The properties of GaMnN films grown by metalorganic chemical vapour deposition using Raman spectroscopy*

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An investigation of room-temperature Raman scattering is carried out on ferromagnetic semiconductor GaMnN films grown by metalorganic chemical vapour deposition with different Mn content values. New bands around 300 and 669 cm^{-1}, that are not observed in undoped GaN, are found. They are assigned to disorder-activated mode and local vibration mode (LVM), respectively. After annealing, the intensity ratio between the LVM and E_2(high) mode, i.e., $I_{LVM}/I_{E_2(high)}$, increases. The LO phonon-plasmon coupled (LOPC) mode is found in GaMnN, and the frequency of the LOPC mode of GaMnN shifting toward higher side is observed with the increase in the Mn doping in GaN. The ferromagnetic character and the carrier density of our GaMnN sample are discussed.

Keywords: diluted magnetic semiconductor, metalorganic chemical vapour deposition, Raman scattering

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1. Introduction

To introduce an additional degree of freedom into the next generation of electronic devices, great efforts have been made to develop operating ferromagnetic semiconductors with a Curie temperature (T_c) above room temperature. Gallium nitride has potential applications in electronic and optoelectronic devices, such as light emitting diodes and blue laser diodes.[1−3] In addition, the theoretical predictions have shown that it may be possible for GaN doped with Mn to realize ferromagnetism at room temperature or higher. Therefore, GaMnN may be one diluted magnetic semiconductor (DMS) candidate for practical applications. Its room-temperature ferromagnetism has been achieved by a number of different methods, such as ion implantation,[4,5] molecular beam epitaxy (MBE),[6] and metalorganic chemical vapour deposition (MOCVD).[7] However, the experimental results have shown significant discrepancies and the magnetic origin is still unclear. Therefore, an extensive study and further analysis of the layer are required before high-quality and efficient spintronic devices are launched commercially.

It is important to investigate the vibronic properties to understand the change in the material property of GaMnN and the magnetic origin behind Mn-doped GaN. Nondestructive characterization such as Raman scattering is a convenient way to study the vibronic properties of films.[8−11] In the early stages, many groups found that the Raman spectra of GaMnN were quite different,[12−16] and the interpretation of the difference is also controversial. As an optimal technique for growing high-quality III-nitrides, MOCVD is a desirable method to produce room-temperature ferromagnetic GaMnN. However, few reports on the Raman spectra of GaMnN film grown by MOCVD can be found. In the present paper, the Raman spectra for a series of GaMnN samples with different Mn concentrations grown by MOCVD are investigated.

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2. Experimental procedure

The samples examined here were prepared by MOCVD. Details of the growth conditions have been presented elsewhere.[17] In the present paper, four samples named A, B, C, and D were fabricated with a doping content value of 0.0%, 1.5%, 1.8%, and 2.0%, respectively. The qualities of all the samples were studied by a high-resolution x-ray diffraction diffractometer. Except for the peaks corresponding to GaN and sapphire, no second phase related to Mn was observed for Mn-doped GaN film in the ω–2θ scan curves.[17] The micro-Raman scattering experiments were carried out in a backscattering geometry of $z(x,-)z$ configuration, with a 514.5 nm argon laser used as the excitation light source. The spectral resolution was better than 1 cm^{-1} in a spectral range from 50 to 9000 cm^{-1}. A suitable notch filter was used to reduce the Rayleigh scattering light, and the slit width was reduced to about 100 μm to prevent background noise.

3. Results and discussion

Figure 1 shows the Raman spectra of the GaN and GaMnN samples with different Mn concentrations at room temperature. The spectra are normalized by the peak intensity of the E_2(high) phonon mode at 568.5 cm^{-1}, and shifted toward the vertical direction for comparison. The Raman peak of the undoped GaN sample located at 144, 568.5, and 733 cm^{-1} correspond to the E_2(low), E_2(high), and A_1(LO) phonon modes, respectively, while the peak at 416 cm^{-1} comes from the sapphire substrate. Weak bands are visible at 380, 430, and 449 cm^{-1}, and a shoulder peak at 750 cm^{-1}, is observed at the high-energy part of A_1(LO). Compared with the case of the undoped GaN sample, expect for the characteristic features of E_2(low), E_2(high), and A_1(LO) of GaN that remain there, some other new bands show up in the GaMnN sample. First, new bands around 300 and 669 cm^{-1} are observed. Moreover, the intensities of the two bands increase with Mn content without the shift of their positions. Second, the A_1(LO) mode becomes strongly asymmetric broadening towards lower frequency with increasing Mn content. In addition, weak bands are also visible at 380, 416, 430, and 449 cm^{-1}, and a shoulder peak at 750 cm^{-1} is also observed at a higher frequency of A_1(LO), but their intensities and peak positions do not change with Mn content.

