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Room temperature ferromagnetism in new diluted magnetic semiconductor AlN:Mg nanowires†

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Room-temperature ferromagnetism has been observed in Mg-doped AlN (AlN:Mg) nanowires. The saturation magnetization and the coercivity of the AlN:Mg nanowires are about 0.051 emu g^{-1} and 127 Oe, respectively. The Al vacancy and substitutional Mg could play very important roles in room temperature ferromagnetism. These findings confirmed the room temperature ferromagnetism in diluted magnetic semiconductor AlN:Mg nanowires by doping with the nonmagnetic element Mg.

In the past couple of decades, a great deal of effort has been devoted to the exploration of new multifunctional spintronics materials for practical applications. While the ferromagnetism in a diluted magnetic semiconductor (DMS) such as (In, Mn)As was discovered,[1,2] it is desirable to fabricate a novel material including both charge carriers and localized spins which may open up a new branch of magneto-electronic materials science area.[3] Among the most promising candidates of DMS, much interest has been focused on III–V semiconductor based DMSs. They have demonstrated a successful combination of high optoelectronic properties and very unique room-temperature ferromagnetism properties (low magnetization and high spin polarization), which can lead to potential industrial applications in the emerging field of spintronics.[3–7] Numerous efforts have been made to study III–V semiconductor based DMSs both experimentally and theoretically. For example, the magnetic transition metals such as Mn, Cr, Fe, Co, V, and Ni have been widely used as magnetic dopants to fabricate GaN, GaAs, and AlN based DMSs to raise the Curie temperature (T_c) above the room temperature.[8–13] However, the origin of ferromagnetism in DMSs are still being debated theoretically.[14–16] Recently, it has been reported that dopant semiconductors with intrinsically nonmagnetic elements (Cu, Sc and Y *etc.*) also exhibit room-temperature ferromagnetism by introducing a high concentration of magnetic ions.[17–19] In addition, magnetism in the geometry of one-dimensional chains has been predicted in atoms with only s- or sp-valence electrons, like Na, Mg, Al, and Si.[20] Cai *et al.* also studied the electronic and optical properties of Zn and Mg doped AlN using density functional theory.[21] First-principle calculation by Tang *et al.* indicated that double Mg atom doped passivated AlN nanowires display ferromagnetic properties.[22] Recently, Hui *et al.* observed ferromagnetism in AlN:Mg zigzag nanowires.[23] Using *ab initio* calculation, Wu *et al.* also predicted that room temperature ferromagnetism may be expected in AlN doped with 7% Mg.[24] Therefore, we decided to explore the possibility of synthesizing AlN:Mg nanowires as a diluted magnetic semiconductor. Nanowires offer thermodynamical stability and one-dimensional structural features, which may be helpful in developing spintronic devices.[25]

In previous reports, we have shown the experimental fabrication of a DMS in AlN nanoprisms doped with nonmagnetic rare-earth-elements, Sc and Y.[17,18] In order to explore new nanoscale DMS materials and to verify the theoretical prediction of a potential room temperature ferromagnetism produced by AlN:Mg,[22,24] we set out to fabricate a DMS in AlN nanowires doped with a nonmagnetic element, magnesium, using the simple arc discharge plasma method. Nanowires have many advantages over thin films in the study of ferromagnetism in DMS, including nanoscale size, low dimensionality, and single-crystallinity.[4,7,8] The magnetic characterization of the fabricated AlN:Mg nanowires shows that they have room temperature ferromagnetism, with saturation magnetization and coercive fields (H_c) being 0.051 emu g^{-1} and 127 Oe, respectively. These findings confirm that it is possible to produce DMSs in AlN nanowires without doping magnetic element.

