

Optical studies of MOCVD-grown GaN-based ferromagnetic semiconductor epilayers and devices

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Ga_{1-x}Mn_xN epilayers and p-i-n device structures have been grown by metalorganic chemical vapor deposition. Optical studies were found to investigate the role of Mn concentration and the role of different codopants to elucidate the origin of the room temperature ferromagnetism in Ga_{1-x}Mn_xN epilayers. Increasing Mn concentration was found to significantly affect long-range lattice ordering. This observation was supported by the existence of a disorder-induced Raman mode at 300 cm⁻¹ and local vibrational modes (LVMs) at 669 cm⁻¹ that has been attributed to the formation of self-compensating nitrogen. The E₁(TO) phonon frequency was found to linearly increase with Mn composition, which is expressed by (558 + 2.7x) cm⁻¹. The intensity and the linewidth of an absorption band near 1.5 eV was found to increase with Mn concentration, and is assigned to the e to t₂ transition in the split ⁵T₂ band of Mn³⁺. No absorption was detected in Si co-doped Ga_{1-x}Mn_xN. In this case, a significantly increased EPR signal of Mn²⁺ ions confirmed the trapping of electrons provided by the shallow Si donor and reduced the available states for ferromagnetic exchange. A change in the measured magnetization is observed under ultraviolet illumination, though the nature of this phenomenon is still not understood.

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1 Introduction

Wide-bandgap diluted magnetic semiconductors have been considered attractive candidate materials for spintronics based on theoretical predictions of ferromagnetism (FM) at room temperature [1]. These predictions of FM are based on observations in Ga_{1-x}Mn_xAs, where long range ferromagnetic coupling between the dilute magnetic centers within the semiconductor lattice is mediated by holes introduced by shallow Mn acceptors. This model may not hold in Ga_{1-x}Mn_xN as substitutional Mn is a deep trap compared to shallow acceptor in Ga_{1-x}Mn_xAs [2]; nevertheless there are several reports of room temperature FM in this system [3–5]. Double exchange d-d exchange interactions have also been suggested to stabilize FM in the nitrides, though this interaction is typically short-ranged and should not lead to FM above 100 K [6]. Moreover, the low solid Mn_{Ga} solubility in Ga_{1-x}Mn_xN has led to the assertion that all of the observed ferromagnetic behaviour is due to secondary phases [7]. Also, spintronic devices in the nitrides

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have not been demonstrated, largely because the FM nature of the alloy is still not universally understood. In this work, optical studies have been used to explore these issues in $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ layers and initial devices have been produced by metalorganic chemical vapor deposition (MOCVD).

2 Experimental

$\text{Ga}_{1-x}\text{Mn}_x\text{N}$ films were grown on 2" sapphire (0001) substrates with GaN templates in a highly-modified commercial rotating-disk reactor with a short jar configuration and specially designed reactant injection system. Details of the growth process are described in more detail elsewhere [5]. Subsequent characterization included high-resolution X-ray diffraction (Philips X'Pert Pro Diffractometer), Raman spectroscopy (Renishaw micro-Raman system with a 488 nm excitation source), room temperature magnetometry (Lakeshore 7404 Vibrating Sample Magnetometer), and infrared reflectance (Perkin-Elmer system 2000 Fourier Transform Infrared spectrometer). Magneto-transmission experiments at 1.7 K up to 7-T were performed using lock-in techniques using circularly polarized light from a 250 W tungsten lamp in combination with a RG9 filter. Transmitted light was detected by a Ge photomultiplier.

3 Results

The optimally grown Mn epilayers were specular and had a reddish color that increased in intensity with the thickness of the Mn layer, consistent with incorporation of substitutional Mn in the GaN layers. X-ray diffraction revealed good crystalline quality of the epilayer with no evidence of secondary phases. Hall measurements are consistent with the conclusion that Mn is a deep center, as the measured Hall concentration tracks with any underlying GaN layer. When only Mn containing layers are grown with no GaN templates, the sample becomes too resistive to measure via standard techniques and the contact resistances increase several orders of magnitude. The magnetic properties of the as-grown layers are discussed in more detail elsewhere [5, 8]. Optimally grown layers exhibited magnetic hysteresis at room temperature, and a large decrease in the strength of the magnetization is observed with either silicon co-doping or annealing. The average contribution from the individual Mn atoms decreases with increasing Mn incorporation. This is expected in the context of an impurity band model and recent reports on heavy doping, where a significant conversion from Mn^{3+} to Mn^{2+} at high Mn doping has been reported [9]. This indicates a transfer of the Fermi level out of an impurity band that could stabilize the FM in this system.

