Synthesis and analysis of magnetic semiconductor nanowires (Mn-doped GaP and GaN nanowires)
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1. Introduction

Diluted magnetic semiconductors (DMS) are expected to be key materials in future spintronicdevices, since theyare an excellent media in which charge and spin degrees of freedom accommodatedinto single matter resulting in interesting magnetic, magneto-optical, magnetoelectronics, and other properties [1-6]. The demonstration of unique propertiesof DMS, such as field-effect control of ferromagnetism, efficient spin injection to produce circularly polarized light, and spin-dependent resonant tunneling, opens a rich and diverse landscape for technological innovation in magnetoelectronics.Searchingfor high Curi temperature DMS materials is presently challenging subject with respect to applications as well as theoretical viewpoints. The integration of 1D DMS nanostructures into electronics is particularly of importance in order to make real use of the advantages offered by the spins. Here, we investigate the synthesis of Mn-doped GaN and GaP nanowires (NWs) exhibiting ferromagnetism at room temperature. We synthesized exclusively 5-7 at. % Mn-doped GaN and GaP NWs with high purity via thermal chemical vapor deposition (CVD). The structure, composition, and magnetic properties were thoroughly investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-voltage TEM (HVEM) using 1.25 MV (Jeol JEM ARM 1300 S, 1.25 MV), energy-dispersive X-Ray fluorescence,and high-resolution X-ray diffraction (XRD).

2. Experimental

Ga/GaN/$MnCl_2$ or GaP/$MnCl_2$ mixture was placed in a quartz boat loaded inside a 2.5 cm diameter and 80 cm long quartz tube reactor. Alumina substrates were coated with 0.01 M $HAuCl_4 \cdot 3H_2O$ (98+%, Sigma) ethanol solution. The substrate was positioned at a distance of 10 cm away from the quartz boat. Argon (Ar) flowed with a rate of 500 sccm while raising or lowering the temperature. The temperature of the Ga/Mn source was set at 1100 °C, and that of the substrate was

approximately 950 °C. NH_3 (99.999 %, Solkatronic) or Ar was introduced with a rate of 100 sccm for 1 h.

3. Results and Discussion

TEM image reveals the general morphology of the nanowires (Figure 1(a)). They have either straight or periodically bumpy surface. Few catalytic nanoparticles attach to the endof the nanowires. The diameter of nanowires is in the wide range 40-100 nm. The bumpy nanowires usually have the larger diameter than the straight nanowires. The HVEM image of straightnanowires shows the defect lines perpendicular to the growth direction (Figure 1(b)). The inset is Fourier-transformed ED pattern, showing that of twin-crystalline zinc blende structured GaP crystal. The growth direction is [111], which is same as that of undoped GaP NWs. The defect lines existing betweenwell-crystalline zinc blende structured GaP crystals The (111) fringes perpendicular to the wire axis are separated by about 3.1 Å, which is consistent with that of zinc blende GaP (a=5.4506 Å JCPDS Card No. 32-0397). The detailed feature of the bumpy GaP NW is shown in Figure 1(c). The bumpy parts are apparently sheathed by amorphous-like outerlayers. The atomic-resolved image for the edge of crystalline parts reveals perfect GaP crystals (Figure 1(d)). The ED pattern (not shown) confirms the single-crystalline GaP crystals. At the bumpy parts,the polycrystalline GaP nanosize crystals are embedded in the amorphous layers sheathing the crystalline GaP MW (Figure 1(e)). The inset is corresponding ED pattern showing the polycrystalline nature of GaP crystals.

The XRD pattern has been measured for the undoped and Mn-doped GaP NWs, showing a typical one of zinc blende structure GaP crystal (Figure 2(a)). The undoped GaP NWs were synthesized by the procedure described previously. No other crystalline phases such as Ga-Mn, Mn-O, or Mn-P were detected. The Mn-doped GaP NWs have the narrower width and the peak position shifted to a slightly lower angle. The narrower width indicates that the Mn doping would cause the less surface defects than the undoped GaP crystals.

Figure 3(a) corresponds to a SEM micrograph showing the high-density Mn-doped GaN nanowires grown homogeneously on a large area of the substrates. The length is about 20 ㎛. They usually have triangle cross-section and smooth/clean surface without any particle impurities. TEM image reveals the general morphology of the nanowires that most of them are straight and their diameter is uniformly 40-70 nm with a mean value of 50 nm (Figure 3(b)). The nanowires are terminated with few catalytic particles. HVEM image of a GaN nanowire is shown in Figure 3(c). Atomic-resolved view reveals negligible defects in the lattice planes (Figure 3(d)). No clusters or

other crystal domains embedded in the wurtzite structured GaN crystals were found over the entire nanowire. The inset is its corresponding ED pattern, showing the single-crystalline GaN crystal and the growth direction parallel to the [100] direction of hexagonal unit cell. All of the nanowires, we observed, are grown with the same structure.

