Transition metal ion implantation into AlGaN

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n- and p-type Al$_x$Ga$_{1-x}$N ($x = 0.38$ for n-type, $x = 0.13$ for p-type) layers grown on Al$_2$O$_3$ substrates were ion implanted with the transition metals Mn, Cr, and Co at high concentrations (peak doping levels ~3 at. %). After implantation and annealing at 1000 °C, only impurity transitions at ~2.9 and 3.9 eV and no band-edge photoluminescence could be observed in all the samples. X-ray diffraction did not detect any peaks associated with second phase formation. Room-temperature hysteresis loops were obtained for Co-implanted n-type AlGaN, while there was no convincing evidence for ferromagnetism in the Mn- or Cr-implanted n-AlGaN. By sharp contrast, Mn implantation in p-AlGaN did produce ferromagnetic behavior and 300 K hysteresis. Both carrier type and crystalline quality can influence the resulting magnetic properties. © 2003 American Institute of Physics. [DOI: 10.1063/1.1613375]

INTRODUCTION

Very few studies of the properties of ion-implanted AlGaN have been reported, even though the GaN/AlGaN heterostructure is a key component of devices such as high electron mobility transistors, UV lasers, light-emitting diodes, and solar blind UV photodetectors. There is interest in the use of transition metal doped semiconductors is proportional to the band gap of the material. Accordingly, GaN has been a focus of attention above room temperature. In this regard, theoretical predictions suggest that the Curie temperature in transition metal doped semiconductors is proportional to the band gap of the material. Accordingly, GaN has been a focus of attention in this regard, with the transition metals introduced during epitaxial or bulk growth or postgrowth by implantation or diffusion. The use of ion implantation allows for rapid screening of the effectiveness of different transition metal elements in producing ferromagnetic behavior. The properties of implanted transition metals in AlGaN are of particular relevance for realization of polarized light emitters or spin transistors since they could serve as the cladding layer in the former and the wide-band-gap part of the heterostructure in the latter.

In this article we report on the optical, structural, and magnetic properties of n- and p-type AlGaN implanted with doses of Mn, Cr, or Co sufficient to produce peak transition metal concentrations of a few atomic percent. The material exhibits carrier concentrations ~3 × 10$^{16}$ cm$^{-2}$ after implantation and annealing, indicating that the transition metals introduce deep states into the band gap and that free-carrier-induced ferromagnetism is not likely to be the mechanism for the observed magnetic properties.

EXPERIMENT

The n-type undoped ($n \sim 5 \times 10^{17}$ cm$^{-3}$) Al$_{0.35}$Ga$_{0.65}$N layers were grown on c-plane Al$_2$O$_3$ substrates by hydride vapor phase epitaxy, as described in detail previously. The layer thicknesses were ~0.4 μm in each case. The p-type ($p \sim 3 \times 10^{16}$ cm$^{-3}$), Mg-doped Al$_{0.15}$Ga$_{0.85}$N layers were also grown on sapphire (0001), but were grown by metal-organic chemical vapor deposition. The layer thickness was ~1 μm. Implantation of Mn$^+$, Cr$^+$, or Co$^+$ ions was performed at 250 keV energy, corresponding to a projected range of ~1500 Å. The dose was held constant at 3 × 10$^{16}$ cm$^{-2}$, producing a peak concentration of each transition metal of ~3 at. % in AlGaN. During the implant step, the samples were held at a temperature of ~300 °C to produce dynamic annealing and substitutionality of the transition metal atoms. Postimplant annealing was carried out at

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1000 °C for 2 min under a flowing N₂ ambient in a Heatpulse 610T system, with the samples in a face-to-face configuration with other AlGaN layers. Characterization included photoluminescence (PL) measurements performed with a quadrupled Ti:sapphire laser as an excitation source together with a streak camera. X-ray diffraction (XRD) was performed in a Philips powder diffractometer. Magnetic characterization was carried out in a quantum design superconducting quantum interference device system.

RESULTS AND DISCUSSION

Figure 1 shows θ–2θ XRD scans from the n-AlGaN before and after Mn⁺ implantation and annealing at 1000 °C. Similar results were found for the Co⁺ and Cr⁺ implanted samples and the n- and p-AlGaN did not show any observable differences. The highest intensity peaks in all spectra correspond to the expected AlGaN(0 0 0 2) and (0 0 0 4) lines and Al₂O₃(0 0 0 2), (0 0 0 6), and (0 0 0 12) substrate peaks. We did not observe any peaks due to second phases that could exhibit ferromagnetism. For example, in the Mn implanted material, Mn₅N is ferromagnetic with a Curie temperature of 745 K and GaMn is also ferromagnetic with a Curie temperature near 300 K (metallic Mn is antiferromagnetic). In the Co⁺ implanted AlGaN, metallic Co has a Curie temperature of 1382 K and CoₓN phases are all Pauli ferromagnetic. Finally, in the Cr⁺ implanted AlGaN, CrO is half metallic, while Cr, CrN, Cr₂N, Al₂Cr, and Ga₅Cr₅ are not ferromagnetic. However, in such thin layers, it could be possible for small quantities of second phases to be present and remain undetectable by XRD.

