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Mn-doped AlN nanowires with room temperature ferromagnetic ordering

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Mn-doped AlN nanowires were synthesized by *in situ* doping of Mn using a chemical vapor deposition method. Analyses of microstructure and chemical compositions indicate that the as-prepared samples were homogenously Mn-doped AlN nanowires. The low temperature photoluminescence, and magnetization as a function applied magnetic field of the Mn-doped AlN nanowires were investigated. A Curie temperature higher than 300 K was observed from the as-doped nanowires. The room temperature ferromagnetic properties of the synthesized Mn-doped AlN nanowires make it an excellent candidate for applications in future spintronic nanodevices.
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In the past two decades, much attention has been paid to spintronics because of the possibility of using both the freedoms of spin as well as charge of carriers for next generation devices. Diluted magnetic semiconductors (DMSs) are believed to be the most promising candidate for spintronics.[1–4] Nowadays, much research work has mainly focused on syntheses and magnetic property of transition metal doped III-V and II-VI semiconductors since theoretical work predicted that these materials can exhibit high Curie temperature (T_C) above room temperature,[5–7] which is of great importance in point of view of application. As one of the important III-V semiconductors, AlN has a very wide direct band gap of ~6.2 eV and plays an important role in many solid-state devices.[8] AlN may also be a good candidate for spintronics due to its predicted room temperature ferromagnetism when doped with transition metals.[9,10] Moreover, near or above room temperature ferromagnetism of transition metal (Mn, Co, Cr)-doped AlN thin films was observed by several groups recently,[10–14] and the resistivity reduced significantly.[14] One-dimensional DMS nanostructures are of great importance, since they are not only well-defined building blocks to fabricate nanoscale electronic and optoelectronic devices but also could potentially achieve high carrier concentrations and efficient injection of spin-polarized carrier.[15] Recently, Mn-doped GaN nanowires with a Curie temperature higher than 300 K through chemical vapor deposition (CVD) method have been reported.[15–17] However, though AlN is also an important III-V semiconductor, room temperature ferromagnetism of transition metals doped AlN one-dimensional nanostructures has not been reported. In this work, Mn-doped AlN nanowires were synthesized via a simple vapor phase deposition method, and room temperature ferromagnetism of the as-synthesized sample was observed.

Mn-doped AlN nanowires were synthesized in a typical horizontal furnace CVD system. An alumina boat with Al powder (99.9%) was placed in the center of a quartz tube. A clean silicon (100) substrate of about 1 cm^2 coated with 10 nm Al firstly and then 5 nm Au by E-beam evaporation is covered on the alumina boat at a distance of 1 cm from the surface of the source material in the boat. Another alumina boat with 3 g $MnCl_2$ was placed at one end of the furnace near the gas input. The quartz tube was transferred into a horizontal tube furnace and evacuated to vacuum to move out oxygen. During growth, the pressure inside the tube was kept at 100 Torr. The furnace was heated at a rate of 20 °C/min to 890 °C and kept at this temperature for 30 min under a mixed gas flow of argon and ammonia with flow rates of 100 and 5 SCCM (cubic centimeter per minute), respectively. The temperature was then increased to 960 °C quickly and kept for another 15 min. After the furnace was cooled down to room temperature, the substrate was found covered with a gray layer. X-ray diffraction (XRD) technique was carried out to investigate the phase structure of the products. A field emission Strata DB235 focus ion beam system working at scanning microscope (SEM) mode was employed to investigate the morphology of the as-grown sample. A Tecnai F30 transmission electron microscope (TEM) operating at 300 kV with a field emission gun was used together with a Gatan imaging filter to analyze the microstructure and the chemical composition of the sample. Inductively coupled plasma (ICP) spectroscopy (Leeman Labs. Inc.) was used to further investigate the content of manganese. Low temperature photoluminescence was excited by a 325 nm wavelength laser. Magnetic properties of the nanowires were studied using a superconducting quantum interference device (SQUID) magnetometer.

A typical SEM image of the Mn-doped AlN nanowires was shown in Fig. 1(a). It can be seen that the as-grown nanowires cover surface of the substrate in high density. The average length of the nanowires was about several to ten micrometers and diameters vary between 100 and 200 nm. X-ray diffraction was first used to characterize the structure of the product. All peaks in the corresponding x-ray diffraction analysis can be assigned to the wurtzite structure of pure AlN. No other phases were found. The microstructure of the Mn-doped AlN nanowires was further investigated with TEM. Figure 1(b) shows a TEM image of the nanowires, and shows that the nanowires have average diameter between 100 and 200 nm. The corresponding electron diffraction pattern shown in inset revealed that the as-grown Mn-doped AlN nanowires are polycrystalline, and the diffraction ring pattern is consistent with the structure of the wurtzite alumi-

