Ultraviolet photoluminescence from ferromagnetic Fe-doped AlN nanorods

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Fe-doped AlN (AlN:Fe) nanorods on silicon substrates were fabricated using a catalysis-free vapor phase method. The AlN:Fe nanorods exhibited high crystalline quality and preferred *c*-axis orientation. The spontaneous saturated magnetization of the AlN:Fe nanorods was determined to be $\sim 0.64 \mu_B$/Fe at room temperature. Room temperature photoluminescence measurement of the AlN:Fe nanorods revealed two strong ultraviolet emissions at 3.69 and 6.02 eV which could be attributed to Fe^{3+}-related and band edge emissions, respectively. The Fe-doped AlN nanorods not only exhibited ferromagnetism but also significantly enhanced the band edge emission as compared to the undoped AlN nanorods. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2738370]

Diluted magnetic semiconductors (DMSs) are attractive materials for the spintronics, as they can have the inherent properties of both semiconductor and ferromagnetic materials. The most direct method to induce spin-polarized electrons into a semiconductor is by introducing appropriate transition metals (TMs) or rare-earth dopants to produce a DMS. Meanwhile, the integration of future spintronic devices into nanodevices would require the fabrication of one-dimensional (1D) DMS nanostructures in well-defined architectures.[1] The behavior of carriers in nanostructures may also allow for the enhancement of the ferromagnetic semiconductor behavior, because nanostructures are expected to have longer coherence times than in the bulk, which may provide a pathway for increasing the spin life-time in ferromagnetic semiconductor devices for practical applications.[2] Besides the well studied oxides and III-V DMSs, group III nitrides are getting more attractive because of the theoretical prediction[3] and experimental realization of room temperature ferromagnetism. Although AlN-based DMS bulk materials have been extensively studied and modeled,[4–8] there are very few reports on the synthesis of 1D nanostructures[9] because of the limited TM equilibrium solubility in semiconductors as well as in the intrinsic difficulty in nanocrystal doping. So far, TM dopants in AlN such as Mn, Cr, Co, and Cu have been employed. Meanwhile, Fe^{3+} ($3d^5$) having a high magnetic moment of $5\mu_B$/Fe could lead to the high spin state.[10] In this work, magnetic and photoluminescence (PL) properties of Fe-doped AlN nanorods were investigated.

AlN:Fe nanorods were prepared in a horizontal tube furnace. The experimental procedure has been reported elsewhere.[9] Briefly, aluminum chloride powder ($AlCl_3$, Sigma-Aldrich, 99.99%), ferric chloride anhydrous ($FeCl_3$,

Sigma-Aldrich), and ammonium (NH_3) were used as sources. AlN:Fe nanorods were grown on Si substrate without catalyst at 1000 °C for about 2 h. Crystallography of the nanorods was determined by using Siemens D5005 x-ray diffractometer (XRD) with Cu $K\alpha$ irradiation at 40 kV and 40 mA. Field emission scanning electron microscopy (SEM, JEOL JSM-6340F) and transmission electron microscopy (TEM, JEOL JEM-2010) were used for the morphologies and structural analysis. X-ray photoelectron spectroscopy (XPS, VG ESCAlab MKII) was engaged using Al $K\alpha$ as x-ray source to analyze the element content. Deep ultraviolet PL spectroscopy under a 197 nm laser excitation was employed to study the optical properties of the nanorods at room temperature. Magnetic hysteresis loops of the AlN:Fe nanorods were measured by an alternating gradient magnetometer with a maximum field of 10 kOe.