In summary, the Mn-doped GaP and GaN nanowires were synthesized by CVD. The HVEM images reveal that the majority of nanowires have bumpy surface sheathed by the GaP nanocrystals. The HVEM images also detect no other clusters or crystal domains embedded in the GaN crystals. Hysteresis curves measured at 5 and 300 K provide an evidence for the room-temperature ferromagnetism with T_C higher than 300 K. Therefore we conclude that Mn is incorporating into the GaP and GaN nanowires and forming the ferromagnetic semiconductor nanowires.

References

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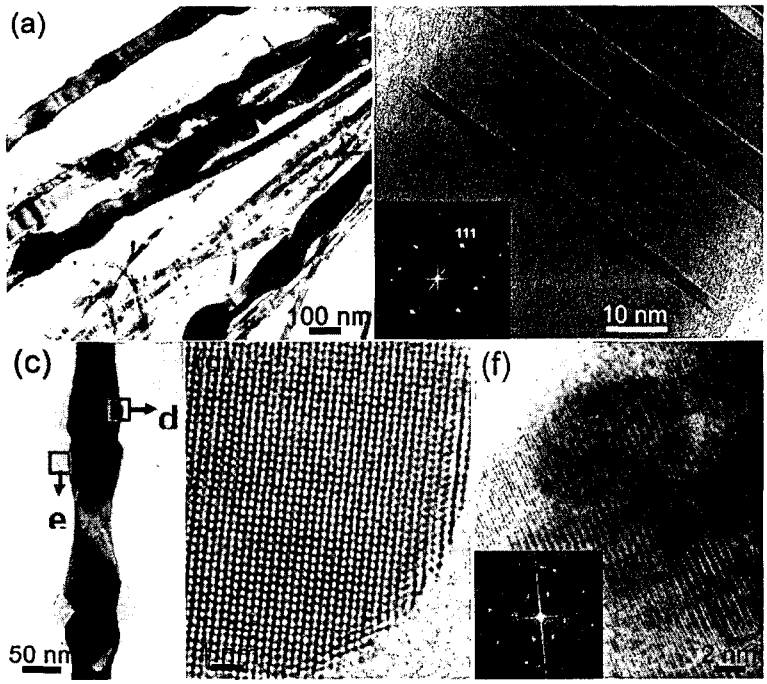

Fig. 1. (a) TEM image showing the typical morphology of Mn-doped GaP NWs. The diameter is 40-100 nm. The inset corresponds to the SAED pattern of single nanowire, showing the [111] growth direction (b) The straight nanowires shows the defect lines perpendicular to the growth direction (c) Atomic-resolved view shows the highly crystalline (001) planes along the wire axis. (d) HVEM image for a selected bumpy nanowire. (e) Atomic-resolved view shows the highly crystalline GaP crystals with cracks indicated by the arrows. (f) The polycrystalline GaP nanosize crystals embedded in amorphous outerlayers sheath the crystalline GaP NW.

