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Original Research Article

Co-precipitation synthesis of ZnO nanoparticles and their characterization

Manjeet Singh*

Department of Physics, Government College Matanhail, Jhajjar – 124106, Haryana, India *Corresponding author, E-mail: <u>manjeetgur@gmail.com</u>

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ABSTRACT

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ZnO Nanoparticles; Structural and Optical Properties; Magnetic Resonance. The co-precipitation method was successfully used to synthesize a series of ZnO nanoparticles at different temperatures (100°C to 600°C). Numerous experimental techniques, including x-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDX), thermal analysis (TG-DTA), UV-vis spectroscopy, infrared absorption spectroscopy (FTIR), and electron spin resonance spectroscopy (ESR), were used to analyze the samples. All of our ZnO samples have the hexagonal wurzite structure, according to XRD measurements, and the average crystallite size grew between 19 and 23 nm as the temperature increased. Optical absorption spectra demonstrate that when particle size increased, the band gap moved to the lower energy. Electron center resonance was demonstrated by ESR studies with g values of roughly 1.96. We noticed that the ESR signal intensities increased and the g values decreased as the temperature increased. Furthermore, OH local vibrational modes clearly diminish as the temperature rises. The findings from heat analysis and infrared absorption spectroscopy measurements provide strong support for the ESR measurement results.

1. Introduction

Research on ZnO semiconductors began in 1935 [1], but it wasn't until the 1950s that they gained significant recognition, primarily because of their optical characteristics [2]. ZnO is frequently regarded as an electronic semiconductor with a wide band gap because it falls somewhere between the homo-polar semiconductors group IV elements and the hetero-polar alkali halides. When zinc atoms are replaced by an element of group I-A or I-B, or oxygen atoms by an element of group V-A, acceptor centers should form. Conversely, when zinc atoms are replaced by an element of group III-A, or oxygen atoms by an element of group VII-A, donor centers should form [3], and zinc and oxygen vacancies may act as acceptor and donor, respectively. It has recently been demonstrated that ZnO has superior qualities, including a high exciton binding energy, a low lasing threshold density, and a strong resistance to highenergy particle bombardment [4]. For usage in optoelectronic devices and UV lasers that operate in severe environments and at high temperatures, it is one of the most promising alternatives to GaN. Nonetheless, the regulation of conductivity from n-type to p-type is necessary for practically all optoelectronic applications. The challenge of discovering an effective p-type dopant is one of the main challenges that must be addressed in order to enable the successful development of optoelectronic devices and lasers.

ZnO nearly always displays n type conductivity when developed, with charge carriers being electrons in the conduction band. There has been much debate over the years regarding the origin of this conductivity. This conductivity's nature has always been ascribed to inherent faults. Nonetheless, Van de Walle [5] proposed that the hydrogen atom in ZnO may behave as a shallow donor in his firstprinciples study, which was based on density functional theory. In contrast to its function as a compensatory center that counteracts the prevalent conductivity in other semiconductors, its behavior is surprising and significantly different. It is exceedingly difficult to prevent hydrogen from being incorporated into the sample during the crystal-growth process, therefore its presence in the process is not surprising.

ZnO is extremely important in nanoscale semiconductor materials, and a significant number of studies have been published discussing ZnO nanoparticles (NPs). Additional characteristics of the material include: (i) the quantum-size effect, which affects the bandgapsize [6,7] and, in turn, the optical and electronical properties of the material, and (ii) a high surface-to-volume ratio in comparison to bulk materials. The latter characteristic is important for catalysis and hydrogen storage. In recent years, a number of ZnO nanoparticle synthesizing techniques have been documented, including solgel chemistry [8], co-precipitation [7], hydrothermal [10], combustion [11], and sono-chemical [9]. Since different synthesis techniques result in different nanoparticle characteristics, controlling the synthesis condition is crucial. Different parameters, including pH, aging period, reaction temperature, and dry temperatures, are attributed to variations in optical and electronical properties.