The AlN:Mg nanowires were synthesized in an improved arc discharge plasma setup.[17] Al (purity 99.99%), Mg (purity 99.99%) and N_2 gas (purity 99.99%) were used as sources. The N_2 pressure was at 40 kPa, input current was maintained at 100 A, and the voltage was slightly higher than 25 V. After reaction for 10 min, a large number of cotton-like samples deposited on the substrate. Phase, structural and chemical composition analyses of the AlN:Mg nanowires were carried out using X-ray diffraction (XRD)

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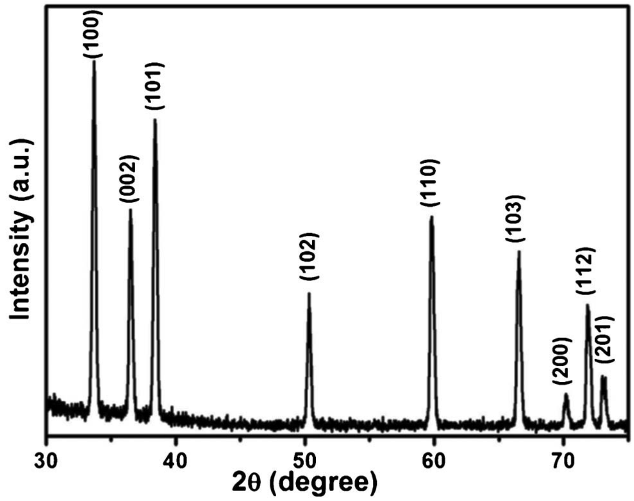

Fig. 1 XRD of the sample with indexed peaks.

with Cu Kα radiation, Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microcopy (TEM), and energy-dispersive X-ray spectroscopy (EDX). The magnetic properties were measured using a vibrating sample magnetometer (VSM) at room temperature.

Fig. 1 displays the powder XRD pattern of the sample. All peaks can be readily indexed to wurtzite-structure (space group: *P*63*mc* (no. 186)) AlN (JCPDS file No. 08-0262), showing only a single phase. No peaks corresponding to Al metal or Al–Mg alloy could be found in the XRD patterns.

Scanning electron microscopy (SEM) images of the as-synthesized AlN:Mg nanowires (Fig. 2a–c) show that the product consists primarily of 1D structures with diameters of the order of 200 nm and lengths greatly exceeding 5 μm, a very high aspect ratio. Energy dispersive spectroscopy (EDS) analysis (Fig. 2d) reveals the doping of Mg ions in AlN corresponds to a concentration of approximately 3%. Other impurity phases have not been detected.

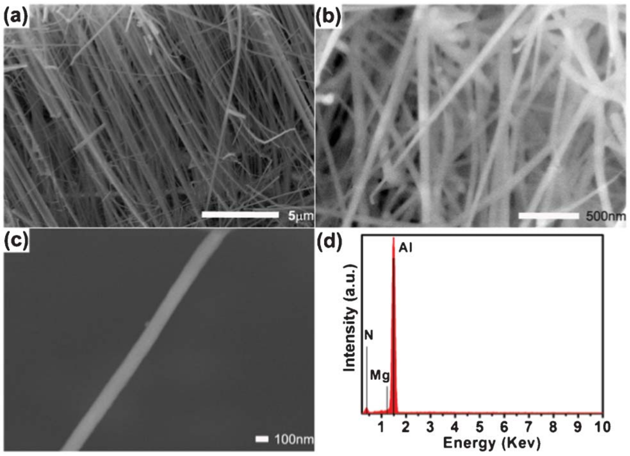

Fig. 2 (a) and (b) Low-magnification SEM image of AlN:Mg nanowires; (c) high-magnification SEM image of a nanowire; (d) EDS spectrum of AlN:Mg nanowires.

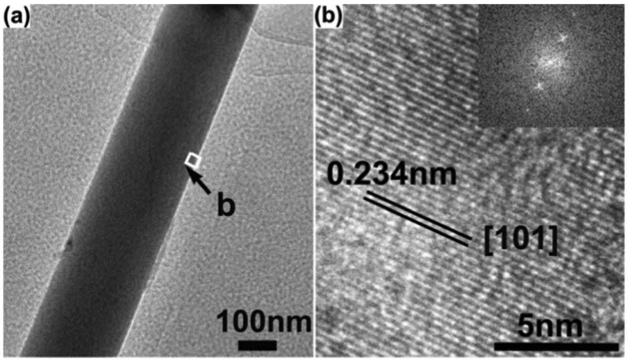

Fig. 3 (a) TEM image of the typical nanowire. (b) HRTEM lattice image the surface of a nanowire, its FFT patterns inserted.

