Oxygen-vacancy-induced green emission and room-temperature ferromagnetism in Ni-doped ZnO nanorods

Javed Iqbal¹,4, Baiqi Wang², Xiaofang Liu¹, Dapeng Yu², B He³ and Ronghai Yu¹,4

¹ Laboratory of Advanced Materials, Department of Material Science and Engineering, Tsinghua University, Beijing 100084, People’s Republic of China
² State Key Laboratory for Mesoscopic Physics and Electron Microscopy Laboratory, School of Physics, Peking University, Beijing 100871, People’s Republic of China
³ National Synchrotron Radiation Laboratory (NSRL), University of Science and Technology of China, Hefei 230029, People’s Republic of China

E-mail: javedsaggu73@yahoo.com and rhyu@tsinghua.edu.cn

Abstract. Single-crystalline Ni-doped ZnO nanorods have been synthesized through a chemical method. The average length and diameter of these nanorods are in the ranges of 400–700 nm and 25–40 nm, respectively. Structural analyses reveal that the Ni-doped ZnO nanorods are of pure wurtzite hexagonal phase and grow along the preferred c-axis direction. X-ray photoelectron spectroscopy (XPS) gives evidence that the Ni dopant is in the +2 valence oxidation state and is uniformly distributed in the nanorods. Full multiple-scattering ab initio calculations of Ni K-edge x-ray absorption near edge structure (XANES) analysis reveal that Ni impurity atoms are substitutionally incorporated into ZnO host without formation of secondary phases (Ni metal and Ni₂O₃). The comparison of experimental and simulated XANES spectra on Ni K edge shows the presence of the oxygen vacancy (native defect) in the prepared nanorods. Photoluminescence spectrum shows two emission peaks, which are ascribed to near band edge (NBE) transitions and broadened intensive green emission associated with oxygen-vacancy defects. Furthermore, the magnetic measurements reveal that the nanorods exhibit intrinsic room-temperature ferromagnetism.

4 Authors to whom any correspondence should be addressed.
ferromagnetism. Ferromagnetic ordering is interpreted by the overlapping of polarons mediated through oxygen vacancy based on the bound magnetic polaron (BMP) model.

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1. Introduction

ZnO has received considerable attention in the field of semiconductor materials due to its direct wide band gap (3.37 eV) and transparency in the visible range [1, 2]. It is a promising candidate for transparent electronics as well as ultraviolet (UV) optoelectronics including laser development because of its high exciton binding energy (60 meV) at room temperature [3, 4]. In recent years, there has been a significant interest towards semiconductor devices that operate not only with electron charge but also utilize the electron spin as an additional degree of freedom [5, 6]. Therefore materials of combined ferromagnetic and semiconducting nature, preferably at room temperature, are needed. Many experiments have been tried to inject spin-polarized electrons into non-magnetic semiconductors by constructing junction between the ferromagnetic metal and the semiconductor [7]. However, the spin orientation is limited up to a short distance from the junction (called the dead layer) due to the scattering of electrons at the Schottky barrier of metal–semiconductor interface [8]. To overcome the scattering problem, it was theoretically predicted that the ferromagnetic state in Mn-, Fe-, Co- and Ni-doped ZnO diluted magnetic semiconductors (DMSs) can be stabilized at room temperature [9, 10]. However, on the experimental side, the origin of ferromagnetism in ZnO DMSs remains a very controversial topic. A number of studies indicate that the ferromagnetism in TM-doped ZnO DMSs may arise from the precipitation of magnetic clusters or from the secondary magnetic phases [11]. On the other hand, there are reports that ruled out the presence of magnetic clusters or secondary phases and support intrinsic ferromagnetic origin [12]. In order to understand the exact mechanism of magnetic properties, the accurate determination of structural information of the TMs dopants with advanced technique (such as XANES) is highly desired.