In this work, we describe the synthesis of ZnO NPs at different dry temperatures using the co-precipitation method. We also describe the NPs' optical characteristics, structural characteristics, vibrational modes, and magnetic resonance. X-ray diffraction (XRD) is used to characterize the structure, UV-vis and infrared absorption spectroscopy is used to study optical characteristics and vibrational modes, and electron spin resonance (ESR) spectroscopy is used to deploy magnetic resonance. We try to correlate one property to the others using these data. Our findings are contrasted with those found in previous research.



2. Experimental

Zinc sulfate hepta hydrate (99.9%) ZnSO₄•7H₂O, 25% aqueous NaOH, and ethanol were employed in this investigation to synthesize ZnO NPs. These materials were purchased from Aldrich. Every chemical used was of analytical reagent grade and was utilized straight away, without any additional purification. The co-precipitation approach was used to synthesize ZnO NPs. 250 ml of de-ionized water was vigorously stirred with 24.6 mmol of analytical grade ZnSO₄•7H₂O from Aldrich at 80°C. At the same time, 500 milliliters of de-ionized water were mixed with the proper amount of NaOH. After that, both solutions were combined for half an hour at 75°C while being constantly stirred, until a milky white solution was achieved. Following the reaction, the solution was centrifuged for 15 minutes at 2800 rpm and repeatedly cleaned with ethanol and de-ionized water to get rid of the sodium sulfate (NaSO₄) byproduct. After cooling, the precipitate was allowed to mature for 24 hours at room temperature. The precipitate was dried for 6 hours at different dry temperatures, T_d (100°C to 600°C), in a vacuum oven to produce different hydrogen concentrations. For 5 hours, some materials were annealed at temperatures as high as 800°C.

The radiation of wavelength $\lambda = 1.54060$ Å in the 10° to 80° range was used to perform the structural characterization. Si powder was used to calibrate the diffractometer. The specimens' XRD patterns were confirmed by comparing them with the JCPDS data. The Scherrer peak broadening method was used to estimate the average size of precipitate crystallites (A conventional x-ray diffractometer (Philips PW1710) operating at 40 kV and 20 mA with monochromatic Cu-K α := $k\lambda/\Delta \cos\Theta$, where k = shape factor (0.89), λ is the x-ray wavelength, Δ is the line widening at half-height, and Θ is the particle's Bragg angle. The Debye-Scherrer formula is used to determine the average crystallite size from the highest intense peak, which corresponds to (101) reflection. Using a scanning microscope and energy dispersive x-ray spectroscopy (EDX), the samples' elements were analyzed. Optical characterizations were performed using diffuse reflectance spectroscopy measurements. A Shimadzu UV-vis spectrophotometer with an integrating sphere attachment and a spectralon reflectance standard was used to capture all of the spectra in the 200-800 nm range.

A Shimadzu Fourier transform spectrometer was used to analyze infrared absorption in the 400–4000 cm⁻¹ spectral range in order to investigate the bonding arrangement. For the infrared absorption tests, a pellet composed of KBr powder and nanoparticles was utilized. Electron spin resonance (ESR) was performed at room temperature utilizing X-band JEOL JES-RE1X to gather data on defects and vacancies. Standard numerical techniques were used to assess the ESR spectra's area and shape. Setaram TAG 24 was used for simultaneous thermo-gravimetric and differential thermal analysis (TGA-DTA) measurements. The samples were heated at a rate of 10° C min⁻¹ from ambient temperature to 800°C.

3. Results and discussion

The XRD patterns of samples created using coprecipitation techniques with dry temperature T_{ds} of 100°C, 200°C, 400°C, and 600°C for 6 hours are displayed in Figure 1(a). The spectra nearly match those of ZnO NPs' usual XRD spectra from prior experiments [12, 13]. Nine peaks can be seen around $2\Theta = 32.12$, 34.48, 36.6, 47.76, 56.84, 63.02, 66.95, 68.23, and 69.24 in all of our XRD patterns. These correspond to (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. All of the observed peaks for each sample may be indexed as ZnO's hexagonal wurzite structure, which has space group P63mc. Apart from the wurzite structure, no other impurity compound is seen.



