Co-DOPED ZnO NANOWIRES GROWN BY VAPOR-LIQUID-SOLID METHOD: STRUCTURAL, OPTICAL AND MAGNETIC STUDIES

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We report on the growth of Co-doped ZnO nanowires (NWs) on Si substrate using a self-catalytic vapor deposition method from a Co-doped ZnO nanopowder source and study its structural, optical and magnetic properties for the as-grown and rapid thermal annealed samples. Co (5%) doped ZnO (ZnCoO) nanoparticles are used as source material for the growth process. The field emission scanning electron microscopy and high resolution transmission electron microscopy images clearly reveal formation of long ZnO NWs with uniform diameter. X-ray diffraction analysis confirms the single crystalline hexagonal structure of Co-doped ZnO NWs without impurities of metallic cobalt or other phases. Micro-Raman studies of doped samples show doping/disorder induced additional modes at ~621, 671 cm\(^{-1}\) as compared to the undoped ZnO. Room temperature photoluminescence spectra of the doped ZnO NWs show strong emission band at ~380 nm and no significant emission was observed in the visible region indicating low defect content in the NWs. The field dependent magnetization (M–H curve) measured at room temperature exhibits paramagnetic nature for the NWs with the magnetic moment in the range 2-3.7 m-emu/cm\(^2\) for the applied field 2 Tesla, while the source ZnCoO powder exhibit room temperature ferromagnetism with saturation magnetization ~6 emu/g. Possible mechanism of alteration in magnetic behavior in doped NWs are discussed based on the growth conditions and influence of defects.

Introduction

Considerable research efforts have been focused on ZnO-based dilute magnetic semiconductors (DMS) in recent years\(^1\)\(^-\)\(^3\) due to the prediction of possible ferromagnetic properties with Curie temperature (T\(_C\)) above room temperature.\(^4\) In particular, ZnO-based materials have been receiving considerable attention due to its abundance and environment-friendly nature and also due to its potential as a suitable optoelectronic material with a wide band gap (~3.34 eV) and high exciton binding energy of 60 meV. With the advancement of experimental techniques, interest in zero-dimensional and one-dimensional (1D) ZnO-based materials as building blocks of new electronic and spintronic devices is rapidly increasing. The study of the effect of dimensionality on magnetic, optical,
and mechanical properties is therefore important not only for technological applications but also to strengthen our basic understanding in low dimensions. Among all the forms of ZnO-based DMS nanocrystals with room-temperature ferromagnetism, 1D nanowires (NWs) and nanorods (NRs) are supposed to have specific applications in fields such as sensors, field-emitters, p-n diodes, short-wave magnetooptical and spintronics devices.\(^5\-^8\)

Based on current available reports on DMSs, it is clear that the vast majority of research on ferromagnetic properties of transition metal (TM) doped ZnO system are often observed in thin films and nanosized particles\(^9\,^10\) instead of well-crystallized bulk materials, which reveals that defects may stabilize ferromagnetism (FM) in those low-dimensional materials.\(^11\,^12\) Recently transition-metal (TM) doped 1D ZnO nanowires of varying diameter were grown by various experimental techniques and ferromagnetic ordering has been found at a range of temperatures from low to room temperature.\(^3\,^13\)

Considerable effort has also been devoted for introducing two different 3d-TM impurities into ZnO matrix in order to explore the effect of codoping on transition temperature.\(^14\,^15\) Liu et al.\(^13\) successfully synthesized (Fe/Co) codoped 1D ZnO nanowires via chemical vapor deposition growth method and observed Curie temperature was higher than 300 K. Previous theoretical study by Park and Min\(^16\) on bulk Zn\(_{1-x}\)(FeCo)\(_x\)O indicated that there is no indication of charge transfer between Fe and Co. They suggested that double exchange mechanism will not be effective for observed ferromagnetism and one needs to invoke other exchange mechanism between Fe and Co. Defects such as O vacancy or Zn interstitial (n-type defect) and Zn vacancy (p-type defect) seem to play important role and need to be investigated. Anisotropic ferromagnetism dependent on nanowire geometry and density at room temperature was reported by Cui et al.\(^17\) in Co and Ni-doped ZnO NWs. Photoluminescence (PL), electroluminescence (EL), cathodoluminescence (CL), and magnetic properties were investigated in undoped and Mn-doped ZnO nanowires and nanorods.\(^18\-^19\) PL, EL, and CL emitted in the visible region were observed and were attributed to the ionized oxygen vacancies.

