Properties of Co-, Cr-, or Mn-implanted AlN

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AlN layers grown on Al_2O_3 substrates by metalorganic chemical vapor desposition were implanted with high doses (3×10^{16} cm^{-2}, 250 keV) of Co^+, Cr^+, or Mn^+. Band-edge photoluminescence intensity at ~6 eV was significantly reduced by the implant process and was not restored by 950 °C annealing. A peak was observed at 5.89 eV in all the implanted samples. Impurity transitions at 3.0 and 4.3 eV were observed both in implanted and unimplanted AlN. X-ray diffraction showed good crystal quality for the 950 °C annealed implanted samples, with no ferromagnetic second phases detected. The Cr- and Co-implanted AlN showed hysteresis present at 300 K from magnetometry measurements, while the Mn-implanted samples showed clear loops up to ~100 K. The coercive field was <250 Oe in all cases. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1586987]

INTRODUCTION

AlN plays an important role in many areas of solid-state devices, including thin film phosphors,[1,2] nitride-based metal–insulator–semiconductor heterostructure transistors,[3,4] thin-film gas sensors,[5] acoustic wave resonators,[6,7] ultraviolet light-emitting diodes,[8–10] distributed Bragg reflectors,[11,12] heat spreaders,[13] and heterojunction diodes.[14] AlN may also be promising in the emerging field of spintronics, due to its predicted high Curie temperature (T_C) when doped with particular transition metals.[15] Room temperature ferromagnetism has been reported for Cr-doped AlN thin films deposited by reactive sputtering[16] or molecular beam epitaxy.[17] Ion implantation provides a versatile and convenient method for introducing transition metals into semiconductors for examination of their effects on the structural and magnetic properties of the resulting material.[18] AlN is an ideal host in this regard, since Kucheyev *et al.*[19] reported that single crystal epilayers of AlN grown on sapphire substrates did not become amorphous even at LN_2 temperatures for high doses of keV heavy ions such as Au. In addition, very high quality AlN on sapphire has recently been reported by several groups,[20,21] providing well-characterized material in which to examine the properties of transition metals.

In this article we report on the characteristics of Co-, Cr-, or Mn-implanted AlN. These appear to be the most promising elements for creation of robust ferromagnetism in AlN. In addition to the theory and experiments discussed above for AlN,[15,17] room temperature ferromagnetism has been reported by several groups for Cr-doping of GaN.[22–24] The expected deep acceptor nature of the transition metals in AlN suggests that carrier-mediated ferromagnetism will be unlikely, but other mechanisms such as bound polarons may be applicable.[25]

EXPERIMENT

The AlN epilayers were grown by metalorganic chemical vapor deposition on sapphire (0001) substrates, as described in detail elsewhere.[20] The layers were 1 μm thick, with full-width-half-maximum values of 150–500 arc sec for the AlN (0002) rocking curves. Implantation of Cr^+, Co^+, or Mn^+ ions was carried out at an energy of 250 keV (corresponding to a projected range of ~1500 Å in each case) and a fixed dose of 3×10^{16} cm^{-2}. The substrate temperature was held at ~300 °C to promote dynamic annealing.[26] As a rough guide, the peak transition metal concentrations, located at the projected range, are ~3 at. % in the AlN. After implantation, the samples were annealed at 950 °C, 2 min under flowing N_2 in a Heatpulse 610T system. Photoluminescence (PL) measurements were carried out with a quadrupled Ti:sapphire laser as an excitation source together with a streak camera, providing an excitation power of ~3 mW at 196 nm.[27] X-ray diffraction (XRD) was carried out on a Philips powder diffractometer while magnetic measurements were performed in a Quantum Design superconducting quantum interference device magnetic properties measurement system.