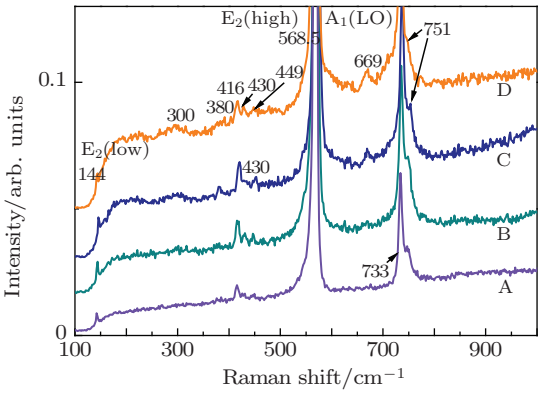


Fig. 1. (colour online) The Raman spectra of GaMnN with different Mn concentrations at room temperature.

The new band near 300 cm^{-1} arises from the disorder-activated mode.[12,13,18] We agree on the interpretation of this band, and think that it is the characteristic feature of GaMnN, which is caused by lattice disordering after Mn-doped GaN. The observed 669 cm^{-1} mode is assigned to the local vibration mode (LVM) by occupying the Ga site with Mn. This is due to the following reasons. First, the intensity of the peak at 669 cm^{-1} increases with Mn content. Second, no additional peaks from the Mn-related secondary phases or impurities are observed for Mn-doped GaN films in the ω–2θ scan curves.[17] This result indicates that the GaMnN sample is of single phase, which is associated with the previous result (as shown in Fig. 2),[19] and Mn is shown to occupy the Ga site in the GaMnN sample. Third, GaMnN films are still long-rang lattice ordered and symmetric after Mn-doped GaN because the characteristic modes of GaN remain in GaMnN. Fourth, GaMnN samples are rapidly annealed at 600 °C for 30 min in a flowing N_2 gas, and then their Raman spectra are measured. The changes in the E_2(high) and 669 cm^{-1} of GaMnN before and after annealing were observed. For comparison, the Raman spectra of annealed and unannealed GaMnN are also displayed in Fig. 3. In order to see this clearly, only the higher doped GaMnN (sample D) is shown in Fig. 3.

The intensity of the peak at 669 cm^{-1} is found to be sharp and increase after annealing, and the relative intensity ratios between LVM (669 cm^{-1}) and E_2(high), i.e., $I_{\mathrm{LVM}}/I_{\mathrm{E_2(high)}}$ are 0.013 and 0.02 before and after annealing, respectively. The increase of

$I_{\mathrm{LVM}}/I_{\mathrm{E_2(high)}}$ implies that the crystalline quality of GaMnN is improved after annealing, and the LVM can be enhanced after annealing due to the substitution of incorporated Mn for Ga. For these reasons, the band at 669 cm^{-1} relates to the LVM, which is due to the substitution of Mn for Ga in the GaN lattice.

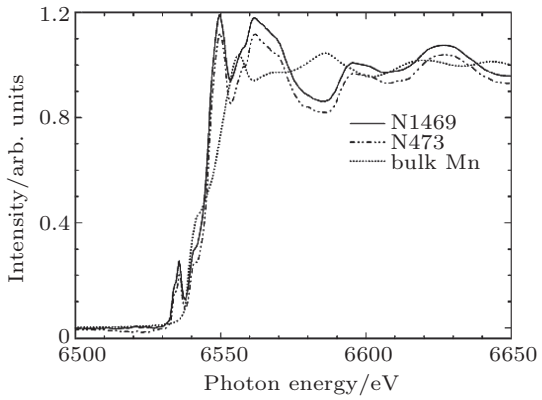


Fig. 2. Experimental X-ray absorption near-edge structure (XANES) spectra of the GaMnN samples called N1469 and N1473 in Ref. [19]. The pre-edge peaks at 6535.6 eV indicate that Mn atoms can replace Ga atoms in the samples.

