10 s is weak compared with those annealed at 800 and 850 °C for 10 s because of low annealing temperature. We selected the low annealing temperature and short annealing time because of the low concentration of Mn^{+} (1%). These results mean that the carrier activation in samples annealed at 800 and 850 °C for 10 s well took place. It is suggested that the transition at 2.5 eV is (D, Mn) which means a donor-Mn acceptor pair transition and that around 3.1 eV is (e, Mn) which means a free electrons or electrons bound to donors-Mn acceptor transition, respectively. Mn (ionic radius of 0.66 Å) must substitute for Ga (ionic radius of 1.41 Å) since the molar refractivity of an ion is proportional to the cube of its radius. In relation to Mn-related transitions, there are ferromagnetic types of Mn centers possibly formed in III–V compounds.

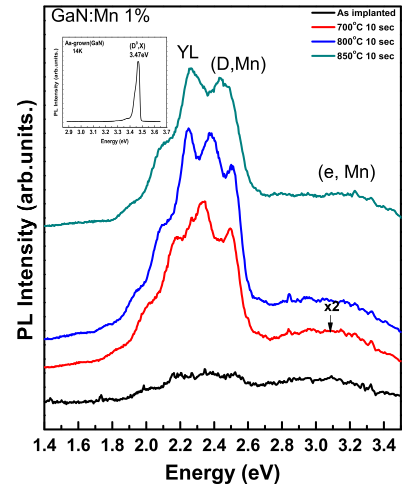

Fig. 1. PL spectra measured at 14 K for the as-grown GaN epilayer (inset) and the GaN:Mn epilayers with Mn concentrations of 1%.

Type I: the first type of neutral Mn center (A^0) is substitutional Mn_{Ga}^{+3} (d^4) with the ground state spin $S=2$ and its related transition was found mainly in GaP:Mn [21].

Type II: the second type of neutral Mn center (A^0) is [d^4 core + e (tightly bound electron)] + h (weakly bound hole, binding energy = 0.113 eV in the case of GaAs:Mn) → Mn_{Ga}^{+2} (d^5) + h with the ground state total angular momentum $J=4$ and has the properties