AIP Applied Physics Letters

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Citation: Applied Physics Letters **94**, 151909 (2009); doi: 10.1063/1.3117203
View online: http://dx.doi.org/10.1063/1.3117203
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/94/15?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **94**, 151909 (2009)

Magnetophotoluminescence properties of Co-doped ZnO nanorods

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(Received 26 February 2009; accepted 12 March 2009; published online 15 April 2009)

We present the detailed experimental results of the magnetic and optical properties of cobalt doped ZnO nanorods, especially the temperature and magnetic field dependence of photoluminescence up to 14 T. The Raman measurements indicate that our Co-doped ZnO nanorods have the same lattice constant as crystalline bulk ZnO. Sharp luminescence peaks centered at around 670 nm were observed at low temperature and their intensity decreased with increasing magnetic field. The luminescence peaks were attributed to *d-d* transitions in the Ligand field from the doped Co ions. We also observed a diamagnetic shift at a temperature of 1.5 K when the magnetic field was scanned from 0 to 14 T. The exciton radius of the Co-doped ZnO nanorods was deduced from the magnetophotoluminescence results. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3117203]

Diluted magnetic semiconductors (DMSs), in which a fraction of nonmagnetic elements are substituted by magnetic transition metal ions, are ideal candidates for spin-transport electronics. Wide band gap zinc oxide DMSs have been extensively studied due to their possible applications in spintronics and UV devices.[1,2] ZnO has a high solubility for transition metal ions[3,4] when compared to its other III-V compound semiconductor counterparts. This makes the oxides ideal candidates for fabricating DMSs. The existence of room temperature ferromagnetism in transition metal doped GaN and ZnO thin films was predicted by Dietl *et al.*[5] and Sato and Katayama-Yoshida[6] and was demonstrated experimentally in Co-doped ZnO thin films by Lin *et al.*[7] The ferromagnetism measured at various temperatures was reported in Co-, Ni-, Mn-, and Fe-doped ZnO thin films,[8–12] as well as nanostructures,[13–16] in the past few years. Recently, anisotropic ferromagnetism dependent on nanowire geometry and density at room temperature was reported by Cui *et al.*[17] in Co- and Ni-doped ZnO nanowires. More recently, photoluminescence (PL), electroluminescence (EL), cathodoluminescence (CL), and magnetic properties were investigated in undoped and Mn-doped ZnO nanowires and nanorods.[18–20] PL, EL, and CL emitted in the visible region were observed and were attributed to the ionized oxygen vacancies.

In this paper, we apply optical spectroscopy techniques in a low temperature and high magnetic field dilution refrigerator to investigate the optical properties of hydrothermally prepared Co-doped ZnO nanorods. We report Raman measurements, as well as temperature and magnetic field dependence of PL peaks observed at the visible regions. The luminescence peaks exhibited a weak diamagnetic shift due to the increase in wave function separation between the electron and hole pairs as the magnetic field intensity was increased.

The Co-doped ZnO nanorod samples studied in this work were prepared by the hydrothermal method. Zinc nitrate hydrate [$Zn(NO_3)_2$, 0.06 g] and hexamethyleneteramine (0.028 g) were first added to 40 mL of de-ionized (DI) water to form a 5 mM clear solution. Cobalt nitrate with different weight percentages from 0% to 200 %, with respect to zinc nitrate hydrate, was dissolved into the above solution. The mixture was heated in a Teflon-coated stainless steel autoclave at 95 °C for 2 h. After cooling to room temperature, the solid product was put into a centrifuge tube and was repeatedly cleaned with DI water to wash away the remaining Co ions for five to ten times, depending on the amount of cobalt nitrate added. The solid was dried at 70 °C for 5 h to obtain the ZnO nanorod powder. Doping concentration varied by adjusting the weight percentage of the cobalt nitrate. The color of the ZnO nanorod powder turned green as the doping became heavier. The composition of the solid was found by powder x-ray diffraction (XRD) to be ZnO. The doping concentration of Co was analyzed using the inductively coupled plasma mass spectrometry.

The XRD patterns of the ZnO samples with different doping concentrations and the scanning electron microscopy (SEM) image are given in Ref. 21. The strong peaks in the data indicate that well aligned ZnO nanorods with wurtzite structures were obtained, and the crystal structure was not altered by the doping. The nanorods were uniform in size, with a diameter of about 200 nm. However, the length of the rod varied from 6 to 1 μm as the doping concentration was increased from 0 % to 90 %. Figure 1 shows the hysteresis behavior of 90% Co-doped ZnO ($Zn_{0.998}Co_{0.002}O$) nanorods at room temperature. The sample exhibited weak ferromagnetic behavior with remanence permanent magnet of the order of 10^{-3} emu/g.