Representative XRD pattern of the AlN:Fe nanorods is shown in Fig. 1(a). Several diffraction peaks were observed, which corresponds to the wurtzite AlN structure. No diffraction peaks of Fe–N or Al–Fe compounds were found within the sensitivity of XRD. The strong (002) intensity indicates that the AlN:Fe nanorods preferentially grow along the *c* axis. The inset of Fig. 1 is the typical cross-sectional SEM image of the AlN:Fe nanorods. It is observed that a high density AlN:Fe nanorod array was grown either perpendicular or slantingly from the wafer to form the quasiarrays. These nanorods are ~500 nm in length with decreasing diameters along the growth direction. Figure 1(b) shows the TEM image of the AlN:Fe nanorods which exhibits a sharp tip of 15–20 nm in diameter. The corresponding high-resolution TEM images and the selected area electron diffraction as shown in Fig. 1(c) reveal that the nanorod is a single crystal with a spacing of 0.49 nm between the neighboring lattice planes [the distance between the neighboring
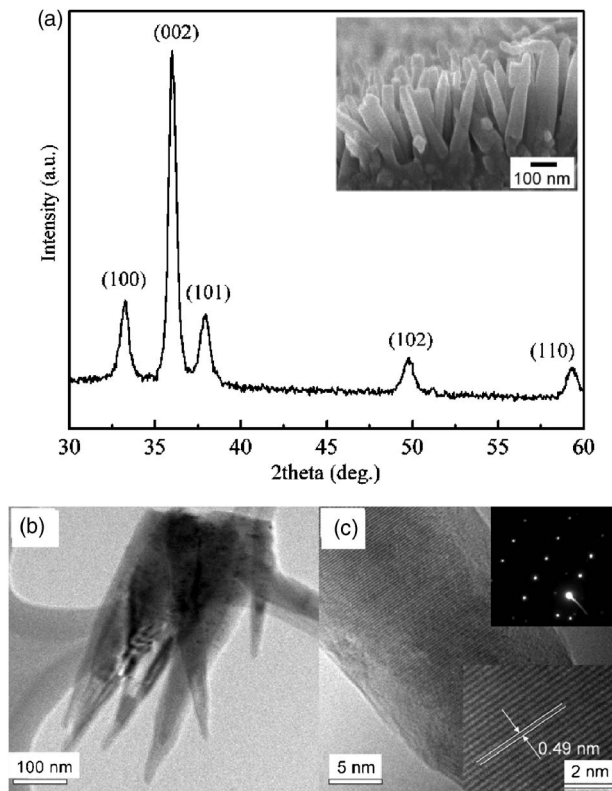
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FIG. 1. (a) XRD spectrum of the AlN:Fe nanorods. The inset is the cross-sectional SEM image of AlN:Fe nanorods. (b) TEM image of the AlN:Fe bundle. (c) A single nanorod with the corresponding electron diffraction pattern and high-resolution image.

lattice planes is noted as $d_{(hkl)}$], which is in agreement with $d_{(001)}$ of hexagonal AlN.

Figure 2 shows the XPS spectra of the undoped and Fe-doped AlN nanorods. Besides the absorbed carbon and oxygen, Al and N were clearly evident from both spectra. The atomic ratios of N/Al of undoped and Fe-doped AlN are estimated to be 0.91 and 0.79, respectively, suggesting that the AlN nanorods are Al rich. The atomic concentration of Fe is about 3.5% in the Fe-doped AlN nanorods. It is noted that the binding energy of Fe $2p_{3/2}$ is located at 710.19 eV, which indicates that Fe ions are in high spin state.[11]
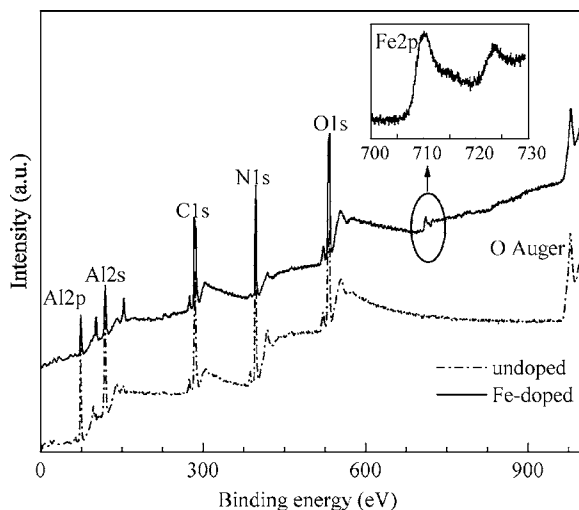

FIG. 2. XPS spectra of the undoped and Fe-doped AlN nanorods. The inset shows the magnification of Fe $2p$ peak.
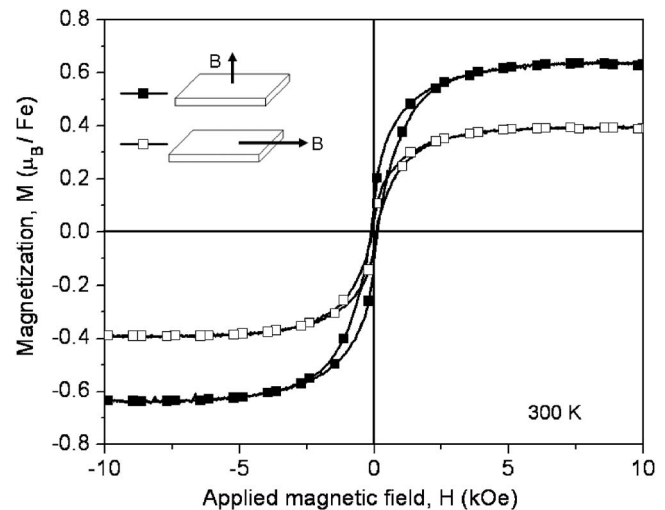

FIG. 3. Magnetization hysteresis loops of the AlN:Fe nanorods measured at room temperature with applied field parallel and perpendicular to the sample.

