Mid-gap photoluminescence and magnetic properties of GaMnN films grown by metal–organic chemical vapor deposition*

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Metal–organic chemical vapor deposition (MOCVD) grown ferromagnetic GaMnN films are investigated by photoluminescence (PL) measurement with a mid-gap excitation wavelength of 405 nm. A sharp PL peak at 1.8 eV is found and the PL intensity successively decreases with the addition of Mn, in which the Mn concentration of sample A is below 1% ($[\mathrm{Mn}]_\mathrm{A} = 0.75\%$) but its PL intensity is stronger than other samples'. The 1.8-eV PL peak is attributed to the recombination of electrons in the t_2 state of the neutral Mn^{3+} acceptor with holes in the valence band. With Mn concentration increasing, the intensity of the PL peak decreases and the magnetic increment reduces in our samples. The correlation between the PL peak intensity and ferromagnetism of the samples is discussed in combination with the experimental results.

Keywords: GaMnN, photoluminescence, magnetism, metal–organic chemical vapor deposition

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1. Introduction

Research on diluted magnetic semiconductors (DMSs), especially GaMnN, has received much attention due to their potential for the integration of photonic, electronic, and magnetic devices on a single chip.[1] Some properties such as the nature of the electronic states and the light emission mechanism are essential for electro–optical properties and spintronic devices. In this aspect, the most relevant and significant issue is the natural state of the Mn doped into GaN. Successful growth of GaMnN films has been used to obtain important information about the position of Mn levels in GaN by optical absorption, cathodoluminescence, photoconductivity spectrum, etc.[1–8] Graf *et al*. thought that the level at 1.42 eV is the internal absorption between the $^5T_2$ and ^5E levels of the Mn^{3+} (d^4) state for the GaMnN grown by molecular beam epitaxy (MBE).[2] Korortov *et al*. indicated that Mn forms a deep acceptor level close to $E_\mathrm{v} + 1.4$ eV in a GaMnN film grown by metal–organic vapor phase epitaxy (MVOPE).[4] The sharp photoluminescence peaks located at 1.6 eV and 1.8 eV are assigned to excited state $^4T_1$ to defect and $^4T_2$ to defect of Mn^{2+}, respectively.[5] An absorption peak with an onset at 2.0 eV is also reported in Ref. [3], but its assignment and other properties are not discussed. A similar feature above 1.8 eV related to a transition from the valence band (VB) is observed by photoconductivity and optical absorption studies,[2,8] but seldom detected in photoluminescence (PL), not even at Mn concentrations below 1%. In addition, most of these studies focused on optical properties; correlation between optical and magnetic properties for GaMnN films has been rarely investigated, especially for GaMnN films grown by metal–organic chemical vapor deposition (MOCVD).

PL measurement is a standard optical characterization technique for probing the electronic structure, the light emission mechanism, etc. In the present paper, we investigate the GaMnN films grown by MOCVD, and all the samples have well established magnetic properties. There were no interesting experimental results for the above band gap excitation in previous PL measurements. Now, to excite the Mn band, the GaMnN films are excited using a mid-gap excitation wavelength of 405 nm.

2. Experimental procedure

The samples examined here were prepared by MOCVD. The details of the growth conditions have been presented elsewhere.[9] Trimethylgallium (TMGa) and ammonia were used as gallium and nitrogen sources. Bis(monomethycyclopentadienyl) manganese ((MCp)2Mn) was used as a dopant source during the growth of GaMnN layers. The Mn concentration of the GaMnN film was controlled by varying the ratio between the molar flow rates of Mn and Ga flowing into the reactor. In this paper, three samples named A, B, and C were fabricated at doping content x values of 0.75%, 1.8%, and 2.0%, respectively. X-ray analysis showed that no second-phase-related Mn was observed

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in any of the samples.[9] The results of magnetic properties and Raman measurements have been already published in Refs. [9] and [10]. In short, these measurements indicated that the samples remained ferromagnetic at 300 K and were still long-range lattice ordered and symmetric after Mn doping into GaN, identifying that Mn occupied the Ga site in GaMnN samples. PL measurement was carried out using a semiconductor laser with an excitation wavelength of 405 nm. The maximum output power of the laser was 250 mW; the excitation density was 320 mW/cm^2. The laser beam was focused on the samples with a beam size of about 500 μm in diameter. The wavelength of the monochromator was calibrated by measuring mercury lamp spectra. A silicon photodiode was used to detect the signal. The diagram of the PL experiment set-up is shown in Fig. 1.