For the optical measurements under low temperature and high magnetic field, we first put the 90% Co-doped ($Zn_{0.998}Co_{0.002}O$) ZnO nanorod powder on a 1×1 cm^2 silicon wafer. A 0.2 mm thick cover glass was placed on top and was sealed onto the silicon wafer using putty and silicone. The sample was stuck to a sample holder with N-grease at the bottom of an insert equipped with a fiber probe. The insert was put into a dilution refrigerator and cooled down to 1.5 K. We performed the Raman and PL spectroscopy measurements through the fiber for above samples at excitation wavelengths of UV and 488 nm. In Fig. 2 it is shown that we compared the Raman signal from the Co-doped nanorods

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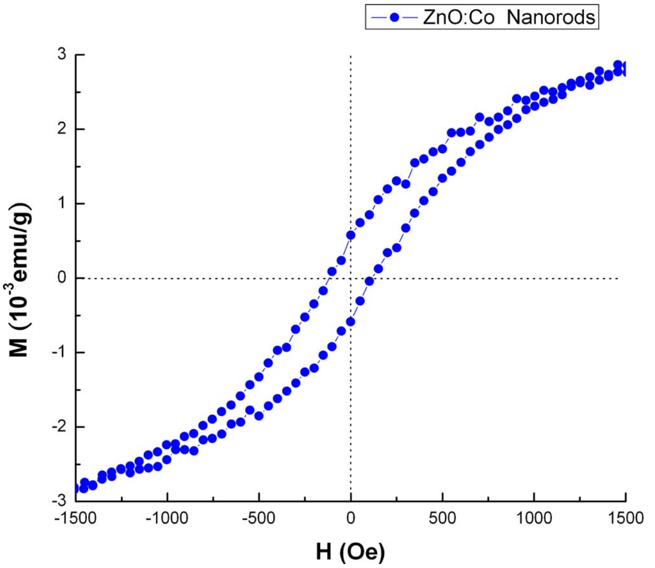

FIG. 1. (Color online) Room temperature magnetic hysteresis loops (M-H curve) of Co-doped ZnO nanorods.

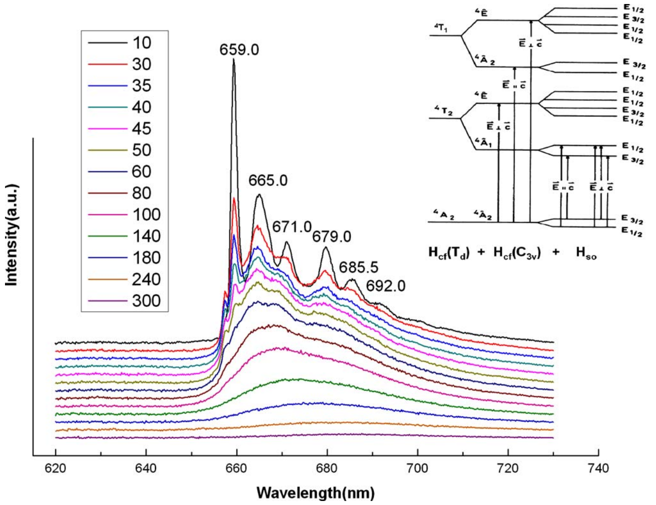

FIG. 3. (Color online) Temperature dependence of the PL spectra centered at 680 nm from $T=10$ K to $T=300$ K. The inset shows the schematics of energy transitions.

with pure ZnO nanorods. The spectra agree well with earlier reports.[22–25] It also indicates that our samples have the same lattice constant as crystalline bulk ZnO.

The Co-doped nanorods showed a PL peak near 380 nm due to the near-band-edge emission.[26] We also found two weak bands, centered around 500 and 670 nm, at an excitation wavelength of 266 nm. The green luminescence is generally attributed to the single ionized oxygen vacancy in the ZnO.[27] However, the emission band at around 670 nm deserves greater attention.

Figures 3 shows the temperature dependence of PL spectra excited at 405 nm from $T=10$ to $T=300$ K. Sharp peaks were revealed at 659, 665, 671, 679, 685.5, and 692 nm at low temperature, respectively. We believe that the light absorption is due to the isolated Co^{2+} ions in the ZnO lattice and the mechanisms are the competing superpositions of $^4A_2(F)$ to $^2E(G)$, and $^4A_2(F)$ to $^4T_1(P)$ and $^4A_2(F)$ to $^2T_1(G)$ energy levels.[28,29] The observed emissions resulted from the transitions of the $^4T_1(P)$, $^2T_1(G)$, $^2E(G)$ levels to the $^4A_2(F)$ ground state of the isolated Co^{2+} ions on zinc sites.[30] Schematics of the energy transitions are given in Fig. 3.

