Understanding the Room Temperature Ferromagnetism in GaN Nanowires with Pd Doping

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Abstract. We report the first synthesis and characterization of 4d transition metal palladium-doped GaN nanowires (NWs). Room temperature ferromagnetism has been observed in high quality Vapor Liquid Solid (VLS) epitaxy grown undoped n-type GaN nanowires. It was proposed that this type of magnetism is due to defects which are not observed in Bulk GaN because of large formation energy of defects in bulk GaN. Here we have successfully doped 4d transition metal Pd in GaN NWs. We find fairly strong and long-range ferromagnetic coupling between Pd substituted for Ga in GaN . The results suggest that 4d metals such as Pd may also be considered as candidates for ferromagnetic dopants in semiconductors.

1. Introduction
Doping semiconductor nanostructures with selected dopant ions represents an effective means of imparting new electrical[1], optical[2, 3], and magnetic[4], properties into these promising materials, thereby expanding their intrinsic functionalities. In particular, nanostructured diluted magnetic semiconductors (DMSs)[5], obtained by substitutional doping of nanocrystalline compound semiconductors with paramagnetic transition-metal ions, can enable simultaneous control and manipulation of electron spins and charges at the nanoscale. This approach is pivotal in the formulation of spin-based electronics, or spintronics, which has emerged as a potential alternative to conventional charge-based electronics[6]. Diluted magnetic semiconductor nanowires (DMS-NWs)[2, 7, 8] have, therefore, attracted significant interest in recent years due to the possibility of expanding devices functionality using electronic spin as an additional degree of freedom. Moreover, shape anisotropy of DMS-NWs may potentially allow for a reduced magnetostatic energy and, therefore, easier magnetization of the NWs along the growth direction. Considerable effort has gone so far into the study of 3d transition metals, such as manganese and chromium as dopants in GaN nanowires . As far as 4d metals are concerned, only the optical spectra of niobium and molybdenum impurities in GaN have been considered thus far. It has previously been shown that palladium, which is nonmagnetic in its fcc ground state, does exhibit ferromagnetic order when in a hcp or double-hcp (dhcp) phase[9]. A Pd atom in these phases experiences an environment of similar symmetry as in a wurtzite semiconductor such as gallium nitride.

Herein, we synthesized high-purity single-crystalline Ga_{1-x}Pd_{x}N NWs with controlled Pd contents, $x = 0, 0.0049, 0.0076$ and 0.016 exhibiting room-temperature ferromagnetism, using a
simple vapor transport method. We attempted to correlate the magnetization of these nanowires with their electronic structures.

2. Experimental

Pure and Palladium doped GaN NWs were prepared via metal-catalyzed Vapor Liquid Solid (VLS) method using ammonia (99.99%, Matheson), gallium metal (99.99%, Aldrich), PdCl$_2$ (99.99%, Aldrich) as the N, Ga and Pd sources respectively, and phosphorus doped n-type Si (100) as the growth substrate. First bulk GaN precursor was prepared by dissolving gallium metal in 69% HNO$_3$ (Aldrich) solution such that the Ga: HNO$_3$ molar ratio was greater than 1:3 under ultrasonication. This solution was then diluted by adding into 2-propanol under stirring such that the molar ratio of Ga:2-propanol was 1:90 and allowed to stir for 30 min. A white precipitate was obtained on slow addition of 25% NH$_4$OH (ammonia solution) to this solution under vigorous stirring, which was separated by centrifugation, washed in ethanol, and dried at 60°C for 24 h. Nitridation was carried out in an alumina boat kept in a quartz tube with an inner diameter equal to 24 mm under ammonia flow. The tube was flushed with nitrogen for 30-45 min, and ammonia was allowed to flow into the tube. The flow was set to around 200 sccm, and the temperature was fixed to 900°C for 60 min. A yellow color pure GaN bulk powder was obtained. These GaN powders are taken as a source material. GaN powders and PdCl$_2$ powders were placed separately in two alumina boats, which loaded inside a quartz tube reactor. A silicon substrate, on which a 3-5 nm thick Au film was deposited, was positioned at a distance of 10 cm away from the GaN source. Ammonia was allowed to flow at a rate 300 sccm while raising and lowering the temperature. The temperature of Ga and Pd sources were set to 1100°C and 800°C, respectively, and the substrate was approximately set at 900°C. Argon gas was continuously flowed at a rate of 500 sccm for 60 min during the synthesis. The Pd content was controlled by adjusting the evaporation temperature of PdCl$_2$. Undoped GaN nanowires was prepared under identical conditions, but without PdCl$_2$.

![Figure 1](image_url)

**Figure 1.** (a) Full range XRD patterns taken from Ga$_{1-x}$Pd$_x$N ($x=$ 0.0049, 0.0076, and 0.016) NWs and (b) the magnified scaled (100) peak.

