Structure and Elemental Distribution of (Ga,Mn)N Nanowires

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ABSTRACT: (Ga,Mn)N nanowires were grown by plasma-assisted molecular beam epitaxy on p-type Si(111) substrates. Chemical composition and elemental distribution of single nanowires were analyzed by energy dispersive X-ray spectroscopy revealing an inhomogeneous Mn distribution decreasing from the surface of the nanowires toward the inner core region. The average Mn concentration within the nanowires is found to be below 1%. High-resolution transmission electron microscopy shows the presence of planar defects perpendicular to the growth direction in undoped and Mn-doped GaN nanowires. The density of planar defects dramatically increases under Mn supply.

KEYWORDS: Nanowire, GaN, Mn, MBE, defects

Diluted magnetic semiconductors (DMS) are appealing systems for the development of spin electronics devices. Much effort has been devoted in the past decade to find out whether the requirement of room temperature (RT) ferromagnetism can be fulfilled by DMSs. Mn is the prototypical magnetic impurity in II–VI and also III–V semiconductors. However, in the latter, the low solubility hinders coupling among the magnetic impurities to give rise to a collective ferromagnetic state. Several attempts have been made in layered structures and the best results have been obtained through low temperature growth of GaMnAs, yet with a Curie temperature (T_C) far below room temperature. Higher T_C have been foreseen for wide-gap semiconductors and oxides,¹ but up to now no convincing proof of a real DMS at room temperature has been provided experimentally. For instance the higher growth temperature of GaN as compared with GaAs makes it even more difficult to reach the high concentrations of dilute magnetic impurities, e.g., Mn, necessary for the coupling.

An alternative approach to layered structures is to consider low-dimensional GaN nanostructures such as nanowires (NW). The magnetic coupling of Mn atoms in (Ga,Mn)N nanowires has been calculated to be ferromagnetic with the Mn atoms having a clear preference for the outermost surface sites over the interior sites.² A slightly different picture has been predicted for Mn-doped GaAs NWs. For this system the influence of the crystal structure on the incorporation and magnetic properties of Mn has been studied by first principle calculations.³ Here Mn is shown to incorporate in the interior of NWs with wurtzite structure and to give rise to ferromagnetic coupling, whereas in zinc blende NWs the Mn remains at the surface and no ferromagnetic coupling occurs.

Experimentally, the magnetic properties of (Ga,Mn)N NWs grown by various methods have been reported to vary between paramagnetic and ferromagnetic up to room temperature.^{4–10} In some reports also the distribution of Mn has been investigated and is found to be homogeneous within the NWs.^{4,7,9–12}

In this Letter we report on the growth of (Ga,Mn)N NWs by molecular beam epitaxy (MBE) with the main focus on the

structural and chemical composition which could play an important role in determining the magnetic properties as already pointed out above. The NWs all grow in the stable wurtzite structure, and Mn is preferentially incorporated at the surface. Two main effects of the Mn supply are observed, i.e., an increased density of basal plane stacking faults, and the formation of semipolar $\{\bar{1}101\}$ facets for NWs grown without sample rotation.

All samples were grown on Si(111) substrates in a Veeco GenII MBE system equipped with a rf-plasma source (UNIBulb), a SUMO dual filament effusion cell for gallium, and a standard effusion cell for manganese. The p-type Si(111) substrates were degreased with acetone and propanol in an ultrasonic bath for 2 min before insertion into vacuum. In situ outgassing took place at 600 °C and at 1000 °C shortly before growth to remove the native oxide. The substrate temperature is measured by a thermocouple. Highly perfect thin GaN(0001) layers are produced in our MBE at a substrate temperature of about 770 °C and slow growth rates (≈ 3 nm/min) under conditions not far from equilibrium between the growing solid and the source materials right at the interface. In fact, under slightly Ga-rich conditions optimum growth occurs in the range of a Ga-bilayer formation and retention at the surface, which is the energetically favorable GaN(0001) surface structure.¹³ On the other hand, N-rich conditions at the growing surface dramatically increase roughness up to the limit of self-organized growth of NWs. The nitrogen plasma source was run with a nitrogen flux of 1 sccm and a plasma excitation power of 400 W. The growth conditions were about 10 times richer in nitrogen than at stoichiometry. The Mn supply was in the range of 5–35% of the total metal flux as given by the sum of the beam equivalent pressure (BEP) of Ga and Mn. Unless stated otherwise the growth commences with a 30 min nucleation phase of undoped GaN NWs in order to ensure comparable starting conditions for subsequent growth under Mn supply.

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Figure 1. Side and top view SEM micrographs of undoped (a, b) and Mn-doped (c, d) GaN NWs grown at a substrate temperature of 850°C . The (Ga,Mn)N NWs were grown with the same Ga flux and a Mn supply of 9%. (e) Average relative Mn concentration as a function of the Mn supply for several samples grown with different Ga/N ratios at temperatures of 775 and 850°C .

