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Synthesis of Bulk $Ga_{1-x}Mn_xN$: A Prospective Spintronic Material

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During recent years rapid development of spintronics has occurred.[1−3] Roughly speaking, in contrast to conventional electronics, which is based on the electron charge, spintronics is based on effective use of the electron spin. Moreover, it is anticipated that $Ga_{1-x}Mn_xN$, heavily p-type doped, should reveal ferromagnetic ordering at ambient temperatures.[4] In view of this, considerable effort has been taken worldwide to synthesize this material. Various techniques have been used to obtain GaN doped with certain metals endowed with magnetic properties.[5−10] Here, we report a method of obtaining free-standing single crystals of $Ga_{1-x}Mn_xN$. The method of codoping with Mn and Si was also used. The dimensions of the crystals obtained were up to 4.8 × 2.5 × 0.4 mm.

GaN single crystals doped with Mn were prepared from a mixture of gallium nitride and manganese powders, or from a mixture of gallium and manganese, in reactions with ammonia at temperatures of 1000−1250 °C. The concentration of Mn was determined by electron microprobe (CAMECA SU30). Raman investigations were done by DilorXY equipment. X- ray measurements were performed on a Kuma KM4CCD diffractometer (Poland). The EXAFS experiments were performed at the HASYLAB synchrotron facility (Hamburg, Germany). Magnetic properties were studied by superconducting quantum interferometer (SQUID).

The highest level of concentration of Mn in our crystals was 7.9 atomic percent. X-ray structure refinement, EXAFS measurements, and Raman investiga-

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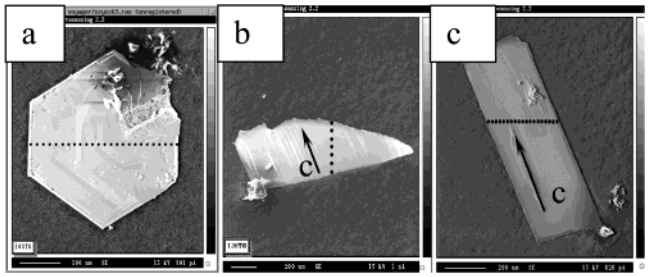

Figure 1. Photographs of single crystals: (a) $Ga_{1-x}Mn_xN$, $x = 0.0185$; (b) $Ga_{1-x}Mn_xN$, $x = 0.0475$; and (c) $Ga_{1-x}Mn_x(Si)N$, $x = 0.079$.

tions showed a quite good GaN wurtzite-type structure of bulk single crystals was obtained. In the reactions of mixtures of polycrystalline GaN and Mn powders with ammonia at 1230 °C hexagonal platelets with dimensions of up to 2.5 × 1.5 × 0.4 mm were prepared (all the crystals obtained in our works were etched in concentrated HNO_3 to remove the residues of metals or manganese nitrides). Figure 1a is a photograph of one of these crystals. The areas of the crystal analyzed by means of electron microprobe are marked as black spots. The concentration of Mn was measured as 1.85±0.1 atomic % (the measurement error was ±0.12 at. %). The concentration of manganese inside the crystal determined after breaking was 1.85 at. %. The Raman investigations have shown a good quality of these crystals, and also that the *c*-axis is perpendicular to the dominating plane of the platelets.

In the reaction of the mixtures of gallium and manganese with ammonia in the temperature range 1000−1070 °C irregular platelets were formed in which the *c*-axis was parallel to the platelet plane. The dimensions of these crystals were up to 4 × 2 × 0.4 mm. Figure 1b is a photograph of the crystal of gallium nitride heavily doped with manganese. The concentration of Mn measured (also inside the crystal after breaking) was 4.75 ± 0.05 at. % (the measurement error was ±0.12 at. %).