Figure 1: (a) X-ray diffraction patterns of ZnO NPs synthesized at various dry temperatures; (b) EDX spectra of ZnO NPs.

These findings align with those derived from the EDX spectra shown in Figure 1(b). As previously validated by XRD data, the successful synthesis of ZnO NPs was indicated by the observation of Zn signals at around 1.01, 8.7, and 9.5 keV in addition to an oxygen peak at 0.6 keV.

Figures 2(a) and (b) display the lattice parameter values that were determined from XRD data using the Rietveld refinement approach. The Gaussian distribution was used to fit all of the available reflections. The lattice parameters for ZnO synthesized at dry temperature $T_d = 100^{\circ}$ C are a = b = 3.255 Å and c = 5.218 Å, according to analysis of XRD patterns shown in Figure 1(a). When the dry temperature is raised from 100°C to 600°C, the computed lattice parameters do not significantly change. The normal JCPDS parameter for bulk ZnO, a = b = 3.2498 Å and c = 5.206 Å, is marginally lower than these measurements.



Figure 2: Using the (101) and (002) peaks as a function of dry temperature, Panels (a) and (b) display the lattice parameters *a* and *c* of hexagonal wurzite ZnO; Panel (c) displays the average size of ZnO NPs derived from Scherrer's formula.

Furthermore, a thorough examination of peak positions indicates that there is compressive strain in the samples since there is a slight shift in its value toward a lower 2Θ as the temperature rises [14]. Additionally, it is demonstrated that when the temperature rises, the reflection peaks for the whole samples get sharper and the full width at half maximum (FWHM) somewhat decreases.

According to Figure 2(c), the average size of ZnO NPs determined using the Scherrer peak broadening method is around 18 nm for T_d of 100°C, 19 nm for T_d of 200°C, 21 nm for T_d of 400°C, and 23 nm for T_d of 600°C. This suggests a little increase in average crystallite size at higher dry temperatures.

TG-DTA analyses were performed from room temperature to 600°C in atmosphere to show the alterations that took place during the precursor's thermal treatment (Figure 3). The TG curve shows that the precursor loses weight in two main stages.



Figure 3: ZnO NPs weight loss as a function of temperature is displayed by the TG curve and the DTA curve that goes along with it.

The dehydrogenation process of surface-adsorbed water molecules is revealed by the first significant stage, which occurs in the temperature range below 100° C and shows a loss of 3.2 wt.%.

The second stage of weight loss (2.6 wt.%) that occurred between 100°C and 220°C may have been caused by the diffusion of hydrogen atoms or OH-ions from the ZnO network. At temperatures above 220°C, a little reduction in the TG curve indicates a further out diffusion of OH^- ions or H atoms. Given that fewer than 8% of the total weight was lost throughout the thermal analysis investigation, this indicates that a significant amount of ZnO was formed during synthesis. Two endothermic peaks in the DTA curve of the precursor produced by heat treatment match the two main weight loss phases of the TGA curve.

Diffuse reflectance spectroscopy was used to measure optical characteristics. Every spectrum was recorded between 200 and 800 nm. For the samples in Figure 1(a), Figure 4 displays the diffuse reflectance spectra R as a function of wavelength. Given that our samples are powder, our spectra's low reflectance values show that there is a lot of absorption in the relevant wavelength range. In the 350–800 nm range, there was a noticeable variation between the samples, according to the room temperature data. Applying the Kubelka-Munk function F(R), which is provided by the relation $F(R) = (1 - R)^2/2R$, where R is the magnitude of reflectance, makes the relevance of this more apparent [15]. The square of the Kubelka-Munk function $F(R)^2$ as a function of energy was plotted to estimate the optical gap (inset of Figure 4) from diffuse reflectance spectra.



Figure 4: ZnO NPs synthesized at different temperatures and their diffuse reflectance spectra. The associated optical gap of ZnO NPs as a function of temperature is displayed in the inset.