The morphology of the samples was investigated by scanning electron microscopy (SEM) in top and side view geometry. The structure, chemical composition, and elemental distribution of selected single NWs were assessed by transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) analysis. To this aim the NWs were transferred with a cleanroom wipe to a Cu grid covered with a thin amorphous carbon foil. Measurements were carried out using a Philips CM200-FEG-UT operated at 200 keV which is equipped with a Si:Li detector (Oxford Link ISIS). Ex situ X-ray photoelectron spectroscopy (XPS) was also performed on the (Ga,Mn)N NWs samples with monochromatized Al K α for the photoexcitation.

Figure 1 shows the sample morphologies for undoped (a, b) and Mn-doped GaN NWs (c, d) grown at 850°C . In this specific case the (Ga,Mn)N NWs were grown without any preceding GaN nucleation. In general the growth at higher temperature results in an improved morphology of the NWs as shape uniformity is concerned. Mn-doping leads to a lower NW density and for comparable Ga fluxes to an enhanced axial growth rate of the (Ga,Mn)N NWs. This is consistent with a nanowire growth partially controlled by Ga diffusion. Due to the lower nanowire density more Ga atoms are available from the surface of the substrate for each nanowire. Furthermore tilting of the (Ga,Mn)N NWs relative to the substrate is observed. This is most likely due to increasing roughness of the substrate for increasing Mn supply. Interdiffusion of Mn at the Si surface induces precipitates extending several tens of nanometers deep into the substrate as observed by cross sectional EDX analysis in scanning TEM.

Figure 1e reports the average relative Mn concentration as a function of the Mn supply for several samples grown with

Figure 2. (a) Scanning TEM images of a (Ga,Mn)N NW and details of the selected area for chemical analysis. Line and point scan positions are given by the blue dotted line and the red circles, respectively. (b) EDX intensity profiles of Ga (red, open circles) and Mn (black, filled circles) for the line scan AA'. The Mn intensity has been multiplied by a factor of 20 for clarity. (c) Relative Mn concentration from the AA' line scan (blue, filled circles) and from the point scan (red, open circles). (d) EDX intensity profiles as in (b) measured for the line scan BB'.

different Ga/N ratios at temperatures of 775 and 850°C . The average Mn concentration is determined by an EDX point analysis and given in percentage of the Ga atom concentration within the nanowires. For each point measured along the NW axis, a volume across the whole NW thickness is sampled. On average less Mn is incorporated within the NWs at the higher growth temperature. This behavior shows that the solubility limit

Figure 3. TEM images of an undoped GaN nanowire (a) and a Mn-doped NW with a Mn supply of 15% (b). Both samples were grown with substrate rotation at a temperature of 850 °C. (c) TEM image of a nonrotated Mn-doped GaN NW grown at a temperature of 850 °C and a Mn supply of 15%. (d) HRTEM close-up of the faceted region along with the Fourier transform.

has already been reached under the applied growth conditions. The average incorporation of manganese is found to be below 1%, independent of the Mn supply for the investigated range between 5 and 35%. A comparable observation is reported in the literature for samples grown by chemical vapor deposition (CVD).¹² These results point to a more general difficulty in incorporating high manganese concentrations in GaN nanowires, even though reports of (Ga,Mn)N nanowires with Mn concentrations as high as 10% do exist.⁶

The Mn distribution in the (Ga,Mn)N NWs was further analyzed by spatially resolved EDX with the electron beam crossing the NW along the radial direction. The results are reported in Figure 2. Line scans across the NW as well as selected positions have been measured as marked in Figure 2a. The Ga and Mn intensity profiles for the AA' line scan are shown in Figure 2b. The relative Mn concentration evaluated for the line scan AA' and for the selected points is shown in Figure 2c. Due to the low Mn concentration and the short dwell time of the electron beam, a poor signal-to-noise ratio is obtained for the line scan method. Therefore in Figure 2c only data were considered for which the Mn K signal clearly exceeds three times the standard deviation of the background signal. In general point scan data provide better statistics. Therefore the low Mn concentration in the central region of the NW was determined by this method only. Furthermore point scan data can serve as a consistency check for the line scan results in the outer region.

The average Mn concentration at the center of the NW amounts to about 1%, whereas at the surface a value up to about 2% is reached. Considering the high spatial resolution of the probe (1 nm), the measured relative Mn concentration profile points to an inhomogeneous distribution continuously decreasing from the surface toward the inner core region. This tendency is even more pronounced toward the faceted NW surface as shown in Figure 2d. A simple core-shell model with a Mn-free core is not able to reproduce the measured profiles quantitatively.

