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J. Am. Chem. Soc., **2007**, 129 (36), 10980-10981• DOI: 10.1021/ja073310r • Publication Date (Web): 16 August 2007

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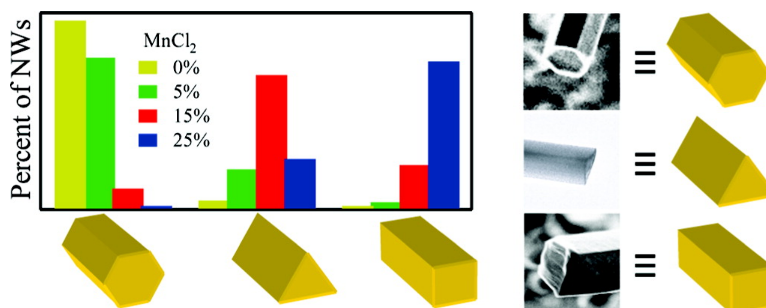

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Published on Web 08/16/2007

Dopant Ion Concentration Dependence of Growth and Faceting of Manganese-Doped GaN Nanowires

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The prospect of coexistence and control of multiple functional properties in materials is of both scientific and technological importance. Materials that combine electrical and magnetic properties have attracted much attention for their promise in spin-electronics, or spintronics.[1] Semiconductor nanowires (NWs) have emerged as key components for future photonic and electronic devices.[2] Imparting magnetic properties into semiconductor NWs by controlled doping with transition-metal ions is therefore of a particular interest.[3−7] These materials, known as diluted magnetic semiconductor NWs (DMS-NWs), are seen as prime candidates for spintronics applications.[3−7] Synthesis of DMS-NWs is a challenging task, however, because of difficulties in doping control during quasi-one-dimensional (1-D) crystal growth. Little is known about the mechanism of dopant ion incorporation and the effects of dopants on the growth, structure, and properties of DMS-NWs. Moreover, directional growth and well-defined faceting make NWs an excellent model system for studies of crystal growth in the presence of impurities.

Manganese-doped GaN (Mn:GaN) is an attractive material for spintronics because of proposed high-temperature ferromagnetic ordering of Mn in the GaN lattice.[8] Different morphologies and faceting of Mn:GaN NWs were reported,[3−5] in some cases without addressing rigorously the dopant locale and speciation.[5] Theoretical studies have suggested that growth direction, shape, and surface topology are important factors for magnetic properties of Mn:GaN NWs.[7] In this Communication we report on the effect of Mn dopant ions on the growth and faceting of Mn:GaN NWs. We show that an increasing concentration of Mn precursor in the reaction mixture alters systematically the growth and faceting of Mn:GaN NWs and demonstrate that NW morphology can be controlled using Mn dopants.

Mn:GaN NWs were synthesized by adapting the chemical vapor deposition method for the growth of II−VI and III−V NWs, as described previously.[3] We applied this approach to study growth dependence on the concentration of Mn precursor. All samples were synthesized under identical conditions at 990 °C in a single step process from a mixture of elemental Ga and varying amounts of $MnCl_2$ in a flow of H_2 and NH_3 gases. Nickel nanoclusters, prepared in-situ on sapphire substrates, were used as the NW growth catalysts. The amount of $MnCl_2$ in the reaction mixture was varied from 0 to 30 mol % with respect to Ga.

The morphologies, crystal structures, and faceting of Mn:GaN NWs were examined with transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure 1). In all samples we observed three distinct cross sections: hexagonal, triangular, and rectangular (Figure 1a, b, and c, respectively). These were present in different ratios depending on the starting concentrations of $MnCl_2$. SEM images of the corresponding cross sections are shown as lower insets (also Figure S1 in Supporting Information). Low resolution (left panels) and high-resolution (right panels) TEM