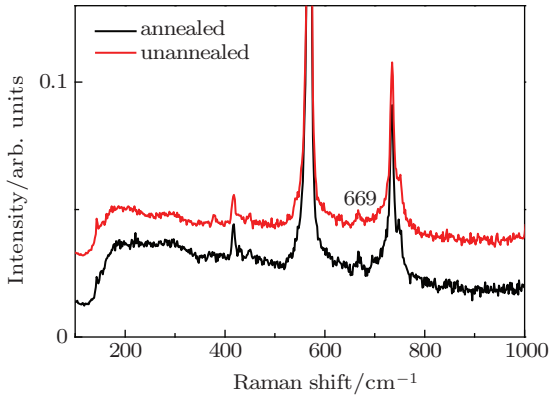


Fig. 3. (colour online) (colour online) The Raman spectra of annealed and unannealed GaMnN (sample D).

Raman spectroscopy is an alternative technique for estimating the free carrier density in lattices.[20,21] The principle is detailed as follows. Free carriers in semiconductors generate a collection of electronic excitations called plasmons. Plasmons interact with the A_1(LO) mode, resulting in the LOPC mode.[22] The frequencies of the LOPC mode shift toward higher frequency side with the increase in the carrier density in the layer. In Fig. 1, the A_1(LO) mode is broadened and its frequency shifts toward the high-frequency side with the increase in the amount of Mn doping in the GaN layer, which indicates the presence of the LOPC mode. Figure 4 demonstrates the interaction of fore-side plasmons with the A_1(LO) mode to develop into the LOPC mode in respect of the Mn doping content in the GaN. The frequencies of the LOPC mode of GaMnN shifting toward the high-frequency side is observed with the increase in the amount of Mn doping in the GaN. Thus, the result is probably caused by the increase in the carrier density in our GaMnN sample with the increase of the Mn content in the GaN. Asghar *et al.*,[23] Li and Lu,[24] and Cheng *et al.*[25] also observed the LOPC mode in their Raman scattering measurements. Moreover, Asghar *et al.*,[23] and Li and Lu[24] estimated the free carrier densities of their samples. The carrier density in the magnetic semiconductor directly relates to the ferromagnetic character of the material.[26] Accordingly, we can estimate that the ferromagnetic character of our GaMnN sample is improved with the increase of the Mn content in the GaN. The result is in agreement with our previous magnetic measurement.[17]

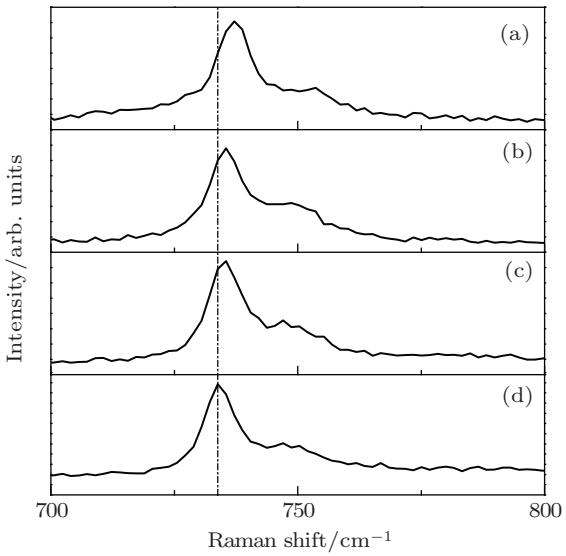


Fig. 4. Raman shift due to increasing interaction between the LO phonon and plasmon excitations with respect to the Mn content in GaN films for sample (a) D, (b) C, (c) B, and (d) A.