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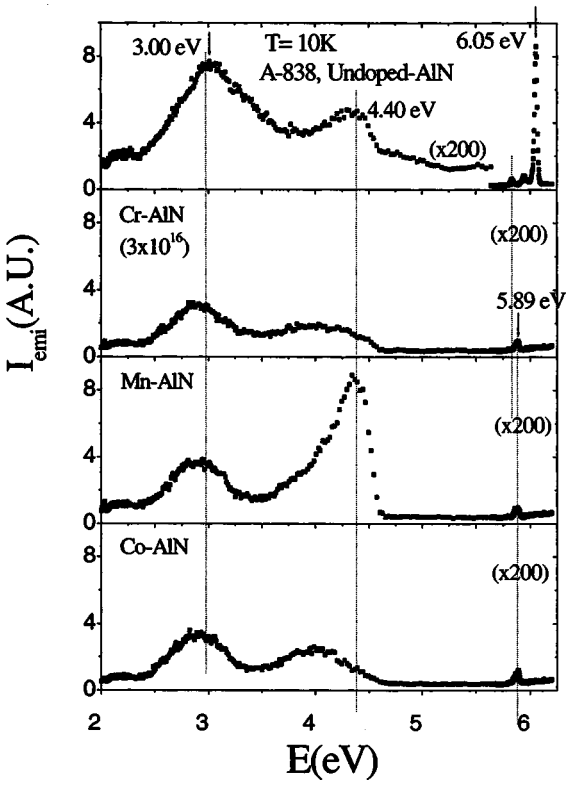

FIG. 1. 10 K PL spectra from AlN either before (top) or after Cr^+, Mn^+, or Co^+ implantation (3×10^{16} cm^{-2}, 250 keV), followed in all cases by 950 °C, 2 min anneals.

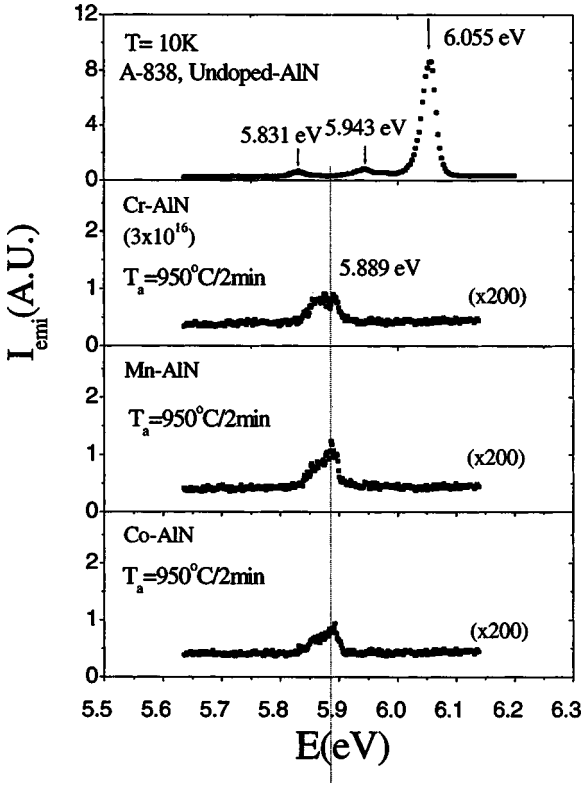

FIG. 2. 10 K AlN band edge region PL either before (top) or after Cr^+, Mn^+, or Co^+ implantation (3×10^{16} cm^{-2}, 250 keV), followed in all cases by 950 °C, 2 min anneals.

RESULTS AND DISCUSSION

Figure 1 shows PL spectra taken at 10 K of the AlN implanted with Cr, Mn, or Co after annealing at 950 °C for 2 min. The spectra look basically identical in each case, even without annealing. The unimplanted AlN shows strong band-edge emission at ~6.05 eV and two broad emission bands related with deep level impurities at ~3.0 and 4.40 eV, each of which has peak intensity of ~1% of the band-edge emission intensity. The Cr-, Mn-, and Co-implanted AlN show an absence of band-edge emission, which suggests that the point defect recombination centers created during implantation are stable against annealing at 950 °C. This is consistent with the conclusions of Kucheyev *et al.*,[19] who found that structural lattice disorder produced in AlN by 300 keV Au^+ at doses comparable to those employed here was stable against rapid thermal annealing at 1000 °C.

