

Research Article

Oxygen Defects Mediated Magnetism of Ni Doped ZnO

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Ni doped ZnO nanoparticles were synthesized by a solution route and annealed in O₂, air, and Ar, respectively. X-ray diffraction and X-ray photoelectron spectroscopy measurements show that the samples possess typical wurtzite structure and have no other impurity phases. Magnetization loops for ZnO samples were measured and clearly show typical ferromagnetic saturation behavior. With the defect analysis based on photoluminescence spectroscopy, the effect of defects on the nature and origin of ferromagnetism was investigated. The results suggest that oxygen vacancies, especially single ionized oxygen vacancies, play a crucial role in mediating ferromagnetism in the Ni doped ZnO.

1. Introduction

Diluted magnetic oxide semiconductors (DMOSs) have gained much attention recently due to the possibility to control spin and charge simultaneously for future spintronics [1, 2]. These oxide semiconductors with a wide band gap are optically transparent in visible region and important for the development of spin related optoelectronic devices. After the theoretical prediction by Dietl et al. suggesting the existence of room temperature ferromagnetism (FM) in doped ZnO, the system has been extensively studied [3, 4]. Remarkable progress has been made in the realization of transition metal (TM) doped ZnO with Curie temperature (T_c) at or above room temperature (RT). It was also reported that even doping “nonmagnetic” atoms such as Cu or Bi leads to RT FM in ZnO [5, 6]. More recently, FM had been observed in undoped ZnO, which opened an extensive debate on the origin of FM [7, 8]. Therefore, some researches suggested that induced FM is due to oxygen defects in ZnO, not TM ions or secondary phases. Although the origin of FM in TM doped and undoped ZnO has not been fully understood so far, oxygen (or Zn) defects are broadly recognized as an important reason for the FM behavior of doped and undoped ZnO, which is also consistent with our previous work on FM of undoped ZnO [9].

In the present work, we have focused our attention on further research of the role of oxygen (or Zn) defects by investigating the effect of different annealing atmospheres on

the FM properties of Ni doped ZnO nanoparticles based on an analysis of photoluminescence (PL) spectroscopy.

2. Experimental

2.1. Preparation of Ni Doped ZnO Nanoparticles. Ni doped ZnO nanoparticles were prepared by a solution method. A total of 0.01 mol of zinc acetate (Zn(AC)₂·2H₂O) and Nickel acetate (Ni(AC)₂·4H₂O) in the chosen atomic rations were dissolved in 200ml deionized water as the precursor together with 0.01 mol methenamine (C₆H₁₂N₄, HMT). Then they were mixed under vigorous stirring for 30 min in a glass beaker. Before growth, a glass substrate was cleaned carefully and put into the glass beaker. The growth time and temperature were 24 h and 95°C, respectively. After growth, the substrate was taken out the solution, thoroughly rinsed with deionized water, treated in an ultrasonic water bath for 10 min, and dried in air at room temperature. To investigate the influence of defects on the inducing magnetic moment, the resulting sample was divided into three parts for the followed anneal at 800°C for 30 min in Ar, air, and O₂, respectively.

2.2. Characterization. The structure of Ni doped ZnO nanoparticles was determined by X-ray diffraction (XRD) with Cu *K*_α radiation ($\lambda = 0.1542$ nm) at RT. The effective concentration and binding state of the ions in the

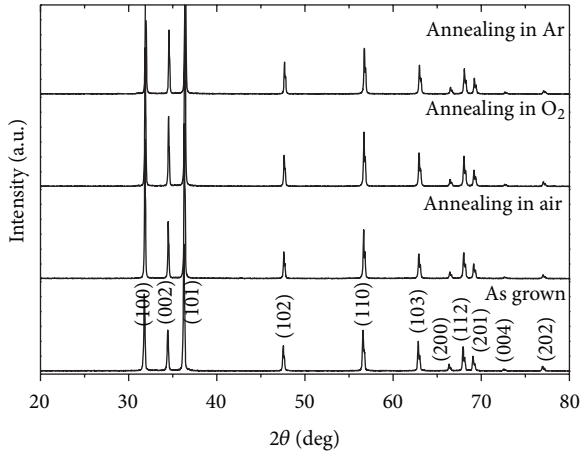


FIGURE 1: X-ray diffraction of Ni doped ZnO samples as grown and thermal annealed in different atmosphere.

