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Study of (Ga, Mn)N prepared by Mn-ion implantation using optical techniques*

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This paper reports that (Ga, Mn)N is prepared using implantation of 3at.% Mn Ions into undoped GaN. Structural characterization of the crystals was performed using x-ray diffraction(XRD). Detailed XRD measurements have revealed the characteristic of Mn-ion implanted GaN with a small contribution of other compounds. With Raman spectroscopy measurements, the spectra corresponding to the intrinsic GaN layers demonstrate three Raman active excitations at 747, 733 and 566 cm^{-1} identified as $E_1(\mathrm{LO})$, $A_1(\mathrm{LO})$ and E_2^H, respectively. The Mn-doped GaN layers exhibit additional excitations at 182, 288, 650–725, 363, 506 cm^{-1} and the vicinity of E_2^H mode. The modes observed at 182, 288, 650–725 cm^{-1} are assigned to macroscopic disorder or vacancy-related defects caused by Mn-ion implantation. Other new phonon modes are assigned to Mn_x-N_y, Ga_x-Mn_y modes and the local vibrational mode of Mn atoms in the (Ga, Mn)N, which are in fair agreement with the standard theoretical results.

Keywords: Mn-ion implantation GaN, diluted magnetic semiconductors, Raman spectroscopy, x-ray diffraction

PACC: 7550P, 6170T, 6110, 7830

1. Introduction

In recent years, III–V diluted magnetic semiconductors (DMSs) have attracted much attention as the materials to be applied in spintronic devices. Ferromagnetism has been discovered in InMnAs[1] and GaMnAs.[2−4] However, the highest Curie temperature $T_\mathrm{C} = 61\,\mathrm{K}$ and 173 K,[5] obtained for these materials by heavy p-type doping is still far from room temperature demanded by commercial applications. In the area of DMSs related to III–V compound semiconductors, wide bandgap semiconductor GaN has very recently received great interest as promising host material for making DMSs, since theoretical studies predict that its Curie temperature (T_c) is higher than room temperature.[6] This allows spintronic devices to operate at room temperature. GaN-based DMSs materials can be fabricated by molecular beam epitaxy (MBE), metal organic chemical vapour deposition (MOCVD) or ion implantation. A major obstacle to form III–V magnetic semiconductors has been the low solubility of magnetic elements (e.g. Mn) in these compounds. Because the magnetic intensity is roughly proportional to the concentration of the magnetic elements, no significant changes in the magnetic properties can be observed if the doping level is around $10^{18}\,\mathrm{cm}^{-3}$, which is the upper limit of the dopant solubility in the materials.[6] It is well known that ion implantation has many advantages including independent control of the doping level, selective area doping, and the ability to fabricate planar devices and self aligned structures without any limitation of solubility. Although some experimental studies on the magnetic characteristics of GaN-based DMSs have been reported,[7−13] many fundamental properties, especially the magnetic ion related properties, about (Ga, Mn)N are still not clear and required to be investigated further. For our knowledge, few report of Roman scattering study on (Ga, Mn)N prepared by Mn-ion implantation with different post-annealing temperatures, especially the magnetic Mn-ion related Roman behaviour, has been found in the literature up to now. It is, therefore, very important to investigate the vibrational properties for understanding the change in material properties of (Ga, Mn)N after Mn-ion implantation with different post-annealing tem-

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peratures.

In this paper, we have presented Raman results obtained from the (Ga, Mn)N prepared by Mn-ion implantation GaN with different post-annealing temperature. Energy dispersive x-ray (EDX) was performed to monitor the compositional properties of the samples. Detailed XRD measurements have revealed the characteristic of Mn-ion implanted GaN at various annealing temperatures.

2. Sample preparation

The GaN samples were grown by MOCVD on sapphire substrates. GaN buffer of 25 nm was grown firstly at a substrate temperature of 540°C, followed by 3 μm epitaxial growth of undoped GaN at ∼950°C. Mn-ions were implanted at an energy of 300 keV and doses of 4.67×10^{16} cm^{-2} to produce average volume concentrations about 3 at.% in the top 300nm of the GaN. After the implantation of Mn ions, the samples were annealed at 700°C, 800°C, 900°C for 5 min and at 1050°Cfor 2min in the ambience flowing N_2 gas with the samples face down on GaN wafers.

Raman scattering experiments were performed at room temperature in the backscattering configuration by employing the 514.5 nm line of an argon-ion laser. The laser beam was focused and then the scattered light was collected with a 50× objective lens. The scattered light was dispersed with a Renishaw-RM2000 model spectrometer and detected with a CCD detector. EDX was performed to monitor the compositional properties of the samples. The XRD measurements were used to investigate the existence of secondary phases as well as the structural changes.

3. Result and discussion

Figure 1 shows an EDX spectrum of the as-implanted (Ga, Mn)N layer formed by Mn ions implantation into the undoped GaN epilayer. The well resolved x-ray fluorescences of Ga, N, Mn, and O elements are observed clearly, and the fraction of Mn is determined to be approximately 3 at.%.

