Electric-Field Control of Ferromagnetism in Mn-Doped ZnO Nanowires

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Supporting Information

ABSTRACT: In this Letter, the electric-field control of ferromagnetism was demonstrated in a back-gated Mn-doped ZnO (Mn-ZnO) nanowire (NW) field-effect transistor (FET). The ZnO NWs were synthesized by a thermal evaporation method, and the Mn doping of 1 atom % was subsequently carried out in a MBE system using a gas-phase surface diffusion process. Detailed structural analysis confirmed the single crystallinity of Mn-ZnO NWs and excluded the presence of any precipitates or secondary phases. For the transistor, the field-effect mobility and n-type carrier concentration were estimated to be 0.65 cm²/V·s and 6.82 × 10¹⁸ cm⁻³, respectively. The magnetic hysteresis curves measured under different temperatures (T = 10–350 K) clearly demonstrate the presence of ferromagnetism above room temperature. It suggests that the effect of quantum confinement in NWs improves Tc and meanwhile minimizes crystalline defects. The magnetoresistace (MR) of a single Mn-ZnO NW was observed up to 50 K. Most importantly, the gate modulation of the MR ratio was up to 2.5 % at 1.9 K, which implies the electric-field control of ferromagnetism in a single Mn-ZnO NW.

KEYWORDS: Diluted magnetic semiconductor, Mn-doped ZnO, nanowire, carrier-mediated ferromagnetism, quantum confinement

Spintronics, utilizing electron spin as a new degree of freedom for information processing, has emerged as a promising solution for the challenges of continuous scaling of CMOS technology.¹ Spin field-effect-transistor²–⁴ (spin-FET) aims to meet the requirements of novel electronic devices, including ultrahigh density, low power consumption, and nonvolatility. There are spin-FETs to manipulate spin transport by a gate voltage through the Rashba effect⁵ or to modulate spin-polarized carriers by the magnetization configuration (parallel or antiparallel) of half-metallic source and drain.⁶ Beyond those, the ferromagnetic phase change could also be used as a state variable to minimize the charge current dissipation. One of the approaches is to manipulate the ferromagnetism in a diluted magnetic semiconductor (DMS) channel by a gate voltage, called nonvolatile transspinor device, which controls the communication between the source/drain terminals through the exchange interaction.⁴,⁵

Previously, Dietl⁶ applied the Zener model to predict room temperature ferromagnetism (RT-FM) in Mn-doped compound semiconductor, and Mn-ZnO became one of the most promising DMS materials for spintronics for which could function at RT. In 2003, Sharma et al.⁷ first demonstrated the RT-FM in Mn-ZnO thin film, but Kundaliya et al.⁸ argued that the origin of RT-FM was due to oxygen-vacancy-stabilized phases. To clarify this controversy, in 2005 Coey et al.⁹ proposed a spin-split impurity band model to explain the RT-FM in Mn-ZnO, and many other groups subsequently reported high temperature FM (Tc > 400 K) in Mn-ZnO thin film¹⁰–¹² and NWs.¹³ They claimed that the high Tc was due to electrons from shallow donor impurities, which form magnetic polaron and a spin-split impurity band.⁹ However, a comprehensive study of the electric-field control of FM has not been reported yet, particularly in the nanoscale material system.

Only recently, Xiu et al.⁴ have used quantum confinement in quantum dots to enhance the exchange interaction between the confined carriers and the Mn dopants, and hence improve Tc in Mn-doped Ge quantum dots; likewise Tang et al.⁵ have demonstrated the spin injection and detection in Mn₅Ge₃/Ge/Mn₅Ge₃ nanowires transistors. For Mn-ZnO NWs, it has been shown to have better crystallinity by taking advantages of the well-developed synthesis process of ZnO nanostructure¹⁴ as well as the high solubility of 3d metals in ZnO.¹⁵ In this work,
we report the studies of Mn-ZnO NWs from material characterizations to electrical and magneto-transport measurements. The clear $M-H$ hysteresis loop of an assembly of Mn-ZnO NWs was observed up to 350 K, and meanwhile the magnetoresistance (MR) ratio was measured up to 50 K. More importantly, by using a typical back-gated transistor structure, the effective manipulation of FM of a single Mn-ZnO NW was clearly observed at 1.9 K, which sets the stage for RT spin-FET devices in the future.

