Magnetic Properties of Mn–Doped III–Nitrides Grown by MOCVD

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Dilute Magnetic Semiconductor (DMS) research has mainly focused on II–VI and III–V materials, where a maximum Curie temperature (T_C) of 110K was reported in (Ga,Mn)As.[1] However, (Ga,Mn)N has shown ferromagnetic behavior with Curie temperature (T_C) exceeding room temperature.[2],[3],[4] The elevated Curie temperatures exhibited in this material has obvious and practical technological implications. Efforts to grow (Ga,Mn)N by metal–organic chemical vapor deposition (MOCVD) have produced much information on the optical properties of the films. Korotkov[5] *et al*. shows that Mn forms a deep acceptor level with optical transitions at 1.4 and 2.06 eV, and photoluminescence measurements of Mn–doped films indicated the presence of an intra 3*d*–shell transition of the Mn ion. However, there were no reports on the magnetic properties or crystalline quality of this material system grown by MOCVD. The purpose of this study is to demonstrate room temperature ferromagnetic MOCVD grown (Ga,Mn)N. We also discuss the growth parameters and their effect on the solubility limits of Mn in GaN as well as magnetic response.
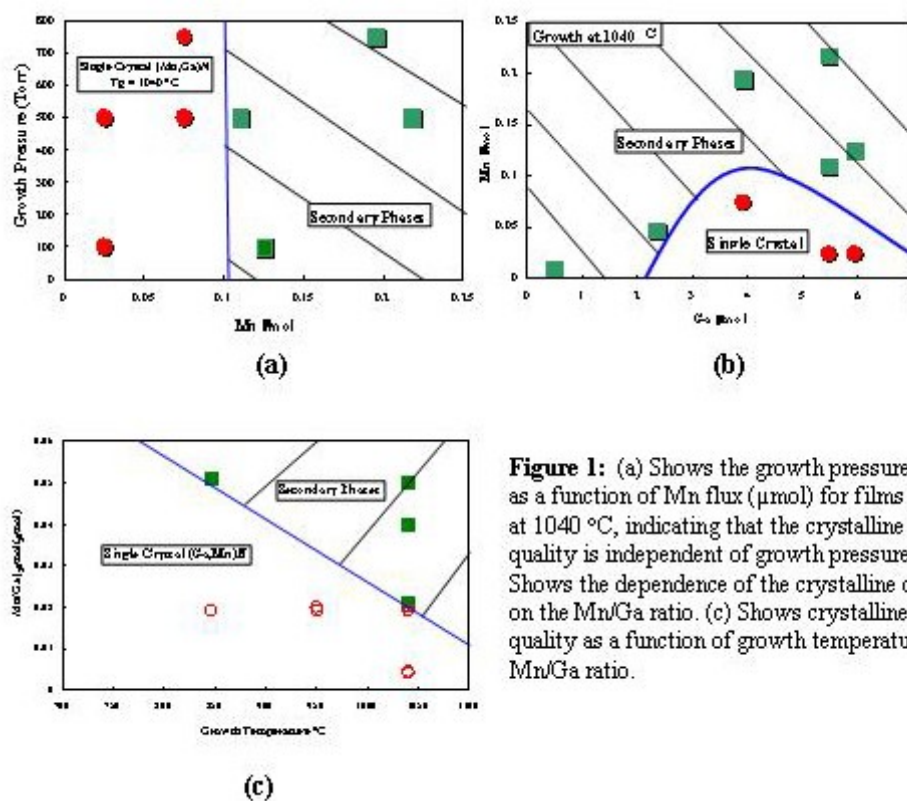

Figure 1: (a) Shows the growth pressure (Torr) as a function of Mn flux (μmol) for films grown at 1040 °C, indicating that the crystalline quality is independent of growth pressure. (b) Shows the dependence of the crystalline quality on the Mn/Ga ratio. (c) Shows crystalline quality as a function of growth temperature and Mn/Ga ratio.

(Ga,Mn)N films were grown by MOCVD on *c*–plane sapphire substrates in a radio frequency inductively heated vertical chamber. Trimethylgallium (TMGa), bisethylcylo–pentadienyl manganese (EtCp)$_2$Mn, and NH$_3$ were used as precursors. A low temperature (500 °C) GaN buffer layer of ~ 40 nm thick is grown. An undoped GaN epitaxial layer ~0.1 ¼m was grown at 1040 ºC to serve as a template for (Ga,Mn)N. The growth temperatures and pressures used for (Ga,Mn)N varied from 850 °C to 1040 °C, and from 100–760 Torr, respectively. The (Ga,Mn)N film thickness ranged from 0.6–1.4 μm for this study. X–ray diffraction (XRD) and Transmission Electron Microscopy (TEM) were utilized to determine their crystal quality and the nature of any secondary phases (if formed). Secondary Ion Mass Spectrometry (SIMS) provided the chemical composition of Mn in the resulting