In addition, the doping of TM in ZnO is not only interesting from the ferromagnetism point of view, it is also a good candidate for improving the optical and electrical properties, which are crucial for its practical applications. It was reported that ZnO nanorods showed
different emission bands depending on the doping material [13]. Doping of Pb$^{2+}$ into ZnO nanorods exhibited violet and blue emission bands [14]. Nickel (Ni$^{2+}$), due to its unique chemical stability, is also recognized as one of the most efficient doping element to improve and tune the optical, electrical and magnetic properties of ZnO nanomaterials. Thus, the study of optical and magnetic properties of Ni-doped ZnO is important from both fundamental and applied points of view. Usually, doped ZnO nanowires and nanorods are synthesized by thermal evaporation, vapor phase transport and condensation methods, all of which require high-temperature conditions. It has been noted that such high-temperature synthesis strongly influences the properties of ZnO nanomaterials. However, wet chemical synthetic approach provides a promising option for low-temperature in situ doping during the synthesis of ZnO nanorods. This method is easily reproducible and applicable to large industrial scale fabrication of products. In this paper, we report the synthesis, structure, microstructure, photoluminescence and room-temperature ferromagnetism of the Ni-doped ZnO nanorods. The objective of this study is to see the effect of Ni doping on the emission spectrum and magnetic properties of ZnO nanorods using the low-temperature wet chemical approach. On the basis of theoretical analysis and observed interesting results, the origins of intensive green band emission and room-temperature ferromagnetism are discussed in detail.

2. Experiment and calculation

2.1. Sample preparation and characterization

Direct chemical syntheses of TM-doped ZnO may provide better control over materials composition than high-temperature vacuum deposition or solid-state syntheses, which generally use dopant source materials that are themselves undesirable contaminants (e.g. Co metal for Co$^{2+}$: ZnO, NiO for Ni$^{2+}$: ZnO and MnO$_2$ for Mn$^{2+}$: ZnO) or require some special conditions that promote phase segregation. Ni-doped ZnO nanorods were fabricated by simple low-temperature wet chemical method. The formation of the nanorods was controlled by the growth parameters such as reactant concentration, pH value, reaction time and temperature without using any catalyst. All chemicals used here were of analytical grade. The synthesis process of Ni-doped ZnO nanorods was similar to the method previously reported for other dopants [15] but the growth parameters were precisely optimized in the present work. In this process, 0.5 M NaOH ethanol solution as a precipitant agent was slowly dropped into a constantly magnetically stirred mixture containing 0.05 M Zn(NO$_3$)$_2$.6H$_2$O and 0.003 M NiCl$_2$.6H$_2$O at 0°C. The resultant achieved solution was transferred into a Teflon autoclave and kept at 120°C for 10, 15, 24, 36 and 48 h, respectively. The precipitates were collected, washed and then centrifuged. Finally, these cleaned precipitates were dried at 110°C for 10 h. Nanorods with diameter 40 nm and length up to 700 nm can be achieved by increasing the reactant concentration, adjusting pH value and increasing the growth time up to 15 h.

The crystal structure and phase composition of the Ni-doped ZnO nanorods were characterized by x-ray diffraction (XRD) and selected area electron diffraction (SAED). The morphology and microstructure of as-prepared nanorods were investigated by TEM and HRTEM. The existence, composition and valance state of Ni dopant were determined by x-ray photoelectron spectroscopy (XPS) using a spherical capacitance analyzer (SCA) with Al K$_\alpha$ x-ray monochromatic source with resolution of ±0.01 eV and energy-dispersive x-ray spectroscopy (EDS). The Ni K-edge XANES spectra of the prepared nanorods were carried
Figure 1. XRD pattern of Ni-doped ZnO nanorods.

out at beam line U19 of National Synchrotron Radiation Laboratory (NSRL) in Hefei, China. The soft x-ray beam from a bending magnet was monochromatized by a varied line spacing plane grating monochromator and refocused through a toroidal mirror. The room-temperature photoluminescence spectrum was recorded on Renishaw in Via Raman spectroscope using He–Cd laser with a wavelength of 325 nm as an excitation source. The magnetic measurements were carried out on VSM and SQUID, which were capable of detecting the signals up to $10^{-6}$ and $10^{-8}$ emu g$^{-1}$, respectively.

2.2. Calculation details

To corroborate the incorporation of Ni into the ZnO lattice, XANES spectra have been simulated by the real space multiple-scattering (MS) approach using ab initio self-consistent FEFF 8.2 code on Ni K edge [16]. The position- and energy-dependent Hedin–Lundqvist potential has been used in this simulation for the exchange–correlation part of the potential. The condition parameters have been optimized to produce good potentials for the accurate XANES calculation of Ni-doped ZnO nanorods.

