Ferromagnetism in Mn-doped GaN nanocrystals prepared solvothermally at low temperatures

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3% and 5% Mn-doped GaN nanocrystals of different sizes, with the average diameters in the range of 4–18 nm, have been prepared by two independent routes under solvothermal conditions starting with two different precursors. The reaction temperature was around 350 °C in all the preparations. The nanocrystals so prepared exhibit ferromagnetism with magnetization (M) and Curie temperature (T_C) values increasing with percent of Mn and particle size. The observation of ferromagnetism in Mn-doped GaN nanocrystals prepared at relatively low temperatures is of significance in understanding this potential in spintronics materials. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2357927]

Mn-doped GaN (GaMnN) was predicted by Dietl *et al.*[1] to be ferromagnetic with a high Curie temperature, with possible use in spintronics. Several workers have since investigated GaMnN because of its potential applications.[2,3] Thus, magnetic, optical, and electronic properties of GaMnN, specially in the form of thin films, have been reported widely.[2–12] Thus, Thaler *et al.*[12] found room temperature ferromagnetism in GaMnN films, without the presence of any second phase, for Mn levels below ~10%. Overberg *et al.*[4] have reported that GaN films doped with 7% Mn to be ferromagnetic with a low T_C (between 10 and 25 K), while Zajak *et al.*[10] reported that Mn-doped GaN to be paramagnetic. The highest T_C reported so far in GaMnN films is by Sasaki *et al.*[6] who prepared the films by reactive molecular beam epitaxy using ammonia as the nitrogen source. Some of the studies have suggested the possible presence of second phases such as Ga–Mn or Mn–N alloys as being responsible for the observation of ferromagnetism.[8,11] It has, however, been pointed out that 5% Mn-doped GaN films grown under optimum conditions show no second phase but exhibit room temperature ferromagnetism.[2] One of the limitations in most of the studies of thin films is that they are generally prepared at temperatures in the range of 750–1250 °C. Such temperatures can give rise to Ga–Mn alloy impurities with high ferromagnetic T_C's.

Incorporation of Mn into GaN nanowires has been reported by a few workers.[3] Thus, Deepak *et al.*[13] have shown that GaMnN nanowires, with an average diameter in the 25–75 nm range containing 1%–5% Mn, are ferromagnetic at 300 K. Han *et al.*[14] also find GaMnN nanowires with 5% Mn to be ferromagnetic with a T_C of at least 300 K. The preparation of nanowires is also carried out generally at high temperatures, just like the thin films. We, therefore, considered it important to investigate the magnetic properties of GaMnN samples prepared at relatively low temperatures to ensure that the secondary ferromagnetic phases are not present. For this purpose, we have prepared 3% and 5% Mn-doped GaN nanocrystals of different sizes by employing low-temperature solvothermal reactions.

The method of synthesis of the GaMnN nanocrystals involved the solvothermal decomposition of solid solution of gallium(III)-manganese(II)cupferronate, $(Ga_{1-x}Mn_x)(C_6H_5N_2O_2)_{3(1-x)+2x}$, in the presence of hexamethyldisilazane (HMDS) or the reaction of a mixture of $GaCl_3$ and $MnCl_2$ with HMDS around 350 °C. 3% Mn-doped GaN nanocrystals were obtained by the reaction of 150 mg (0.320 mmol) of the cupferronate solid solution, $Ga_{0.97}Mn_{0.3}(C_6H_5N_2O_2)_{2.97}$, with 4 ml of HMDS in 6 ml of toluene in a Swagelok autoclave at 350 °C for 20 h. Figure 1(a) shows the x-ray diffraction (XRD) pattern of the as-prepared sample, revealing broad reflections similar to those observed earlier with small size of GaN nanocrystals.[15–17] The (100), (002), and (101) reflections of hexagonal GaN merge to form a broad peak in the XRD pattern. Transmission electron microscope (TEM) images shown in Fig. 2(a) indicate that the particles have an average diameter of 4 nm. Larger nanoparticles of 3% Mn-doped GaN nanoparticles could be prepared by increasing the initial concentration of solid solution precursor (starting with 600 mg or 1.28 mmol of the cupferronate) and keeping the other reaction parameters the same. A TEM image of such a sample shown in Fig.