There are very few reports on the synthesis of Co doped ZnO NWs by high temperature vapor-phase growth.\(^20\-^21\) Although this approach has proven quite effective for the production of a multitude of nanoscale semiconductors, gas-phase synthesis has some considerable limitation in regards to homogeneous doping and sustaining ferromagnetic characteristics because of high growth temperature. Here, we have grown Zn\(_{1-x}\)Co\(_x\)O nanowires by a self-catalytic vapor phase thermal evaporation method and systematically investigated their magnetic properties under different growth conditions. The crystal structure, morphology and chemical composition of the products was examined through x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), Transmission Electron Microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). Micro Raman and PL studies were carried out to check the doping induced peaks and the presence of defects in doped ZnO. Vibrating sample magnetometer (VSM) is employed to measure the room temperature (RT) magnetic properties and the variation of magnetization with temperature. The observed magnetization and its temperature dependence are discussed with reference to the role of defects and doping in the ZnO sublattice.

**Experimental details**

Co-doped ZnO NWs are grown on Si substrates using a self-catalytic vapor liquid-solid (VLS) method from a Co-doped ZnO nanopowder source. The starting materials are commercial ZnO nanopowder (purity 99.999%, Sigma Aldrich) and cobalt (Co) powder (99.5%, Loba Chemie). 5% Co powders is mixed with the ZnO nanopowder. After mixing, the powders are grinded for 10 minutes and milled in a mechanical ball-milling machine (Retsch, PM 100) at 350 rpm for duration of 5 hrs in a zirconium oxide vial under atmospheric pressure and temperature. Zirconium oxide balls of diameter 5 mm are used in this experiment. The ball to powder mixture weight ratio is taken as 10:1. Zn\(_{1-x}\)Co\(_x\)O NWs are synthesized in a horizontal muffle furnace via thermal vapor deposition method. The mixture of doped ZnO nanopowder and high quality graphite powders was used as source material for the growth of the doped NWs. The source material was heated at 950°C and the thermally produced vapor was deposited on the cleaned Si (100) substrates which were placed at 700°C and 800°C in downstream direction. The deposition was carried out for 30 min under a constant Ar flow at 70 sccm. The
chamber pressure was maintained at 750 mbar during the growth. After the deposition, samples were cooled down to room temperature and taken for characterization.

The crystal structures of the obtained samples are characterized by XRD patterns (Bruker D8 Advance, CuKα radiation) and micro-Raman spectroscopy (LabRam HR800, Jobin Yvon). Morphology of as-synthesized samples is observed by FESEM (Sigma, Zeiss, Germany) and TEM (200KV, JEM2100, JEOL, Japan)). Composition analysis is done by energy-dispersive X-ray spectroscopy (EDS) to confirm the presence of Co atoms in the as grown NWs. The magnetic properties of the samples are measured by using a Lakeshore (model no. 7410) VSM. The UV-Vis absorption spectroscopy measurements are recorded using a commercial spectrophotometer (Varian) with a monochromated Xenon lamp source. PL measurement was performed at RT using 325 nm excitation in a commercial high resolution fluorimeter (Edinburg, FSP920).