3. Results and discussion

3.1. Structure and microstructure of Ni: ZnO nanorods

Figure 1 shows a typical XRD pattern of Ni-doped ZnO nanorods. All diffraction peaks can be indexed to the wurtzite structure of the ZnO (space group P6$_3$mc). There is no indication of any secondary phase or clusters, which confirms that it is highly pure and single ZnO phase. The lattice parameters of Ni-doped ZnO calculated from XRD data are $a = b = 3.198$ Å and $c = 5.204$ Å, which are to some extent less than those of undoped ZnO ($a = b = 3.2509$ Å and
$c = 5.2069 \text{ Å}$. This decrease in lattice constants is due to contraction of the crystal structure as the slightly smaller ionic radius of Ni$^{2+}$ (0.69 Å) substituted that of Zn$^{2+}$ (0.74 Å) in tetrahedral co-ordination of ZnO wurtzite structure [17].

The morphology and further structural characterization were performed by TEM and HRTEM, as shown in figures 2 and 3, respectively. From figure 2, it can be observed that the sample consists of large quantities of thin and uniform nanorods of average diameter 25–40 nm and length 400–700 nm. In order to be sure that there are no precipitates of the impurity phase and Ni metal clusters in the nanosize range, HRTEM and SAED experiments have been performed to investigate the microstructure of nanorods. Figure 3 shows the HRTEM and SAED images of Ni-doped nanorods with clearly resolved lattice fringes and crystalline nature. From figure 3(a), it can also be observed that the lattice spacing of the (001) planes is 0.276 nm, which demonstrates that the Ni-doped ZnO nanorods are single-crystalline structure and growth direction of nanorods is orientated along the preferred $c$-axis. Figure 4 illustrates a typical EDS analysis of the single Ni-doped ZnO nanorod. The EDS spectrum of the nanorods shows that each nanorod is composed of Ni, Zn and O (the Cu signal comes from the copper grid). Furthermore, the quantitative analyses of EDS reveal that nearly 3% Ni concentration is doped into ZnO crystal and the atomic ratio of (Zn + Ni) : O in the ZnO nanorods is 1 : 1.

3.2. Local Ni dopant structure in Ni: ZnO nanorods

The valance state, substitution and contents of Ni cations in ZnO nanorods were examined by XPS spectrum as shown in figure 5. The peaks of Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ core levels are found to be centered at 855.51 ± 0.10 and 873.01 ± 0.10 eV, respectively, whereas the corresponding satellite structures are clearly observed at 861.014 ± 0.10 and 879.214 ± 0.10 eV, which are comparable to the results presented in the literature [18, 19]. The peak positions depend on
the local structure of the Ni atoms and provide the information about the chemical state. The Ni 2p$_{3/2}$ (855.51 ± 0.10 eV) position is quite different from that of metallic Ni (852.7 eV), NiO (853.8 eV) and Ni$_2$O$_3$ (856.7 eV) [20]–[22]. The absence of Ni metallic clusters can also be explained on the basis of energy difference between Ni 2p$_{3/2}$ and Ni 2p$_{1/2}$ core levels. For Ni-doped ZnO, the difference is 17.50 eV, which is different from the value of metallic Ni (17.27 eV) [20]. This energy difference for NiO (17.49 eV) is very close to the observed (17.50 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 ($T_N$ 520 K) [20, 36], 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 [20]. 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

Figure 3. HRTEM images (a, b) and SAED image (c) of Ni-doped ZnO nanorods.
impurity phase, such as Ni metal, Ni$_2$O$_3$ and NiO. Moreover, XPS also verifies the EDS results that the Ni contents are doped uniformly up to 3 at.% into ZnO nanorods.