nanostructures were characterized with X-ray photoelectron spectroscopy (XPS) (ESCA-LAB 250, Thermo-VG Scientific). The optical properties were characterized by photoluminescence (JobinYvon-800 HR). The magnetic properties were investigated by means of a SQUID magnetometer (MPMS, Quantum Design-PPMS 9).

3. Results and Discussion

3.1. Microstructure. The structure of Ni doped ZnO particles was characterized by XRD at RT, as shown in Figure 1. No other diffraction peaks besides those of wurtzite ZnO can be observed. Thus, it was demonstrated that the samples possess the typical wurtzite structure and no impurity phases are present.

3.2. XPS Analysis. X-ray photoelectron spectroscopy is the most useful tool to analyze the surface valence states of the elements in a material. To further investigate the composition and structure of the prepared particles, XPS spectra of Ni doped ZnO sample were measured and are shown in Figure 2.

An extended scan is reproduced in Figure 2(a). The Zn2p3 spectrum exhibits an asymmetry feature, indicating the possibility of existence of multicomponent Zn. Gaussian resolving is performed and two peaks obtained were centered at 1020.93 and 1022.42 eV (see Figure 2(b)). The peak centered at 1020.93 eV corresponds to the binding energies of Zn2p3 of undoped ZnO. The peak centered at 1022.42 eV is attributed to the Zn2p3 of Ni doped ZnO. This increase of binding energy is due to the substitution of parts of the lattice Zn in ZnO by Ni²⁺ ions with the larger ionic radius and the formation of Zn–Ni bonding structure.

To investigate the distributing of Ni element, gaussian resolving is also performed on the Ni2p spectrum. The peaks of Ni 2p3/2 and Ni 2p1/2 core levels are found to be centered at 855.54 and 873.1 eV, respectively, whereas the corresponding satellite structures are clearly observed at 861.3 and 878.7 eV. The peak positions depend on the

local structure of the Ni atoms and provide the information about the chemical state. The Ni 2p3/2 (855.54 eV) position is quite different from that of metallic Ni (852.7 eV), NiO (853.8 eV), and Ni₂O₃ (856.7 eV). The absence of Ni metallic clusters can also be explained on the basis of energy difference between Ni 2p3/2 and Ni 2p1/2 core levels. For Ni doped ZnO, the difference is 17.56 eV, which is different from the value of metallic Ni (17.27 eV). This energy difference for NiO (17.49 eV) is very close to the observed (17.56 eV) value, which gives the evidence that Ni is in +2 valance state; however, the presence of NiO can be ruled out as NiO is antiferromagnetic (TN 520 K), whereas in this case, room temperature ferromagnetism is observed. Furthermore, the shape of peaks for Ni metallic with satellites structure is narrow and different from the observed spectrum of Ni doped ZnO nanorods. These results give evidence that Ni ions with valence +2 are successfully substituted into tetrahedral sites of the ZnO wurtzite structure without forming any detectable impurity phase, such as Ni metal, Ni₂O₃, and NiO. The atomic concentration of Ni is about 2.90%.

The XPS spectrum of O1s is asymmetric (see Figure 2(d)), indicating the presence of multicomponent oxygen species in the near-surface region. It can be fitted with three components, which are centered at 529.92 eV, 531.2 eV, and 531.74 eV, respectively. The peak at about 529.92 eV is attributed to the ZnNiO crystal lattice oxygen. The peak at about 531.2 eV is associated with oxygen-deficient regions in the ZnNiO matrix. The peak at about 531.74 eV is due to the chemisorbed oxygen of the surface hydroxyl, –CO₃, adsorbed H₂O, or adsorbed O₂ [10–12].

