

## Effects of hydrogen incorporation in GaMnN

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Single-phase (Ga,Mn)N layers grown by molecular beam epitaxy with  $\sim 3$  at. % Mn were exposed to  $^2\text{H}$  or  $^1\text{H}$  plasmas under conditions designed to permeate layers with hydrogen. No evidence of the formation of Mn–H complexes could be detected from either infrared spectroscopy or the changes in magnetic properties. However, the residual magnetization increased  $\sim 20\%$  after hydrogenation, consistent with passivation of crystal defects in (Ga,Mn)N. Hydrogenation may be an attractive method for improving the magnetic properties of these heteroepitaxial materials. © 2003 American Institute of Physics. [DOI: 10.1063/1.1637151]

(Ga,Mn)N is one of the most promising candidates for realization of a room temperature ferromagnetic semiconductor. Numerous groups have reported on the magnetic properties of GaN doped with Mn during epitaxial or bulk growth or by doping after growth by direct implantation or diffusion.<sup>1–16</sup> Depending on the synthesis conditions, it appears possible to prepare single-phase (Ga,M)N with Mn concentrations of a few atomic percent. The origin of the ferromagnetism is somewhat controversial, with the contribution of phases such as Ga–Mn or  $\text{Mn}_x\text{N}_y$  compounds apparent in some cases.<sup>5,17</sup> In addition, the free carrier concentration in most (Ga,Mn)N does not appear to be high enough for conventional carrier-induced ferromagnetic coupling between the Mn ions and the deep nature of the Mn acceptor level ( $E_V + 1.4$  eV) precludes it contributing a significant number of free holes at normal temperatures.<sup>18</sup> Recent theories suggest that at percolation limits, localized holes near the magnetic impurity are polarized and the energy of the system is lowered when the polarization of the localized holes is parallel and therefore ferromagnetism is possible in insulating or low carrier density materials.<sup>19,20</sup>

The effects of atomic hydrogen on the magnetic properties of (Ga,Mn)N is of interest since potentially it could have a large influence if it were to passivate the deep Mn acceptors.<sup>21,22</sup> In addition, the hydrogen may passivate crystalline point and line defects that would otherwise degrade the magnetization. In this letter we demonstrate that hydrogen does not form a detectable concentration of (Mn–H)<sup>0</sup> complexes in *n*-type (Ga,Mn)N, but that there is an increase in the magnetization from the material upon hydrogenation.

The *n*-type ( $n \sim 5 \times 10^{16} \text{ cm}^{-3}$ ) (Ga,Mn)N was grown by plasma-assisted molecular beam epitaxy on undoped 3  $\mu\text{m}$  thick GaN buffer layers grown by metalorganic chemical vapor deposition on *c*-plane  $\text{Al}_2\text{O}_3$  substrates. The (Ga,Mn)N

layer thickness was  $\sim 0.15 \mu\text{m}$  and the Mn content was  $\sim 3$  at. % as determined by Auger electron spectroscopy. The as-grown samples showed clear hysteresis at 300 K with coercivities of 52–85 Oe and residual magnetization of  $\sim 1.6$  emu/g at this temperature. Both x-ray diffraction and high resolution transmission electron microscopy showed the material was single phase within the resolution of these techniques. The samples were exposed to  $^2\text{H}$  or  $^1\text{H}$  plasmas for periods of 0.5–3 h at 250 °C in a rf (13.56 MHz) reactor operating at 300 mTorr pressure and 100 W forward power. Depth profiling of  $^2\text{H}$ ,  $^1\text{H}$  and Mn was performed with secondary ion mass spectroscopy (SIMS) measurements in a Cameca system using 14.5 keV  $\text{Cs}^+$  beams for  $^2\text{H}$  and 3 keV  $\text{O}^{2+}$  beams for Mn. Infrared spectra were measured with a Bonem DA3 spectrometer equipped with a KBr beamsplitter and InSb detector. The samples were cooled to 4.2 K in an Air Products helium cryostat. Magnetic properties were measured in a superconducting quantum interference device (SQUID) magnetometer. Three samples of each type were measured in the SQUID to check the reproducibility of the results and one sample of each type was remeasured for a similar reason. In each case, the magnetization was the same to within  $\pm 5\%$ .