These days, XANES is considered to be a powerful analytical and characterizing tool for the study of local structure and geometry of doped materials. In order to further investigate the structure and substitution of Ni$^{2+}$ dopant into ZnO lattice, Ni K-edge spectra of Ni$_{0.03}$Zn$_{0.97}$O,
metal Ni and Ni$_2$O$_3$ have been carried out in a high-vacuum chamber as shown in figure 6(a). An evident difference in the XANES spectral shapes and edge positions among Ni$_{0.03}$Zn$_{0.97}$O, Ni metal and Ni$_2$O$_3$ indicates that the Ni dopant is substituted without forming any secondary clusters (Ni and Ni$_2$O$_3$). In order to elucidate the local geometry of Ni$^{2+}$, the qualitative analysis of XANES spectrum for prepared Ni$_{0.03}$Zn$_{0.97}$O nanorods is not sufficient and needs some calculations for its confirmation. The ab initio XANES spectrum using FEFF 8.2 code has been simulated for substitutinal Ni into Ni$_{0.03}$Zn$_{0.97}$O and shown in figure 6(c). These calculations are made by considering a cell, which contains 77 atoms within a sphere of radius 6 Å from the central Ni atom (which substitutes central Zn in ZnO atomic arrangement). The simulated results demonstrate that more coordination shells do not lead to a significant change in the line shape of the calculated spectrum. The most interesting finding here is that the calculated spectrum exhibits three main peaks (named A, B and C towards increasing photon energy values), which exactly replicate the observed peaks in the experimental XANES spectrum in figure 6(b). However, it can be obviously distinguished from figures 6(b) and (c) that the intensity of peak C is significantly suppressed in the experimentally measured spectrum of Ni$_{0.03}$Zn$_{0.97}$O nanorods. The suppression of peak C is usually linked with the number of native defects in structure. These defects include oxygen vacancy (V$_{O}$), Zn vacancy (V$_{Zn}$) and zinc interstitials (Zn$_i$) [23, 44]. In order to study the behavior of peak C and thus the nature of defects, we performed a simulation by introducing V$_{Zn}$, Zn$_i$ and V$_O$ into Ni$_{0.03}$Zn$_{0.97}$O under the same conditions as for Ni$_{0.03}$Zn$_{0.97}$O, which is shown in figures 6(d) and (e). The calculated results, figure 6(d), demonstrate that the intensity of peak C remains the same in the simulated spectra for V$_{Zn}$ and Zn$_i$ defects. Whereas, with the introduction of V$_O$ (by considering the Ni central atoms surrounded by three oxygen atoms and a V$_O$), simulated results show a trend similar to that observed in the experimental spectrum of Ni$_{0.03}$Zn$_{0.97}$O prepared nanorods. It is therefore concluded that Ni is successfully substituted into the ZnO lattice and the prepared Ni$_{0.03}$Zn$_{0.97}$O nanorods have mainly the oxygen-vacancy (V$_O$) defects in structure.

3.3. Photoluminescence and ferromagnetic properties of Ni: ZnO nanorods

As a prospective photonic material, it is important to study the optical properties of Ni-doped ZnO nanorods. Photoluminescence spectroscopy (PL) is an effective method to investigate the presence of defects in the semiconductors. The PL spectra of the un-doped and Ni-doped ZnO nanorods were recorded at room temperature, and are shown in figure 7. There are two emission peaks in the spectrum of doped nanorods, one peak in the UV region and another broad green emission in the visible luminescence (VL) region. The UV emission peak for both doped and un-doped ZnO nanorods is found at 3.26 eV, which usually originates from the near band-edge (NBE) transition of ZnO and is generally attributed to the recombination of free excitons through collision process [24]. The VL band is highly quenched for un-doped nanorods but it is found with significantly high intensity centered at 2.18 eV for doped nanorods. It is observed that the VL band (green emission) becomes broader and very intense with doping of Ni in ZnO nanorods using low-temperature synthesis approach. Before this, weak green emission observed due to defects in ZnO nanostructures [25]–[27] and also in some reports green emission completely disappeared in the PL spectrum [28]. Under the same conditions and parameters our results for strong green emission in doped ZnO nanorods are found to be reproducible. There are many possibilities responsible for the origin of this observed intense and broadened green emission. It is often attributed to the radiative recombination of