3.3. Photoluminescence Properties. To investigate the presence of defects, the RT PL spectra of Ni doped ZnO as grown and annealed at three different atmospheres are shown in Figure 3(a). Each spectrum displays ultraviolet (UV) near band-edge (NBE) emission. It is well known that, at RT, ZnO typically exhibits UV band-edge emission and broad visible emissions at green, orange, yellow, and red spectral bands. The UV band-edge emission is attributed to free excitonic emission. It is reasonable to assume that this PL mechanism is the same for all our investigated Ni doped ZnO samples. We observed the UV near-band-edge emission peak at 380–400 nm. Here, we only report data for visible emission, which is referred to as deep-level emission and attributed to recombination of electrons deeply trapped in oxygen/Zn vacancies and interstitials, with photo-generated holes.

Many reports have focused on the origin of the PL in doped and undoped ZnO. There are three peaks in the visible band, 527 nm, 575 nm, and 657 nm. The green emission (527 nm) is generally attributed to the recombination of electrons trapped in single ionized oxygen vacancies (V_o⁺) with photo generated holes [13, 14]. The green emission (575 nm) is related to the doubly ionized oxygen vacancy (V_o⁺⁺) [15–17]. The red emission around 657 nm originates from the intrinsic defects of oxygen interstitials (O_i) [18–20], which act as traps for photo-generated holes.

