INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S5811–S5814 PII: S0953-8984(04)79480-1

Optical studies on GaN-based spintronics materials

N Hasuike[1], **H Fukumura**[1], **H Harima**[1], **K Kisoda**[2], **M Hashimoto**[3], **Y K Zhou**[3] **and H Asahi**[3]

[1] Department of Electronics and Information Science, Kyoto Institute of Technology, Kyoto 606-8585, Japan
[2] Department of Physics, Wakayama University, Wakayama 640-8510, Japan
[3] Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

Received 17 April 2004
Published 19 November 2004
Online at stacks.iop.org/JPhysCM/16/S5811
doi:10.1088/0953-8984/16/48/054

Abstract

Structural properties of GaN layers doped with magnetic impurities (Mn, Cr) were investigated by Raman scattering. In the case of Mn-doping, an impurity mode was observed at around 585 cm^{-1} with concentrations of Mn up to 1–2%. This mode was assigned to a local vibrational mode of Mn substituting the Ga site, and interpreted as spectral evidence of a uniform solid solution in the samples. For Cr-doping, good crystalline quality was also confirmed up to [Cr] = 3–5%. Cr is more miscible in GaN than Mn. Resonance enhancement of LO phonon signal was observed in GaCrN layers when excited by a deep UV laser at 266 nm (4.7 eV). This indicates generation of photo-carriers.

1. Introduction

GaN doped with dilute magnetic impurities is an attractive candidate for future 'spintronics' devices based on carrier-induced ferromagnetism [1, 2]. Great difficulties lie, however, in growing high quality samples because of the low miscibility of magnetic elements. This is the main reason for conflicting experimental results on ferromagnetism [3, 4], and makes it indispensable to precisely investigate the structural properties of each sample. In this work, Raman scattering characterization was performed on $Ga_{1-x}Mn_xN$ and $Ga_{1-x}Cr_xN$ epitaxial layers with $x < 12\%$ to focus on the miscibility of magnetic elements and their local atomic arrangements.

2. Experiment

The samples had structures of $Ga_{1-x}Mn_xN$ (200 nm)/GaN (200 nm)/GaN (buffer)/sapphire (0001) and $Ga_{1-x}Cr_xN$ (500 nm)/GaN (20 nm)/GaN (buffer)/sapphire (0001). The top layers were grown by molecular beam epitaxy (MBE) at 750–850 °C and 620 °C, respectively. NH_3 gas was used as the nitrogen source. The conductivity was n-type for both samples according

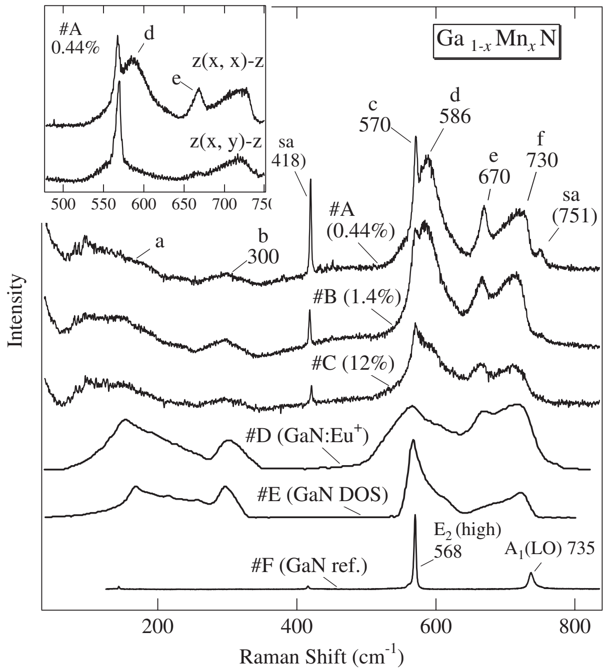

Figure 1. Raman spectra of $Ga_{1-x}Mn_xN$ with $x = 0.44$–12% (#A–#C). Typical spectra of a high quality GaN (#F) and an ion-implanted one (#D), and a calculated phonon DOS (#E) [7] are also shown for comparison. The inset shows a polarized spectra of sample #A.

to a photo-voltaic effect. Further details are described elsewhere [5, 6]. Raman scattering was observed at room temperature by a confocal microscope in backscattering geometry using Ar ion laser at 514.5 nm and fourth harmonics of a YAG laser at 266 nm, and a double monochromator of focal length 85 cm equipped with a liquid-N_2-cooled CCD (charge coupled device) detector. The concentration of magnetic elements was evaluated by electron probe micro-analysis (EPMA).