New Journal of Physics 11 (2009) 063009 (http://www.njp.org/)
Figure 6. (a) Experimental spectra of Ni\textsubscript{0.03}Zn\textsubscript{0.97}O, Ni metal and Ni\textsubscript{2}O\textsubscript{3}. (b–e) Comparison of experimental and simulated XANES spectra of Ni\textsubscript{0.03}Zn\textsubscript{0.97}O.
The green emission has been attributed to photogenerated holes with electrons occupying the singly ionized oxygen vacancy ($V_0$) [29, 30]. Based on the band-structure calculations, the green emission has also been believed due to $V_0$ and Zn$_{in}$ [31]. It was reported that the green emission defects can be enhanced by annealing at higher temperatures above 600°C (due to out diffusion of O) [32]. However, in our case nanorods are synthesized at very low temperature, revealing that the green emission defects in Ni-doped ZnO nanorods are independent of the annealing temperature. There is convincing evidence that the defects causing the enhancement of the green emission are located at the surface. It has been reported that coating ZnO nanostructures with a surfactant suppressed the green emission [33]. Polarized luminescence experiments from aligned ZnO nanorods have also indicated that the green emission originated from the surface of the nanorods [34]. The surface recombination layer is responsible for the visible emission in ZnO [35]. From our XANES experimental and theoretical results, it is found that the prepared nanorods structure is not affected by the introduction of Zn$_{in}$ and Zn$_i$ defects and shows the presence of a large number of $V_0$ defects. Therefore, it is believed that the observed green emission originates from the deep levels of Ni-doped ZnO nanorods and is due to the presence of oxygen-vacancy ($V_0$) defects (figure 7).

Figure 8 shows the magnetic hysteresis ($M$–$H$ curve) of Ni-doped ZnO nanorods at room temperature. The saturation magnetization ($M_s$) of these nanorods is estimated to be about 0.036 $\mu_B$ Ni$^{-1}$, and remanent magnetization ($M_r$) and coercivity ($H_c$) are about 5.6 \times 10^{-3} $\mu_B$ Ni$^{-1}$ and 271 Oe, respectively, as shown in the inset of figure 8. The temperature-dependent magnetization ($M$–$T$ curve) has also been measured in the range of 2–400 K and shown in figure 9. The $M$–$T$ result depicts that the prepared nanorods maintain the ferromagnetic ordering above room temperature.
Figure 8. Magnetization hysteresis ($M–H$) curve of Ni-doped ZnO nanorods at $T = 300$ K.

Figure 9. Temperature-dependent magnetization ($M–T$) of Ni-doped ZnO nanorods.

The origin of observed ferromagnetism at room temperature in these nanorods could arise from a number of possibilities, such as NiO, Ni metal and Ni$_2$O$_3$ and intrinsic property of the doped nanorods. The existence of a secondary phase such as NiO could be easily ruled out, as NiO in bulk shows antiferromagnetism with a $T_N$ of 520 K [36] and super-paramagnetism at nanocrystalline scale, whereas our $M–T$ measurement illustrates ferromagnetic ordering [37, 38]. Another possibility is Ni metal, which is a well-known ferromagnetic material.
However, our nanorods are synthesized in air using ethanol, where Ni metal is unable to exist. Furthermore, the XPS, XRD, HRTEM and XANES results also clearly demonstrate that the structure is in single wurtzite phase and there is no indication of extra phases like Ni metal and Ni$_2$O$_3$ in the prepared nanorods. Therefore, ferromagnetism is expected to arise from the intrinsic exchange interaction of magnetic moments in doped nanorods.