In the PL characterization, no band-edge luminescence was observed after implantation and annealing of any of the samples and only impurity transitions were observed. Figure 2 shows 10 K PL spectra from the implanted AlGaN, in which broad deep level emissions at ~2.9 and 3.9 eV are observed in all implanted samples, independent of the element introduced. One possible assignment of those lines is that of lattice disorder introduced by the implant step. The absence of appreciable band-edge luminescence in the implanted samples indicates that at least some of the point defect damage is stable to at least 1000 °C, similar to the case of pure AlN.

Well-defined hysteresis at 300 K was observed for the Co-implanted Al₀.₃₈Ga₀.₆₂N, as shown at the top of Fig. 3. The coercive fields were ~85 Oe at 300 K and ~75 Oe at 10 K. The saturation magnetization was ~0.4 emu/cm³ or ~0.76μ₀ calculated saturation moment. This is slightly higher than the value reported for Co⁺ implantation into pure AlN under similar conditions (0.52 μ₀). This is consistent with the higher vacancy concentrations expected to be created in AlGaN due to its lower bond strength. The bottom part of Fig. 3 shows the temperature dependence of field-cooled (FC) and zero field-cooled (ZFC) magnetization for the Co⁺ implanted AlGaN. The fact that these have dif-

![FIG. 1. X-ray diffraction spectra of AlₓGa₁₋ₓN (x = 0.38) both before (top) and after Mn⁺ implantation (3 x 10¹⁶, 250 keV), followed by a 1000 °C, 2 min anneal.](image1)

![FIG. 2. 10 K PL spectra from p-AlGaN before and after Mn⁺ implantation and n-AlGaN before and after Cr⁺, Co⁺, and Mn⁺ implantation (3 x 10¹⁶, 250 keV in all cases), followed in all cases by a 1000 °C, 2 min anneal.](image2)
different values out to \( \sim 230 \) K is a further indication of the presence of ferromagnetism in the material. In both epitaxial and ion implanted transition metal doped semiconductors, we have found the general result that the hysteresis can be detected to higher temperatures than the difference in FC and ZFC magnetization.\(^{44}\) As mentioned earlier, the samples exhibited low carrier densities \( (\leq 3 \times 10^{16} \text{ cm}^{-3}) \) from Hall measurements after implantation and annealing and, therefore, carrier-mediated ferromagnetism by free electrons is not expected to be operative. In addition, the Co ionization level is expected to be deep in the AlGaN band gap\(^{45–47}\) so that there will be no significant contribution to the carrier density from the substitutional fraction of these atoms. More recent percolation network models for ferromagnetism in dilute magnetic semiconductors suggest that localized carriers may mediate the interaction between magnetic ions in low carrier density systems.\(^{48,49}\)

Mn-implanted \( p \)-type AlGaN also showed a well-defined hysteresis loop at 300 K, with a coercivity of \( \sim 60 \) Oe (Fig. 4, top). The saturation moment, \( M_s = g \mu_B S \), where \( g \) is the degeneracy factor, \( \mu_B \) the Bohr magneton, and \( S \) the total number of spins, was calculated to be \( \sim 0.57 \mu_B \). The theoretical value would be 4 if all of the implanted Mn was participating towards the ferromagnetism, so the lower experimental value indicates that only a fraction of the Mn is substitutional and magnetically active. The saturation moment for AlGaN is significantly larger than the value of \( 0.17 \mu_B \) reported for Mn implantation into pure AlN.\(^{43}\) The temperature dependence of FC and ZFC magnetization is shown at the bottom of Fig. 4. The ferromagnetism is very weak above \( \sim 125 \) K, but is detectable through the hysteresis.

By sharp contrast to the case of Mn implanted into \( p \)-AlGaN, when we performed the same implants into \( n \)-AlGaN, the resulting differences in FC and ZFC magnetization were very weak (Fig. 5, top) and hysteresis loops even at 10 K did not show clear evidence of ferromagnetism. The differences from the \( p \)-type material may result from the higher AlN mole fraction in the \( n \)-type AlGaN, which makes it harder for the implanted ions to become substitutional upon annealing. An alternative explanation is that holes are more efficient at ferromagnetic coupling between the Mn spins than are electrons. This has been reported previously for both \( n \)- and \( p \)-type GaAs (Ref. 17) and GaP doped with Mn.\(^{44}\) We also did not observe any clear evidence for ferromagnetism in the Cr implanted \( n \)-AlGaN (Fig. 5, bottom).
Some calculations suggest it is energetically favorable to form ferromagnetic transition metal ion dimers and trimers at second nearest-neighbor sites. Distant pairs would be weakly ferromagnetic or antiferromagnetic. These predictions suggest that the ferromagnetism will be a very strong function of the synthesis conditions used for the magnetic semiconductor. They also suggest that nonequilibrium methods such as ion implantation possess inherent advantages in trying to maximize the Curie temperature because of their ability to achieve solid solubilities for dopants well above those possible with equilibrium synthesis methods.

**SUMMARY AND CONCLUSIONS**

Atomic percent concentrations of Mn, Cr, or Co were introduced into epitaxial AlGaN layers by ion implantation. X-ray diffraction did not observe any secondary phase formation after annealing at 1000 °C. No band-edge luminescence was detected in these samples, indicating that nonradiative recombination centers related to implantation damage are not removed at this annealing temperature. Ferromagnetic ordering was observed for Co-implanted samples, but not for Cr. The saturation moments for the ferromagnetic samples were higher than those reported for AlN doped using similar conditions.

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