Ferromagnetic GaN:MnAlSi nanowires

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The fabrication of crystalline Al-codoped GaN:Mn nanowires with a Mn doping rate of approximately 7 at. % is reported. The magnetism measurements show that the Curie temperature is above 350 K. X-ray and electron diffractions do not show the presence of any secondary magnetic phases. The electrical transport measurement indicates that the nanowires are of n-type semiconductor. © 2006 American Institute of Physics. [DOI: 10.1063/1.2174125]

I. INTRODUCTION

Much research has been focused on the preparation of diluted magnetic semiconductor (DMS) based on GaN since Dietl et al. predicted that p-type GaN doped with about 5 at. % of Mn (a high concentration of holes, 3.5 × 10²⁰ cm⁻³) should exhibit a Curie temperature (T c) above room temperature.¹ Progress has been made in both the realization of high-quality (Ga, Mn)N films and the theory of ferromagnetism in DMS. By diffusing Mn into GaN, Reed et al. prepared an n-type (Ga, Mn)N film, which exhibited ferromagnetism with a T c ranging from 220 to 370 K.²–⁴ Thaler et al. and Sonoda et al. also fabricated n-type GaMnN thin films which showed room temperature ferromagnetism by means of molecular-beam epitaxy (MBE).⁵ Theodoropoulou et al. prepared GaMnN by implanting Mn ions into p-type GaN and demonstrated its ferromagnetism with a T c ≈ 250 K.⁷ GaN:Mn films generally exhibit n-type DMS characteristics because of nitrogen vacancies and/or oxygen impurities.²–⁴

DMS nanostructures have recently attracted interest since they are promising components for nanodevices in spintronics,⁸–¹⁰ such as electronic-optic switches, ultrasensitive magnetic field sensors, magnetic hard disk media, and nonvolatile computer memory chips.¹¹–¹³ Room-temperature ferromagnetism in Mn-doped GaN nanowires has been demonstrated by Han et al.¹⁴ and Choi et al.¹⁵ Our efforts have been to fabricate single crystal Mn-doped GaN nanowires via vapor phase transport method without a catalyst. A series of experiments with different weight ratios of manganese acetylacetonate and GaN without a catalyst showed that the Mn content is not larger than 2.5 at. % in the case of no secondary phase. This was consistent with a previous report,¹⁶ where the maximum solubility of Mn in a GaN film without a secondary phase has been shown to be about 3 at. % in the case of a MBE-grown Mn-doped GaN film. The Mn doping rate of smaller than 3.5 at. % is far less than 5 at. % predicted in the theory. It is therefore of interest to increase the Mn contents in GaN to more than 5 at. % without conventional catalysts such as Ni and Au. Here the codoping approach has been selected because it may provide a way to control the conductivity and ferromagnetic behavior, as demonstrated in ZnO.¹⁷ The introduction of Al to Ga solution should improve the wettability and subsequently enhance the solution of Mn into GaN.¹⁸,¹⁹ Nonetheless, little is known about the preparation and physical properties of Al-codoped GaN:Mn nanowires.

In this article, we present the fabrication of GaN:MnAlSi nanowires by vapor phase transport route and the characterization of them using various techniques. In particular, the room-temperature ferromagnetism and current-voltage characteristics of GaN:MnAlSi nanowires are discussed.

II. EXPERIMENTAL PROCEDURE

An alumina boat containing the mixture of GaN powder (Aldrich, 99.99%), manganese acetylacetonate powder (Aldrich, 99.99%), and aluminum powder was located at the center of a quartz tube placed horizontally in a tubular furnace. A sapphire substrate was placed ~250 mm downstream from the boat. The base vacuum was kept at 95 mTorr. The mixture was heated up to 900 °C at a rate of 20 °C/min with a flow of Ar 95% +H 2 5% at 80 SCCM (SCCM denotes cubic centimeter per minute at STP). Ammonia gas (99.999%) was introduced at 150 SCCM after the Ar+H 2 gas was turned...
off. The furnace was then heated up at a rate of 10 °C/min to 1080 °C for 300 min and the pressure was kept at 500 torr. After the furnace was cooled down to ambient temperature with NH₃, yellow-colored products were collected from the sapphire substrate.

A structural analysis was conducted using scanning electron microscopy (SEM), x-ray diffraction (XRD), and transmission electron microscopy (TEM) equipped with energy-disperse x-ray fluorescence (EDX). The magnetic properties were measured using a superconducting quantum interference device (SQUID) magnetometer. A two-terminal technique was used to measure the electrical characteristics.

III. RESULTS AND DISCUSSION

The morphologies of as-prepared samples grown on the sapphire substrate were investigated by SEM. As shown in Fig. 1(a), a bulk quantity of nanowires were obtained with an average diameter of around 50 nm and lengths of up to a few microns. The crystal structure of the nanowires was determined by XRD. The diffraction peaks [Fig. 1(b)] can be completely indexed to those of a bulk GaN with a hexagonal wurtzite structure \( a=3.095 \text{ Å}, \ c=5.00 \text{ Å} \) (ICSD No. 067769). No typical diffraction peaks corresponding to Mn, Al, Si, and/or their compound impurity phases were observed.