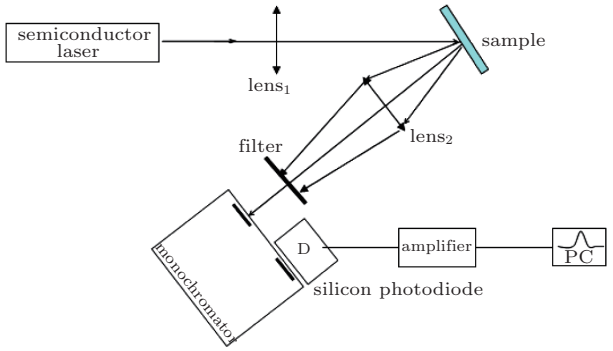


Fig. 1. (color online) Diagram of PL experiment set-up.

3. Results and discussion

The normalized PL spectra of GaMnN samples with different Mn concentrations at room temperature are shown in Fig. 2. A yellow luminescence (YL) band around 450 nm–600 nm[11–13] is observed in all samples, where the peak is situated near 540 nm (2.3 eV). The intensity of the YL bands reduces with increasing Mn concentration. A sharp peak around 695 nm (1.8 eV) is visible on the lower energy side in each of the three samples. Their intensities decrease systematically with increasing Mn concentration, but without shifting their positions.

According to our previous first-principles calculations[14,15] and the *ab initio* calculation by using the local spin density approximation in Ref. [16], the crystal field of the lattice splits the fivefold degenerate d shell of Mn into doublet e and pseudotriplet t_2 states. Both the e and t_2 states of the Mn acceptor level are within the band gap of GaN. In an intrinsic GaMnN sample, the Mn ion has d^4 (Mn^{3+}) configuration, with two electrons in the e and two electrons in the t_2 state, respectively, and E_F is located within the t_2 state of the Mn^{3+} level, which is partially filled and offers the required holes to mediate ferromagnetism. In the present paper, the observed sharp PL peak at 1.8 eV is attributed to the recombination of electrons in the t_2 state of the neutral Mn^{3+} acceptor with holes in the valence band (VB), for the following reasons: (i) the intensity of the 1.8 eV PL peak decreases with increasing Mn concentration, indicating it is are Mn related; (ii) Mn^{3+} (d^4) was observed by the X-ray absorption spectrum of synchrotron radiation in our GaMnN films;[17] (iii) the energy required for a charge transfer at the $Mn^{3+/2+}$ levels was estimated in earlier studies[18–20] and the estimated energy position of the Mn^{3+} acceptor of 1.8 eV is consistent with our PL measurement result; (iv) the photoconductivity spectra exhibit a photoionization shoulder with the onset at 1.8 eV, which was understood as hole emission from the Mn acceptor into VB,[8] which can further explain our attribution. Based on the above points, the PL spectral peak position, and Ref. [21], we obtain our attribution for the 1.8 eV PL peak in our samples. Although the luminescence peak at this position was believed to come from sapphire substrate,[22,23] previous photoconductivity and optical absorption studies reported in Refs. [2], [8], and [9] and our PL measurement here all show that the 1.8-eV peak is related to Mn content.

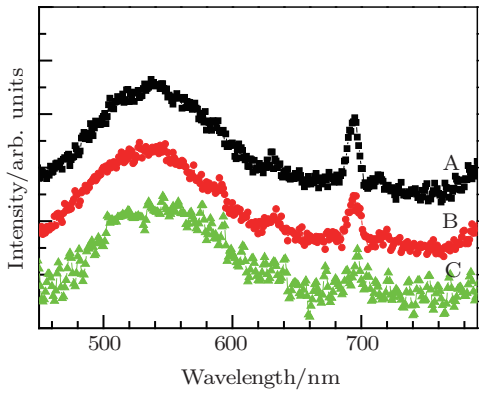


Fig. 2. (color online) Room temperature PL spectra of GaMnN with different Mn content values.