Figure 1 shows Raman spectra for the as-grown $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ samples. The spectra are dominated by the GaN $E_2(\text{high})$ mode at 569 cm^{-1} . Other Raman modes from the host GaN lattice were detected at 735 cm^{-1} , 560 cm^{-1} , and 533 cm^{-1} , the $A_1(\text{LO})$, $E_1(\text{TO})$ and $A_1(\text{TO})$ modes, respectively. The presence of a strong $A_1(\text{LO})$ mode confirms the absence of free carriers [10].

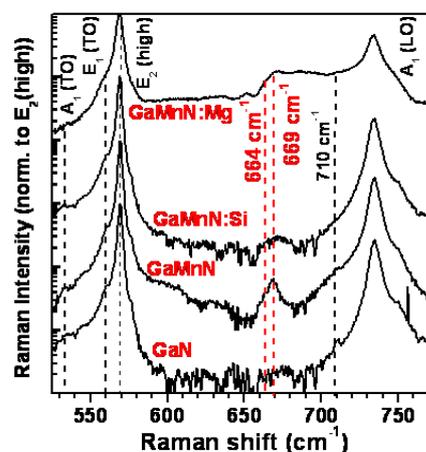


Fig. 1 Raman spectra of $\text{Ga}_{0.985}\text{Mn}_{0.015}\text{N}$ with and without Mg and Si codoping. Note the sensitivity of the vacancy-induced LVM at 669 cm^{-1} on co-doping.

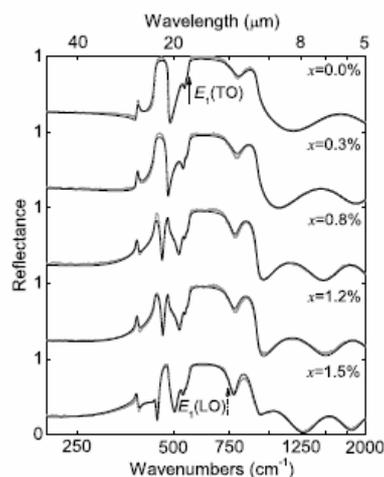


Fig. 2 Infrared reflectance spectra with increasing Mn doping used for analysis of $E_1(\text{TO})$ and $E_1(\text{LO})$ modes.

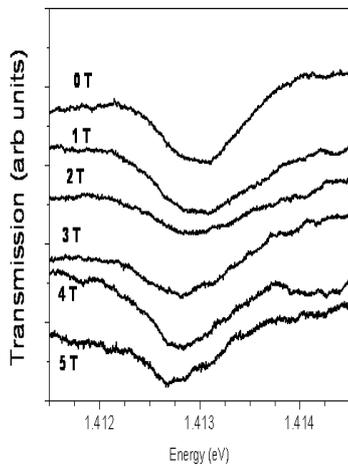


Fig. 3 Transmission spectra as a function of magnetic field at 2 K near the Mn^{3+} d-d transition at 1.413 eV for $\text{Ga}_{0.985}\text{Mn}_{0.015}\text{N}$.

there is a broadening in the $E_1(\text{TO})$ mode from 5.0 to 9.6 cm^{-1} . This suggests that the Mn alloying reduces the bonding forces in the GaN alloy and weakens the translational symmetry, which is consistent with the vacancy formation observed in the Raman spectra.

Optical transmission studies allow for the exploration of the Mn valence state of the material through monitoring the relative intensity of a d-d transition near 1.41 eV [13]. It is an indication of Mn^{3+} character within the sample because this transition requires a partially filled level in order for a spin-conservation during the transition. Figure 3 shows the optical transmission at 2 K for $\text{Ga}_{0.985}\text{Mn}_{0.015}\text{N}$. The peak absorption shifts to lower energies with increasing magnetic field. The zero phonon line of the Mn transition is observed at 1.413 eV broadens with increasing Mn concentration as expected. In samples with Si codoping, this line is not observed. This observation is coincident with the appearance of a strong Mn^{2+} signal via electron paramagnetic resonance, as well as the disappearance of a ferromagnetic magnetization signal. Transmission measurements showed little or no difference to the degree of circular polarization of the incident light.

GaN-based p-i-n structures with Mn integrated into the intrinsic region have been grown to further investigate the fundamental properties of $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ layers. Mn-doped layers of 50 to 200 nm at ap-