To calibrate the incorporation depth of  $^2\text{H}$  and  $^1\text{H}$  in (Ga,Mn)N, SIMS measurements were performed on a sample exposed to either of these plasmas for 30 min at 250 °C in the case of  $^2\text{H}$  and 1 h in the case of  $^1\text{H}$ . Figure 1 shows both the  $^2\text{H}$  and  $^1\text{H}$  depth profiles, demonstrating that both readily diffuse into the material. Note that the diffusivity ( $D$ ) of  $^1\text{H}$  will be  $\sqrt{2}$  times faster than for  $^2\text{H}$ , through the relation for isotopic diffusion,

$$\frac{D(^1\text{H})}{D(^2\text{H})} = \left[ \frac{M(^2\text{H})}{M(^1\text{H})} \right]^{0.5},$$

where  $M$  represents the atomic mass. The results in Fig. 1 are evidence that hydrogen and deuterium are not trapped to any

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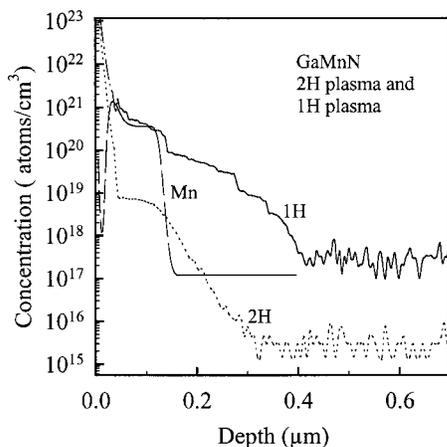


FIG. 1. SIMS depth profile of  $^2\text{H}$ ,  $^1\text{H}$  and Mn in a (Ga,Mn)N sample exposed to  $^2\text{H}$  plasma for 30 min at 250 °C or to  $^1\text{H}$  plasma for 1 h.

marked extent by the Mn, since the profile shapes are consistent with the bulk of the hydrogen and deuterium diffusing in the absence of significant trapping.<sup>23</sup> To ensure complete permeation of the hydrogen through the Mn-doped region in the samples, we used 3 hour plasma exposures of  $^2\text{H}$  for subsequent IR and magnetic characterization.

In order to achieve the highest sensitivity in the IR absorption measurements, two samples were used to produce the differential spectrum shown in Fig. 2. One of the (Ga,Mn)N samples was treated in a  $^1\text{H}$  plasma and the second reference was treated in a  $^2\text{H}$  plasma. Figure 2 presents the difference between the two samples, with positive peaks those that were stronger in the  $^1\text{H}$  plasma treated sample and negative peaks those that were stronger in the  $^2\text{H}$ -treated sample. No new  $^2\text{H}$  or  $^1\text{H}$  lines were detected over the range of 1700–4000  $\text{cm}^{-1}$ , with the lines at 2340 and 3200  $\text{cm}^{-1}$  due to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  frozen onto the (Ga,Mn)N surfaces and the three lines near 2900  $\text{cm}^{-1}$  due to oil vapor in the spectrometer vacuum. Clearly, no Mn–H lines were detected within the sensitivity of the IR measurements, and if these were present they would be easily observable under our conditions. The charge state of hydrogen in *n*-type GaN is not firmly established, but one can speculate on the basis of other semiconductors that it might be in a negative charge state

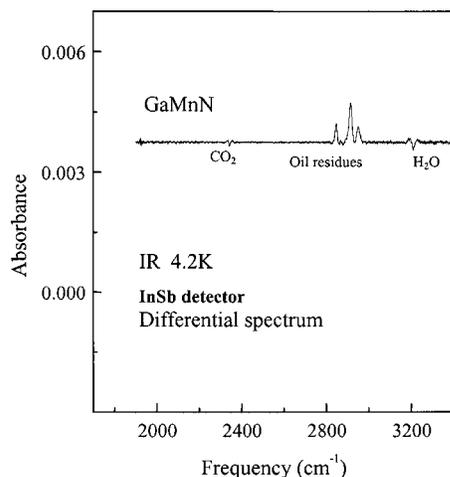


FIG. 2. Differential IR spectrum of (Ga,Mn)N hydrogenated or deuterated for 3 h at 250 °C.