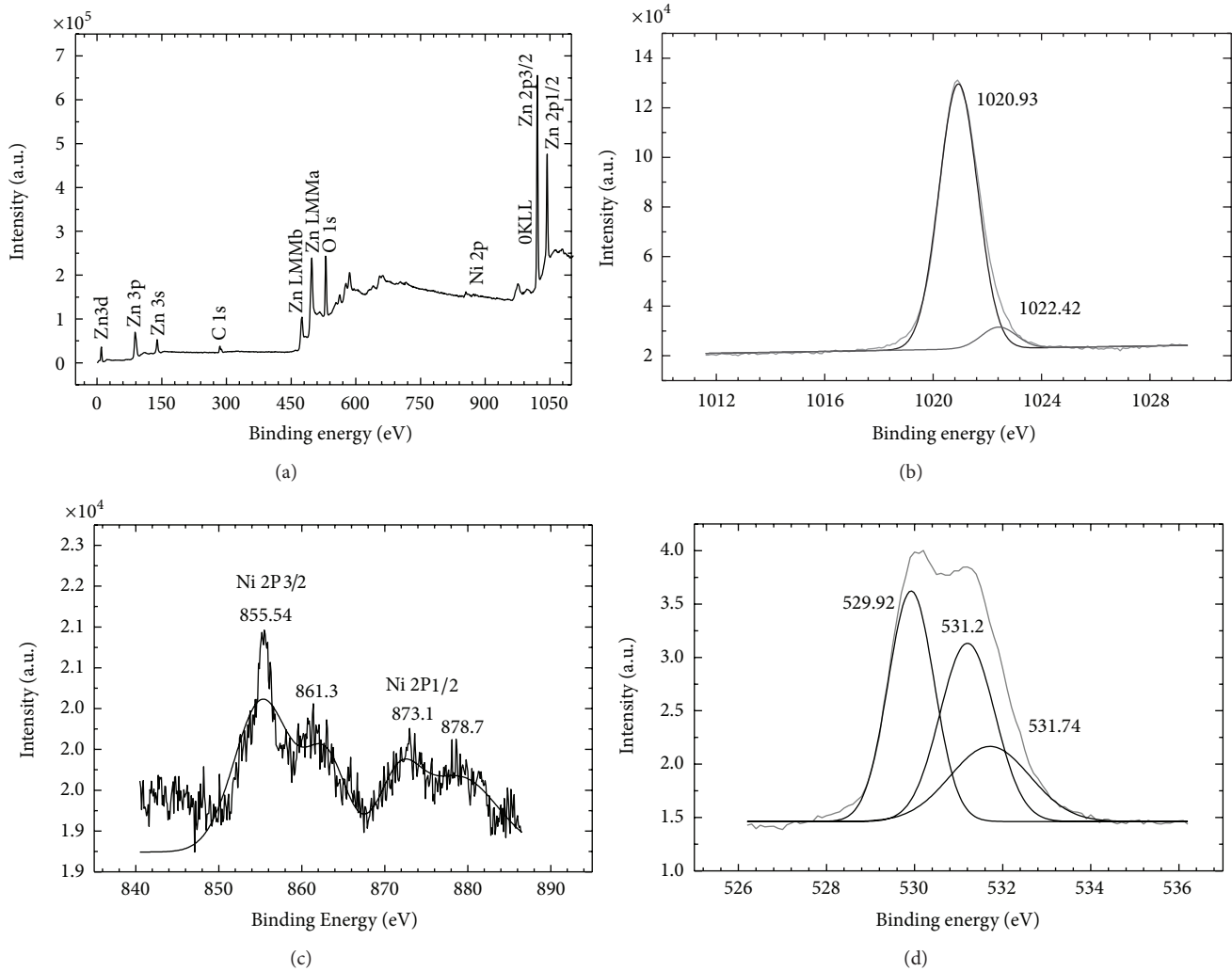


FIGURE 2: XPS spectra of as grown Ni doped ZnO samples: (a) Extended scan; (b) Zn2p3 spectrum; (c) Ni2p3 spectrum; (d) O1s spectrum. (The gray lines represent experimental results and the black solid curves are Gaussian fits of the components).

Gaussian fitting is performed on each spectrum to investigate the distributing of the above three defects, which is shown in Figure 3(b). Figure 4 displays the contents of oxygen related defects in Ni doped ZnO samples as grown and postannealed in different atmospheres (O_2 , air, and Ar).

During the annealing process in Ar and air, oxygen easily escapes from the ZnO particles, the concentration of oxygen vacancies (V_o^+ and V_o^{++}) increases, and the concentration of O_i decreases. After annealed in O_2 , the oxygen vacancies in the sample are filled to a large extent and the concentration of oxygen interstitials have increased. At the same time, the relative contents of V_o^+ increases due to the fact that part of V_o^{++} have been transformed into V_o^+ during the annealing process.

3.4. Magnetic Properties. Magnetization loops for the samples in capsules were measured at 300 K using a VSM magnetometer and the M-H curves are shown in Figure 5. The actual magnetization of the samples was determined by subtracting the diamagnetic contribution of the capsule and substrate

from the raw data. Our experimental results presented indeed show that all the samples are ferromagnetic at RT. The M-H curves clearly show that the typical ferromagnetic saturation behavior. Particularly, it is observed that the post-annealing in different atmospheres does not change the essential FM of the samples but does change significantly the saturated magnetic moments (M_s) of the samples.

3.5. Discussion. The mechanism of intrinsic FM in TM doped oxides still remains controversial, whether it is an intrinsic or extrinsic property of these materials. A diversity of theories has been proposed. For instance, the magnetism of the TM doped ZnO has been attributed to ferromagnetic coupling of the local moment of TM dopants through the carrier-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction [21], indirect double-exchange [22, 23] or super-exchange [24], and so forth. There are even proposals that the observed FM originate from the local magnetic moment of defects such as the Zn vacancies [25] or O vacancies [26–29].