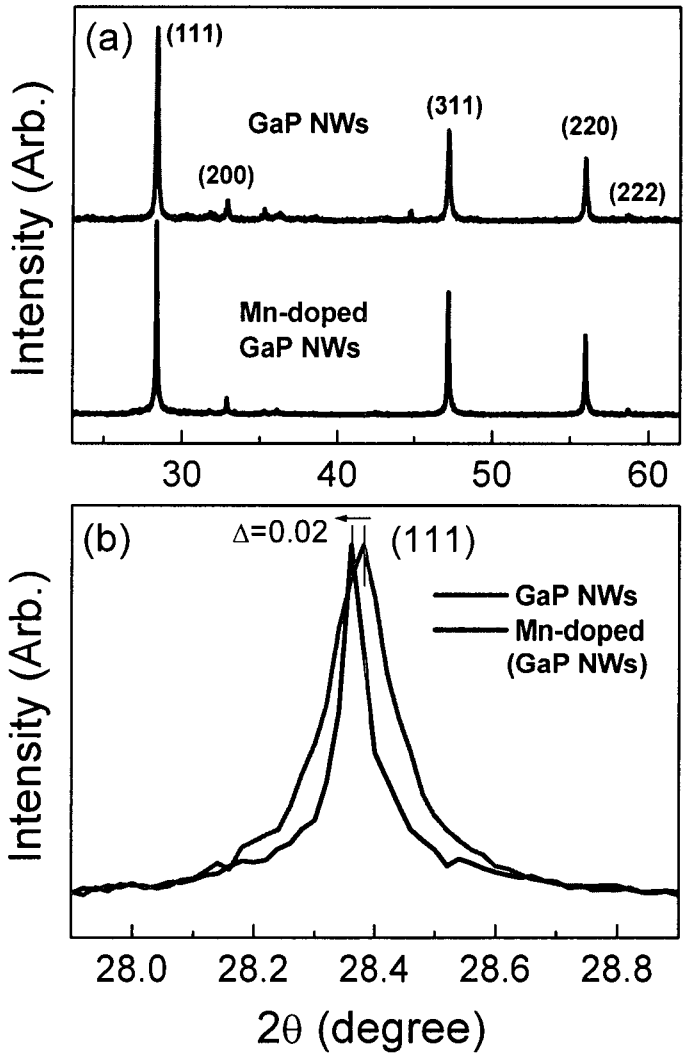

Fig. 2. (a) Full-range XRD pattern and (b) magnified (111) peak of undoped and Mn-doped GaP NWs.

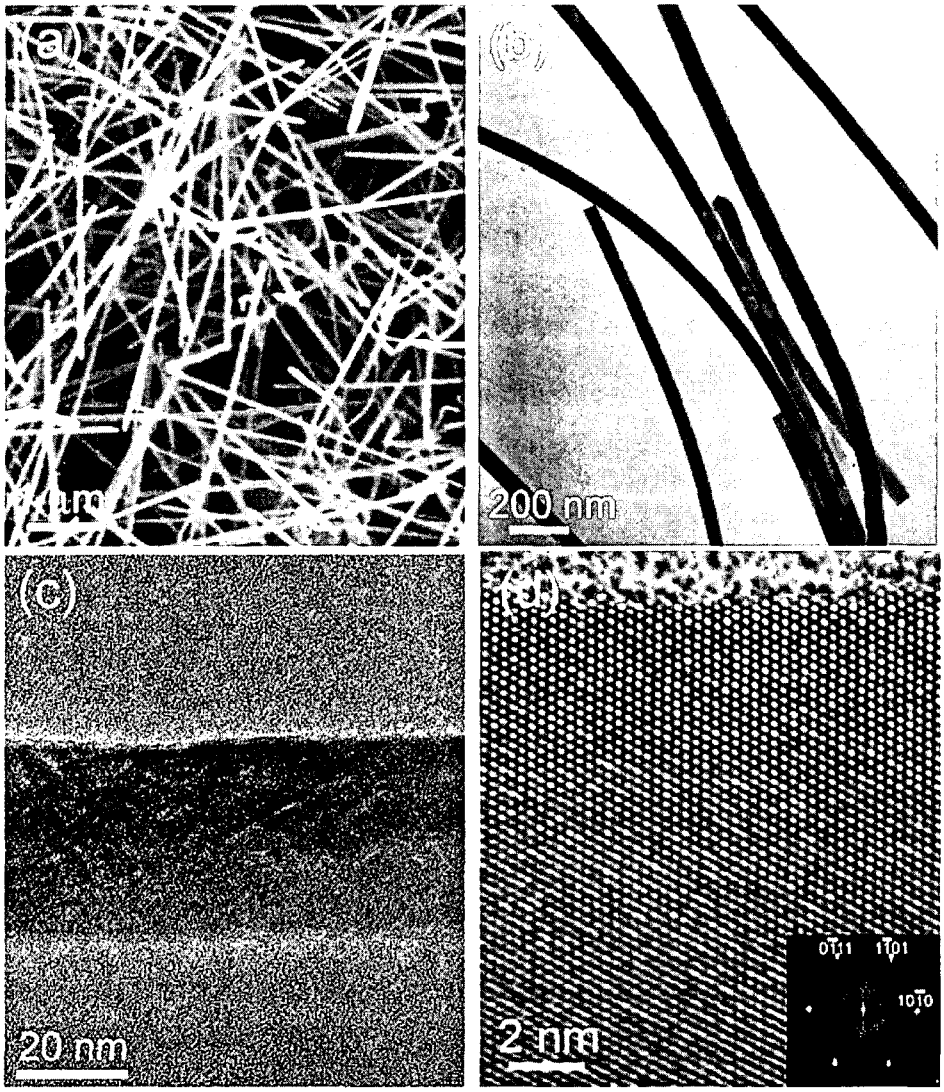

Fig. 3. (a) SEM micrograph of high-density nanowires homogeneously grown on the substrate. (b) TEM image reveals the uniform diameter 50 nm. (c) HVEM image for a Mn-doped GaN nanowire, and (d) magnified image showing single-crystalline phase with no embedded clusters. The SAED pattern confirms the [100] growth direction.