The crystalline structure can be studied by means of XRD. Figure 2 shows XRD profiles of the as-grown sample and Mn-implanted GaN samples with various annealing temperatures. The as-grown samples show only the GaN and Al_2O_3 peak. However, after Mn

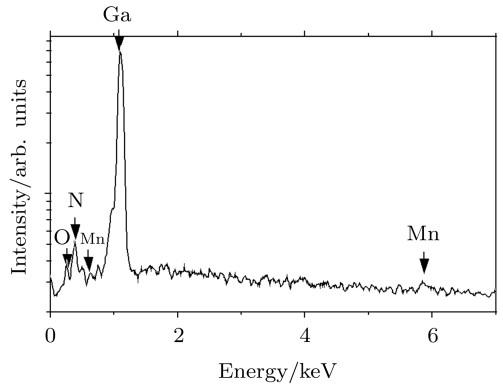


Fig.1. EDX spectrum of Mn Ions implanted GaN.

ions implantation, GaN peak and Al_2O_3 peak are decreased because of the crystal damage due to implantation. After annealing in the temperature higher than 700°C, as shown in Fig.2, the sample shows the recovered crystal property. And also, additional peak at P1(48°) appears. After annealing at 900 and 1050°C, another new peak at P2(39°) is observed. Both these two peaks are associated with the Mn occupying the Ga site or the Ga-Mn phases and the Mn-N compounds.

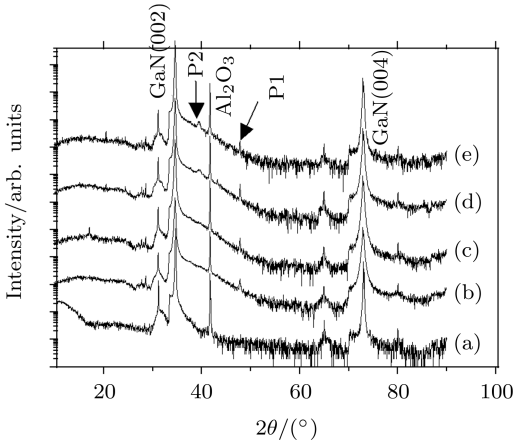


Fig.2. XRD profiles for (a) as-grown GaN and Mn-implanted GaN annealed at (b) 700, (c) 800, (d) 900, (e) 1050°C.

In order to obtain further information about the samples of Mn-implanted into the GaN crystal layer, Raman scattering experiments were carried out. Figure 3 shows Raman spectra for the Mn-implanted GaN samples with different annealing temperatures. For the as-grown sample, as shown in Fig.3(a), the A_1(LO) (733 cm^{-1}), E_1(LO) (747 cm^{-1}), and E_2^H (566 cm^{-1}) are observed as expected from the Raman selection rules in wurtzite GaN films.[14] The peak at 416 cm^{-1} stems from the sapphire substrate. For the Mn-implanted sample shown in Fig.3(b), the intensities

of the A_1(LO), E_1(LO), and E_2^H modes decrease and several weak peaks occur at 182, 288, 650–725 cm^{-1}. But the intensities of the A_1(LO), E_1(LO), and E_2^H increase with annealing temperature, and the intensities of the modes at 182, 288, 650–725 cm^{-1} decrease. In particular, a high temperature annealing higher than 800°C leads a drastic decrease in intensities for these modes. This means that such modes are independent of the local vibrations of Mn impurities. Therefore, we believe that these modes at 182, 288, 650–725 cm^{-1} originated from the macroscopic disorder or vacancy-related defects due to the Mn implantation. After annealing at 700°C, new peaks at 363 and 506 cm^{-1} appear. These peaks become obvious after annealing at 800°C. The origination for the new peaks at 363 and 506 cm^{-1} will be discussed later. Another significant feature of Raman scattering from the present Mn doped GaN layers is the appearance of left and right shoulders (S_L, S_R) around E_2^H (in Fig.3). In order to understand the shoulders around E_2^H, Lorentzian-shaped distribution function is useful for resolving multi-peaks. The results of the decomposition are displayed in Fig.4, and we can see at least two peaks constituting each shoulder S_L and S_R at frequency positions (a: 543 cm^{-1}, b: 553 cm^{-1}) and (c: 576 cm^{-1}, d: 588 cm^{-1}) respectively. Its positions are different from the lattice damage induced by doping in the GaN system.[15,16]. Hence, it is thus surmised that two peaks constituting each shoulder (S_L, S_R) around E_2^H may be correlated with Mn. The reduced mass model gives us a rough estimate of the local vibrational mode (LVM) of Mn atoms in GaN:[17,18]

$$\frac{\omega_{\mathrm{GaN}}}{\omega_{\mathrm{LVM}}} \approx \sqrt{\frac{\mu_{\mathrm{LVM}}}{\mu_{\mathrm{GaN}}}}.$$