The magneto-PL spectra of Co-doped ZnO nanorods, as shown in Fig. 4, were recorded at 1.5 K by scanning the magnetic field up to 14 T with steps of 0.2 T at a time. The luminescence intensity decreased with increasing magnetic field, and dropped by about 25% at 14 T. These results suggest that the wave functions of the electron hole pairs in the excitons were separated under high magnetic field. However, the mechanism is not clear at this moment and needs further investigation.

Other than the intensity variations, a weak diamagnetic shift in luminescence peaks was also detected. The energy shift in the peak at 664 nm as a function of the applied magnetic field is plotted in the inset of Fig. 4 as an example. The diamagnetic shift was also clearly observed when the magnetic field was ramped down. The amount of energy shift is related to the magnetic field by the following equation:[31] $\Delta E=\beta\langle B^2\rangle=e^2\langle\rho^2\rangle/8m^*\langle B^2\rangle$, where β is the diamagnetic coefficient, ρ is the radius of exciton, m^* is the exciton effective mass, and B is the applied magnetic field. By fitting the curve

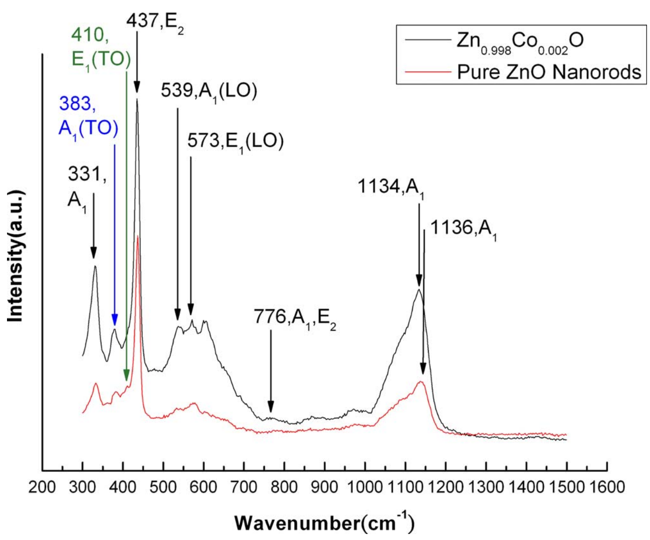

FIG. 2. (Color online) Raman spectra of the Co-doped ZnO nanorods and pure ZnO nanorods.

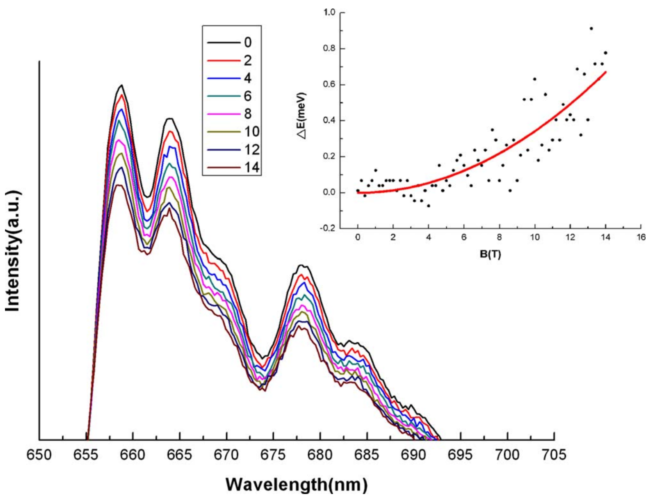

FIG. 4. (Color online) Magneto-PL spectra of the Co-doped ZnO nanorods recorded at 1.5 K. Diamagnetic shift in the PL peak of 664 nm is shown in the inset.

in the inset of Fig. 4, the diamagnetic coefficient β was found to be 3.37 $\mu\mathrm{eV}/\mathrm{T}^2$. From the above equation, we obtained an exciton radius of 4.899 nm. It is in good agreement with the size of the exciton (3.38 nm) obtained with the equation $\rho=(\varepsilon_r)m_0/m_*(a_B)$, where $\varepsilon_r=10$ in ZnO nanostructures.[32] The weak diamagnetic shift observed in the experiments can be due to the smaller exciton radius in this particular material.

To conclude, we have measured the Raman, PL, and magneto-PL of hydrothermally prepared Co-doped ZnO nanorods in a dilution refrigerator with high magnetic field. The PL peaks at around 670 nm were attributed to the transitions between energy levels of doped Co ions. PL intensity was also found to decrease with an increasing magnetic field. The diamagnetic shift in the luminescence peaks was found at a low temperature and allowed us to extract the exciton radius in Co-doped nanorods.

This work was supported by the National Science Council of Republic of China under Contract No. NSC 96-2112-M-009-024-MY3 and NSC 96-2120-M-009-004, the MOE ATU program, and National Nano Device Laboratories.

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