The exact mechanism of intrinsic ferromagnetism in TM-doped oxides is still under debate. A diversity of theories has been proposed, such as super-exchange, double-exchange between the d states of TMs, free-carrier-mediated exchange and sp–d exchange mechanism, etc [39]. All these proposed theories cannot well accord with the experimental results in DMSs [40]. In addition to the magnetic doping effect, oxygen vacancy (V$_{O}$) defects have been suggested to play an important role in the magnetic origin for oxide DMSs [41]. The theoretical studies suggest that V$_{O}$ can cause an obvious change of the band structure of host oxides and makes a significant contribution to the ferromagnetism [42, 43]. The formation of bound magnetic polarons (BMPs), which include electrons locally trapped by oxygen vacancy, with the trapped electron occupying an orbital overlapping with the d shells of TM neighbors, has also been proposed to explain the origin of ferromagnetism [41]. Experimentally, oxygen vacancy might easily be generated during various growth processes owing to the vacuum environments. On the basis of XANES simulated and experimental results, and the observed green emission centered at 2.18 eV, the oxygen-vacancy defects lay in the deep levels with localized carriers. Our systematic study shows that oxygen-vacancy defect constituted BMPs are a promising candidate for the origin of room-temperature ferromagnetism in this system. Within the BMP model, the greater density of oxygen vacancy (V$_{O}$) yields a greater overall volume occupied by BMPs, thus increasing their probability of overlapping more Ni ions into ferromagnetic domains and enhancing ferromagnetism as shown in figure 10. The small observed net magnetism can be explained; as there are also some isolated Ni ions outside polarons (as shown in figure 10), which may reduce the net magnetic moment due to their random distribution [44]. The observed intrinsic ferromagnetism makes these DMSs nanorods potential for future spintronics devices.

Figure 10. Oxygen-vacancy-induced ferromagnetism through overlapping of polarons.
4. Conclusions

Highly ordered Ni-doped ZnO nanorods have been fabricated by a wet chemical process. The preferred growth direction of these nanorods is along the c-axis with 400–700 nm in length and 25–40 nm in diameter. The doped Ni atoms have substituted the Zn positions in the ZnO crystal, and the amount of doping is about 3% in Ni-doped ZnO nanorods. Photoluminescence measurements have shown two obvious peaks in the band spectra. The prominent UV peak at about 3.26 eV is related to NBE and interesting strong green emission in VL band is closely associated with oxygen-vacancy defects. In addition, the Ni-doped ZnO nanorods exhibit room-temperature ferromagnetism, which is related to the oxygen vacancy based on structural analysis and the observed green emission. The exact mechanism is discussed on the basis of the BMP model with overlapping of polarons and alignment of magnetic moments.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant nos. 50525101, 50729101 and 50771058), (NFS, 90606023), National 973 projects (no. 2002CB613505, MOST) and project from Engineering Research Institute of Peking University. Financial support from the Higher Education Commission (HEC), Pakistan (for Javed Iqbal Saggu) is also gratefully acknowledged.

References

[1] Kligshirn C 1975 Phys. Status Solidi b 71 547
[2] Xu H Y, Liu Y C, Mu R, Shao C L, Lu Y M, Shen D Z and Fan X W 2005 Appl. Phys. Lett. 86 123107
[3] Chen Y F, Ko H J, Hong S K and Yao T 2000 Appl. Phys. Lett. 76 559
[4] Bagnall D M, Chen Y F, Zhu Z, Yao T, Koyama S, Shen M Y and Goto T 1997 Appl. Phys. Lett. 70 2230
[5] Ohno H 1998 Science 281 951
[6] Matsumoto Y, Murakami M, Shono T, Hasegawa T, Fukumura T, Kawasaki M, Ahmet P, Chikyow T, Koshihara S and Koinuma H 2001 Science 291 854
[7] Gregg J F et al 1997 J. Magn. Magn. Mater. 175 1
[8] Hammar P R, Bennett B R, Yang M J and Johnson M 1999 Phys. Rev. Lett. 83 203
[9] Dietl T, Ohno H, Matsukura F, Cibert J and Ferrand D 2000 Science 287 1019
[10] Katayama-Yoshida H and Sato K 2000 Japan. J. Appl. Phys. B 39 555
[11] Park J H, Kim M G, Jang H M, Ryu S and Kim Y M 2004 Appl. Phys. Lett. 84 1338
[12] Lee H J, Jeong S Y, Cho C R and Park C H 2002 Appl. Phys. Lett. 81 4020
[13] Bae S Y, Na C W, Kang J H and Park J 2005 J. Phys. Chem. B 109 2526
[14] Chu D, Zeng Y P and Jiang D 2006 Mater. Lett. 60 2783
[15] Iqbal J, Baiqi W, Liu X F, Zhu H C, Yu D P and Yu R H 2009 J. Nanosci. Nanotechnol. at press
[16] Ankundinov A L, Ravel B, Rehr J J and Conradson S D 1998 Phys. Rev. B 58 756
[17] Zhang B, Zhang X T, Gong H C, Wu Z S, Zhou S M and Du Z L 2007 Phys. Lett. A 185 1–4
[18] Pei G Q, Wu F, Xie C, Zhang J G, Li X and Xu J 2008 Curr. Appl. Phys. 8 18–23
[19] Wang H, Chen Y, Wang H B, Zhang C, Yang F J, Duan J X, Yang C P, Xu Y M, Zhou M J and Li Q 2007 Appl. Phys. Lett. 90 52505
[20] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 Handbook of X-ray Photoelectron Spectroscopy (Eden Prairie: Perkin Elmer) pp 84–5
[21] Yu G H, Zeng L R, Zhu F W, Chai C L and Lai W Y 2001 J. Appl. Phys. 90 4039

