Synthesis and electronic properties of ZnO/CoZnO core-shell nanowires

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ZnO/CoZnO core-shell nanowires have been synthesized by depositing an epitaxial layer of $Co_xZn_{1-x}O$ ($x=0.05-0.25$) onto single-crystalline ZnO nanowires via pulsed-laser deposition. Detailed material analysis confirmed the core-shell structure and revealed a homogeneous distribution of Co atoms in the ZnO lattice. Field-effect transistors have been fabricated based on individual ZnO/CoZnO nanowires. These devices exhibited *n*-type transistor characteristics and intriguing magnetoresistance below 30 K. © *2006 American Institute of Physics*.
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ZnO nanostructures have been the focus of intense research in recent years. They are emerging as versatile building blocks for a diversity of nanoscale functional devices ranging from UV lasers,[1] nanocantilevers,[2] chemical sensors,[3] light-emitting diodes,[4] to acoustic wave resonators[5] and field-effect transistors.[6] In addition, ZnO has also been demonstrated as an ideal host material for diluted-magnetic-semiconductors (DMSs).[7–16] In particular, calculations by Dietl and co-workers[7] showed that ZnO and GaN would exhibit ferromagnetism above room temperature when doped with substitutional Mn^{2+} ions and sufficiently high levels of *p*-type dopants. Sato *et al.*[8] further revealed that *n*-type Co-doped ZnO would remain ferromagnetic above room temperature as well. Such ZnO-based DMSs are expected to exhibit a number of intriguing magnetic and magnetooptical properties that arise from spin-exchange interactions between the dopant ions and the semiconductor charge carriers.[17] The above theoretical findings have stimulated extensive interest among experimental researchers. Driven by the possibility of utilizing these materials for semiconductor spin-based electronics or spintronics, considerable research efforts have been focused on the synthesis and characterization of ZnO-based DMS, with primary interest in ZnO thin-film and bulk materials.[9–14]

On the other hand, the integration of DMS materials into modern electronics will require very low dimensions in order to make real use of the advantage offered by spins, where dimensionality and size are known to play a significant role in determining various properties of the systems. DMS-based nanostructures such as nanowires and nanobelts are therefore attracting increasing research interest very recently. A number of interesting DMS nanowires including Mn-doped GaN,[18,19] CdS, and ZnS (Ref. 19) have been synthesized and investigated. In contrast, studies of one-dimensional ZnO DMS nanostructures are still at a nascent stage despite very limited previous efforts.[15,16] The existing synthetic approaches such as ion implantation[15] and vapor-phase transport method[16] may not offer precise control over the chemical composition and morphology of the ZnO DMS nanowires. Moreover, electron-transport study conducted on individual magnetic ZnO nanostructures is still unavailable at the current stage.

In this context, we have carried out systematic studies on ZnO/CoZnO core-shell nanowires synthesized using a nano-casting technique recently developed in our group.[20] This technique provides a generic approach for the synthesis of nanowires with complex compositions. The key feature is to employ proper single-crystalline nanowires as templates, and then use pulsed-laser-deposition (PLD) to coat the templates with desired materials to form epitaxial core-shell nanowires. In this report, we used vertical ZnO nanowires as templates, while $Co_xZn_{1-x}O$ ($x=0.05-0.25$) was deposited via PLD to form ZnO/CoZnO core-shell nanowires. Detailed material analysis confirmed the core-shell structure and revealed a homogeneous distribution of Co atoms in the ZnO lattice. Field effect transistors based on individual ZnO/CoZnO nanowires exhibited *n*-type transistor characteristics and intriguing magnetoresistance.