To increase the concentration of manganese in gallium nitride the so-called co-doping with silicon was carried out. In the reactions of mixtures of Ga with Mn and Si with ammonia at 1000−1030 °C bulk single crystals of $Ga_{1-x}Mn_x(Si)N$ with dimensions up to 4.5 × 2.5 × 0.4 mm were grown. A photograph of this crystal is presented in Figure 1c. The concentrations of dopants were Mn and Si 7.9±0.12 at. % and 0.5 ± 0.2 at. %, respectively (the concentrations of Mn and Si inside the crystals were the same). It was confirmed by Raman measurements that a slightly disordered GaN hexagonal lattice (similar to that in the crystals presented in Figure 1a and b) was formed and the *c*-axis was parallel to the plane of the platelet.

The refined structure of doped GaN crystals obtained in our investigations is illustrated in Figure 2. Doped GaN (as pure GaN) crystallizes in the same polar *P*6(3)*mc* (No. 186) space group from the hexagonal crystal system forming a layered structure of Wurtzite 2H type. The discrepancy factors obtained (for $[I > 2\sigma(I)]$ $R_1 = 0.0118$ for $x = 0.0185$ of Mn doping and 0.0203 for $x = 0.0475$ of Mn doping, and 0.0146 and 0.0217 for all data for these two concentrations of Mn ions) are lower than those found in the literature for pure gallium nitride.[11,12]

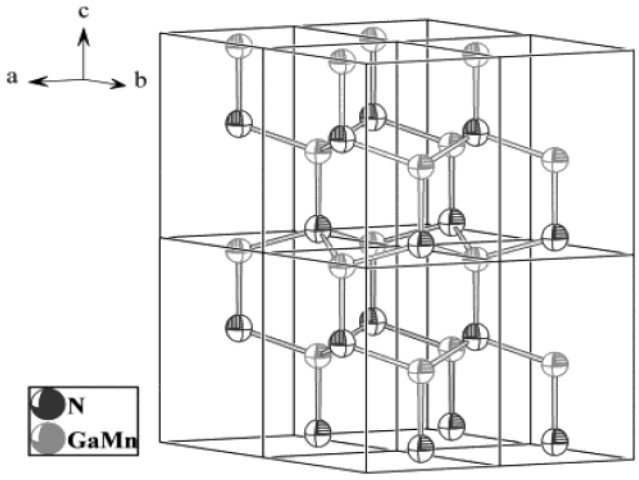

Figure 2. View of 8 unit cells of 1.85 at. % Mn doped GaN crystal. Probability factor of the thermal ellipsoids (ADPs) is equal to 99.99%.

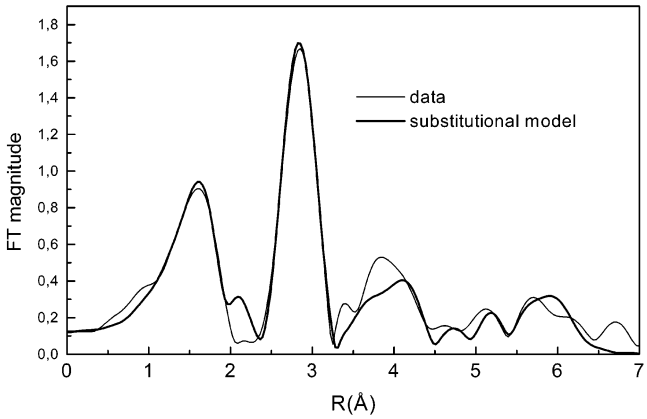

Figure 3. Magnitude of the Fourier transform of EXAFS oscillations for Mn K-edge.

They evidence a good consistency of the refined structural parameters with the real structure.