Results and Discussion

A. Structural characterization

Figure 1 shows some typical XRD pattern of the as-grown 5% Co doped ZnO NWs. All the observed diffraction peaks can be indexed to a ZnO wurtzite structure (space group P63mc), and no other impurity phase was found, which indicates that the Co ions successfully occupy the lattice site rather than interstitial ones. In addition, very slow scans XRD near the peaks of both hexagonal and cubic cobalt phases reveal no signatures of any kind of additional phases in the NPs. XRD pattern of source powder (ZnCoO) shows additional strong peaks corresponding to (100) and (101) planes of ZnO.22 Measurement of Co powder shows one intense peak around 44° which does not appear for the doped samples indicating Co is doped well in the ZnO sublattice.

Fig. 2(a) and 2(b) shows FESEM and TEM images of the Co doped ZnO NWs deposited at 800°C, respectively. The micrograph reveals clearly the formation of long ZnO NWs with diameter in the range 25-55 nm and length in the range 1.5-2.0 µm. HRTEM lattice images are presented in Fig. 2(c). The d-spacing of the crystal plane is calculated as 2.58 Å that matches with the crystal growth plane (002). Inset of Fig. 2(a) shows the results of EDX analysis on the ZnO NWs, revealing the presence of Co, Zn, O confirming that doping of Co inside the ZnO matrix. The doped NWs grown at lower substrate temperature are short and less smooth compared to that grown at higher temperature. We have observed that the NWs deposited at further lower temperature are rope like form and less crystalline. So, deposition at higher temperature is preferred in order to make smooth and long NWS and NRs. But high temperature deposition
might cause a disturbance for ferromagnetic interaction among the TM ions. Therefore, optimum choice of growth temperature/substrate temperature is crucial for the systematic growth of RT ferromagnetic NWs.

**B. Raman scattering studies**

In order to investigate the influence of Co doping on microstructure and vibrational properties, Raman scattering experiments were carried out. Raman scattering is a versatile technique for detecting the incorporation of dopants and the resulted defects and lattice disorder in the host lattice. Figure 3(a) shows the room temperature Raman spectra of the source doped NPs and the undoped ZnO NPs, while that of the as-grown doped NWs are shown in Fig. 3(b) in the range 400 to 800 cm\(^{-1}\). One sharp and strong peak at ~437 cm\(^{-1}\) can be seen for all the samples and it is assigned to \(E_2\) (high) mode in ZnO, which is the strongest mode in wurtzite crystal structure. \(E_2\) (high) mode is associated with the motion of oxygen atoms in ZnO lattice. Note that as compared to undoped NPs, the doped source NPs shows strong Raman band at 574 cm\(^{-1}\), which is deconvoluted into two peaks, as shown in the inset of Fig. 3. The peak at 574 cm\(^{-1}\) is the \(E_1\) (LO) mode and can be attributed to defects due to O vacancies, Zn interstitial defect states. The 2\(^{nd}\) peak is observed at ~547 for the Zn\(_{1-x}\)Co\(_x\)O (x=0.03, 0.05). Wang et al.\(^{23}\) and Cheng et al.\(^{26}\) also observed this mode in (Co, Al) and Ce-doped ZnO. According to the literature, this mode is induced by host lattice defects, such as oxygen vacancies and Zn interstitials. With the doping content, the host lattice defects in ZnO are activated and amplified and then this mode appears. In the present case, due to the smaller ionic radius of Co\(^{2+}\) than that of Zn\(^{2+}\), when Co\(^{2+}\) was doped into ZnO lattice, more oxygen vacancies and Zn interstitials are created. Therefore, the appearance of 547 and 574 cm\(^{-1}\) can be used to characterize Co\(^{2+}\) doped into ZnO lattice. However these defects related peaks do not appear in Raman spectrum of the doped NWs deposited on the Si substrate. Appearance of Si substrate peak might be one obstruction for the observation of any weak peak in this region, but most probably those peaks are absent as confirmed by the PL measurement and from the M-H curve parameters. Instead, we observed disorder induced additional modes at ~621, 671, cm\(^{-1}\). Due to relaxation of the selection rule, disorder induced additional Raman modes becomes active in such doped NW structures.