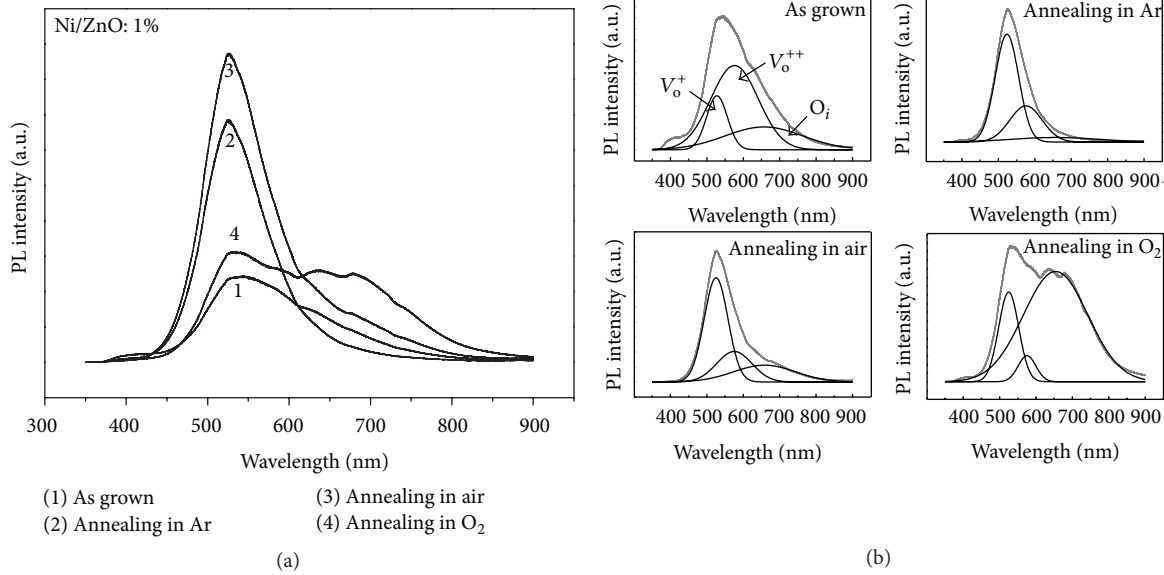


FIGURE 3: RT photoluminescence spectra of Ni doped ZnO samples as grown and annealed in different atmosphere (a) and Gaussian fit of each PL spectrum (b) (The gray lines are the experimental results and the black solid curves are Gaussian fits).

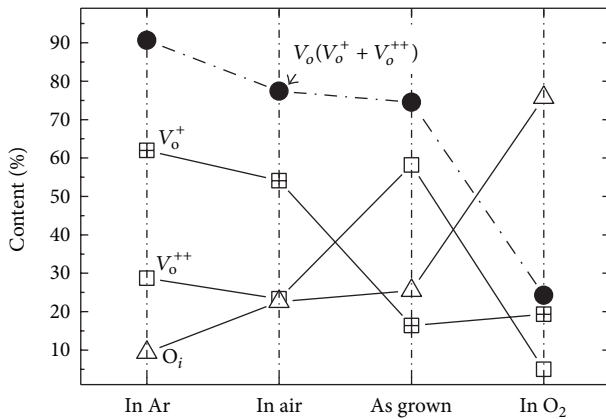


FIGURE 4: The contents of oxygen related defects (V_o^+ , V_o^{++} and O_i) in as grown Ni doped ZnO nanoparticles, and samples with thermal annealing in O_2 , air, and Ar, respectively.

In the present work, XRD and XPS results clearly demonstrate that the samples have a single wurtzite phase and there is no indication of additional phases, such as the Ni magnetic precipitation. So, we expect that FM is from an intrinsic exchange interaction of magnetic moments in Ni doped ZnO. Although the exact mechanism of intrinsic FM in Ni doped oxides is still under debate, defects have greatly been suggested to play an important role in the magnetic origin in the Ni doped ZnO system. As the postannealing is expected to have remarked effects on the defects rather than on the TM dopants, the combination of the present defects analyses based on the PL and the magnetic measurements provides a good opportunity to clarify the physical nature of the local magnetic moment.

In the PL results, Zn vacancies and interstitials were not observed in the prepared Ni doped ZnO system. So the