There are no reflections belonging to other phases, which is consistent with the Mn ions located at the same positions as the Ga ones. Compared to pure GaN data, $a = 3.1891(1)$ Å, $c = 5.1853(3)$ Å and $a = 3.190(1)$ Å [11] and $c = 5.189(1)$ Å,[12] the unit cell parameters of doped samples are slightly bigger because the ionic radius of the doping ions is higher than the radius of the host Ga ions: $a = 3.2026(5)$ Å, $c = 5.1987(10)$ Å for $Ga_{1-x}Mn_xN$ ($x = 0.0185$) and $a = 3.1968(5)$ Å and $c = 5.1901(10)$ Å for $Ga_{1-x}Mn_xN$ ($x = 0.0475$). Also, certain increase in temperature factors for the Ga ion is observed, although because they are heavier than the nitrogen atom they should have a significantly smaller temperature factor. The shortest interatomic distances between nitrogen and gallium ions equal 1.968(3) Å and 1.950(8) Å for smaller and larger doping, and the second shortest N(1)−Ga(1) distances equal 1.9538(10) Å and 1.955(3) Å for $x = 0.0185$ and $x = 0.0475$ of Mn doping, respectively.

To study the local environment around the Mn ions in $Ga_{1-x}Mn_xN$ crystals ($x = 0.0475$), we measured the

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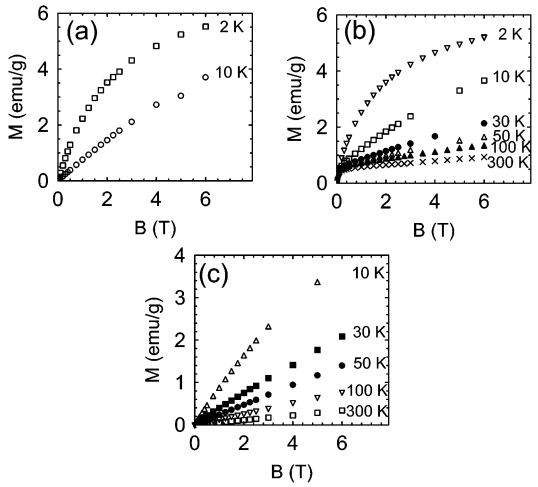

Figure 4. Magnetization as a function of magnetic field at different temperatures of single crystals: (a) $Ga_{1-x}Mn_xN$, $x = 0.0185$;l (b) $Ga_{1-x}Mn_xN$, $x = 0.0475$; and (c) $Ga_{1-x}Mn_x(Si)N$, $x = 0.079$.

extended X-ray absorption fine structure (EXAFS) spectra at the K-edge of manganese. Figure 3 shows the magnitude of the Fourier transform of EXAFS oscillations extracted from the absorption data (thin line). The thick line corresponds to the calculation based on a model with Mn substituting Ga. The calculation was performed within the multiple-scattering approach represented by the FEFFIT fitting procedure.[13] The results of fitting show increased interatomic distances as compared with the GaN lattice: the Mn−N distance is $R_1 = 2.08 \pm 0.01$ Å (the Ga−N distance in GaN is 1.95 Å) and $R_2 = 3.20 \pm 0.01$ Å (3.183 Å in GaN).

To characterize the magnetic properties of our $Ga_{1-x}Mn_xN$ single crystals, magnetization was measured as a function of magnetic field (up to 6 T) and temperature (2−300 K). The representative magnetization data are depicted in Figure 4. In general, magnetization of the crystals shows a typical paramagnetic behavior: a pronounced tendency to saturation at the lowest temperatures (2−5 K) and fast decay with temperature at a fixed magnetic field. This behavior is well described by classical Brillouin function with spin $S = {}^5/_2$, as expected for Mn^{2+} (d^5) centers. The analysis of the magnetization for crystals with higher Mn concentration (e.g., $x = 0.0475$) reveals an anti-ferromagnetic coupling between Mn ions.[14] On the other hand, a ferromagnetic contribution to the total magnetization was also observed for some samples (e.g., $x = 0.0475$). This contribution most likely results from Mn_xN_y phases which appear during the synthesis process.

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Supporting Information Available: Crystallographic information for $Ga_{1-x}Mn_xN$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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