X-ray diffraction patterns of the samples were recorded by high resolution X’Pert PRO Pananalytical X-ray diffractometer in the range 30-65° using Cu K$_\alpha$ radiation. Microstructure and crystal structures of the nanowires were obtained using Field Emission Scanning Electron Microscope (FESEM, JEOL) Transmission Electron Microscope (TEM) and high-resolution TEM.
Figure 2. (a) Low magnified SEM micrograph of high density Ga$_{0.983}$Pd$_{0.016}$N NWs, homogeneously grown on the substrate. (b) TEM image of single 40 nm diameter GaN nanowire that terminates in a faceted nanoparticle of higher contrast (c) HRTEM image of same nanowire. Inset shows a FFT pattern of HRTEM image (HRTEM, JEOL 2010) studies. The metal contents in the nanowires were determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES), (Perkin Elmer). Doped samples were characterized by X-ray photoelectron spectroscopy (XPS,5400 ESCA). Magnetization measurements were carried out by SQUID Magnetometer, Quantum Design, MPMS XL (evercool).

3. Results and Discussion
The high-resolution XRD patterns of the undoped GaN NWs and Ga$_{1-x}$Pd$_x$N NWs are displayed in Figure 1a. The peaks of the GaN NWs exactly match those of wurtzite GaN. All of the GaN NW samples have a highly crystalline nature without the presence of other phases. Panels b in Figure 1 display the magnified (100) peaks.

Figure 3. (a) EDS elemental mapping reveals the homogeneous composition of Ga, Pd and N. (b) Pd Core level XPS spectra for all Pd doped GaN NWs.

The peak position shifts to a lower angle most significantly with the Pd content. The maximum shifts 2$\Theta$ of the (100) peaks is 0.14. The lattice constant also increases with doping concentration of pd. As the Ga$^{3+}$ ions ($r_{Ga} \sim 0.61$ ) at the tetrahedral sites were substituted with the larger radius Pd$^{2+}$ ions ($r_{Pd} \sim 0.98$ ), the lattice constant would expand because
of the difference in the ionic radius. This expansion of lattice constant can be ascribed to the hybridization between the Pd dopants and host defects (holes).

The growth mechanism of the nanowires follows the vapour-liquid-solid mechanism, which makes use of Au catalytic nanoparticles. Thermal decomposition of PdCl₂ occurs above 680°C: PdCl₂ = Pd + Cl₂. Liquid Au droplet on Si substrate forms alloy with GaN and Pd. The supersaturation state of liquid alloy by absorbing vapor of constituent elements leads to nucleation at liquid-solid interface. The dopant Pd content was controlled by adjusting the evaporation temperature of Pd precursor. Figure 2a shows the low-magnified SEM micrograph of the high-density and uniform 1.63% Pd doped GaN(Ga₀.₉₈₃Pd₀.₀₁₆N) NWs grown on the substrates. The TEM image of the individual GaN nanowire explicitly reveals their smooth surface and average diameter of 40 nm and 30-40 μm in length (Figure 2b). The lattice resolved TEM image and corresponding Fourier-transform electron diffraction (FFT ED) pattern of a selected nanowire reveal that it is composed of single-crystalline wurtzite structured GaN (Figure 2c and inset). It shows a spacing between neighboring (100) planes of ca. 0.27 nm (JCPDS Card no. 50-0792). The FFT ED pattern generated from the inversion of the TEM image using Digital Micrograph GMS1.2 software (Gatan Inc.) at the [0001] zone axis, confirms that it has the [1010] growth direction.

Figure 4. Magnetization (M) versus magnetic field (H) of pure GaN NWS at room temperature (a) without background correction. (b) After diamagnetic background correction. M vs H at 300 K (c) and 5 K (d) for all Pd doped GaN NWs. Inset shows the magnified M-H curves in the vicinity of H=0.

The EDS mapping for a selected Ga₀.₉₈₃Pd₀.₀₁₆N nanowires is shown in Figure 3a. EDS line-scanning analysis indicates the Pd content (x= [Pd]/([Pd]+[Ga])) of the individual nanowire to
be about $x=0.02\pm0.01$ with a homogeneous distribution being observed along the nanowires. The Pd content in the doped GaN NWs also determined from Inductive Couple Plasma Atomic Emission Spectroscopy (ICP-AES) with a high accuracy. The concentration of Palladium for highest doped sample as determined from ICP-AES is $\sim 1.63\%$. Electronic structure of Ga and dopant Pd is determined from XPS study. The fine scanned Pd3d core level spectra for all Pd doped GaN NWs are shown in Figure 3b. Which confirmed that in the sample palladium exists in Pd$^{+2}$. The peak of the nanowires appears in the lower energy region compared to that of O(in PdO), due to the lower electronegativity of N. Therefore, the peaks would be expected to originate mainly from Pd(II)-N bonding structures. The carrier concentration and conductive type of these Pd-doped GaN nanowires were determined by Hall measurements at room temperature by Van der Pauw methods. The carrier concentration of Pd doped p-type GaN nanowires is $3.0\times10^{18} \text{cm}^{-3}$ and a mobility of 118 cm$^2$V$^{-1}$s$^{-1}$. It was suggested, in p-type GaN, there exists a shallow acceptor’s hole transfer process onto Pd$^{+2}$ to form Pd$^{+3}$, where the Pd$^{+3}$ ions act as effective shallow donors. This hole transfer process can be described as $\text{Pd}^{+2} + \text{h}^+ (\text{acceptor}) \rightarrow \text{Pd}^{+3}$. So there is a strong hybridization between the Pd dopant and the acceptor in the Pd doped GaN nanowires.