Figure 5: ESR spectra of ZnO NPs dried at 200°C, 400°C, and 600°C.

Using the above approach, the optical gap of ZnO dried at 100°C was found to be 3.52 eV, larger than the optical gap of bulk ZnO (3.32 eV). As the temperature rises, the corresponding optical gaps are observed to shift to lower energies. At 100°C, 200°C, 400°C, and 600°C, the optical gap of our ZnO samples was approximately 3.52 eV, 3.46 eV, 3.38 eV, and 3.35 eV, respectively. Several publications have noted the variance in the optical gap in ZnO [12, 16], and they have explained this variation by citing variations in the average particle size.

Figures 5(a)–(c) display the typical ESR spectra of ZnO dried at $T_d = 200$, 400, and 600°C, respectively. A nearly symmetric resonance was detected, and the *g*-value decreased as the resonance moved to a higher field. As the temperature rises, the line-width is observed to be quenched. Conversely, as the temperature increased, the intensity increased as well. In comparison to samples dried at higher temperatures (not included in the image), the ESR signal in the sample dried at $T_d = 100^{\circ}$ C was found to be extremely feeble. The spectrum's resonance position is 1.9680 for samples dried at $T_d = 200^{\circ}$ C, 1.9676 for samples dried at $T_d = 400^{\circ}$ C, and 1.9665 for samples dried at $T_d = 600^{\circ}$ C.

The literature has shown that the paramagnetic signal around a g value of 1.96 frequently arises due to intrinsic defects like oxygen vacancies or Zn interstitial, as well as residual impurities in ZnO (F, Cl, Br, and Al, Ga, In; the gvalue is essentially independent of the type of impurities), even though the origin of the signal with these g-values is still unknown [3, 17-23]. Hoffmann et al. [22] recently performed high-field ESR and ENDOR experiments on ZnO single crystal at microwave frequencies of 95 and 275 GHz. Their results showed the ESR signal with g-values of $g'' = 1.9569 \pm 0.00005$ and $g^{\perp} = 1.9552 \pm 0.00005$ (g parallel and perpendicular to the crystal c-axis), D1 and D2 centers. It was demonstrated that the hydrogen atom is engaged in the D₁ center using the ENDOR approach. This outcome was consistent with van de Walle's prediction [5]. The D₂ center's genesis is still uncertain, though. It was demonstrated in early papers [3, 17, 19] that the g-value at 1.96 comes from shallow donors and coincides with electron conductivity. Kasai [3] and Hausmann et al. [18] argued that this line are related to the oxygen vacancies, whereas the EPR signal with the g values of g'' = 1.9945 and $g^{\perp} = 1.9960$ was attributed by Hausmann and Schallenberger [18] to the oxygen atom in the tetrahedral interstitial position. Several authors [21, 24-27], however associated the EPR signal at g'' = 1.9945 and $g^{\perp} = 1.9960$ to an oxygen vacancy V_0^+ charge states, that are observed only in irradiated ZnO crystals under illumination and stable up to 400°C - 500°C annealing.

We concluded that the g values in our samples were associated with the oxygen sublattices that may be occupied by hydrogen atoms by comparing our findings with those found in the literature mentioned above.

It was challenging to detect the ESR signal at lower dry temperatures because nearly all of the oxygen sub-lattices were filled by hydrogen. As a result, samples dried with T_d below 400°C were the only ones in which we could detect a modest ESR signal. An ESR signal is generated when the occupation number of hydrogen in the oxygen sublattices decreases with increasing dry temperature. Additionally, it is demonstrated that an increase in dry temperatures essentially results in an increase in the integrated area. Our *g*-values are consistent with those previously reported for ZnO powder, ceramic, and single crystal [3, 17, 18]. These findings demonstrated that, in the absence of irradiation or concurrent lighting of the samples, the

ESR signal at $g \sim 1.96$ in our samples appeared at its maximum intensity.