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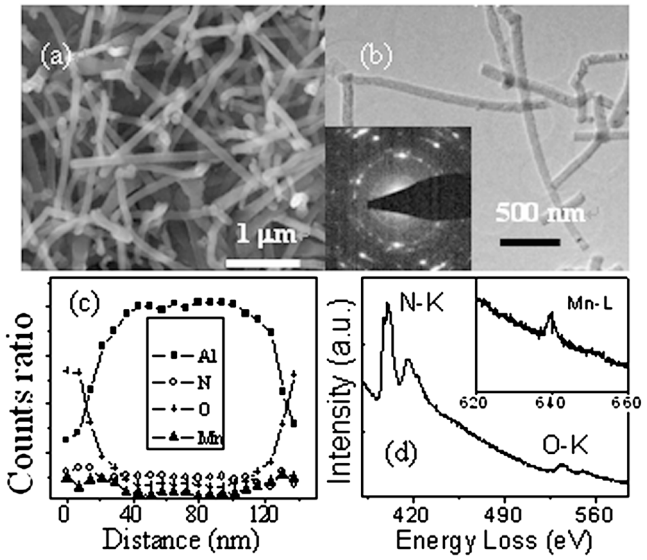

FIG. 1. (a) Low magnification SEM image of high-density as-grown nanowires. (b) TEM image of a single Mn-doped AlN nanowire. Inset: corresponding electron diffraction revealing that the nanowires are polycrystalline. (c) EDS line-scan profile from a representative Mn-doped AlN nanowire, which reveals the radial Al, Mn, N, and O element distributions in a single Mn-doped AlN nanowire. (d) EELS spectrum showing *K* edges of nitrogen and oxygen. The inset shows the Mn-*L* peaks.

num nitride. Energy dispersive spectroscopy (EDS) of the nanowires shows distinct peaks corresponding to nitrogen (N-*K*), Al (Al-*K*), and Mn (Mn-*L*) edges. The Mn/(Mn+Al) atomic percent was determined to be about 3. Analysis of ICP spectroscopy showed that the exact ratio was 2.6%, which is consistent with EDS results. Figure. 1(c) displays the EDS line-scan profiles of Al, N, Mn, and O for a crossing of a typical nanowire. To present the relative proportion of different elements, the counts ratio is calculated as follows. At every point, the value of a certain element is the count of this element divided by the sum of counts of all four elements at that point. The result indicates that the Mn distributes uniformly over the cross section of the nanowire. The composition of the nanowires is also homogenous along the nanowire axis and the variation of manganese content from different nanowires is very small ($<0.5\%$), indicating a uniform doping of manganese in the products. From the profile, oxygen impurity was also observed with an atomic concentration below 5%, and is mainly distributed in the outer layer of the nanowire to form an amorphous sheathing layer, most probably caused by surface oxidation. In the inner layer, oxygen distributes homogenously, suggesting that it was doped into the crystal lattice, but not form secondary phases. No peaks corresponding to Au were observed in the nanowires, indicating that the growth is not vapor-liquid-solid mechanism, but possibly via vapor-solid. The role of Al/Au thin film can change the reaction conditions, such as the roughness of substrates, which was reported to influence the morphology of GaN nanowires.[18] These results are further confirmed by electron energy-loss spectroscopy (EELS), as shown in Fig 1(c). It shows distinct peaks corresponding to nitrogen (N-*K*). The $L_{2,3}$ ionization edge of Mn appears at 640 eV. O impurity (O-*K*) is also detected at 532 eV.

Photoluminescence measurements were also performed at both 10 and 300 K. The as-grown sample exhibited a red luminescence as exemplified by the solid lines in Fig. 2.

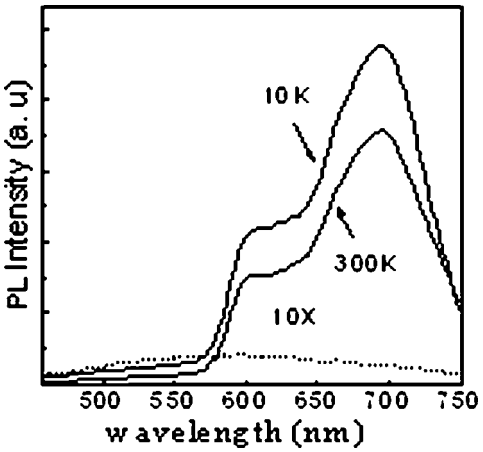

FIG. 2. Photoluminescence measured at 10 and 300 K for the Mn-doped AlN nanowires (solid line) and the undoped AlN layer (dashed lines).

They consist of two intensive emission peaks around 600 and 695 nm. A small band with the peak at about 670 nm was also observed. The red-orange band at 600 nm is a characteristic of the luminescence from the Mn center in AlN.[19] The other two peaks were also reported in previous work of Mn-doped AlN films with O impurity.[20] The emission could be observed with naked eyes even at room temperature. In contrast, the PL spectra of undoped AlN nanowires were also measured, exhibiting very weak broad bands located between 550 and 600 nm, as shown by dashed lines in Fig. 2 with a magnification of 10.