Figure 2 shows an expanded view of the PL spectra in the band-edge region. Once again, the spectra were virtually unchanged as a result of the anneal at 950 °C. The transition lines at 5.943 and 5.831 eV are the one and two longitudinal optical (LO) phonon (112 meV) replica of the 6.055 eV emission line. The implanted samples all show a band at 5.889 eV, which is independent of the implanted species and most likely is related to lattice disorder induced by the implantation.

Figure 3 (top) shows a representative plot of magnetization versus field at 300 K for the Cr implanted AlN annealed at 900 °C. There is well-defined hysteresis present, with a coercive field of ~160 Oe at 300 K and 230 Oe at 10 K. The diamagnetic contributions from the substrate have been subtracted out of the data. At 300 K, the saturation moment, $M_O = g\mu_B S$, where g is the degeneracy factor, μ_B the Bohr magnetron, and S the total number of spins, was calculated to be ~0.65 μ_B for Cr. This value is lower than the theoretical value of 3 μ_B expected for a half-filled d band of Cr, if all of the Cr ions were participating in the ferromagnetic signal. Disorder effects due to implantation-induced change may contribute to creating a distribution of exchange couplings that favor antiferromagnetism and reduce the effective magnetism. Plots of magnetization at 500 Oe versus temperature under field-cooled (FC) and zero-FC (ZFC) conditions are shown for the Cr-implanted AlN in the center of Fig. 3. This subtraction of FC and ZFC magnetization eliminates para- and diamagnetic contributions and indicates the presence of hysteresis if the difference is non-zero. The bottom of Fig. 3 shows the temperature dependence of this difference, ΔM, with magnetization present to the 225–300 K range.

Similar data are shown in Fig. 4 for the Co-implanted AlN. Once again there is hysteresis present at 300 K, with a coercive field of ~1750 Oe at 300 K and 240 Oe at 100 K and a calculated saturation moment of 0.52 μ_B for Co. The FC and ZFC magnetization versus temperature are shown at the bottom of the figure. In this case the differences extend to ~100 K.

Figure 5 (top) shows magnetization versus field at 100 K for Mn-implanted AlN. This was the highest temperature for which clear hysteresis could be obtained. The coercive field

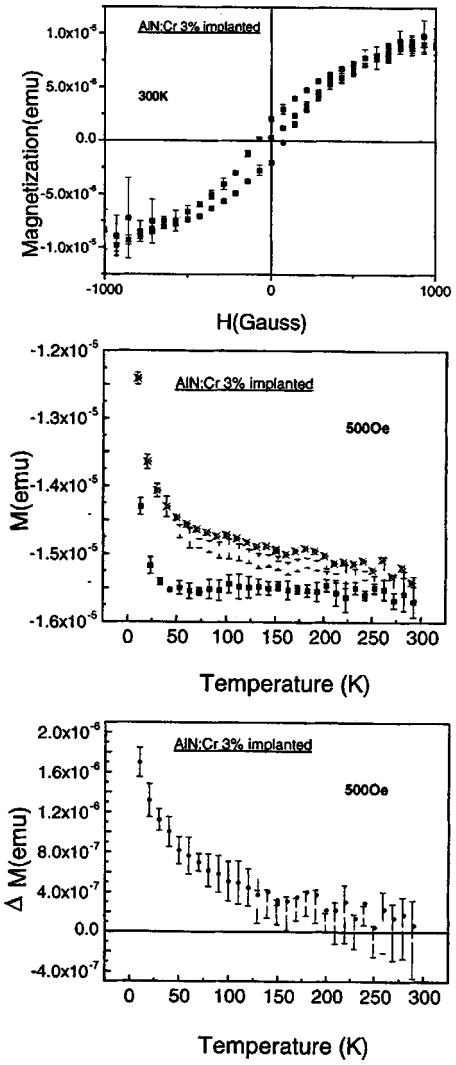

FIG. 3. 300 K magnetization as a function of field (top), field-cooled (FC), and zero-field-cooled (ZFC) magnetization vs temperature (center) and difference in FC–ZFC magnetization vs temperature for AlN implanted with 3×10^{16} cm^{-2} Cr^{+} and annealed at 950 °C, 2 min.