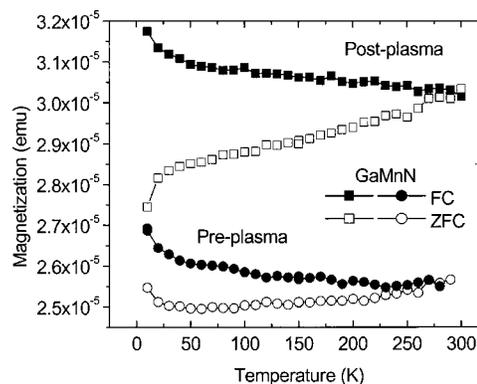


FIG. 3. Temperature dependence of FC and ZFC magnetization of (Ga,Mn)N before and after hydrogenation for 3 h at 250 °C. The results for deuteration under the same conditions were the same within experimental error ( $\pm 5\%$ ).

and formation of complexes with Mn acceptors would be unfavorable.<sup>20,21</sup> The vertical electron mobility in the layers, measured from the reverse saturation current in mesa Schottky diodes,<sup>24</sup> increased from 840 to 903  $\text{cm}^2/\text{V s}$  after hydrogenation, which is consistent with a reduction in scattering by charged defects.

Figure 3 shows field-cooled (FC) and zero field-cooled (ZFC) magnetization as a function of the temperature for the (Ga,Mn)N before and after  $^1\text{H}$  plasma hydrogenation for 3 h at 250 °C. The overall magnetization increases  $\sim 20\%$  upon hydrogenation and this is much larger than the uncertainty in the measurement ( $\pm 5\%$ ). Similar results were obtained for the 2 h exposed samples. The data are also clear evidence that Mn is not passivated nor does it form complexes with hydrogen or else the change in unpaired spin density would be expected to have a profound effect on the magnetic properties. The results are consistent with hydrogen passivation of point and/or line defects that would otherwise degrade the magnetization. The much lower density of these defects relative to the atomic percent levels of Mn means they escape detection in the IR. Numerous reports have shown that the residual magnetization of (Ga,Mn)N is a strong function of the crystal quality and can be significantly increased when the material is grown on high quality, thick GaN layers compared to direct growth on sapphire substrates.<sup>1,2,4,15</sup>

In summary, hydrogen plasma exposure of (Ga,Mn)N produces an increase of  $\sim 20\%$  in residual magnetization. No evidence of the formation of Mn–H complexes is found in *n*-type (Ga,Mn)N. The results are consistent with hydrogen passivation of defects in the material that otherwise degrade the magnetic properties. Similar experiments should be performed in *p*-type (Ga,Mn)N where hydrogen may be in a positive charge state. In this context, the recent successful synthesis of *p*-type InMnAs with room temperature ferromagnetism<sup>25,26</sup> may provide another materials platform for examining the effects of hydrogen in dilute magnetic semiconductors.