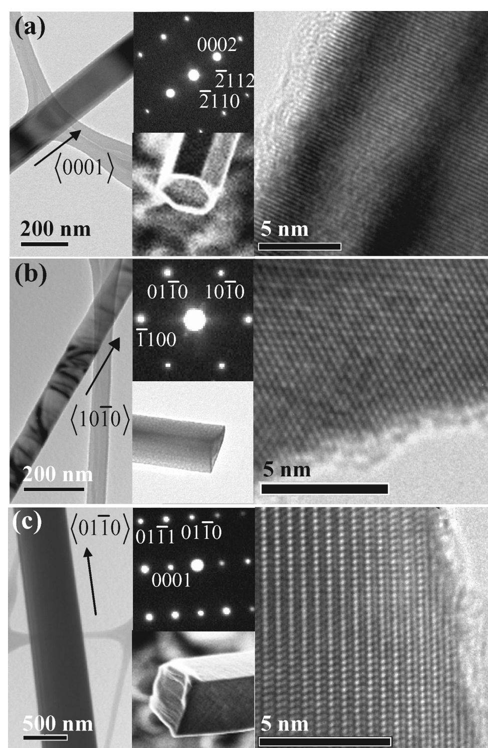

Figure 1. Low resolution (left) and high resolution (right) TEM images of (a) hexagonal, (b) triangular, and (c) rectangular Mn:GaN NWs. The insets show respective electron diffraction patterns (upper insets) and cross-section SEM images (lower insets).

images of typical Mn:GaN NWs reveal that the NWs are single crystalline and have uniform thicknesses and smooth surfaces along the growth directions. Electron diffraction (ED) pattern of the hexagonal NW (Figure 1a, upper inset) recorded along [01−10] zone axis, can be indexed to wurtzite crystal structure and allows the assignment of the growth direction as ⟨0001⟩. ED of the triangular NW (Figure 1b, upper inset), imaged along the [0001] zone axis, enables the determination of the NW growth direction as ⟨10−10⟩. The NW with rectangular cross section grows along ⟨01−10⟩ direction, as evidenced from the ED pattern obtained along the [2−1−10] zone axis (Figure 1c, upper inset).

Energy dispersive X-ray spectroscopy (EDX) measurements were carried out to estimate doping concentrations and to determine dopant ion distributions in the NWs. The NW doping concentrations from Figure 1 are estimated to be ca. 0.85%, 0.52%, 0.64% for hexagonal, triangular, and rectangular NWs, respectively. We found that doping concentrations for individual NWs were comparable regardless of the starting concentration of $MnCl_2$ and of the NW morphologies. Ga and Mn EDX elemental line scan profiles for hexagonal, triangular, and rectangular NWs from Figure 1, collected

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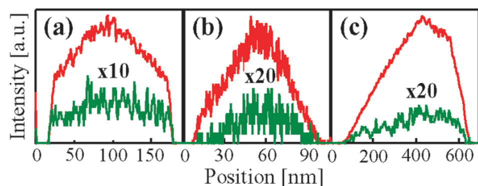

Figure 2. EDX line scan profiles of hexagonal (a), triangular (b),, and rectangular (c) Mn:GaN NWs for Ga (red line) and Mn (green line). The average doping concentrations are 0.85% (a), 0.52% (b), and 0.64% (c). The Mn profiles are multiplied for clarity, as indicated.

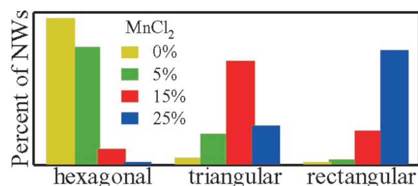

Figure 3. Percentage of Mn:GaN NWs having hexagonal triangular and rectangular cross sections in samples synthesized with $MnCl_2$ starting concentration of 0% (yellow), 5% (green), 15% (red), and 25% (blue). Distribution was determined based on a minimum of 50 NWs for each sample.