The additional Raman peaks at 380, 430, 449 cm^{-1}, and the shoulder peak at 750 cm^{-1} originate from the sapphire substrate. Harima[14] reported similar Raman peaks at 418 and 751 cm^{-1}, which are considered to come from the sapphire substrate. Islam *et al.*[27] reported that the 450 cm^{-1} mode was not observed in Mn–ion implantation GaMnN samples before rapid thermal annealing, but it was observed after annealing (see Fig. 1 in Ref. [27]). Islam

et al. also found that the vibrational mode may relate to interstitial defects or vacancy-related defects in the GaN matrix, which can occur in their sample, owing to the implantation of Mn ions with high energy. The D and C samples in the present study were annealed under the same condition as that in Ref. [27] and the Raman spectra were measured at room temperature. The mode at 449 cm^{-1} was observed before and after annealing. In addition, the undoped GaN is rapidly annealed separately at 600°C and 900 °C. It can be clearly seen from Fig. 5 that for the GaN and GaMnN samples, the 449 cm^{-1} mode is observed at room temperature. Figure 6 shows the Raman spectrum of the sapphire substrate, and the 449 cm^{-1} mode can also be observed. Therefore, the 449 cm^{-1} mode originates from the sapphire substrate, but neither from interstitial defects nor from the vacancy-related defect in the GaN matrix. In addition, peaks at 380, 416, 430, and 751 cm^{-1} can be seen clearly in Fig. 6.

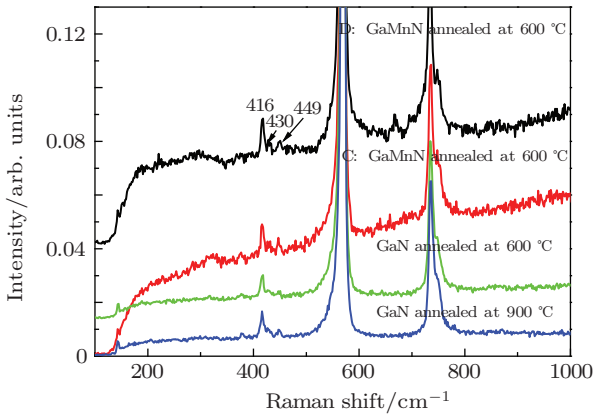


Fig. 5. (colour online) The Raman spectra for GaN and GaMnN (D,C) after being annealed at room temperature.

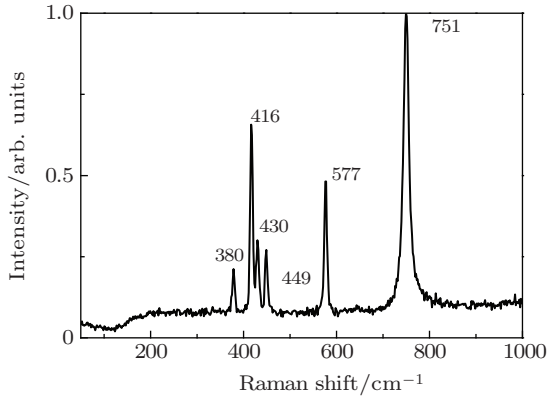


Fig. 6. The Raman spectrum for Al_2O_3 at room temperature.

4. Conclusions

In this paper, room-temperature Raman scattering is performed on ferromagnetic semiconductor GaMnN grown by MOCVD with different values of Mn content. In addition to the characteristic modes of GaN, new bands around 300 and 669 cm^{-1} are observed. The disorder-activated mode and local vibration mode by occupying the Ga site with Mn are responsible for the new Raman bands observed in GaMnN, respectively. After annealing, the LVM can be enhanced, and the intensity ratio between the LVM (669 cm^{-1}) and the E_2(high) mode, i.e., $I_{LVM}/I_{E_2(high)}$, increases. The LOPC mode is found in GaMnN, and the frequencies of the LOPC mode shift toward higher-frequency side with the increase in the Mn doping content in the GaN. Accordingly, we estimate that the carrier density in our GaMnN samples and the ferromagnetic character of GaMnN increase with the Mn doping content in the GaN. In addition, through annealing and Raman scattering, we find that the 449 cm^{-1} mode originates from the sapphire substrate, but neither from interstitial defects nor from vacancy-related defects in the GaN matrix, as reported by Islam.

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