We have annealed our samples in a vacuum to diffuse hydrogen out of them in order to bolster this theory. Figure 5 presents the findings. It is evident that annealing the samples above 400°C affected both the integrated area and the ESR signal's strength. Both improve as the annealing temperature rises, suggesting that there are more paramagnetic centers as the annealing temperature rises. Therefore, we think that our ESR data match oxygen sub-lattices. Compared to the asgrown samples, our annealed samples have a significantly smaller number of hydrogen atoms occupying the oxygen sublattice. The results from the infrared absorption spectra support our ESR results.

Measurements of infrared absorption make it possible to examine the hydrogen bonding patterns of both grown and annealed samples. Figure 6 shows the typical infrared absorption spectra of samples that were produced at various dry temperatures.



Figure 6: FTIR spectra of ZnO NPs synthesized at different dry temperatures (curve (a)-(e)). The FTIR spectra of ZnO NPs that were annealed at 800°C are also displayed.

The infrared spectra for the sample that was dried at 100°C for four hours and then annealed at 800°C for 6 hours is also displayed (curve e). ZnO stretching modes may be responsible for the significant absorption peaks in the 400-700 cm⁻¹ region for all as-synthesised samples [28, 29]. According to XRD and EDX research, these stretching modes are a sign of successfully synthesized ZnO NPs. Simultaneously, we can see an absorption peak at approximately 1646, 1390, and 1121 cm⁻¹, which, respectively, correspond to the OH bending mode, C-OH in-off plane bending, and C-OH out-of-plane bending [30]. Physically absorbed water, O-H stretching modes, and C-H stretching modes overlap in a broad band in the 2900-3700 cm⁻¹ range. Amorphous silicon carbon (a-SiC:H), GaAs, and GaN are among the semiconductors that have been found to exhibit C-H local vibrational modes between 2800 and 3100 cm⁻¹ [31-33]. Both symmetric and anti-symmetric C-H stretching modes are identified as the local vibrational modes in these materials.

We concentrated our investigation on the infrared absorption range of interest, specifically in the wave number range of 2900 - 3700 cm⁻¹, in order to better understand which

local vibrational modes correspond to OH modes. All spectra can be de-convoluted into two peaks, the CH stretching mode at around 2990 cm⁻¹ and the physically absorbed water and O-H stretching modes at about 3400 cm⁻¹ (shown as the dashed line in Figure 7).



Figure 7: The deconvolution of the C-H stretching (dash line) and O-H stretching (dotted line) modes of the infrared absorption band for ZnO NPs synthesized at different dry temperatures falls between 2400 and 3900 cm⁻¹.



Figure 8: C-H stretching mode at 2990 cm⁻¹ and O-H stretching mode at 3400 cm⁻¹ are both integratedly absorbed.

It is observed that a general drop in the absorption peak height and a notable alteration in the spectral distribution occur when the dry temperature is raised from 100°C to 600°C. Specifically, an absorption band shift to the higher wave number. The samples were annealed at 800°C for 6 hours, which caused the peak height to decrease, the peak maximum to shift even further towards a higher wave number, and the absorption peaks to drop. The OH band was still present in the spectra of the samples that were dried at higher temperatures and those that were annealed at temperatures lower than 800°C, suggesting that the hydrogen atoms in the ZnO network were still chemically bound to the oxygen. Figure 8 plots the total integrated absorption of the CH and OH stretching bands against dry temperatures. The total of the fits' absorption areas is used to calculate the integrated absorption. The majority of the hydrogen atoms in our samples prefer to attach to oxygen atoms over carbon atoms, as shown in Figure 8.



Figure 9: ESR spectra of ZnO NPs after being annealed at 600°C (a) and 800°C (b).

Overall, the integrated absorption decreased as the dry temperature increased. This figure demonstrated unequivocally that the assimilation of hydrogen atoms bound in the form of CH and OH groups is limited by the dry temperature. This outcome is in line with the previously described ESR results. Our ESR signal is dominated by paramagnetic centers because of oxygen sublattice, as demonstrated by the effect of hydrogen incorporation on *g*-value in our ESR data, which are displayed in Figures 5 and 9.