The experimental spatially resolved chemical analysis clearly shows evidence of a preference of Mn to incorporate at the NW surface region as compared to the inner part. This behavior was

found for various NWs from different samples with the electron beam crossing the NWs perpendicular to the growth direction, as well as for a cross sectional prepared sample with the electron beam crossing the NW almost parallel to the *c* direction. A tendency of Mn segregation toward the surface was also observed in other experiments during MBE growth of thin (Ga,Mn)N(0001) epitaxial layers at a substrate temperature of 775 °C.¹⁴

Also theoretical calculations predict a more stable configuration of the Mn atoms in the outermost surface sites as compared to the interior ones for various Mn-doped GaN systems: (i) Mn-doped GaN(0001) NW,² (ii) Mn-doped GaN(11 $\bar{2}$ 0) layers,¹⁵ and (iii) Mn-doped GaN(0001) layers.¹⁶ In particular, Mn-doped nanowires have been studied by density functional theory with a supercell geometry extending infinitely along the [0001] direction.² The nanowire diameter is 1.0 nm, and the Mn concentration is 4.2%. Atomic relaxation on the outermost surface layer with a contraction of the Ga–N bond corresponds to a total energy minimum for the undoped GaN nanowire. Different configurations have been then calculated with two Mn atoms within the supercell, and minimum energy is found for Mn occupying Ga sites at the outer surface. In this configuration a ferromagnetic (FM) coupling between the Mn atoms results which is mediated by N and critically depends on the Mn–N distance.

The magnetic behavior of selected NW ensembles has been assessed by superconducting quantum interference device (SQUID) magnetometry. No clear magnetic signal from the NWs has been detected. The measured signal remains after mechanical removal of the NWs and is ascribed to the Mn–Si precipitates formed at the substrate interface. The formation of precipitates within or on the substrate can be a critical point in the magnetic analysis of NW samples.

Concerning a possible FM coupling of the Mn at the surface of the NWs, it must be noted that the real surface is oxidized as expected and as measured by XPS (not shown). The surface reaction should modify the Mn configuration at the surface which has been predicted to be critical for the Mn–Mn FM coupling.

Furthermore the limited Mn concentration at the surface (2%) is much too low to induce a macroscopic FM order by double-exchange due to the very short-range character of this interaction.¹⁷

Investigations of the crystal structure of single undoped and Mn-doped GaN NWs were carried out by TEM. The results are shown in Figure 3. The Fourier transforms (FT) of the HRTEM images show a wurtzite crystal structure with the growth direction along $\langle 0001 \rangle$.

It is often stated that NWs grow free of any extended defects. However the majority of the investigated undoped GaN NWs show the presence of planar defects perpendicular to the growth direction (Figure 3a). The incorporation of Mn significantly increases the density of planar defects which are most likely basal plane stacking faults (BSF) (Figure 3b). This is deduced from intensity contributions within the FTs recorded from selected areas of the Mn-doped NWs which can be assigned to short segments of cubic GaN. It is worth noting that a proper choice of the zone axis is a prerequisite for the observation of these defects. For instance BSFs in wurtzite structures imaged along the $[01\bar{1}0]$ zone axis will be invisible.¹¹

It is known that the stacking fault energy (SFE) for BSFs in bulk GaN is low compared to InN and AlN ($E_{\text{BSF}}^{\text{GaN}} < E_{\text{BSF}}^{\text{InN}} < E_{\text{BSF}}^{\text{AlN}}$).^{18–20} Furthermore it was theoretically predicted that Mn doping may lead to the stabilization of the cubic zinc blende phase in bulk GaN for Mn concentrations above a critical value.^{16,21} As the energy difference between wurtzite and zinc blende structure mirrors the stacking fault energy, Mn doping should lead to a reduction of the stacking fault energy.¹⁸ Our achieved Mn-dopant concentrations lie far below the theoretical critical values for the stabilization of cubic GaN, but the observed trend of an increased density of BSFs for Mn-doped GaN NWs is consistent with these calculations.

Panels c and d of Figure 3 further show anisotropic faceting for (Ga,Mn)N NWs when grown without sample rotation. An analysis of the inclination shows that the facets are $\{1101\}$ planes. As shown in Figure 2 an increase of the Mn K intensity is revealed for the faceted side as compared with the opposite side of the NW. These results indicate that the formation of these facets is most likely due to a locally increased Mn concentration lowering the surface energy of these facets. Therefore the formation of these facets could be significantly lowered by rotating the samples during MBE growth. The formation of specific nanowire facets in the presence of Mn can be even more drastic for other growth methods. In the case of CVD grown (Ga,Mn)N nanowires, the shape and the growth direction can be altered depending on the concentration of the Mn precursor.^{12,22} However, in our case the epitaxial relation with the substrate and the growth direction are maintained for a similar range of Mn supply.

In summary, *c*-oriented (Ga,Mn)N NWs with an average Mn incorporation below 1% were grown by plasma-assisted MBE under N-rich conditions on p-type Si(111). Different Ga/N ratios and Mn supplies were applied, and no clear correlation with the Mn incorporation was found. On average the higher growth temperature induces a lower Mn concentration in the NWs. Spatially resolved EDX analysis along the radial direction reveals an inhomogeneous Mn concentration profile with an enhanced Mn incorporation toward the sidewalls. TEM analysis shows that the NWs have mainly wurtzite crystal structure with the presence of planar defects in undoped and Mn-doped GaN NWs. These defects are most likely basal plane stacking faults whose density strongly increases by Mn doping. Furthermore, it is argued that a local increase of Mn concentration at the sidewalls leads to the formation of $\{1101\}$ facets. The poor incorporation of Mn within the MBE

grown GaN nanowires suggests that this system might hardly be suited for spintronic applications.

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