Under laser excitation at 405 nm, an electron from the VB is moved to the t_2 state of the Mn level and then can relax to the VB, thereby emitting a photon at 1.8 eV. As shown in Fig. 2, the PL intensities of samples A, B, and C successively decrease with increasing Mn concentration. The Mn concentration of sample A is below 1% ($[Mn]_A = 0.75\%$) but its intensity is stronger than those of B and C. At an appropriate Mn concentration, E_F is located in the t_2 state of the Mn^{3+} level. The partially filled t_2 state gives a higher PL intensity at 1.8 eV. With the addition of Mn, the intensity of 1.8-eV PL peaks decreases in each of the samples, presumably due to the introduction of donor-like intrinsic defects such as nitrogen vacancies (V_N). The increase of Mn concentration and the presence of defects both change the position of E_F and thus the charge state of Mn. Our previous studies indicated that the V_N concentration would increase with increasing Mn concentration in our samples.[24] Thus, V_N increases with increasing Mn

concentration in GaN, and as it is donor-like, V_N can raise the E_F toward the conduction band, and lead to the t_2 state tending to be filled. A tendency to fill the t_2 state of Mn^{3+} will prevent an electron from being moved from the VB to the t_2 state under laser excitation at 405 nm, and the PL intensity at 1.80 eV is reduced. Our calculations demonstrate that V_N can induce the antiferromagnetic (AFM) coupling and reduce the ferromagnetism (FM), because $\Delta E_{GaMnN:V_N} < 0$ (ΔE is the total energy difference between AFM and FM of GaMnN:V_N).[15] In addition, due to E_F moving up, the electrons will move to the Mn level and cause Mn^{3+} (d^4) to transform into Mn^{2+} (d^5). This transformation induces the Mn^{3+} concentration ratio to decrease. So a reduced intensity of the 1.8-eV PL peak is observed with increasing Mn concentration. Because of the transformation between Mn^{3+} and Mn^{2+}, they should be coexistent in the present GaMnN samples. Based on the double exchange mechanism, a large proportion of Mn^{3+} transforming into Mn^{2+} reduces the magnetic correlation of the Mn atom and leads to the reduction of ferromagnetism in the materials. So the reduced intensity of the 1.8-eV PL peak indicates a decrease of Mn^{3+} concentration ratio, as well as a magnetic increment decrease with increasing Mn concentration in our samples. The reduced increment of saturation magnetization with increasing Mn concentration was also found in our earlier work.[15]

4. Conclusions

MOCVD grown ferromagnetic GaMnN films are studied by PL measurement with a mid-gap excitation wavelength of 405 nm. In addition to the YL band, a sharp PL peak at 1.8 eV is also observed in each of the samples. The normalized intensity of this PL peak decreases with increasing Mn concentration. The PL peak is attributed to the recombination of electrons in the t_2 state of the neutral Mn^{3+} acceptor with holes in the VB. Sample A ([Mn]$<$ 1%) exhibits the strongest emission at 1.8 eV in all the samples. With increasing Mn concentration and introducing V_N, E_F shifts towards the conduction band and then Mn^{3+} transforms into Mn^{2+}; therefore, the intensity of the 1.8-eV PL peak decreases and the magnetic increment reduces in our samples. At an optimum optimal Mn concentration, E_F is in the t_2 state of the Mn^{3+} level, which maximizes the PL intensity of the 1.80-eV peak. Deviation from the optimum Mn concentration raises E_F, and then the t_2 state tends to be filled, thereby reducing the PL intensity of the 1.80-eV peak and the ferromagnetism of the GaMnN film. Hence, the intensity of the 1.8-eV PL peak is correlated with the Mn^{3+} concentration ratio and the ferromagnetism of the GaMnN film. The influence of V_N on the magnetism of the film is one of the reasons for obtaining high quality GaMnN, which should be taken into consideration.

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