**Results and Discussion.** Zinc oxide nanowires (ZnO NWs) were synthesized on a (100) Si substrate using a traditional thermal evaporation method. The doping process was subsequently carried out in a molecular beam epitaxy (MBE) system. The growth was done at 800 °C with a Mn concentration ($x_{Mn}$) < 2 atom % in order to avoid precipitates, because the thermal equilibrium solubility of Mn in ZnO is predicted up to 25 atom % at 800 °C. Under this doping level, the Mn-doped ZnO can be treated as a DMS due to the exchange interaction between magnetic ions. Figure 1(a) is a schematic illustration of the doping process. As-grown ZnO NWs were first rinsed in acetone for 10 min and then loaded into a MBE chamber with a base pressure of $10^{-10}$ torr. To help Mn diffusion and avoid the secondary phase formation, the Mn deposition lasted for 2 hours. The diffusion cell temperature of Mn source was controlled to yield a nominal Mn deposition thickness of 0.7, 1.4, and 2.5 nm, respectively. During the doping process, ZnO NWs were also heated up to 600 °C so that the incident Mn atoms could diffuse into ZnO NWs from the surface through gas-phase surface diffusion. After the doping process, the substrate was cooled down to room temperature.

To estimate the Mn concentration, X-ray photoelectron spectroscopy (XPS) was performed on Mn-ZnO NWs with different Mn source temperature ($T_{Mn}$). Figure 1b shows the XPS spectrum of Mn-ZnO NWs for $T_{Mn} = 850$ °C, in which each element peak (Zn, Mn, and O) is clearly observed. The inset shows the Arrhenius plot of the relation between $T_{Mn}$ and $x_{Mn}$, which is estimated from the high-resolution XPS spectra of Mn 2p$_{3/2}$ and Zn 2p$_{3/2}$ peaks given in Supporting Information Figure S1. On the other hand, the binding energy of the Mn 2p$_{3/2}$ peak located at 641 eV confirms that the Mn atoms substitute the Zn positions as the Mn$^{2+}$ valence state. In the following, we will focus on Mn-ZnO NWs with $x_{Mn}$ ∼ 1 atom %.

$$x_{Mn} = \frac{I_{Mn\, 2p_{3/2}}}{RSF_{Mn\, 2p_{3/2}}} + \frac{I_{Zn\, 2p_{3/2}}}{RSF_{Zn\, 2p_{3/2}}}$$

(1)

where $I_{Mn\, 2p_{3/2}}$ and $I_{Zn\, 2p_{3/2}}$ are integrated areas under the Mn 2p$_{3/2}$ and Zn 2p$_{3/2}$ peaks in the high-resolution XPS spectra; $RSF_{Mn\, 2p_{3/2}} = 1.77$ and $RSF_{Zn\, 2p_{3/2}} = 3.73$ are the relative sensitivity factors for Mn 2p$_{3/2}$ and Zn 2p$_{3/2}$ peaks, respectively. The peak positions from both samples are consistent, which are related to certain crystal planes. No peak from secondary phase formation is observed within the resolution limit of XRD, which indicates the ideal crystalline structure after doping process. The XRD data for Mn-ZnO (upper) and as-grown ZnO NWs, respectively. The peak positions from both samples are consistent, which are related to certain crystal planes. No peak from secondary phase formation is observed within the resolution limit of XRD, which indicates the ideal crystalline structure after doping process. Figure 1d is a SEM image of an assembly of Mn-ZnO NWs, and the inset shows a magnified image of a single Mn-ZnO NW with a gold catalyst on the top. These pictures show that the NWs possess a smooth surface with several micrometer lengths and 70 nm diameters.

To further inspect the presence of Mn precipitates if any, as well as the detailed crystal structure in Mn-ZnO NWs,
transmission electron microscopy (TEM) is used. Figure 2a shows the TEM image of a typical Mn-ZnO NWs with [001] growth direction. The high-resolution TEM (HR-TEM) image in Figure 2b demonstrates that the Mn-ZnO is single crystalline without the formation of Mn clusters (MnO\x). The lattice spacings are determined to be \(d_{(0001)} = 0.52\) nm for (0001) planes and \(d_{(01\bar{1}0)} = 0.26\) nm for (01\(\bar{1}\)0) planes, respectively. The high-temperature TEM image of Mn-ZnO NWs along the [2\(\bar{1}\)\(\bar{1}\)0] zone axis. (d) EDS spectrum of the Mn-ZnO NWs. The estimated Mn atomic concentration is 0.5–1.2 atom %.