**C. Photoluminescence studies**

Photoluminescence (PL) spectroscopy is an effective tool to investigate the information about bandgap related transitions and the presence of defects in semiconductors. The PL spectra of the as grown and RTA annealed Co-doped ZnO NWs recorded at room temperature are shown in Fig. 4. Distinct strong emission band in the spectra of the NWs can be seen in the UV region at ~380 nm. After RTA annealing, the
UV emission band is red shifted by 2nm. The ~380 nm peak usually originates from the near band-edge (NBE) transition of ZnO and is generally attributed to the recombination of free excitons. There is no measurable visible PL emission present in doped NWs sample, while starting doped NPs showed intrinsic defect related broad visible emission band (D) at 520 nm. Similar visible emission has been observed in the doped ZnO reported by Li et al. The D band is often attributed to the radiative recombination of photogenerated holes with electrons occupying the singly ionized oxygen vacancy ($V_o$). Based on the band-structure calculations, the visible emission has been assigned to $V_o$ and Zn$_{in}$. In our earlier work, it was argued that FM in Co doped ZnO samples can be observed due to defect mediated interaction of the TM ions. But there is no defect related band present in the doped NWS. As these doped NWs are grown at relatively high temperature, defect concentration may be too low to be detected in the PL spectra. Therefore, it is believed that due to the absence of defects, ferromagnetic coupling is not favoured in the Co doped ZnO NWs grown by VLS.

D. Magnetic characterization

The magnetic properties are investigated using VSM. Fig. 5 shows the M-H curve measured at room temperature for the as-grown Co-doped ZnO NWs. Fig. 6(a) shows the magnetic hysteresis (M-H) loops for 5% Co doped milled samples (source material) measured at 300 K. NWs exhibit paramagnetic nature with magnetic moment up to 2.0-3.7×10⁻³ emu/cm² for the applied field 2T. However, the as grown source powder (ZnCoO) exhibits strong ferromagnetism at and above room temperature.

The doped source powder (5% Co doped ZnO NPs) shows saturation magnetization (M_s) as large as 6 emu/g and coercive filed (H_c) of the order of 260 G. While no trace of FM was observed in the undoped ZnO NPs that was first tested under similar conditions. We have also measured temperature dependence of magnetization for the doped source powder to check the high temperature behaviour. Fig. 6(b) shows the temperature dependent magnetization in the temperature range 30° to 550° C. The magnetic moment falls down rapidly with temperature at higher temperature (>450°C) region indicating transition of
the material toward paramagnetic phase. This magnetic transition suggests that high-temperature processing causes a rapid decrease of ferromagnetic coupling of the doped Co atoms. From the differential plot of the M-T curve we obtained the Tc at ~518°C for the source material which implies that the ferromagnetism is not due to the Co metal that has a Tc >1100 °C. We also carried out post-growth RTA annealing of the Co doped NWs and tested the magnetic property of the samples. However, no appearance of FM was observed, consistent with the absence of defect related peaks in the PL measurement. In fact, RTA treatment further eliminates the defects in ZnO NWs. This again supports the hypothesis that due to absence of defects or defect mediated interactions, high temperature grown Co doped ZnO NWs is paramagnetic in nature.

Despite large number of studies reported on ZnO-based DMSs, there are different views about the nature and origin of the magnetic properties of the samples prepared by different methods and different groups.3 These conflicting results between research groups suggest that the magnetic properties of DMS materials seem to be very sensitive to the preparation method and the structure of materials.3,34,35 As reported by Choi et al.35 bulk ZnO and carrier-free ZnO NWs are found to favor the anti-ferromagnetic state due to the super-exchange interaction between the Co ions, the FM state can be obtained by additional electron doping which increases the double-exchange interaction. The stability of electron-mediated ferromagnetism is greatly enhanced due to the quantum confinement effect in NW structures, which leads to the increase in the band gap and the lowering of the minority Co ta levels relative to the conduction band edge. FM of NWs is strongly affected by the position of the minority Co ta levels and their concentration.35 Wang et al.36 demonstrated intrinsic RT FM in ZnO:Co thin films, while Qingyu et al.37 reported paramagnetism in Co doped ZnO films deposited by the same PLD technique. Recently, origin of FM ordering in pristine micro- and nanostructured ZnO has been discussed and role of surface defect was emphasized.38 However, the magnitude of FM in such undoped systems is usually too low for any practical application.