New Journal of Physics 11 (2009) 063009 (http://www.njp.org/)
[22] Yin Z G, Chen N F, Yang F, Song S L, Chai C L, Zhong J, Qian H J and Ibrahim K 2005 *Solid State Commun.* **135** 430

[23] Hsu H S, Huang J C A, Huang Y H, Liao Y F, Lin M Z, Lee C H, Lee J F, Chen S F, Lai L Y and Liu C P 2006 *J. Appl. Phys.* **88** 242507

[24] Li C, Fang G, Fu Q, Su F, Li G, Wu X and Zhao X 2006 *J. Cryst. Growth* **292** 19–25

[25] Huang M H, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 *Science* **292** 1897

[26] He J H, Lao C S, Chen L J, Davidovic D and Wang Z L 2005 *J. Am. Chem. Soc.* **127** 16376

[27] Wen F, Li W, Moon J H and Kim J H 2005 *Solid State Commun.* **135** 34

[28] Cheng C W, Xu G Y, Zhang H Q and Luo Y 2008 *Mater. Lett.* **62** 1617–20

[29] Ng H T, Chen B, Li J, Han J, Meyyappan M, Wu J, Li S X and Haller E E 2003 *Appl. Phys. Lett.* **82** 2023

[30] Hu J, Li Q, Meng X, Lee C and Lee S 2003 *Chem. Mater.* **15** 305

[31] Liu X, Wu X, Cao H and Chang R P H 2004 *J. Appl. Phys.* **95** 3141

[32] Meng X Q, Shen D Z, Zhang J Y, Zhao D X, Lu Y M, Dong L, Zhang Z Z, Liu Y C and Fan X W 2005 *Solid State Commun.* **135** 179

[33] Djurisic A B, Choy W C H, Roy V A L, Leung Y H, Kwong C Y, Cheah K W, Gundu Rao T K, Chan W K, Lui H F and Surya C 2004 *Adv. Funct. Mater.* **14** 856

[34] Hsu N E, Hung W K and Chen Y F 2004 *Appl. Phys. Lett.* **96** 4671

[35] Shalish I, Temkin H and Narayananamurti V 2004 *Phys. Rev. B* **69** 245401

[36] Schwartz D A, Kittilatved K R and Gamelin D R 2004 *Appl. Phys. Lett.* **85** 1395

[37] Richardson J T and Milligan W O 1956 *Phys. Rev.* **102** 1289

[38] Kodama R H, Makhouf S A and Berkowitz A E 1997 *Phys. Rev. Lett.* **78** 1393

[39] Pearson S J, Heo W H, Ivill M, Norton D P and Steiner T 2004 *Semicond. Sci. Technol.* **19** R59

[40] Hsu H S, Huang J C A, Huang Y H, Liao Y F, Lin M Z, Lee C H, Lee J F, Chen S F, Lai L Y and Liu C P 2006 *Appl. Phys. Lett.* **88** 242507

[41] Coey J M D, Venkatesan M and Fitzgerald C B 2005 *Nat. Mater.* **4** 173

[42] Jaffe J E, Droubay T C and Chambers S A 2005 *J. Appl. Phys.* **97** 73908

[43] Weng H, Yang X, Dong J, Mizuseki H, Kawasaki M and Kawazoe Y 2004 *Phys. Rev. B* **69** 125219

[44] Song C, Liu X J, Geng K W, Zeng F, Pan F, He B and Wei S Q 2007 *J. Appl. Phys.* **101** 103903