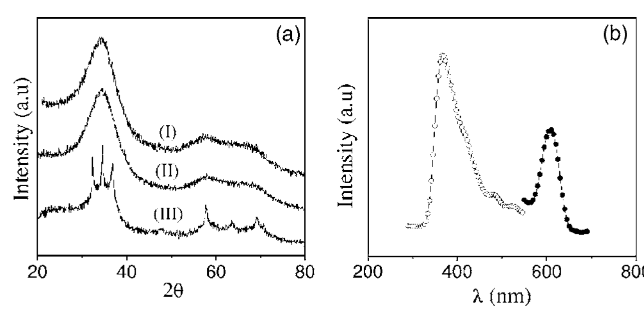

FIG. 1. (a) XRD patterns of (I) 3% Mn-doped GaN of 4 nm diameter, (II) 5% Mn-doped GaN of 4 nm diameter, and (III) 5% Mn-doped GaN nanocrystals of 12 nm diameter obtained by heating the 4 nm particles. (b) Typical PL spectrum of 3% Mn-doped nanocrystals with an average diameter of 4 nm.

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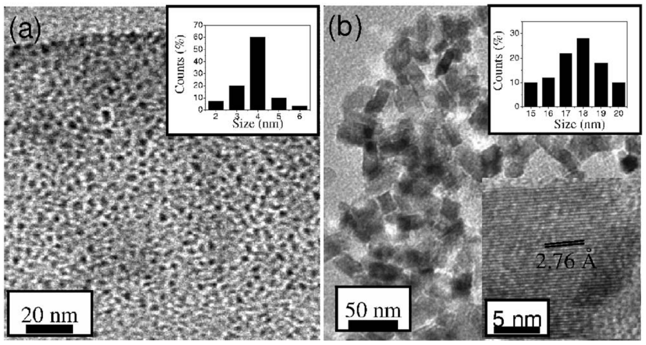

FIG. 2. TEM images of 3% Mn-doped GaN nanocrystals with average diameters of (a) 4 nm and (b) 18 nm prepared by the cupferron route. Insets show the size distribution histograms. The bottom inset in (b) shows the HREM image of an 18 nm nanocrystal.

2(b) shows the average particle size to be 18 nm. The nanoparticles are single crystalline as confirmed by the high-resolution transmission electron microscope (HREM) image [see the inset in Fig. 2(b)], the lattice spacing of 2.76 Å corresponding to the (100) interplanar distance. 5% Mn-doped GaN nanoparticles were prepared starting with the cupferronate precursor, $Ga_{0.95}Mn_{0.5}(C_6H_5N_2O_2)_{2.95}$. The XRD pattern of this sample shown in Fig. 1(a) also has broad reflections due to the small size of the nanoparticles, as also confirmed by the TEM image in Fig. 3(a). On heating these GaMnN nanoparticles at 500 °C in an NH_3 atmosphere for three days, we could obtain the characteristic XRD pattern due to hexagonal GaN [$P6_3mc(186)$] as can be seen from Fig. 1(a). The TEM image of these nanocrystals in Fig. 3(b) shows the average diameter to be ~12 nm. A HREM image of a single crystalline 12 nm particle, shown as an inset in Fig. 3(b), gives a lattice spacing of 2.76 Å corresponding to the (100) interplanar distance. The Mn concentrations of all the GaMnN samples were confirmed by energy dispersive x-ray analysis. Photoluminescence spectra of all the GaMnN nanocrystals showed the band-edge luminescence of the GaN (~360 nm) and the characteristic Mn^{2+} emission ($^4T_1$ to $^6A_1$ transition) around 610 nm.[13] In Fig. 1(b) we show a typical photoluminescence spectrum.

In Figs. 4(a) and 4(b), we show the variable-temperature magnetization (M) data under field-cooled (FC) and zero-field-cooled (ZFC) conditions (H=100 Oe) for the ~4 nm nanocrystals of 3% and 5% Mn-doped GaN, respectively. The inset in Fig. 4(a) shows the M-T curve of the 3% Mn-doped GaN nanocrystals of an average diameter of ~18 nm.