The magnetic properties of the as-grown Mn-doped AlN semiconductor nanowires were investigated at different temperatures using a SQUID magnetometer. Figures 3(a) and 3(b) show the magnetization (M) versus magnetic field (H) measured at 5 and 390 K respectively, which is the limit of the SQUID. The signals of the substrate are already subtracted and clear hysteresis loops can be observed. The whole M-H loops at different temperatures are shown in the insets. The coercive fields (H_C) are 53 Oe at 5 K, 44 Oe at 300 K, and 30 Oe at 390 K, showing that the T_C of the as-grown nanowires is higher than the limit of the SQUID. The spontaneous magnetizations (M_s) are 0.55, 0.073, and 0.030 emu/g at 5, 300, and 390 K respectively. The magnetization at different temperatures is the same or smaller than those in previous reports of Mn-doped AlN thin films, indicating further improvement is possible.[14,21]

Possible secondary phases accounting for ferromagnetism at room temperature is Mn_4N. MnO and Mn_3O_4 nanocrystals were reported to have T_C=40–50 K,[22,23] which could probably contribute to the ferromagnetism at low temperature. They were not observed in the XRD data. It is noted that though no Mn clusters or other secondary ferromagnetic phases that may account for the observed room temperature ferromagnetism were observed under the resolution limit of XRD, their existence cannot be completely excluded. Nevertheless, high-resolution TEM is powerful enough to distinguish different phases. Statistical high-resolution TEM shows no evidence of nanoclusters of secondary phases in a dozen of nanowires examined. Selected area electron diffraction was also performed along many nanowires and all diffraction patterns could be assigned to AlN. Above results prove that room temperature ferromagnetic ordering exists in the as-grown samples and the ferro-

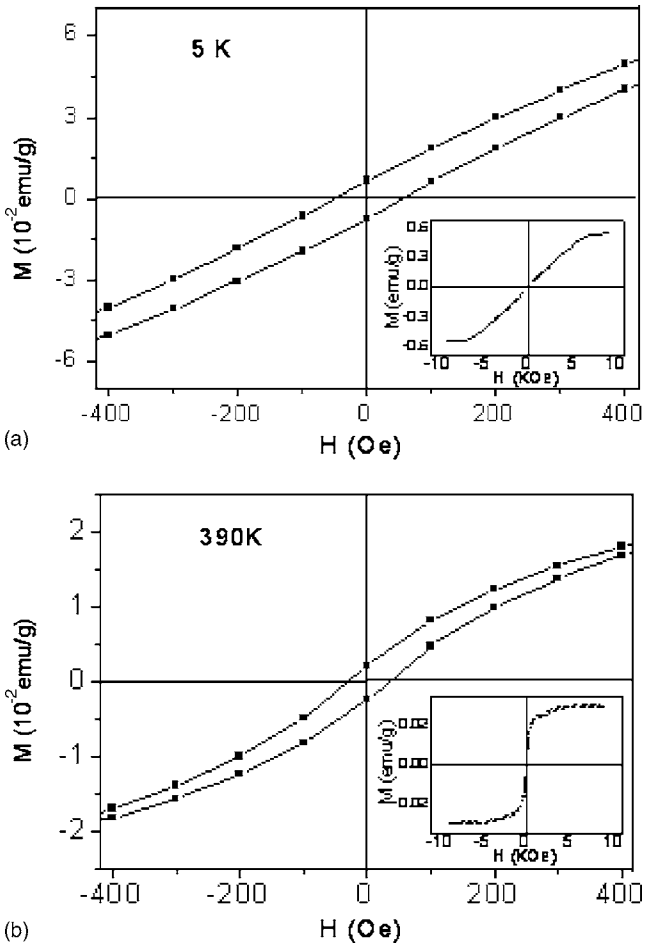

FIG. 3. Magnetic properties of the Mn-doped AlN nanowires. Magnified part in the low-field region of magnetization loop of nanowires measured at (a) 5 K and (b) 390 K. The inset in each figure is the corresponding whole loop of M vs H.

magnetism is likely to be a result of substitution of Al.

Currently, there is no ideal theoretical model which could explain the ferromagnetism in all DMS materials. The Zener model of hole-mediated ferromagnetism has been used to explain the magnetic properties of Mn-doped III-V semiconductors.[5,15] However, it seems not to be an appropriate model for Mn-doped AlN since the defects form near midgap deep levels[24] and AlN is highly resistive at room temperature.[11] The Mn d states split into a triply degenerated t_2 and a doubly degenerated e level for each spin.[24] The majority t_2 would be expected to be 2/3 filled for Mn. This partial filling of the majority t_2 level indicates that the origin of ferromagnetism is likely to be double exchange mechanism.

In summary, Mn-doped AlN nanowires were synthesized by CVD using the reaction of $Al/MnCl_2$ source materials under NH_3 ambient. The length of nanowires is about several to ten micrometers and the diameter of around 150 nm. EDS and line-scan element profiles reveal that Mn distributes uniformly over nanowires with 2.6 at %. PL spectra showed intensive red-band emissions. Hysteresis loops were measured at both 5, 300, and 390 K. T_C of the as-grown nanowires is higher than 390 K, which is the limit of the SQUID. We conclude that the as-synthesized Mn-doped AlN nanowires have room temperature ferromagnetism.

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