Figure 2(a) shows the TEM image of a nanowire. The nanowire has a diameter of about 25 nm. EDX analysis (lower inset) indicates that the nanowire is composed of Ga, N, Mn, Al, and Si with an atomic ratio of 61:31:5:2:1. The presence of Si can be attributed to the quartz tube. The atomic ratio of Ga to Mn is about 93:7. Note that the atomic ratio of Ga to N is nearly 2:1, which indicates N deficiency. The nitrogen loss is probably due to the decomposition of the surfaces of GaN nanowires. The temperature around the sapphire substrate was 700–850 °C, below which the surface of a GaN nanowire starts to decompose. While GaN were being formed, their surfaces were decomposed at a smaller rate. The electron diffraction (ED) does not show any fourfold symmetry patterns, which would be present if either tetragonal or cubic phases such as GaMn and Mn₂N were formed in the nanowires. The diffraction spots only show the sixfold symmetry GaN structure with [001] zone axis, indicating that...
GaN:MnAlSi nanowires are single crystals and have the same lattice structure as GaN. The growth direction of the nanowire is along $[100]$. A typical high-resolution TEM image of a single nanowire is shown in Fig. 2(b). The clear fringes indicate that there is no secondary phase in the GaN:MnAlSi. The spacing between the lattice planes perpendicular to the nanowire axis is about 0.272 nm, which agrees with the $[100]$ spacing of wurtzite GaN. It also further confirms the growth direction of the nanowire to be $[100]$.

Figure 3 shows the field dependence of the magnetization $(M-H)$ of the nanowires at 5 and 300 K, respectively. The magnetic remanence $(M_R)$ is around $5.18 \times 10^{-4}$ emu/g and the coercive field $(H_c)$ approximately $84$ Oe at 5 K, while $M_R$ is $4.57 \times 10^{-4}$ emu/g and $H_c$ is $56$ Oe at 300 K.

The field-cooled (FC) and zero-field-cooled (ZFC) magnetizations as a function of temperature $(M-T)$ for an applied field of 3000 Oe are shown in Fig. 4. The subtraction of FC and ZFC magnetizations can effectively eliminate paramagnetic contributions. The inset of Fig. 4 shows the temperature-dependent difference $\Delta M=M_{FC}-M_{ZFC}$, indicating the presence of hysteresis until 350 K.

Secondary phases should be checked to make sure that this magnetic behavior is due to the doping of Mn. Although the creation of a submicron MnGa phase in GaAs by Mn ion implantation and subsequent heat treatment has been reported, a number of material characterization techniques did not show the presence of any second ferromagnetic phase for Mn contents of below $\sim 10$ at. %. The ED did not show any diffraction spots except for the sixfold symmetry single crystal hexagonal GaN structure. Noting that the XRD measurement rules out the existence of Mn$_4$N and GaMn phases, we believe that the magnetic properties reported in this work are not a result of secondary magnetic phases, but are, rather, intrinsic due to the doping of Mn into the GaN nanostructure.

To identify the electrical properties of GaN:MnAlSi nanowires, a series of $I-V$ measurements was done. Electrical contacts were made to a single nanowire [the inset in Fig. 5(b)] as follows. Alignment marks consisting of a metal dot array with about 1 $\mu$m spacing were fabricated on a heavily doped Si substrate with a 300 nm thermally grown SiO$_2$ layer, which acts as the global backgate. A droplet of dispersed enthanol solution containing nanowires was dropped
on the substrate. Once the solution was blown dry, the nanowires remained fixed on the surface. A suitable nanowire was selected via SEM. While the nanowire was found, its position was determined relative to the alignment marks. A two-layer e-beam resist [polymethyl methacrylate (PMMA)/copolymer] was then spun over the sample and the patterns for electrical leads were generated using e-beam lithography techniques onto the preselected nanowire. Then Ti (∼150 nm) and Au (∼50 nm) were sequentially deposited on the contact area by thermal evaporation. The electrodes were formed by a subsequent lift-off process. The diameter of the nanowire is 42 nm and the distance between the sources and the drain electrodes is 458 nm. Two-terminal electrical resistance \(R_{NW}\) for undoped GaN and Mn-doped GaN nanowires was measured as a function of temperature in a He-3 system. Figure 5(a) shows the temperature dependence of the nanowire resistance \(R_{NW}\) at zero applied field. The temperature was varied from liquid nitrogen to room temperature. The resistivity response of GaN:MnAlSi shows that it goes through the metal insulator transition. The hump in the curve is located at \(T_{1} \sim 270\) K, indicating that the transition temperature marking the loss of ferromagnetic behavior begins from \(\sim 300\) K.\(^{3}\) The absence of this hump in an undoped GaN nanowire [the inset of Fig. 5(a)] indicates that the hump is not an inherent property of GaN nanowires. A current versus source-drain voltage \((I_{sd} \text{ vs } V_{sd})\) plot obtained from a single GaN:MnAlSi nanowire at 9 and 4.5 mV of the gate voltage \(V_{g}\) is shown in Fig. 5(b). The two-terminal \(I_{sd}V_{sd}\) curves exhibit a linear response, thus indicating that contacts behave in a practical sense as Ohmic. The typical contact resistances for the doped GaN are in the range of 1–5 kΩ for each contact. At a certain \(V_{sd}\), \(I_{sd}\) increases (decreases) with increasingly positive (negative) \(V_{g}\), that is, the conductance of the nanowire increases (decreases) with positive (negative) gate voltage \(V_{g}\). This clearly indicates that GaN:MnAlSi nanowires are of \(n\) type. The \(n\)-type conductivity of the present samples is probably related to nitrogen vacancies and/or oxygen impurities under the present growth conditions.\(^{22}\) Further investigations are required.

IV. CONCLUSIONS

In summary, the fabrication and characterization of GaN:MnAlSi nanowires with ∼7 at. % Mn on sapphire substrates are reported. SQUID measurements show ferromagnetism above room temperature. XRD and ED do not identify the presence of any secondary magnetic phases, leading to the conclusion that magnetic properties are due to a solid solution GaN:MnAlSi structure. The \(n\)-type semiconductor property is confirmed via the electrical transport measurement of a nanowire.

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