3. Results and discussion

Figure 1 shows Raman spectra for $Ga_{1-x}Mn_xN$ with $x = 0.44\%$ (#A), 1.2% (#B) and 12% (#C). For comparison, figure 1 includes typical spectra of a high quality GaN (#F) and an ion-implanted GaN (#D), and a calculated phonon DOS (density of states) (#E) [7]. The inset shows a polarized spectra of #A. An x-ray diffraction (XRD) analysis showed that there was no phase separation for #A and #B, while #C showed some secondary phase components due to unassigned precipitates [5]. The spectra #A to #C commonly show signals of the GaMnN layer at 100–200 cm^{-1} (a), 300 cm^{-1} (b), 580–600 cm^{-1} (d), 670 cm^{-1} (e) and 730 cm^{-1} (f). In addition to these signals, sharp phonon signals appear from the underlying GaN layer (c) and the sapphire substrate (sa), which become stronger as the GaMnN layer becomes more transparent from #C to #A. The spectral features (a), (b) and (f) are well reproduced in the ion-implanted sample and resemble the phonon DOS profile. They are defect-induced signals observed when a crystal loses long-range lattice ordering and the Raman selection rule is relaxed. These signals show, therefore, no clear polarization dependence. On the contrary, the peaks (d) and (e) are unique; unlike the defect-induced signals, these two components become well defined or sharp when the Mn content is small, i.e. the sample is less defective. Furthermore, they show clear

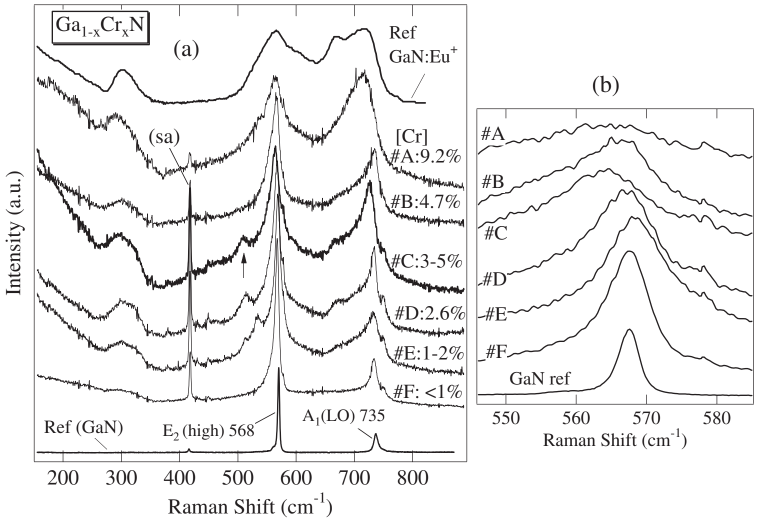

Figure 2. (a) Raman spectra of $Ga_{1-x}Cr_xN$ with $x = 0$–9.2% (#A–#F) with typical spectra of a high quality GaN (bottom) and an ion-implanted one (top) [7] for comparison, and (b) close-up of the E_2 phonon mode.

polarization dependence, as seen in the inset, where $z(x, y) - z$ and $z(x, x) - z$ mean crossed and parallel polarization, respectively, in backscattering geometry from the c-plane. The sharp peak (e) has been assigned as a vacancy-related local vibrational mode (LVM) of the host lattice, and can be observed in parallel polarization [8]. Here we assign the other one, newly observed peak (d), to the LVM of Mn occupying the Ga site because of the following reasons: first, the peak frequency ($\sim$586 cm^{-1}) is close to that of the LVM roughly estimated using the GaN E_2 (high) phonon frequency with consideration of the reduced-mass difference between the Ga–N and Mn–N pairs, i.e. $\omega_{Mn-N} \sim \omega_{Ga-N}[\mu_{Ga-N}/\mu_{Mn-N}]^{1/2} = 582$ cm^{-1}. Second, as shown in the inset, (d) disappears in crossed polarization geometry, which is consistent with the local symmetry around the Mn ion occupying the Ga site (T_d or, more precisely, C_{3v}, if c-axis anisotropy is included) [9]. Recalling that #A and #B showed no precipitation according to XRD, we may conclude that the sharp LVM signal at 586 cm^{-1} is a measure of uniform solid solutions of GaMnN where Mn occupies the Ga site.

A separate experiment on magnetization properties revealed that the non-phase-separated sample (#B) was mainly paramagnetic, while the phase-separated one (#C) was dominated by ferromagnetism at low temperature, which was ascribed to Mn-based precipitates [5].