Figure 2. Structural characterization of Mn-ZnO NWs. (a) Low-magnification TEM image of Mn-ZnO NWs growing along [001] direction. The inset shows the schematic illustration of wurtzite ZnO structure. (b) High-resolution TEM image at Mn-ZnO NW edge confirming its crystalline structure. (c) The corresponding diffraction pattern of Mn-ZnO NWs along the [2\(\bar{1}\)\(\bar{1}\)0] zone axis. (d) EDS spectrum of the Mn-ZnO NWs. The estimated Mn atomic concentration is 0.5–1.2 atom %.

layer of 20 nm Al\(_2\)O\(_3\) was subsequently deposited on top using atomic layer deposition (ALD) at 250 °C to passivate the Mn-ZnO NW surface. Previously, it was reported that the surface conductivity of ZnO could dramatically change with different gas adsorption\(^{23–25}\) therefore, the ALD Al\(_2\)O\(_3\) step is one of the key steps to make a robust Mn-ZnO NW FET when exposing in ambient. In addition, the low-temperature annealing during ALD process helps to form good ohmic contacts because a heavily doped region (n\(^+\)-MnZnO) is formed next to the Ti/Mn-ZnO interface\(^{26–28}\). As shown in Supporting Information Figure S2a, the source/drain current (\(I_{SD}\)) was improved by 3 orders of magnitude after the ALD process (solid circle).

Figure 3a shows the results from both two-probe and four-probe \(I–V\) measurements at room temperature in order to exclude the contact resistance. The inset shows a SE image of a typical Mn-ZnO NW with an effective channel length of 700 nm and a diameter of 70 nm. The resistivity of the Mn-ZnO NW was estimated to be \(\rho \sim 1.41\) Ω cm. The inset of Figure 3b is the schematic illustration of a back-gated Mn-ZnO NW FET. The corresponding diagram, Ti forms a very low Schottky barrier (\(\phi_{SD}\)) versus 1000/T in Arrhenius plot at various drain biases in Supporting Information Figure S2c reveals a consistent Schottky barrier height of \(q\varphi_{SD} = 30\pm2\) meV by assuming that the circuit model of Ti/Mn-ZnO/Ti heterostructure are represented by two back-to-back Schottky diodes, as shown in the inset of Supporting Information Figure S2b. Figure 3d shows the corresponding energy band diagram of a Ti/Mn-ZnO/Ti heterostructure under zero bias, assuming the band structure parameters (such as band gap and electron affinity) of Mn-ZnO are the same as those of nondoped ZnO crystal\(^{29}\). In the band diagram, Ti forms a very low Schottky barrier (\(q\varphi_{Ti} = 4.3\) eV) with the Mn-ZnO surface because the work function of Ti (\(q\varphi_{Ti} = 4.3\) eV) is closed to the electron affinity of Mn-ZnO.
Figure 3. Characterization of a back-gated Mn-ZnO NW FET at room temperature. (a) Two-probe and four-probe $I-V$ measurements of a single Mn-ZnO NW. The inset shows a SEM image of a typical Mn-ZnO NW device with six electrodes. The extracted resistivity is $\rho \sim 1.41\, \Omega\, \text{cm}$. (b) The corresponding $I_{ds}-V_{gs}$ characteristic at $V_{ds} = 20\, \text{mV}$. The extracted field-effect mobility is $\mu = 0.65\, \text{cm}^2/\text{V}\cdot\text{s}$, and the carrier density is $n = 6.82 \times 10^{18}\, \text{cm}^{-3}$. The inset shows the schematic illustration of a back-gated Mn-ZnO NW FET, in which the magnetic field ($H_{//}$) was applied along the nanowire axial direction. (c) The corresponding $I_{ds}-V_{ds}$ characteristics at various gate voltages. (d) Energy band diagram of a Ti/Mn-ZnO/Ti heterostructure while $V_{gs} = 0$. ($q\psi_{Ti} = 4.3\, \text{eV}$ and $\chi_{MnZnO} = 4.0\, \text{eV}$).

Figure 4. SQUID measurements of an assembly of the Mn-ZnO NWs. (a) Magnetic moment as a function of field for an assembly of Mn-ZnO NWs at $T = 10, 100, 200, 300,$ and $350\, \text{K}$. The inset shows the magnified hysteresis loop near the origin of Mn-ZnO NWs at $300\, \text{K}$. The red arrows show the sweeping direction of the magnetic field. (b) The Arrott plots of the data in (a). The $T_c$ is projected to be above $300\, \text{K}$. (c) The normalized saturation magnetization ($M_s/M_0$) as a function of temperature. The power-law fitting ($\beta = 0.365$) approximately predicts the Curie temperature ($T_c$) to be $437\, \text{K}$. (d) Magnetic moment as a function of temperature following FC and ZFC at $H = 100\, \text{Oe}$, in which the blocking temperature is $T_b = 90\, \text{K}$. 