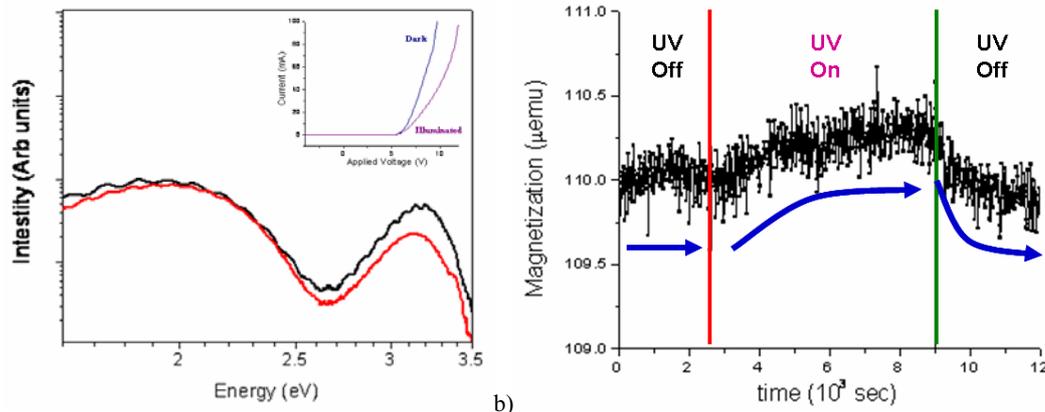


Fig. 4 a) Electroluminescence spectra of two p-i-n diodes with $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ of varying thickness in the active region. The inset shows the light and dark I-V characteristics. b) Measured VSM magnetization for 200 nm thick $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ ($x = 0.015$) layer with and without illumination from the unfiltered radiation of a UV lamp.

The predominant feature with increasing Mn incorporation is a Raman mode near 669 cm^{-1} , which has been attributed to local vibrational modes (LVM) due to vacancies [11]. A weaker intensity is seen in this mode with co-doping with silicon. The intensity is roughly the same in Mg co-doped $\text{Ga}_{1-x}\text{Mn}_x\text{N}$, though there is also an increase in the background signal as seen in Fig. 1a. This suggests that based on doping and formation energy considerations [12], that the 669 cm^{-1} mode is related to nitrogen vacancies, and that donor compensation is significant in the as-grown and Mg co-doped $\text{Ga}_{1-x}\text{Mn}_x\text{N}$. Electronically, the shallow donor nitrogen vacancies are over-compensated by the deep Mn acceptors, leading to semi-insulating material.

Infrared reflection studies were used to examine the $E_1(\text{TO})$ phonon mode, which is not allowed in the Raman back-scattering configuration, Fig. 2. This mode shifts slightly to higher energies with increasing Mn concentration, from a value of 558 cm^{-1} to 561 cm^{-1} at $x = 0.015$. In contrast, the $E_1(\text{LO})$ mode show a slight decrease in the position with increasing concentration. Moreover, with increasing Mn doping,

proximately 1% Mn doping were grown on n-doped GaN layers and subsequently capped with 200 nm p-GaN. The devices were then fabricated into diode structures using standard lithographic techniques used for GaN light emitting diodes. I-V characteristics of the device structures clearly show rectifying behavior as shown in the inset of Fig. 4a. The turn-on voltage and resistance of the devices increases with increasing Mn thickness as would be expected from the highly resistive nature of these centers. Figure 4a shows the electroluminescence (EL) behavior of a sample device. The EL spectra is dominated by two peaks – one at 3.4 eV which is due to the bandedge recombination, and another of approximately equal in magnitude at around 2.1 eV due to Mn-induced defect related emission. A similar emission spectrum has recently been reported in $\text{Al}_{1-x}\text{Mn}_x\text{N}$ devices [14]. The intensity of the near-bandedge emission is several orders of magnitude lower than that of a typical GaN p-i-n LED structure, and visibly, the Mn-containing emitters are yellow-orange compared to blue.

Another feature of $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ which has not been observed to date in $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ is that of optically induced magnetization effects. By controlling the polarization of light near the band edge in $\text{Ga}_{1-x}\text{Mn}_x\text{As}$, carriers can be excited in sufficient quantities to result in an observed FM signal [15]. Optically induced magnetization will take on a different character due to the deeper nature of the d-state related impurity band in $\text{Ga}_{1-x}\text{Mn}_x\text{N}$. In order to study effects of a population of the band, vibrating sample magnetometry (VSM) measurements were taken before and during excitation with the unfiltered, unpolarized light of an ultraviolet lamp, as shown in Figure 4b. After illumination under the UV light, a rise in the measured magnetization can be seen. The effect is slight, less the 0.5% of the total magnetic signal as would be expected from the relative intensity of the source relative to the population of the traps. The signal was above the inherent noise of the measurement and reversible when the illumination is removed. Investigations are underway to explore the spectral, radiant intensity and polarization dependence of this phenomenon and to eliminate the possibility of any contribution from charging, heating, or other potential measurement-dependent effects.

4 Conclusion

Optical studies were performed on MOCVD-grown $\text{Ga}_{1-x}\text{Mn}_x\text{N}$ exhibiting room temperature ferromagnetism and showed a weakening of the lattice with Mn incorporation, resulting in a tendency towards forming nitrogen vacancies in as-grown material. Mn^{3+} character was observed via EPR and optical transmission measurements in samples with strong magnetic character, indicating the importance of valance state and compensation control for achieve strong ferromagnetic signatures in the nitrides.

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