A chemical vapor deposition method was used to grow vertical ZnO nanowires on *a*-plane sapphire substrates following a previous reported method.[21] Au films (2 nm) were used as catalyst for the ZnO nanowires shown in Fig. 1(a). Transmission electron microscopy (TEM) image in Fig. 1(b) shows that the ZnO nanowire surface is very clean, which is critical for the next step of PLD coating. There are two reasons for using vertical ZnO nanowires as templates. The first is that the lattice match between ZnO and $Co_xZn_{1-x}O$ is almost perfect when *x* is small. Therefore, the as-deposited
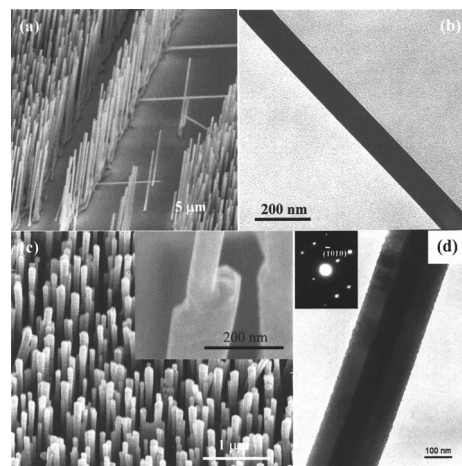

FIG. 1. (a) SEM image of ZnO nanowires grown on *a*-plane sapphire. (b) TEM image of as-grown ZnO nanowires. (c) SEM of ZnO/CoZnO core-shell nanowires after the PLD process. Inset: SEM image of a nanowire revealing both the core and the shell. (d) TEM image of a ZnO/CoZnO core-shell nanowire. The diameter of ZnO core is 50 nm and the $Co_xZn_{1-x}O$ coating layer is 70 nm. Inset is the SAED pattern from the ZnO/CoZnO core-shell nanowire.

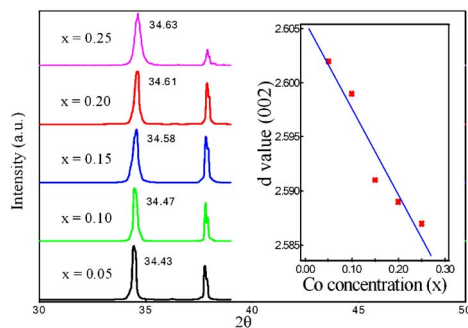[a)]Electronic mail: chongwuz@usc.edu

FIG. 2. (Color online) XRD results of ZnO/Co_xZn_{1-x}O core-shell nanowire samples with different Co content. In each curve, the left peak corresponds to ZnO (002) and the number is its 2θ value. The right peak is indexed to (110) of a-plane sapphire substrates. Inset: a plot of the d value of core-shell nanowires vs the Co content x.

Co_xZn_{1-x}O coating layers can have very high quality. The second reason is that vertically grown ZnO nanowires can have the least shadow effect during the PLD process so that the Co_xZn_{1-x}O layers can be coated uniformly around the ZnO nanowire templates.

After the ZnO growth, pulsed laser deposition of CoZnO was carried out following our previous publication.[20] The Co_xZn_{1-x}O target was prepared by compressing Co and ZnO powder into a pellet. The Co content can be adjusted by varying the ratio of these two powders. The nanowire templates together with the Co_xZn_{1-x}O target were transferred into a tube furnace connected with a Nd:YAG laser (λ =532 nm). PLD was done at 450 °C in oxygen environment. Figure 1(c) shows the scanning electron microscopy (SEM) image of the sample after the PLD process. All the nanowires remained normal to the substrate, and careful examination revealed an increase of the nanowire diameter, as a result of the CoZnO deposition. The inset of Fig. 1(c) shows a SEM image of a ZnO/Co_xZn_{1-x}O core-shell nanowire, which happened to have part of the CoZnO coating broken. One can clearly see the inner ZnO core and the shell layer. Figure 1(d) shows a TEM image of a ZnO/Co_xZn_{1-x}O core-shell nanowire that has 70 nm Co_xZn_{1-x}O coating layer with a deposition time of 25 min. All the nanowires examined by TEM showed uniform and smooth CoZnO coating. The selected-area-electron-diffraction (SAED) pattern of the nanowire [Fig. 1(d) inset] shows that both the ZnO core and the CoZnO coating are single crystalline.