The magnetization versus magnetic field (M-H) curve of the AlN:Fe nanorods measured at room temperature shows a hysteresis loop, revealing its ferromagnetic behavior, as shown in Fig. 3. The spontaneous saturated magnetization and coercivity of the AlN:Fe are estimated to be $\sim 0.64 \mu_B$/Fe and 116 Oe when the field is applied perpendicular to the sample, which is $\sim 61\%$ and 50% larger than the field applied parallel to the sample, respectively. The magnetic anisotropy in TM substituted semiconductor is a common characteristic of DMSs.[12] This indicates that a significant fraction of Fe spins are coupled magnetically in AlN, and the saturated magnetic moment of the AlN:Fe nanorods is significantly larger than Fe-implanted ZnO (Ref. 13) and Cr-doped AlN.[14]

The Fe^{3+}-V_N-Fe^{3+} groups are expected in the structure. An electron trapped in the nitrogen vacancy (V_N) constitutes an F center, where the electron occupies an orbital which overlaps with the d shell of both ion neighbors. Since Fe^{3+}, $3d^5$, only has unoccupied minority spin orbitals, the trapped electron will be spin down ($\downarrow$) and the two ion neighbors spin up ($\uparrow$), resulting in the magnetization. Although no Fe-related secondary phases can be detected by the XRD and TEM, we cannot rule out the possibility of nanosized Fe clusters or Fe oxide phases which may also contribute to the ferromagnetism.

PL emission from the AlN and AlN:Fe nanorods is shown in Fig. 4. The PL spectrum of the undoped AlN nanorods comprises two strong impurity-related emission lines at 3.25 and 4.32 eV, and a weak emission at 5.83 eV. The emission lines of 3.25 and 4.32 eV can be attributed to the transitions between free or donor bound electrons to Al vacancy and vacancy-impurity complex (V_{Al} complex) with different charge states.[15] However, the emission line of 5.83 eV, which is much smaller than the room temperature band edge emission (for example, 5.96 eV) (Ref. 16) of AlN, is likely to be related to an unidentified impurity as the peak position does not shift with temperatures from 300 down to 10 K. Further experiments are currently underway to determine the origin of this peak. It is noted that both impurity emissions are absent from the Fe-doped nanorods, but a 3.96 eV emission becomes apparent in addition to the band edge emission at 6.02 eV. The vanishing of the 3.25 and
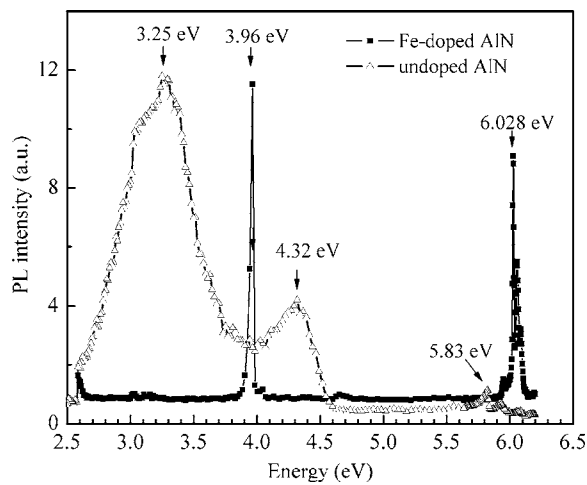
FIG. 4. PL spectra of the undoped and Fe-doped AlN nanorods.

4.32 eV emissions may be due to the formation of the non-radiative defect complex induced by Fe ions. Heitz *et al.*[17] reported that the deep $Fe^{3+/2+}$ acceptor level is 3.17 eV above the valence band maximum in GaN. Assuming band offsets in nitrides following the internal reference rule, the $Fe^{3+/2+}$ acceptor level is expected to be about 3.96 eV above the valence band of AlN, where the valence band offset for GaN/AlN is 0.79 eV.[18] Therefore, the emission line of 3.96 eV with narrow linewidth (18.5 meV) might be related to $Fe^{3+/2+}$ acceptor. The narrow UV emission linewidth of the Fe-doped AlN is very similar to that observed in Gd-implanted AlN epilayer.[19] Therefore, strong dopant-related UV emissions not only can take place in AlN thin films but also in nanostructures. Besides the observed ferromagnetism, Fe doping also seems to play an important role in enhancing the UV emissions in AlN nanorods. AlN:Fe may be a promising DMS material for spintronics.

In summary, Fe-doped AlN nanorods exhibited room temperature ferromagnetism with a saturated magnetic moment of $0.64\mu_B$/Fe when the field was applied perpendicular to the sample. The two UV emission peaks at 3.96 and 6.02 eV from the Fe-doped AlN nanorods could be attributed to $Fe^{3+/2+}$ acceptor and band edge emission, respectively. It is noted that Fe doping plays a significant role in enhancing the UV emissions in the AlN nanostructures.

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