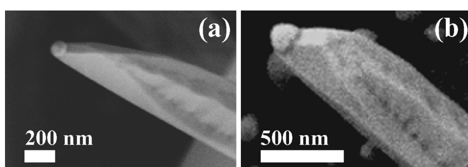

Figure 4. SEM images of Mn:GaN NW faceting during the NW growth: (a) transformation of hexagonal to triangular cross section, and (b) transformation of hexagonal to rectangular cross section.

perpendicular to the NW growth axes, are shown in Figure 2a, b, and c, respectively. For all three NWs the Mn profiles are essentially identical to those of Ga (Figure S2), suggesting homogeneous distribution of dopant ions for the given synthetic conditions, regardless of the NW growth direction or faceting. The forms of the profiles observed are consistent with the NW geometries and orientations.[3,9]

Figure 3 shows the distribution of Mn:GaN NWs having a specific cross-sectional shape, for different Mn concentrations in the reaction mixture. Synthesis of pure GaN NWs in the absence of Mn precursor (yellow) yields NWs with almost exclusively hexagonal or cylindrical cross sections. At $MnCl_2$ concentration of 5 mol % (green), most NWs (77%) still have hexagonal cross sections, while we observed ca. 20% of NWs having triangular cross sections. With further increase in initial Mn concentration to 15 mol % (red) the fraction of hexagonal NWs declines, and the NWs with triangular cross sections become predominant (68%), along with an appreciable fraction of rectangular NWs (22%). At the $MnCl_2$ concentration of 25 mol % (blue), the majority of the NWs attain rectangular cross section (75%), while the percentage of hexagonal NWs becomes negligible. The fraction of NWs having triangular and rectangular cross sections increases at the expense of hexagonal NWs with increasing Mn precursor concentration. We note that the presence of Mn dopant ions in the reaction mixture also lowers the average lengths of NWs. These results show that Mn dopant ions inhibit the growth of Mn:GaN NWs and that NW growth and faceting depend on the concentration of Mn precursor.

Faceting of Mn:GaN NWs during the growth was further studied with SEM (Figure 4). Figure 4a and b show the transformation of Mn:GaN NW morphology from hexagonal to triangular and rectangular, respectively. Appearance of new facets can be observed in the vicinity of the catalyst particles at an early stage of the NW growth. Recent theoretical studies indicate that Mn atoms have a preference for surface sites over the interior sites in GaN NWs.[7] Furthermore, studies of doping Mn into nanocrystals suggest that binding to specific facets is critical for dopant incorporation.[10] Although the doping mechanism for Mn:GaN NWs cannot be definitively elucidated from the structural data alone, our results indicate that Mn binding to the specific facets also plays a key role in governing the growth of, and dopant incorporation into, GaN NWs. We believe that dopant binding to the most stable surface sites formed during NW nucleation inhibits the advancement of the corresponding NW facets, leading to termination of their growth at high Mn starting concentrations. The binding of Mn may then proceed on other available facets with lower binding enthalpies (Figures S3 and S4). Growth of such facets subsequently defines the NW morphology from the onset of the growth. Similar doping concentrations for all three NW morphologies indicate that Mn residence times are similar for the most favorable facets of GaN NWs, which is consistent with the theoretical predictions for II−VI wurtzite lattices.[10] The difference in the reported faceting of Mn:GaN NWs may, therefore, be associated with a difference in starting amounts of Mn precursor. Mechanistic and theoretical studies of Mn:GaN NW growth and dopant incorporation, and of other GaN NW systems are currently under investigation.

In summary, we have shown here that the growth and faceting of Mn:GaN NWs is critically dependent on the concentration of Mn precursor in the reaction mixture. These results allow for preparation of Mn:GaN NWs in a truly controlled fashion, and for experimental studies of the properties of Mn:GaN NWs with respect to their structure and morphology. Furthermore, this work shows that it may generally be possible to use simple ionic impurities to control and manipulate 1-D crystal growth.

Acknowledgment. We thank Fred Pearson (Brockhouse Institute, McMaster University) for assistance with TEM and EDX measurements. P.V.R. acknowledges the financial support of this work by the University of Waterloo and NSERC.

Supporting Information Available: TEM images of NW cross sections and faceting, and normalized EDX Ga and Mn line scans. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA073310R