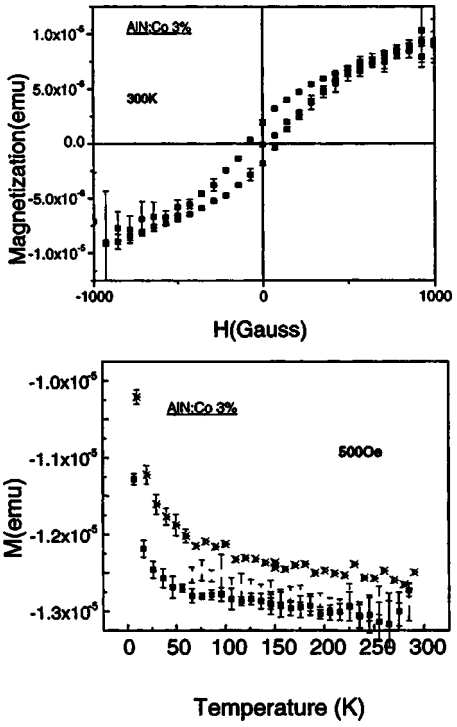

FIG. 4. 300 K magnetization as a function of field (top) and FC and ZFC magnetization as a function of temperature (bottom) for AlN implanted with 3×10^{16} cm^{-2} Co^{+} and annealed at 950 °C, 2 min.

was ~220 Oe at both 100 and 10 K. The FC and ZFC phases are almost coincident at an applied field of 500 Oe, as shown at the bottom of the figure and consistent with lower overall magnitude of the magnetization. The calculated saturation moment was 0.17 μ_B for Mn at 100 K, compared to the theoretical value of 4.

Figure 6 shows representative θ–2θ XRD scans of the Cr or Mn implanted samples after 950 °C annealing. The Co data are not shown for clarity sake, since the spectra was the same as for the Mn and Cr implanted material. The main peaks correspond to the expected AlN(0002) and (0004) lines and Al_2O_3 (0002), (0006), and (0012) substrate peaks and the broad peak at $2\theta=20$ °C is due to short-range disorder from the implantation process and was not observed on the as-grown films. No peaks due to the half-metallic ferromagnetic CrO_2 phase[28] were detected in the Cr-implanted sample and other potential second phases which could form, such as Cr, CrN.[29] Cr_2N and Al_xCr_y, were not detected and in any case are not ferromagnetic at the temperatures used in these experiments.[24] Similarly, in the case of Co implantation, metallic Co has a Curie temperature of 1382 K and Co_xN phases are all Pauli ferromagnetic.[30] Finally, for Mn implantation, metallic Mn is antiferromagnetic[24] while Mn_xN

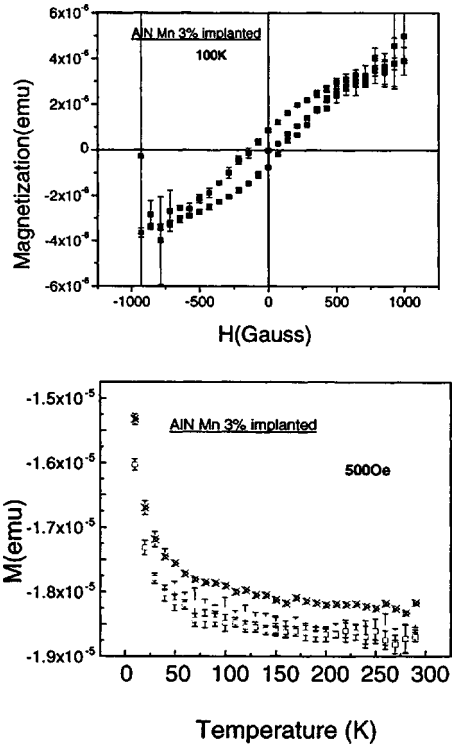

FIG. 5. 100 K magnetization as a function of field (top) and FC and ZFC magnetization as a function of temperature (bottom) for AlN implanted with 3×10^{16} cm^{-2} Mn^{+} and annealed at 950 °C, 2 min.