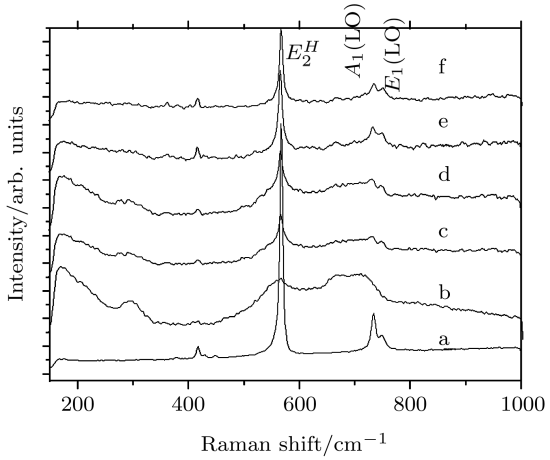


Fig.3. Raman spectra for (a) as-grown GaN, (b) as implanted GaN and annealed at (c) 700, (d) 800, (e) 900, (f) 1050°C.

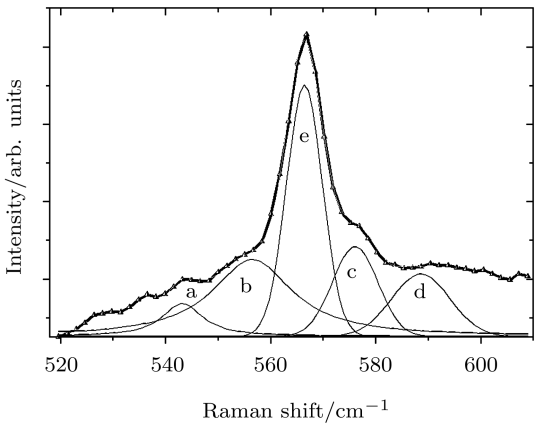


Fig.4. Extended view of the typical experimental data from the annealed (Ga, Mn)N. Shoulders around E_2^H are decomposed using Lorentzian fit. The four component excitations (curves: a, b, c, d) may be due to the LVM of different Mn_xN_y localized structure and the LVM of Mn atoms in the (Ga, Mn)N.

Using GaN, E_2^H (569 cm^{-1})[14] phonon frequency ω_{GaN} with consideration of the reduced mass (μ) difference between the Ga–N and Mn_x–N_y compound, we find that two peaks (a: 543, b: 553 cm^{-1}) in the S_L and other peak (d: 588 cm^{-1}) in the S_R might be related with the LVM of Mn_4N, Mn_2N, and $Mn_2N_{0.86}$ localized structures, respectively. Considering that (Ga, Mn)N should show both GaN- and MnN-like phonon modes, we find that the peak at 576 cm^{-1} should be the LVM of Mn atoms in the (Ga, Mn)N. Although we can not directly observe Raman peak related to (Ga, Mn)N, nevertheless, the reported result indirectly supports our viewpoint that the appearance of additional peaks in the Raman spectra are reasonable, originated from the LVM of Mn occupying the Ga site. Using the same formula, we find that the excitations at 363 and 506 cm^{-1} might be related with the LVM of Ga_x–Mn_y.

4. Conclusion

The structural and optical properties of Mn-ion implanted GaN have been investigated. From XRD measurements, the samples display the characteristic of Mn-ion implanted GaN with a contribution of the Mn occupying the Ga site or the Ga–Mn phases and the Mn-N compounds, and the crystalline quality of Mn-ion implanted GaN has been improved after annealing. Micro-Raman spectra have been performed on (Ga, Mn)N prepared by the Mn ion implantation with different post-annealing temperature. Raman results obtained from the annealed and unannealed

(Ga, Mn)N also demonstrate that crystalline quality of (Ga, Mn)N has been improved after annealing. In addition to GaN like phonon modes, the most significant features of Raman scattering from the present Mn doped GaN layers, are some new phonon modes at 182, 288, 650–725, 363, 506 cm^{-1} and the appearance of left and right shoulders (S_L, S_R) around E_2^H. The excitations at 363 and 506 cm^{-1} is believed to originate from the LVM of Ga_x-Mn_y and the modes observed at 182, 288, 650–725 cm^{-1} are assigned to macroscopic disorder or vacancy-related defects. By applying Lorentzian-shaped distribution function useful for multi-peaks, we can see that there are at least two peaks constituting each shoulder S_L and S_R at frequency positions (a: 543 cm^{-1}, b: 556 cm^{-1} and c: 576 cm^{-1}, d: 588 cm^{-1}) respectively. Using the reduced mass model, we find that the phonon modes at 543 cm^{-1}, 556 cm^{-1}, and 588 cm^{-1} are related with the Mn-related LVM and assigned to the LVM of different Mn_xN_y localized structure. Considering that (Ga, Mn)N should show both GaN- and MnN-like phonon modes and using the same formula, we assign the peak at 576 cm^{-1} to the LVM of Mn atoms in the (Ga, Mn)N.

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