Five kinds of ZnO/Co_xZn_{1-x}O core-shell nanowires were synthesized using the above-mentioned technique by changing the ratio of Co in the targets for PLD (x=0.05, 0.10, 0.15, 0.20, and 0.25). All other conditions were kept the same for these five samples except using different targets. X-ray diffraction (XRD) was used for characterization of the ZnO/Co_xZn_{1-x}O core-shell nanowire samples after PLD. Figure 2 shows the XRD data of the five samples. Only peaks corresponding to ZnO/Co_xZn_{1-x}O core-shell nanowires and sapphire substrates were detected. Detailed examination revealed a consistent shift of the ZnO/Co_xZn_{1-x}O (002) peak when the Co content was varied from 0.05 to 0.25, indicating a decrease of the lattice spacing d between the (002) planes. The values of d for different Co doping levels were calculated using the (110) peak of the sapphire substrate as reference, with the results shown in the inset of Fig. 2. These data points can be fitted with a linear curve: $d=-0.08x+2.605$. This is consistent with previous results
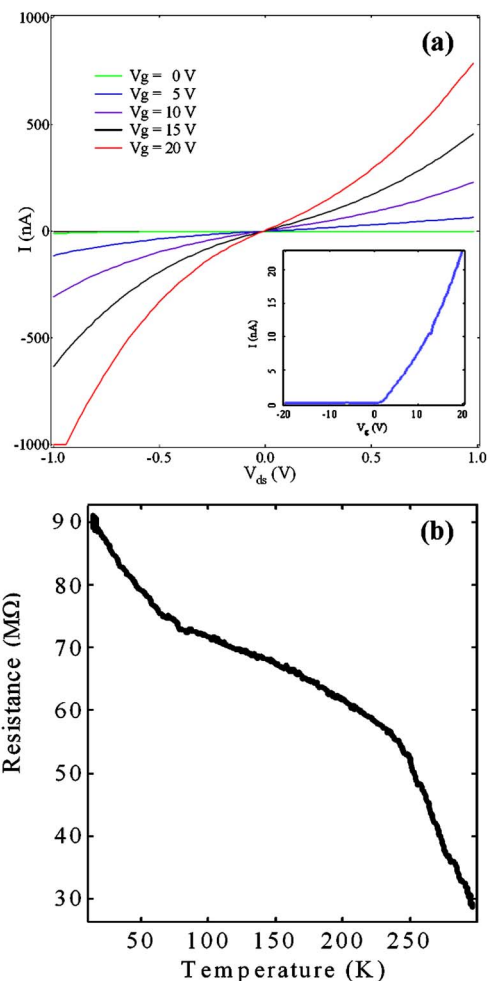

FIG. 3. (Color online) (a) Gate-dependent I-V_{ds} curves recorded at room temperature for a ZnO/$Co_{0.15}Zn_{0.85}$O core-shell nanowire transistor. Inset shows current vs gate voltage at V_{ds}=50 mV. (b) Temperature dependence of the device resistance.

obtained with Co_xZn_{1-x}O film samples,[22] and indicates that the Co atoms distributed homogeneously and replaced Zn atoms in the ZnO lattice, therefore leading to reduced lattice size. Furthermore, no Co-related peaks were identified in our XRD results, thus confirming no Co oxide or Co clusters were formed during the material synthesis. This observation is consistent with previous reports on CoZnO film samples.[12,13]