In figure 2(a), Raman spectra of $Ga_{1-x}Cr_xN$ with $x = 0$–9.2% are shown as #A–#F together with typical spectra of a high quality GaN (bottom) and an ion-implanted GaN (top) [7] for comparison. Figure 2(b) shows a close-up of the E_2 phonon mode. It is easily observed that the E_2 (high) phonon mode is sharply peaked at $x = 0$–3% (#F–#D), but clearly broadened at above 3–5% (#C, #B and #A). The total spectrum of #A in figure 2(a) resembles well that of ion-implanted sample (top), indicating that the long-range lattice ordering is lost. The A_1 (LO) mode at 735 cm^{-1} is also sharp at $x = 0$–3%. We found by a separate polarization experiment that these two phonon modes satisfied well Raman selection rules for wurtzite symmetry at low Cr concentrations.

Figure 2(b) shows furthermore that the E_2 peak gradually shifts to higher frequency with increasing x from 0 to 3% (from #F to #D), while some sudden change occurs at higher x values (#C–#A). Our XRD characterization (θ–2θ scan) showed a well-correlated result with this Raman scattering observation, i.e. the diffraction angle of the GaN(0002) peak gradually increased with increasing x from 0 to 3%, indicating a monotonous decrease in the c-axis lattice constant. The increase in phonon frequency from #F to #D in figure 2(b) means that lattice shrinkage also occurs in the c-plane. We have found by extended x-ray absorption fine structure (EXAFS) that the nearest neighbour of Cr is N at $x <\sim 3\%$. Thus, our results indicate that substitution of Cr to the Ga site happens smoothly at low Cr concentrations, resulting in lattice shrinkage. We consider that this lattice shrinkage increases the lattice distortion energy, and at $x = 3$–5% leads to some local structure re-arrangement as seen in figure 2, #C to #A. Our Raman spectra clearly show, however, that the wurtzite host-lattice structure is well retained in the whole tested range $x = 0$–9.2% with no clear indication of phase transition or secondary phases.

An impurity mode is observed at around 510 cm^{-1} (arrow in figure 2(a)). This mode appears at $x = 1$–2% (#E) and enhances in intensity with x up to 3–5% (#C). Since it showed clear polarization property suggesting T_d or C_{3v} symmetry, it may be attributed to Cr-related LVM. Another impurity mode is observed at #E at around 530 cm^{-1}, but not yet assigned.

In a separate Raman scattering experiment on $Ga_{1-x}Cr_xN$, by using a deep UV laser source at 266 nm (=4.7 eV), we observed a clear enhancement of LO-phonon intensity at $x = 0$–5%. This is due to a resonance Raman effect induced by photo-excitation of free carriers. This suggests a well-defined band structure of the samples, and we think that the generation of photo-carriers may open the way to verify the possibility of carrier-induced ferromagnetism by pure optical means.

4. Conclusion

In GaMnN layers, the formation of a uniform solid solution as ternary alloy was confirmed at [Mn] $<\sim 2\%$. The samples showed a local vibrational mode at 585 cm^{-1}, which was attributed to Mn substituting the Ga site. For larger Mn concentrations, Raman spectra showed deterioration in long-range lattice ordering.

Good crystallinity was also observed in GaCrN layers doped by [Cr]<3–5%. They showed resonance enhancement of LO-phonon signals when excited by a UV laser at 266 nm (4.7 eV). This is a clear indication of the photo-injection of free carriers to a diluted magnetic semiconductor.

Acknowledgments

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT), through MEXT Special Coordination Funds for Promoting Science and Technology (Nanospintronics Design and Realization, NDR).

References

[1] Dietl T, Ohno H, Matsukura F, Cibèrt J and Ferrand D 2000 *Science* **287** 1019
[2] Sato K and Katayama-Yoshida H 2000 *Japan. J. Appl. Phys.* **39** L555
[3] Sonoda S, Shimizu S, Sasaki T, Yamamoto H and Hori H 2002 *J. Cryst. Growth* **237–239** 1358
[4] Das G P, Rao B K and Jena P 2003 *Phys. Rev.* B **40** L724
[5] Hashimoto M, Zhou Y K, Tampo H, Kanamura M and Asahi H 2003 *J. Cryst. Growth* **252** 499
[6] Hashimoto M, Zhou Y K, Kanamura M, Katayama-Yoshida H and Asahi H 2003 *J. Cryst. Growth* **251** 327
[7] Davydov V Yu, Kitaev Yu E, Goncharuk I N, Smirnov A N, Graul J, Semchinova O, Uffmann D and Evarestov R A 1998 *Phys. Rev.* B **58** 12899
[8] Limmer W, Ritter W, Sauer R, Mensching B, Liu C and Rauschenbach B 1998 *Appl. Phys. Lett.* **72** 2589
[9] Brandt M S, Ager J W III, Göez W, Johnson N M, Harris J S Jr, Molnar R J and Moustakas T D 1994 *Phys. Rev.* B **49** 14758