4. Conclusions

In conclusion, the co-precipitation process was used to synthesize ZnO NPs at different dry temperatures. Several measurement techniques were used to describe the characteristics of the as-synthesized and annealed samples. The conventional XRD pattern of ZnO with hexagonal wurzite structure is well-aligned with the XRD pattern of both assynthesised and annealed samples. These outcomes align with the findings derived from EDX spectra. Furthermore, greater peak intensities were found in all diffraction peaks, suggesting that the ZnO NPs obtained have a high degree of crystallinity. The typical grain size of the as-synthesised ZnO particles is between 18 and 23 nm, and it increases as the dry temperature rises. The optical absorption band red-shifted as the average grain size increased, according to UV-vis studies. Our ZnO particles' ESR spectra demonstrate the electron center resonance with a g-value about 1.96. We thought that the resonance was caused by the hydrogen atoms occupying the oxygen sub-lattices. According to the infrared absorption measurement, when the amount of hydrogen integrated in oxygen atoms decreased, the g-value decreased and the oxygen sub-lattices increased.

References

- C.W. Bunn, The lattice dimensions of zinc oxide, *Proc. Phys.* Soc. 47 (1935) 835-842.
- [2] F. Seitz, D. Turnbull, Solid State Physics: Advances in Research and Application, Academic Press Inc., New York (1959).

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- [3] P.H. Kasai, Electron spin resonance studies of donors and acceptors in ZnO, *Phys. Rev.* **130** (1963) 989-995.
- [4] U. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchi-kov, S. Dogan, V. Avrutin, S.J. Cho, H. Morkoc, A comprehensive review of ZnO material and devices, *J. Appl. Phys.* 98 (2005) 041301.
- [5] C.G. Van de Walle, Hydrogen as a cause of doping in zinc oxide, *Phys. Rev. Lett.* 85 (2000) 1012-1015.
- [6] V. Ischenko, S. Polarz, D. Grote, V. Stavarache, K. Fink, M. Driess, Zinc oxide nanoparticles with defects, *Adv. Funct. Mater.* 15 (2003) 1945-1954.
- [7] P.K. Sharma, A.C. Pandey, G. Zolnierkiewicz, N. Gus- kos, C. Rudowicz, Relationship between oxygen defects and the photoluminescence property of ZnO nanoparticles: A spectroscopic view, *J. Appl. Phys.* **106** (2009) 9.
- [8] H.C. Huang, T.E. Hsieh, Preparation and characterization of highly tansparent UV-curable ZnO-acrylic nanocomposites, *Ceram. Int.* 36 (2010) 1245-1251.
- [9] K.V. Rajeswari, P. Gomathisankar, Antibacterial and photocatalytic activities of sonochemically prepared ZnO and Ag-ZnO, J. Alloys Comp. 508 (2010) 587-591.
- [10] Y. Hu, H.J. Chen, Preparation and characterization of nanocrystalline ZnO particles from a hydrothermal process, *J. Nanopart. Res.* **10** (2008) 401-407.
- [11] C.S. Lin, C.C. Hwang, W.H. Lee, W.Y. Tong, Preparation of zinc oxide (ZnO) powder with different types of morphology by a combution synthesis method, *Mater. Sci. Eng.: B* 140 (2007) 31-37.
- [12] P.K. Giri, S. Bhattacharyya, D.K. Singh, R. Kesava- moorthy, B.K. Panigrahi, K.G.M. Nair, Correlation between microstructure and optical properties of ZnO nanoparticles synthesized by ballmiling, *J. Appl. Phys.* **102** (2007) 093515.
- [13] Gao, Z. Zhang, J. Fu, Y. Xu, J. Qi, D. Xue, Room temperature ferromagnetism of pure ZnO nanoparticles, *J. Appl. Phys.* 105 (2009) 113928.
- [14] A. Thurber, K.M. Reddy, V. Shutthanandan, M.H. Engelhard, C. Wang, J. Hays, A. Punnoose, Ferromagnetism in chemically synthesized CeO₂ nanoparticles by Ni doping, *Phys. Rev. B* 76 (2007) 165206.
- [15] M. Naeem, S.K. Hasanain, A. Mumtaz, Electrical transport and optical studies of ferromagnetic cobalt doped ZnO nanoparticles exhibiting a metal-insulator transition, *J. Phys.: Cond. Mat.* 20 (2008) 025210.
- [16] L. Irimpan, V.P.N. Nampoori, P. Radhakrishnan, B. Krishnan, A. Deepthy, Size-dependent enhancement of nonlinear optical properties in nanocolloids of ZnO, *J. Appl. Phys.* **103** (2008) 033105.
- [17] K.M. Sancier, ESR investigation of photodamage to zinc oxide