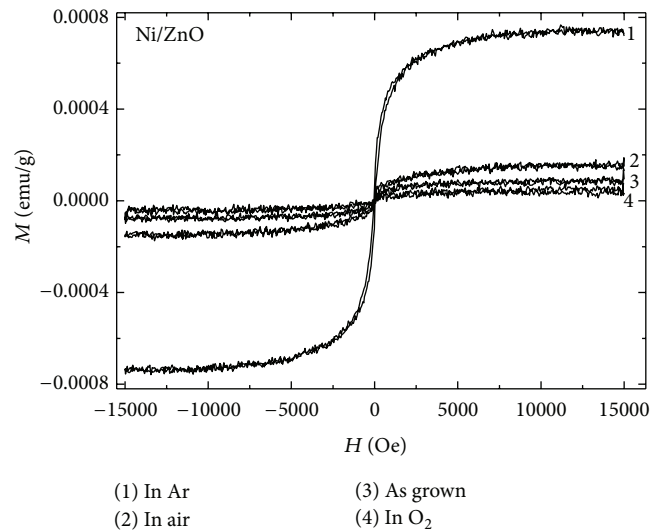


FIGURE 5: Magnetic hysteresis of Ni doped ZnO samples as grown and postannealed in different atmospheres (O_2 , air, and Ar).

contributions of the observed oxygen defects on FM will be discussed below.

From Figure 5 it is observed that the saturated magnetic moment increases after annealing in Ar and air but decreases after annealing in O_2 . We compared the saturated magnetic moments with the optical spectroscopic intensities originated from the oxygen vacancies in two charge states and oxygen interstitials (Figure 4). A definitely positive correlation between the M_s and the intensity of V_o (V_o^+ and V_o^{++}) is observed, while a pronounced negative correlation between the M_s and the intensity of O_i can be seen. These results indicate that the observed three different defects may make different contributions to FM and that oxygen vacancies and

its related defect complexes play an essential role in the Ni doped ZnO system. As the annealing in different atmospheres does not change the concentration of the Ni dopants, it is expected that the dominant differences of FM introduced by annealing among the samples are either the concentrations or the charge states of the oxygen related defects, such as oxygen vacancies (V_o) and V_o -Ni complexes.

Theoretical and experimental studies have later confirmed that ferromagnetism in transition metal doped ZnO system, especially in ZnO thin film, is genuine and commonly believed to be due to an exchange interaction between magnetic moments localized at the TM sites mediated by free charge carriers. And, the magnetic moment can actually be mediated by tuning the concentration of lattice defects, as well as that of the dopants [30]. In the present ZnO:Ni samples, there may coexist two different mechanisms in response to the observed magnetism. There is an indirect RKKY interaction among the magnetic dopants/defects, which is always ferromagnetic in the short-range regime. In addition, there is the antiferromagnetic superexchange interaction via the O anions. The observed magnetism depends on the competition of these two mechanisms. With increasing the oxygen vacancies, the antiferromagnetic superexchange is suppressed so that the positive correlation between the M_s and the intensity of oxygen vacancy is observed. In any sense, based on the present results, we suggest that in addition to the magnetic doping effect, oxygen vacancies, especially V_o^+ , play an essential role in the magnetic origin for Ni doped ZnO. The role of oxygen defects in mediating the FM in TM doped ZnO still needs further theoretical and experimental research.

4. Conclusion

In summary, Ni doped ZnO nanoparticles have been prepared with a solution method. The structure and the surface valence states of the elements in the samples were studied in detail. To investigate the influence of the defects on the inducing magnetic, the particles are annealed in O_2 , air, and Ar, respectively. RT PL spectra were measured to facilitate an investigation of the defects. Magnetization loops for the samples were measured at 300 K and clearly show typical ferromagnetic saturation behavior. A combination of results from the defects analyses based on the PL and the magnetic measurements suggest that oxygen vacancies, especially singly ionized oxygen vacancies, play a crucial role in mediating ferromagnetism in the Ni doped ZnO system.

Conflict of Interests

All the authors declare that they do not have any conflict of interests.

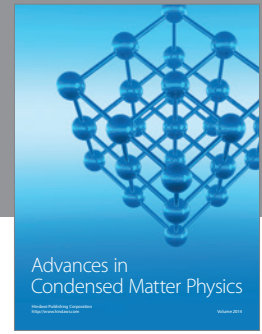
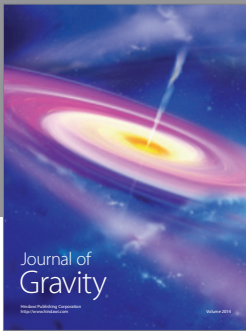
Acknowledgments

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