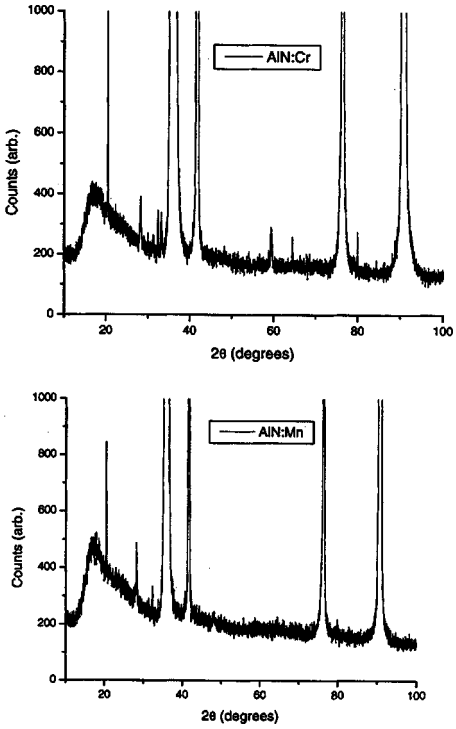

FIG. 6. X-ray diffraction scans of AlN implanted with Cr^+ (top) or Mn^+ (bottom) to a dose of 3×10^{16} cm^{-2} and annealed at 950 °C, 2 min.

is ferromagnetic with a Curie temperature of 745 K.[24] Thus, secondary ferromagnetic phases are not responsible for the observed magnetic properties.

The origin of the observed ferromagnetism is not likely to be carrier-mediated due to the insulating nature of the AlN. Wu *et al.*[17] suggested that substitutional $Al_xCr_{1-x}N$ random alloys would have Curie temperatures over 600 K, as estimated from a multicomponent mean-field theory in which the ferromagnetism occurs in a midgap defect band. Another possible mechanism for the observed magnetic properties is that the Mn is not randomly distributed on Al sites but is present as atomic scale clusters. Some mean field theories suggest that Mn clustering can significantly influence T_c as a result of the localization of spin polarized holes near regions of higher Mn concentration.[31,32] There is also some support for this assertion from local spin density approximation calculations which predict it is energetically favorable for the formation of magnetic ion dimers and trimers at second nearest-neighbor sites which are ferromagnetic.[32] The percolation network-like model for ferromagnetism in low carrier concentration systems suggested by several groups is another potential mechanism.[33,34]

SUMMARY AND CONCLUSIONS

High doses (3×10^{16} cm^{-2}) of ion implanted Co^+, Cr^+, or Mn^+ ions into AlN epilayers on Al_2O_3 substrates severely degrades the band-edge luminescence, which is not recovered by annealing up to 950 °C. In each case the implanted AlN shows ferromagnetic ordering as evidenced by the presence of hysteresis in M versus H loops. The hysteresis persists up to $\geqslant$300 K in the case of Cr^+ or Co^+ implantation and 100 K for Mn^+ implantation. Less than ~20% of the implanted ions contribute to the magnetization, but this might be increased by use of much higher annealing temperatures. Simple two-terminal resistivity measurements show that the implanted AlN remains insulating ($>10^8$ Ω cm) and thus conventional carrier-mediated ferromagnetism is not a likely mechanism for the observed magnetic properties. Implantation provides a versatile method of introducing different transition metal dopants into AlN for examination of their effect on the structural and magnetic properties.

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