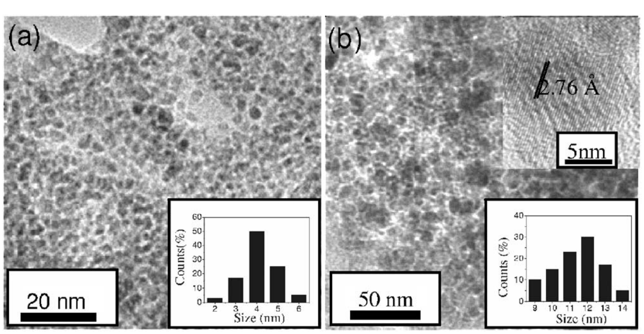

FIG. 3. TEM images of 5% Mn-doped GaN nanocrystals with average diameters of (a) 4 nm and (b) 12 nm, the latter have been obtained by heating 4 nm nanocrystals at 500 °C. Insets show size distribution histograms. The top inset in (b) shows the HREM image of a 12 nm nanocrystal.

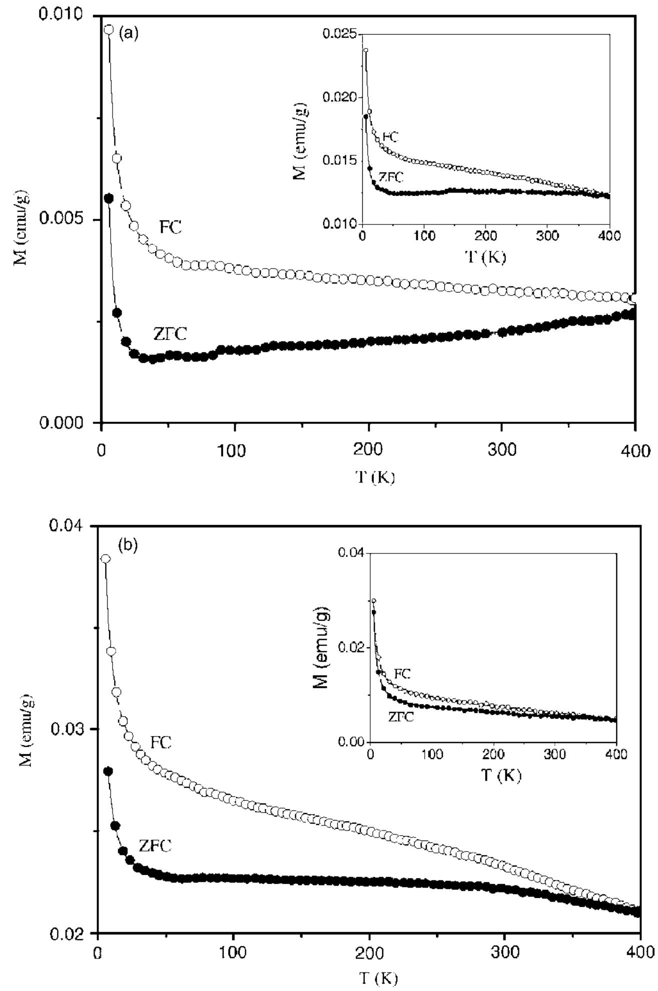

FIG. 4. Temperature variation of magnetization (M) curves of (a) 3% and (b) 5% Mn-doped GaN nanocrystals with an average diameter of 4 nm, prepared by the cupferron route. Inset in (a) shows the M-T curves for the 3% Mn-doped GaN nanocrystals with an average diameter of 18 nm and inset in (b) shows the M-T curves of the 5% Mn-doped GaN nanopcrystals of 12 nm diameter.

Similar data for those ~12 nm nanocrystals of 5% Mn-doped GaN are shown as an inset in Fig. 4(b). The shapes of the M-T curves of the GaMnN nanocrystals found by us are similar to those reported in the literature for the GaMnN films.[2,3] There is a clear divergence between the FC and the ZFC curves above 300 K, considered to be characteristic of a single phase GaMnN system.[2] The values of magnetization of the 5% Mn-doped samples are higher than those of the 3% Mn-doped samples. The magnetization of the 18 nm nanocrystals of the 3% Mn-doped sample is higher than that of the 4 nm nanocrystals. We estimate the T_C values from mean-field approximation to be 655, 858, and 935 K for the 4 nm 3% Mn-doped GaN, 18 nm 3% Mn-doped GaN, and 4 nm 5% Mn-doped GaN nanocrystals, respectively. The T_C value is higher for the 5% Mn-doped GaN than 3% Mn-doped GaN nanocrystals. T_C is also higher for the 18 nm 3% sample than for the corresponding 4 nm sample.