The morphology and structure of the AlN:Mg nanowires have been characterized in further detail using TEM and HRTEM. Fig. 3a shows a typical TEM image of one nanowire. It shows that the nanowire is very straight with a diameter of approximately 250 nm, consistent with the SEM observation. Fig. 3b presents the corresponding HRTEM lattice image taken from the nanowire surface (recorded from the rectangular area in Fig. 3a). The distance between adjacent lattice planes is about 0.234 nm, which corresponds well with the *d*-spacing of (101) crystal planes of hexagonal wurtzite AlN, suggesting a growth direction of the nanowire in the [101] direction. The insert in Fig. 3b shows a fast Fourier transform (FFT) of the image, which further demonstrates that the as-grown nanowire is single crystalline and grows along the [101] direction.

Raman scattering is a useful tool for the characterization of nanomaterials. The space group of the hexagonal wurtzite AlN crystal is *P*63*mc* with all atoms occupying the C_{3v} sites. Six first-order Raman active modes, $2E_2$, $1A_1$(transverse optical (TO)), $1A_1$(longitudinal optical (LO)), $1E_1$(TO), and $1E_1$(LO), may be present.[26] Fig. 4 shows the Raman spectrum of the AlN:Mg

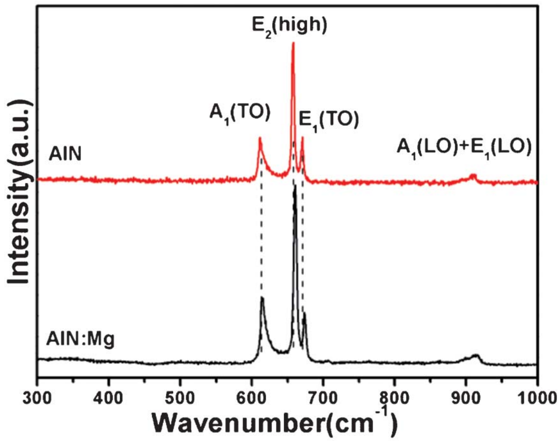

Fig. 4 The Raman spectrum of the as-grown AlN and AlN:Mg nanowires.

nanowires. Three distinct peaks centered at 612.8, 658.2 and 671.4 cm^{-1} are correlated to the first-order vibrational modes of A_1(TO), E_2(high), and E_1(TO), respectively. The low-intensity broad peak around 904.9 cm^{-1} is assigned to the overlap of the modes A_1(LO) and E_1(LO). The slight shift of A_1(TO), E_2(high) and E_1(TO) of the AlN:Mg nanowires relative to those of the undoped AlN nanowires, may be attributed to the distortion of the crystals due to the incorporation of Mg. These results are in good agreement with the results of room temperature DMS Sc and Y doped AlN nanostructures.[17,18]