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- <sup>1</sup>G. T. Thaler, M. E. Overberg, B. Gila, R. Frazier, C. R. Abernathy, S. J. Pearton, J. S. Lee, Y. D. Park, Z. G. Khim, J. Kim, and F. Ren, *Appl. Phys. Lett.* **80**, 3964 (2002).
- <sup>2</sup>K. H. Kim, K. J. Lee, D. J. Kim, H. J. Kim, Y. E. Ihm, D. Djayaprawira, M. Takahashi, C. S. Kim, C. G. Kim, and S. H. Yoo, *Appl. Phys. Lett.* **82**, 1775 (2003).
- <sup>3</sup>N. Theodoropoulou, A. F. Hebard, M. E. Overberg, C. R. Abernathy, S. J. Pearton, S. N. G. Chu, and R. G. Wilson, *Appl. Phys. Lett.* **78**, 3475 (2001).
- <sup>4</sup>M. E. Overberg, C. R. Abernathy, S. J. Pearton, N. Theodoropoulou, K. T. McCarthy, and A. F. Hebard, *Appl. Phys. Lett.* **79**, 1312 (2001).
- <sup>5</sup>S. Dhar, O. Brandt, A. Trampert, L. Daweritz, K. J. Friedland, K. H. Ploog, J. Keller, B. Beschoten, and G. Guntherodt, *Appl. Phys. Lett.* **82**, 2077 (2003).
- <sup>6</sup>H. Hori, S. Sonoda, T. Sasaki, Y. Yamamoto, S. Shimizu, K. Suga, and K. Kindo, *Physica B* **324**, 142 (2002).
- <sup>7</sup>S. J. Pearton, C. R. Abernathy, M. E. Overberg, G. T. Thaler, D. P. Norton, N. Theodoropoulou, A. F. Hebard, Y. D. Park, F. Ren, J. Kim, and L. A. Boatner, *J. Appl. Phys.* **93**, 1 (2003).
- <sup>8</sup>M. C. Park, K. S. Huh, J. M. Myoung, J. M. Lee, J. Y. Chang, K. I. Lee, S. H. Han, and W. Y. Lee, *Solid State Commun.* **124**, 11 (2002).
- <sup>9</sup>M. Sato, H. Tanaka, K. Kato, T. Sasaki, Y. Yamamoto, S. Sonoda, S. Shimiyu, and H. Hori, *Jpn. J. Appl. Phys., Part 1* **41**, 4513 (2002).
- <sup>10</sup>M. Hashimoto, Y. K. Zhou, H. Tampo, M. Kanamura, and H. Asahi, *J. Cryst. Growth* **252**, 499 (2003).
- <sup>11</sup>J. Y. Chang, G. H. Kim, J. M. Lee, S. H. Han, H. J. Kim, W. Y. Lee, M. H. Ham, K. S. Huh, and J. M. Myoung, *J. Appl. Phys.* **93**, 7858 (2003).
- <sup>12</sup>S. E. Park, H.-J. Lee, Y. C. Cho, S.-Y. Jeong, C. R. Cho, and S. Cho, *Appl. Phys. Lett.* **80**, 4187 (2002).
- <sup>13</sup>S. J. Pearton, C. R. Abernathy, D. P. Norton, A. F. Hebard, Y. D. Park, L. A. Boatner, and J. D. Budai, *Mater. Sci. Eng., R.* **40**, 137 (2003).
- <sup>14</sup>J. M. Baik, H. W. Jang, J. K. Kim, and J.-M. Lee, *Appl. Phys. Lett.* **82**, 583 (2003).
- <sup>15</sup>Y. Shon, Y. H. Kwon, S. U. Yuldashev, Y. S. Park, D. J. Fu, D. Y. Kim, H. S. Kim, and T. W. Kang, *J. Appl. Phys.* **93**, 1546 (2003).
- <sup>16</sup>M. L. Reed, N. A. El-Masry, H. Stadelmaier, M. E. Ritums, N. J. Reed, C. A. Parker, J. C. Roberts, and S. M. Bedair, *Appl. Phys. Lett.* **79**, 3473 (2001).
- <sup>17</sup>B. K. Rao and A. Jena, *Phys. Rev. Lett.* **89**, 185504 (2002).
- <sup>18</sup>R. Y. Korotkov, J. M. Gregie, and B. W. Wessels, *Physica B* **308**, 30 (2001).
- <sup>19</sup>M. Berciu and R. N. Bhatt, *Phys. Rev. Lett.* **87**, 107203 (2001).
- <sup>20</sup>V. K. Dugaev, V. I. Litvinov, J. Barnas, and M. Viera, *Phys. Rev. B* **67**, 033201 (2003).
- <sup>21</sup>S. K. Estreicher, *Acta Phys. Pol. A* **102**, 517 (2002).
- <sup>22</sup>S. K. Estreicher, *Mater. Sci. Eng., R.* **14**, 319 (1995).
- <sup>23</sup>D. A. Tulchinsky, J. W. Corbett, J. T. Borenstein, and S. J. Pearton, *Phys. Rev. B* **42**, 11881 (1990).
- <sup>24</sup>J. Kim, F. Ren, G. T. Thaler, R. Frazier, C. R. Abernathy, S. J. Pearton, J. M. Zavada, and R. G. Wilson, *Appl. Phys. Lett.* **82**, 1565 (2003).
- <sup>25</sup>A. J. Blattner and B. W. Wessels, *Appl. Surf. Sci.* (in press).
- <sup>26</sup>A. J. Blattner, P. L. Prabhurashi, V. P. Dravid, and B. W. Wessels, *J. Cryst. Growth* (in press).