![Figure 5](image)

**Figure 5.** (a) Temperature dependent $M_{FC}$ and $M_{ZFC}$ with $H=1kOe$ for undoped GaN NWs. The inset represents its $\Delta M (M_{FC} - M_{ZFC})$ curve. (b) Temperature dependent $\Delta M (M_{FC} - M_{ZFC})$ curve for all doped sample.

The magnetic moment ($M$) versus magnetic field ($H$) curves for pure GaN NWs at 300 K are shown in Figure 4a. The samples exhibit ferromagnetic hysteresis behavior with a strong diamagnetic background signal. Figure 4b corresponds to the field-dependent M-H curve of the undoped GaN NWs after strong diamagnetic correction. Hysteresis occurs with a saturation field of 1 kOe. The saturated magnetization is estimated to be $8.5\times10^{-6} \text{emu/gm}$ and coercivity 148 Oe. Figure 5a displays the field-cooled ($M_{FC}$) and zero-field cooled M ($M_{ZFC}$) versus T curves at $H =1000 \text{ Oe}$ for pure GaN NWs. The inset corresponds to $\Delta M (M_{FC} - M_{ZFC})$ as a function of temperature in the range of 5-300 K. Figure 5b shows the same curve for all Pd doped sample. This magnetization difference is particularly informative when there are small amounts of ferromagnetic material in the presence of a large diamagnetic background. This subtraction indicates the presence of ferromagnetism if the difference is nonzero. This data indicates that the ferromagnetism persists to 320 K.

Both Ga and N vacancies are suggested to be present in the as-grown GaN depending on the growth conditions. Calculations of the energies of formation of Ga and N vacancies in bulk GaN have been reported in the literature[10]. Although the formation of nitrogen vacancy has lower energy, electronic structure calculations have shown that this type of vacancy causes a
paramagnetic state. On the other hand, Ga vacancies introduce magnetic moments which lie on the neighboring N atoms that are spin polarized due to Hund’s rule. This type of magnetism due to defects in bulk GaN has not been observed because of the large formation energy of defects in bulk GaN. However, the defect formation energy at the surface of the nanowires may be significantly different from that in the bulk due to the size effect which involves structural as well as electronic effects. Thus, the defect formation energies at the surface are lower, resulting in high concentration of defects which gives rise to percolative ferromagnetism at the surface of the nanowires of GaN.

Figure 4c-d displays the M-H curves of the Ga$_{1-x}$Pd$_x$N NWs consistently showing hysteresis at 5K and 300 K. The saturated magnetizations of these NWs are estimated to be about $9.33 \times 10^{-5}$, $24.12 \times 10^{-5}$ and $32.78 \times 10^{-5}$ emu/gm at 300 K. The inset displays the curve in the vicinity of $H=0$. The hysteresis curves show that $M_r = 2.07 \times 10^{-5}$, $3.45 \times 10^{-5}$ and $4.35 \times 10^{-5}$ emu/gm and $H_C = 60$, 82, and 100 Oe for $x = 0.0049$, 0.0076, and 0.016 respectively. So as the Pd content increases the magnetization also increases. Theoretically it was predicted that the introduction of palladium introduces an impurity gap state, with both the majority and minority spin components retaining a band gap. Importantly, the Pd impurity related band is spin polarized, with a spin polarization of 0.24-0.31 eV and the Fermi level lying within this band; charge carriers traveling through a Ga$_{1-x}$Pd$_x$N layer will therefore be spin polarized. This additional spin polarized state contribute to ferromagnetism significantly. As a result of it the magnetic moment of Pd doped GaN NWs is enhanced.

4. Conclusion
Single-crystalline Ga$_{1-x}$Pd$_x$N NWs were grown by the vapor transport method, using the evaporation of GaN/PdCl$_2$. We have demonstrated that the undoped GaN NWs show room-temperature ferromagnetism that has been discussed in terms of defects at the surface of the nanowires. We find fairly strong and long range ferromagnetic coupling between Pd substituted for Ga in GaN. The results suggest that 4d metals such as Pd may also be considered as candidates for ferromagnetic dopants in semiconductors.

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6. References
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