Recently, there has been intensive interest in studying AlN based DMSs due to their potential applications in spintronics. However, the origin of ferromagnetism is still not clearly understood. Since magnetic transition metals are intrinsically magnetic, their precipitates or secondary magnetic phases in the host semiconductor may also contribute to the observed ferromagnetism. In order to avoid the problem of magnetic precipitates, doping an intrinsically nonmagnetic element, such as Cu, Sc and Y, has attracted theoretical and experimental attentions to produce AlN-based DMSs. Recently, Wu *et al.*'s *ab initio* calculations based on spin density functional theory have shown that Mg-doped AlN favoured the ferromagnetic ground state because Al vacancy and substitutional Mg impurity in AlN can lead to spin-polarized ground states.[20] However, there has been no report on the magnetic properties of Mg doped AlN experimentally. Our room temperature measurements of the magnetization *versus* magnetic field curve of the synthesized AlN:Mg nanowires shows a hysteresis loop, revealing its ferromagnetic behavior, as shown in Fig. 5. The saturation magnetization of the AlN:Mg nanowires is 0.051 emu g^{-1}, and its coercive field is about 127 Oe. Recently, Hui *et al.*[23] obtained AlN:Mg zigzag nanowires and regular nanowires using a chemical vapor deposition (CVD) method. They found that only the zigzag nanowires show ferromagnetism due to the Mg–N complexes exhibited in the zigzag nanowires (as revealed by the XPS spectrum). However, their regular nanowires do not show ferromagnetism because of the absence of Mg–N complexes in the regular nanowires (confirmed by the XPS spectrum). They concluded that it is difficult to synthesize AlN:Mg regular nanowires with Mg–N complexes using the regular CVD method. It is noted that our arc discharge plasma method can provide very high temperatures up to 5000 K with a temperature gradient which is different to the regular CVD method.[27] The ferromagnetism in our AlN:Mg nanowires may result from the following two factors. Firstly, a large number of Al vacancies and surface defects in this sample can introduce spin polarization to N atoms around the defect site resulting in ferromagnetism. It was found by *ab initio* calculations that Al vacancies in AlN lead to ferromagnetism.[24] Our photoluminescence spectrum (Fig. S2, ESI†) shows a peak at 550 nm, which was related to the Al vacancies and surface defects in AlN:Mg nanowires confirming the results of theoretical calculation.[23] Secondly, substitutional Mg impurities in AlN also lead to a ferromagnetic ground state. The XPS spectrum (Fig. S1, ESI†) shows a binding energy at 95 eV, which is very close to the previously reported value of Mg–N bonding in Mg-doped AlN zigzag nanowires.[23] It confirmed the substitution of Al by Mg in AlN:Mg nanowires. We created crystal structures of Mg doped AlN in the absence and the presence of Al vacancies according to the theoretical calculation[24] and the results of the XPS and photoluminescence spectrum (as shown in Fig. S3, ESI†). When an Mg atom substitutes an Al atom, Mg and its four neighboring N atoms strongly hybridize and it forms a tetrahedron MgN_4 with neighboring N atoms. Recent calculations based on density functional theory predicted that spin-polarized MgN_4 tetrahedra in AlN favor a ferromagnetic ground state.[22] Our results further confirm the theoretical prediction. Therefore, both Al vacancy and substitutional Mg impurity in AlN nanowires lead to ferromagnetic ground states.

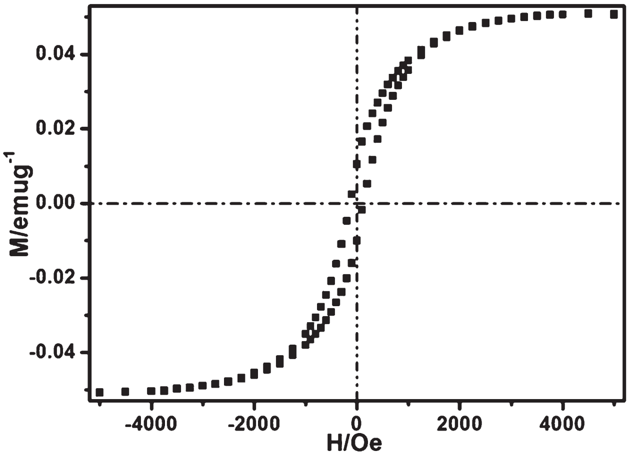

Fig. 5 Magnetic properties of AlN:Mg nanowires.

In summary, we reported the successful synthesis of AlN:Mg nanowires through direct nitrification of Al and Mg metals in arc discharge plasma with N_2 as the working medium. No template or catalyst was used. The synthesized AlN:Mg nanowires with diameter around 200 nm and single-crystalline wurtzite-AlN structure show room temperature ferromagnetism, which may have applications in spintronic and optoelectronic nanodevices.

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References

1 H. Munekat, H. Ohno, S. von Molnar, A. Segmüller, L. L. Chang and L. Esaki, *Phys. Rev. Lett.*, 1989, **63**, 1849.
2 H. Ohno, *Science*, 1998, **281**, 951.
3 H. Ohno, *Nat. Mater.*, 2010, **9**, 952.
4 A. Van Esch, L. Van Bockstal, J. De Boeck, G. Verbanck, A. S. van Steenbergen, P. J. Wellmann, B. Grietens, R. Bogaerts,

F. Herlach and G. Borghs, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, **56**, 13103.

5 A. H. MacDonald, P. Schiffer and N. Samarth, *Nat. Mater.*, 2005, **4**, 195.

6 M. A. Mayerm, P. R. Stone, N. Miller, H. M. Smith, O. D. Dubon, E. E. Haller, K. M. Yu, W. Walukiewicz, X. Liu and J. K. Furdyna, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 045205.