Figures 5(a) and 5(b) show the variation of magnetization with fields at 10 and 300 K for the 3% and 5% Mn-doped GaN nanocrystals of 4 nm diameters. The inset in Fig. 5(a) shows the M vs H curve for the 3% Mn-doped GaN nanocrystals of 18 nm diameters. The coercivity (H_c) values at 10 K are 212, 230, and 260 Oe for the 4 nm 3% Mn-doped, 18 nm 3% Mn-doped, and 4 nm 5% Mn-doped nano-

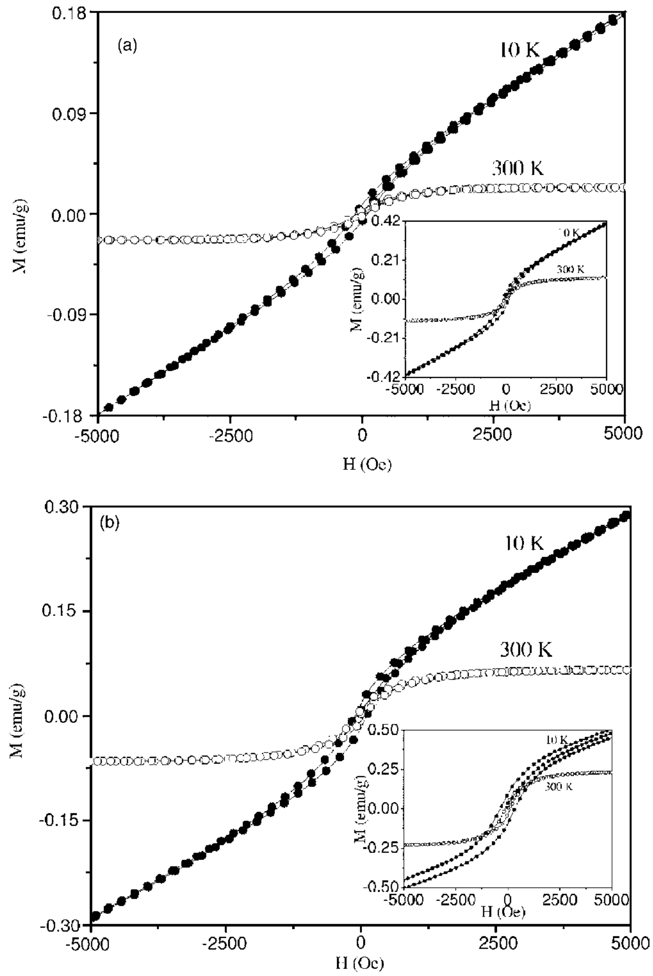

FIG. 5. Field dependence of magnetization of (a) 3% and (b) 5% Mn-doped GaN nanocrystals of 4 nm diameter prepared by the cupferron route. Inset in (a) shows the *M-H* curves of 3% Mn-doped GaN nanocrystals with a diameter of 18 nm prepared by the cupferron route. Inset in (b) shows the *M-H* curves of 3% Mn-doped GaN nanocrystals of 6 nm diameter prepared by the chloride route.

crystals, respectively. The values of H_c parallel the variation of the T_C.

We have also prepared 3% Mn-doped GaN nanocrystals of ~6 nm diameter by the reaction of 100 mg (0.568 mmol) $GaCl_3$ and 2.2 mg (0.017 mmol) $MnCl_2$ with 3 ml of HMDS in 8 ml of toluene at 350 °C under solvothemal conditions. The magnetization-temperature curve of this GaMnN sample was similar to that in Fig. 4, and the estimated T_C is 785 K. Magnetic hysteresis data of this sample recorded at 10 and 300 K are shown as an inset in Fig. 5(b). The hysteresis curves are somewhat superior to those found with the samples prepared by the cupferron route. The H_c values are 700 and 265 Oe at 10 and 300 K, respectively.

In conclusion, we have prepared Mn-doped GaN nanocrystals under solvothermal conditions by employing two different precursors of Ga and Mn by keeping the temperature of the preparation around 350 °C. The average diameters of the different samples of nanocrystals prepared by us vary between 4 and 18 nm. All the nanocrystals show ferromagnetism at room temperature. Values of M, H_c, and the T_C values of the nanocrystals are generally in the ranges reported for GaMnN thin films. Furthermore, all these magnetic properties increase with the increase in Mn concentration as well as the particle size. Observation of ferromagnetic GaMnN nanocrystals prepared at low temperatures is significant since secondary phases are unlikely to be formed under the preparative conditions employed. The results of the present study are somewhat consistent with the theoretical predictions of Das *et al.*[18]

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