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Mn-doped ZnO NWs (0.3 atom %) at 300 K as well as other diluted magnetic semiconductor. To approximately estimate the Curie temperature ($T_c$) of the Mn-ZnO NWs, the $M$–$H$ curves at different temperatures are plotted as $M^2$ versus $H/M$, called Arrott plots. By neglecting the high order terms, the relation between $H$ and $M$ could be expressed as
\begin{equation}
M^2 = \frac{H}{M} + aM^2\quad \text{where } \chi = \frac{N_s}{N_c} \sim 2 \times 10^{18} \text{ cm}^{-3} \quad \text{(carrier concentration)}
\end{equation}
and $a$ is a materials-dependent constant. When extrapolate each curve to $M^2 = 0$, the $T_c$ is obtained when $1/\chi = 0$. As shown in Figure 4c, the intercept of $H/M$ axis does not vanish ($1/\chi \neq 0$) even at $T = 300$ K, which means that the $T_c$ has not been reached yet. By using the slope obtained at 300 K, a dash line that passing through origin point could be drawn at the $T_c$ which is projected to be above 300 K. On the other hand, the temperature dependence of the saturation magnetization is shown in Figure 4c. These data also enable an approximate prediction of the $T_c$ using a power-law equation from the critical behavior model:
\begin{equation}
M_c(T) = M_c(T_c)\left(\frac{T_c}{T}\right)^\beta
\end{equation}
where $M_c(T_c) = M_c(T = 10)$, and $\beta = 0.365$ is the critical exponent in the 3D Heisenberg model. In the figure, the theoretical fitting (solid line) agrees well with the experimental results (empty circles), and shows the $T_c = 437$ K at the intersect of $x$-axis.

The temperature-dependent magnetization measurement is exhibited in Figure 4d via zero-field cooling (ZFC) and field cooling (FC) at $H = 100$ Oe. The ZFC and FC curves show a typical ferromagnetic behavior while no intersection is observed in the temperature range of 10–400 K, which reaffirms that $T_c$.

**Figure 5.** Temperature-dependent magneto-transport measurements on a single Mn-ZnO NW. (a) Temperature-dependent resistance ($R$–$T$) measurements on a single Mn-ZnO NW under an axial magnetic field ($H_T$) of 9 T (solid square) and 0 T (open circle). The inset shows the linear fitting for activation energy, $E_a \sim 33$ meV. (b) Magnetoresistance (MR) ratio as a function of $H_T$ at different temperature. The MR curves are intentionally shifted for clarity, and the height of the double head arrow represents 10 % of the MR ratio. (c) MR ratio as a function of $H/M$ under different gate voltage at 1.9 K, in which $\Delta MR$ is defined as the height of the MR curves. (d) The left axis shows the extracted $\Delta MR$ (solid circle), and the right axis shows the zero-field resistance (open square) under each gate voltage.
is higher than 400 K. However, the FC/ZFC curves of the Mn-
ZnO NWs show the blocking temperature at \( T_b = 90 \) K. Because it is also observed from ZFC/FC curves of the as-
grown ZnO NWs (\( T_b = 50 \) K), as shown in Supporting
Information Figure S3a, the existence of the blocking
temperature may result from intrinsic defects, such as oxygen
vacancy,\(^{33,34}\) which contribute to a weak intrinsic ferromagnet-
ism though the ferromagnetism is significantly enhanced after
the Mn-doping, as shown in Supporting Information Figure
S3b. In Figure 4d, the bifurcation begins to increase as the
temperature goes below 100 K, and the effect of the external
magnetic field starts to overcome the thermal fluctuation and
dominate the overall magnetization when the temperature is
lower than 100 K. This trend is roughly consistent with the
following magneto-transport measurements, in which the MR
ratio of a single Mn-ZnO NW in the Figure 5b also quickly
increases while the temperature is lower than 50 K.

The temperature-dependent magneto-transport measure-
ments on a back-gated Mn-ZnO NW FET were carried out
in a Quantum Design physical property measurements system
(PPMS). To exclude the contact resistance, a standard four-
probe setup was used to measure the channel resistance with a
Keithley 6221 DC/AC current source and a Keithley 2182
nanovoltmeter. Figure 5a shows the temperature-dependent
resistance (R−T) measurements on a single Mn-ZnO NW
under an axial magnetic field of \( H_a = 9 \) T (solid square) and \( H
= 0 \) T (open circle), respectively. The axial magnetic field
was applied along the NW, as shown in the inset of Figure 3b. To
further investigate carrier-mediated ferromagnetism in Mn-ZnO
material system, the impurity band model from Coey et al.\(^{9}\)
is considered to explain the long-range magnetic order at a low
Mn concentration (~1 atom %). In their model, the FM in
dilute ferromagnetic oxide is mediated by shallow donor
electrons, which form bound magnetic polarons and overlap to
create a spin-split impurity band. Because this model relies on
thermal activated carriers, the zero field R−T curve in the inset
of Figure 5a is fitted using modified Arrhenius law under the
polaron assumption:\(^{12,35}\)

\[
R(T) = R_0 T^\alpha \exp \left( \frac{E_p}{kT} \right)
\]