powders, Surf. Sci. 21 (1970) 1-11.

- [18] A. Hausmann, B. Schallenberger, Interstitial oxygen in zinc oxide single crystals, *Zeitschrift fur Physik* **31** (1978) 269-273.
- [19] M. Schulz, ESR experiments on Ga donors in ZnO crystals, *Phys. Stat. Sol.* 27 (1975) K5-K8.
- [20] W.E. Carlos, E.R. Glaser, D.C. Look, Magnetic resonance studies of ZnO, *Physica B* 308 (2001) 976-979.
- [21] V.A. Nikitenko, K.E. Tarkpea, I.V. Pykanov, S.G. Stoyukhin, EPR and thermoluminescence in ZnO single crystals with ionic vacancies, *J. Appl. Spect.* 68 (2001) 502-507.
- [22] D.M. Hoffmann, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, Hydrogen: A relevant shallow donor in zinc oxide, *Phys. Rev. Lett.* 88 (2002) 045504.
- [23] H. Zhou, A. Hofstaetter, D.M. Hofmann, B.K. Meyer, Magnetic resonance studies on ZnO nanocrystals, *Microelect. Eng.* 66 (2003) 59-64.
- [24] J.M. Smith, W.E. Vehse, ESR of electron irradiated ZnO confirmation of F⁺ center, *Phys. Lett. A* 31 (1970) 147-148.
- [25] J.M. Meese, D.R. Locker, Oxygen displacement energy in ZnO, Solid Stat. Commun. 11 (1972) 1547-1550.
- [26] L.S. Vlasenko, G.D. Watkins, Optical detection of electron paramagnetic resonance in room-temperature electron-irradiated ZnO, *Phys. Rev. B* 71 (2005) 125210.
- [27] L.S. Vlasenko, Magnetic resonance studies of intrinsic defects in ZnO: Oxygen vacancy, *Appl. Magn. Res.* **39** (2010) 103-111.
- [28] W. Xie, X. Huang, Synthesis of biodiesel from soybean oil using heterogeneous KF/ZnO catalyst, *Catal. Lett.* **107** (2006) 53-59.
- [29] A. Hernández, L. Maya, E. Sánchez-Mora, E.M. Sánchez, Solgel synthesis, characterization and photo- catalytic activity of mixed oxide ZnO-Fe₂O₃, *J. Sol-Gel Sci. Technol.* **42** (2007) 71-78.
- [30] J. Das, I.R. Evans, D. Khushalani, Zinc glycolate: A precursor to ZnO, *Inorg. Chem.* 48 (2009) 3508-3510.
- [31] R. Saleh, M. Munisa, W. Beyer, Infrared absorption in a-SiC:H films prepared by DC sputtering, *Thin Solid Films* 426 (2003) 117-123.
- [32] D.M. Joseph, R. Balagopal, R.F. Hicks, L.P. Sadwick, K.L. Wang, Observation of carbon incorporation during gallium arsenide growth by molecular beam epitaxy, *Appl. Phys. Lett.* 53 (1988) 2203-2204.
- [33] M.O. Manasreh, J.M. Baranowski, K. Pakula, H.X. Jiang, J. Lin, Localized vibrational mode of carbon- hydrogen complexes in GaN, *Appl. Phys. Lett.* **75** (1999) 659-661.

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