The successful synthesis of ZnO/Co_xZn_{1-x}O core-shell nanowires paved the way for studying Co_xZn_{1-x}O nanowire transport properties. These nanowires were removed from sapphire substrates and then transferred onto Si/SiO_2 substrates. Field effect transistors (FETs) were fabricated using ebeam lithography, and Ti/Au metal contacts were deposited to contact individual nanowires, while the silicon substrate can be used as a gate electrode. These devices were annealed at 350 °C for 30 s to improve the contacts. The following electronic measurement data were all obtained from ZnO/$Co_{0.15}Zn_{0.85}$O core-shell nanowire FETs. Figure 3(a) shows current-voltage (I-V_{ds}) characteristic of a typical ZnO/$Co_{0.15}Zn_{0.85}$O core-shell nanowire transistor at room temperature. Five I-V_{ds} curves at V_g=0, 5, 10, 15, and 20 V are displayed in Fig. 3. With the gate voltage varying from 0 to 20 V, the conductance of the nanowire gradually increased. This confirms that the as-grown ZnO/$Co_{0.15}Zn_{0.85}$O core-shell nanowires are n-type semiconductors. The inset of
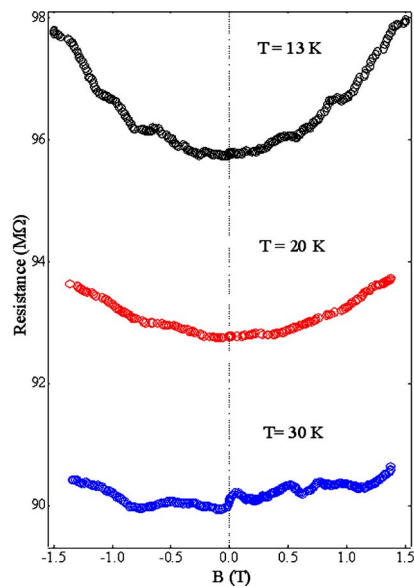
FIG. 4. (Color online) Magnetoresistance recorded at T=13, 20, and 30 K, while a magnetic field applied normal to the sample substrate was swept between ±1.5 T.

Fig. 3(a) displays a current versus gate voltage (I-V_g) curve taken at V_{ds}=50 mV while gate voltage was swept from −20 to 20 V. Again, n-type transistor behavior was clearly observed, as the conductance increased when the gate voltage increased positively. We have further measured the temperature dependence of the nanowire transistor resistance, with the result shown in Fig. 3(b). The device resistance increased monotonically when the temperature decreased, indicating standard semiconductor behavior. The amplitude of the resistance increase, however, is relatively small.

n-type ZnO is predicted to be ferromagnetic with substitutional doing of Co ions. The stabilization mechanism of the ferromagnetic state has been qualitatively investigated in Sato and co-worker's pioneering work.[8] Based on their *ab initio* calculations, the Co-3d states are located at approximately the Fermi level of the semiconductive ZnO matrix, which show pronounced exchange splitting, with the spin-up and -down states being fully and partially occupied, respectively. In this situation, a portion of electron carriers would occupy Co-3d states and participate in the double exchange mechanism when the system is doped with n-type impurities (e.g., oxygen vacancies), which reduces the kinetic energy of the ferromagnetic state. Based on the ZnO/Co$_{0.15}$Zn$_{0.85}$O nanowire FET, we have further carried out studies on their electronic properties in different magnetic fields and temperatures. Figure 4 shows a plot of the device resistance when the magnetic field was swept from −1.5 to 1.5 T at three different temperatures. Modulation of the device resistance can be derived to be ~2.1% at 13 K and 1.1% at 20 K. When the temperature was increased to 30 K, no obvious change of resistance with the magnetic field was observed. For comparison, control experiments were performed with ZnO nanowire transistors using the same fabrication and measurement techniques, and no magnetoresistance was observed even at 10 K with a magnetic field of 1.5 T. This clearly shows that the Co$_{0.15}$Zn$_{0.85}$O coating layer is the origin of the observed magnetoresistance. The negative magnetoresistance shown in Fig. 4 (resistance increases with applied magnetic field) is rather intriguing and deserves further study. We note that there are reports of both positive and negative magnetoresistance in DMS systems,[9,10] likely as a result of the diversity of the material composition and quality under study.

In summary, we have synthesized high-quality ZnO/Co$_x$Zn$_{1-x}$O core-shell nanowires by depositing an epitaxial layer of Co$_x$Zn$_{1-x}$O (x=0.05−0.25) onto single-crystalline ZnO nanowire templates via pulsed laser deposition. Co atoms were shown to replace Zn atoms in the lattice instead of forming Co oxides or Co clusters. Field-effect transistors have been fabricated based on individual ZnO/CoZnO nanowires. These devices exhibited n-type transistor characteristics and intriguing magnetoresistance below 30 K.

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