(Ga,Mn)N films.   Vibrating Sample Magnetometer (VSM) and Superconducting Quantum Interference Device (SQUID) measurements were used to determine the magnetic properties of the films. Hall measurements were performed to determine electrical properties.
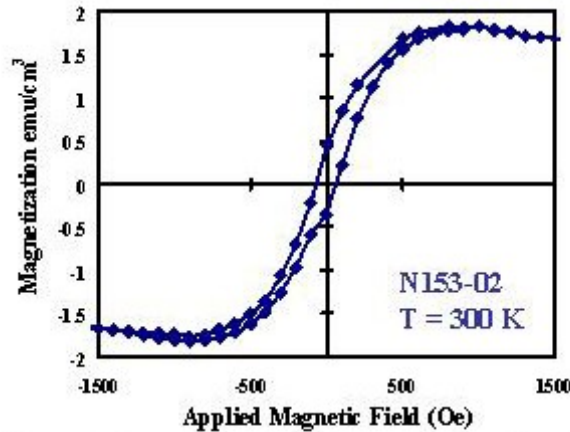

Figure 2. Room temperature SQUID measurement showing perpendicular magnetization for MOCVD grown Mn:GaN sample N153-02. Based on the growth conditions and sample dimensions this sample is estimated to have ~1 μB/Mn atom.

The range of solid solubility of Mn in GaN as a function of (EtCp)$_2$Mn flux, TMGa flux, growth temperature, and growth pressure were studied. Growth conditions resulting in either single crystal (Ga,Mn)N or (Ga,Mn)N containing separated secondary phases are show in Figures 1(a), (b) & (c). Figure 1(a) shows that the formation of secondary phases is independent of growth pressure, but is critically dependent on the (EtCp)$_2$Mn flux for a given TMGa flux and growth temperature, and that single crystal (Ga,Mn)N only occurs for (EtCp)$_2$Mn less than 0.1 ¼mole. However, it appears that the Ga flux (i.e. growth rate) and the EtCp)$_2$Mn/TMGa partial pressure ratio also affect the occurrence of secondary phases at a given growth temperature, as shown in figure 1(b). Even for a fairly low Mn flux (as low as 0.01 *m*mole) secondary phases occur readily at lower growth rates indicating that secondary phase formation depends on growth kinetics as well as thermodynamic considerations. Figure 1(c) shows the effect of growth temperature on the formation of secondary phases. At high growth temperatures it is possible for kinetics to dominate where the Mn diffusivity is increased due to an increase in the total number of Ga vacancies which can enhance the formation of secondary phases. Thus, from figure (1) single crystal (Ga,Mn)N can only be achieved under fairly strict conditions that depend on growth rate, growth temperature and the (EtCp)$_2$Mn flux in the gas phase. It should be mentioned that the boundary between single crystal and multi–phase region shown in figure (1) is an approximation of the Mn solubility limit in GaN and are shown as a general guide line. Therefore, more experimental data are needed to explain the trends in growth.

Most of the (Ga,Mn)N films in the single crystal region were determined to be ferromagnetic at room temperature. Figure (2) shows the room temperature SQUID measurement for a single crystal (Ga,Mn)N sample N153–02 showing ferromagnetic behavior. This sample is estimated to have a Mn concentration [Mn] = 4.313 X 10^{19} atoms/cm^3 within the (Ga,Mn)N film. The saturation moment of this sample is ~ 1 μ_B/Mn atom, with a coercivity of ~ 100 Oe.   Assuming that Mn^{2+} atom substitutes for Ga site in the GaN lattice so that J = 5/2, the Mn concentration [Mn] calculated from the magnetization curves using M_S = [Mn]$g\mu_B$S gives 3.88 X 10^{19} atoms/cm^3, where M_S is the saturation magnetization and the g–factor is 2. This indicates a 17% difference in Mn concentration when compared with values obtained from SIMS, which suggests that not all of the Mn ions are contributing to ferromagnetic coupling.   Growth conditions for sample N153–02 and N174–02 are nearly identical

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with the exception of the growth pressure, where samples were grown at 500 Torr and 760 Torr, respectively. The fact that their magnetic properties are also very similar indicates that the growth pressure does not play a critical role for controlling the magnetic properties of the Mn:GaN films. The saturation magnetization M_S as a function of temperature for N153–02 identifies a Curie temperature of ~ 400 K as measured by SQUID.

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