7 Q. Liu, C. X. Liu, C. Xu, X. L. Qi and S. C. Zhang, *Phys. Rev. Lett.*, 2009, **102**, 156603.

8 S. Y. Wu, H. X. Liu, L. Gu, R. K. Singh, L. Budd, M. Schilfgaarde, M. R. MaCartney, D. J. Smith and N. Newman, *Appl. Phys. Lett.*, 2003, **82**, 3047.

9 D. Kumar, J. Antifakos, M. G. Blamire and Z. H. Barber, *Appl. Phys. Lett.*, 2004, **84**, 5004.

10 R. Frazier, G. Thaler, M. Overberg, B. Gila, C. R. Abernathy and S. J. Pearton, *Appl. Phys. Lett.*, 2003, **83**, 1758.

11 A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, R. M. Frazier, J. Y. Liefer, G. T. Thaler, C. R. Abernathy, S. J. Pearton and J. M. Zavada, *Appl. Phys. Lett.*, 2004, **85**, 4067.

12 R. M. Frazier, G. T. Thaler, J. Y. Leifer, J. K. Hite, B. P. Gila, C. R. Abernathy and S. J. Pearton, *Appl. Phys. Lett.*, 2005, **86**, 052101.

13 J. Zhang, X. Z. Li, B. Xu and D. J. Sellmyer, *Appl. Phys. Lett.*, 2005, **86**, 212504.

14 T. Jungwirth, J. Sinova, J. Masek, J. Kucera and A. H. MacDonald, *Rev. Mod. Phys.*, 2006, **78**, 809.

15 F. Matsukura, H. Ohno, A. Shen and Y. Sugawara, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1998, **57**, R2037.

16 K. Sato and H. Katayama-Yoshida, *Semicond. Sci. Technol.*, 2002, **17**, 367.

17 W. W. Lei, D. Liu, X. Chen, P. W. Zhu, Q. L. Cui and G. T. Zou, *J. Phys. Chem. C*, 2010, **114**, 15574.

18 W. W. Lei, D. Liu, Y. M. Ma, X. Chen, F. B. Tian, P. W. Zhu, X. H. Chen, Q. L. Cui and G. T. Zou, *Angew. Chem., Int. Ed.*, 2010, **49**, 173.

19 K. Osuch, E. B. Lombardi and L. Adamowicz, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2005, **71**, 165212.

20 Z. Z. Zhu, J. C. Zheng and G. Y. Guo, *Chem. Phys. Lett.*, 2009, **472**, 99.

21 X. M. Cai and L. Yuan, *Mater. Sci. Forum*, 2011, **663–65**(1), 195.

22 Z. K. Tang, L. L. Wang, L. M. Tang, X. F. Li, W. Z. Xiao, L. Xu and L. H. Zhao, *Phys. Status Solidi B*, 2012, **249**, 185.

23 Y. Y. Hui, J. Ye, R. Lkortz, K. S. Teng and S. P. Lau, *Phys. Status Solidi A*, 2012, **209**, 1988.

24 R. Q. Wu, G. W. Peng, L. Liu, Y. P. Feng, Z. G. Huang and Q. Y. Wu, *Appl. Phys. Lett.*, 2006, **89**, 142501.

25 H. J. Choi, H. K. Seong and U. Kim, *Nano*, 2008, **3**, 1.

26 V. Y. Davydov, N. S. Averkiev, I. N. Goncharuk, D. K. Nelson, I. P. Nikitina, A. S. Polkovnikov, A. N. Smirnov, M. A. Jacobson and O. K. Semchinova, *J. Appl. Phys.*, 1997, **82**, 5097.

27 W. W. Lei, D. Liu, L. H. Shen, J. Zhang, P. W. Zhu, Q. L. Cui and G. T. Zou, *J. Cryst. Growth*, 2007, **306**, 413.