(3)

where \( \alpha = 3/2 \) for a nonadiabatic polaron model.\(^{35}\) The
activation energy (\( E_p \)) of our Mn-ZnO NW was estimated to be
approximately 33 meV, which is close to the value of 42.4 meV
reported from the Mn-ZnO thin film.\(^{12}\) Figure 5b shows the
MR ratio as a function of axial magnetic field at different
temperature (T = 1.9−50 K). The curves are intentionally
shifted for the purpose of clarity, and the length of double side
arrow represents the 10 % change of the MR ratio. The height
of MR peak is about 8 % at 1.9 K, and it is observable up to 50
K. These positive MR indicate the presence of spin-dependent
scattering, which has been reported previously that the giant
spin-splitting of the impurity band in Mn-ZnO affects the
quantum correction to resistivity and turns the MR behavior
from weak localization to weak antilocalization.\(^{36,37}\) In our Mn-
ZnO NW system, the low temperature (T < 50 K) MR is
proportional to the magnetization. However, it also depends on
the effect of spin-dependent scattering, which is associated with the
phase coherence length that has a strong temperature
dependence of \( L_p(T) \sim T^{-1/2} \).\(^{37}\) The value of MR drops with
raising temperature, and is easily overwhelmed by the thermal
noise at higher temperature. Therefore the MR is only detected
at low temperature (T < 50 K) in our Mn-ZnO NWs.

Although most research focuses on the Mn-ZnO thin films, it
is particular interest to investigate the electric-field control of
FM in nanostructures, because the quantum confinement could
significantly enhance the exchange coupling between the
confined carriers and the localized Mn\(^{3+}\).\(^{438}\) Figure 5c shows the
MR ratio as a function of axial magnetic field under different
gate voltages (\( V_g = -40 \)−40 V), where \( \Delta MR \) is defined as the height of the MR curves and extracted by
averaging the MR value within the saturation region (\( H_a = 8 \)−9
T). Figure 5d summarizes the gate modulation of the MR
measurements. The left (right) axis shows the \( \Delta MR \) (zero-field resistance, \( R_{h=0,T} \)) as a function of the gate voltage, respectively.
The gate-dependence of \( R_{h=0,T} \) in Figure 5d suggests that the
electron density increases as the gate voltage increases. As
predicted by the impurity band model for carrier-mediated
ferromagnetism in diluted ferromagnetic oxide,\(^{9}\) increasing
itinerary electron concentration would enhance the interaction
between each polarons, and hence increase the magnetism.
This enhanced magnetism is evidenced by the electric-field
modulation of MR ratio, which also increases from 5.6 to 8.1 %
when the gate voltage increases from −40 to +40 V. Therefore,
our results are consistent with the carrier-mediated ferromag-
etism model\(^9\) in Mn-ZnO system. Although this work shows that the electric-field modulation of magnetic moment is only observed at low temperature, it is the first demonstration of electric-field modulation of magnetism of diluted magnetic
ZnO NWs.

Conclusions. In this paper, the Mn-ZnO NWs were
synthesized by a gas-phase surface diffusion process in a
dedicated MBE system. The Mn concentration was estimated to be \( x_{Mn} = 1 \) atom %. The presence of Mn precipitates was not
observed based on XPS, XRD, and SEM experiments. The
perfect crystalline of the Mn-ZnO NWs was confirmed by HR-
TEM. Room-temperature FET characterization shows that majority carrier was n-type, and the corresponding mobility
(carrier concentration) was 0.65 cm\(^2\)/V·s (6.82 \times 10\(^{18}\) cm\(^{-3}\)),
respectively. Curie temperature of Mn-ZnO NWs was estimated to be about 437 K from SQUID measurements.
The difference of \( \Delta MR \) is up to 2.5 % as the gate voltage changes from −40 to +40 V at \( T = 1.9 K \), which suggests the
electric-field control of ferromagnetism. The successful
demonstration of gate modulation of FM in a DMS NW
represents an important step toward realizing future all-spin
logic devices.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

Additional information and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.
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