In the present case, Co doped ZnO NPs source material revealed RT FM. Our systematic study have shown that oxygen-vacancy defect constituted BMPs are one of the promising candidate for the origin of FM in the doped NPs, also possible interaction of the Co2+ and extended defects e.g., dislocations/grain boundaries may be responsible for the observed FM at and above RT.22,38 However the as-grown ZnO:Co NWs show paramagnetic behavior at RT, possibly because of their high temperature growth and absence defect related states. Since the growth temperature (>700°C) of doped NWs is much higher than the Tc of the doped source materials, the ferromagnetic ordering might be lost during the growth at such high temperature. Note that no significant amount of intrinsic defects could be found in the as-grown NWs, as evidenced from the Raman and PL spectra. Thus, due to lack of sufficient defects, which according to the majority of the literatures, essentially mediate the magnetic exchange interaction, no FM is observed in the Co doped ZnO NW.14,29 Note that Co doped ZnO thin films grown at or above 700°C have shown room temperature FM, where defects were present.39 Co/Mn-codoped ZnO NWs grown by vapour deposition have shown obvious RT FM characteristics with defects having important role.14 Thus, growth temperature is not the sole factor determining the absence of FM in these NWs. Also absence of FM interaction might be happening for low concentration of Co ions in our sample as reported in other group that the magnetic interaction between the Co ions has the short-range nature and sufficiently high concentrations of the Co ions are needed to achieve FM in ZnO NWs.35 We believe that lack of sufficient concentration of defects in these NWs are primarily responsible for the absence of FM in these NWs. Note that we have not detected any oxide phase formation (e.g., CoO, which is antiferromagnetic) in the as-grown NWs. Hence, secondary phases are unlikely to be responsible for the absence of FM. Further element specific characterization like X-ray magnetic circular dichroism (XMCD), X-ray linear dichroism (XLD), X-ray absorption spectroscopy (XAS) 40,41 may be needed to know about the exact interaction mechanism of observed magnetization behaviour. Also proper control of growth temperature, substrate temperature, gas flow rate might lead to FM quality NWs, having important applications as 1D DMS material which needs further investigation.
Conclusions

Co-doped ZnO NWs of diameter 15-25 nm have been synthesized on Si substrates using a catalyst free vapor deposition method from a Co-doped ZnO nanopowder source. The FESEM and TEM images clearly show formation of long ZnO NWs with uniform diameter. Doping of Co is further confirmed by EDX analysis. Micro-Raman studies of doped samples show doping/disorder induced additional mode at ~621 and 671 cm\(^{-1}\) as compared to the undoped and doped ZnO NPs. Room temperature PL spectra of the doped ZnO NWs show strong excitonic emission band at ~380 nm and no significant PL emission was observed in the visible region indicating very low defect content in the doped NWs. The field dependence of magnetization (M–H curve) measured at room temperature exhibits paramagnetic nature with nominal magnetic moment in the range 2.0-3.7×10\(^{-3}\) emu/cm\(^3\) for the applied field 2 Tesla, while the source powder (ZnCoO) exhibit room temperature ferromagnetism with saturation magnetization ~6 emu/g. The absence of FM in the doped NWs is explained on the basis of high temperature growth process, where no significant amount of intrinsic defects is present in the as-grown NWs. FM in the source NPs is observed for defect mediated interaction. Optimization of the growth parameter like growth temperature, substrate temperature, gas flow rate may lead to FM in the doped NWs, worth important application as 1D DMS material which needs further investigation.

Reference