Study into luminescence and photoconductivity of nano-structured ZnO obtained through sol-gel method

L V Mikhnev, E A Bondarenko, O M Chapura, A A Skomorokhov, A I Nikonov, M S Malorodov, R V Pigulev and D L Gazdinsky

North-Caucasus Federal University, Pushkin Street 1, Stavropol 355009, Russian Federation

*Email: ChapurOL-7@mail.ru

Abstract. Sol-gel method from zinc acetate in water was employed to synthesize nano-sized zinc oxide. The structural features of the ZnO obtained samples, their spectral features of luminescence and photoconductivity were studied. The influence of the treatment temperature on the luminescence and photoconductivity of nano-sized zinc oxide was studied. The type and energy position of the intrinsic defects involved in the luminescence and photoconductivity processes were determined.

1. Introduction

In recent years, a wide range of possible applications of nanomaterials and nanoparticles of zinc oxide in particular has resulted in an interest in their physical and chemical properties. Nanoparticles of zinc oxide themselves and in composites offer potential for the creation of antibacterial agents [1, 2], active materials for toxic waste processing [3], as well as for the detection of fire-hazardous and poisonous gases [4]. Zinc oxide can be used in the ultraviolet range optoelectronic devices while due to the high binding energy of the exciton (60 meV), radiation can be generated at high temperatures reaching 550 K [5]. ZnO nanoparticles can be used in the development of ultraviolet radiation sensors and high-efficiency solar cells [6, 7].

Currently, there are many methods for developing zinc oxide nanostructures, namely – sonochemical [8], sol-gel [9], hydrothermal [10], etc. These methods in combination with the possibilities of varying the synthesis technological parameters make it possible to obtain structures based on ZnO of different morphology. At the same time, the fields of their application are not determined only by the geometric parameters of the nanoparticles, yet also by a set of physical and chemical properties of the resulting group of nanoparticles, while the latter is known to be significantly affected by the defective situation in the synthesized structures.

Most often, the composition of point defects involved in radiative recombination, is successfully evaluated through studying photoluminescence spectra [11-16]. At the same time, the study of photoconductivity spectra allows investigating electronic transitions in a material, including those involving defects that lead to the appearance of free nonequilibrium charge carriers. Therefore, analysis of the luminescence spectra and photoconductivity in a combination stand as a more detailed method for estimating the defect situation.

2. Materials and methods
Zinc acetate dihydrate (Zn(CH$_3$COO)$_2$·2H$_2$O), 25% ammonia solution (NH$_3$·H$_2$O) and distilled water were used as the initial materials for synthesis ZnO nanoparticles. First, a 0.5 M aqueous zinc acetate solution was prepared. To the resulting solution, at intensive stirring, the ammonia solution was added dropwise, with continuous monitoring of the pH level. At pH ≈ 8, the process was stopped, since it is at this acidity value that zinc oxide is formed from its hydroxide. Next, the received gel was centrifuged at 2500 rpm, and the resulting precipitate was triple-washed with distilled water. This procedure is needed to remove various impurity ions remaining after the reaction taking place between zinc acetate and ammonia solution. Further on, the washed gel was dried at a temperature of 110 °C for 12 hours. For the synthesis of experimental samples 1, 2, 3, the powders obtained through drying were subjected to additional thermal treatment at temperatures of 175, 270 and 400 °C, respectively.

The structural features of the obtained particles were studied with X-ray diffraction and scanning electron microscopy, using the PANalytical Empyrean and TESCAN MIRA3 devices, respectively. The measurements of optical, luminescent and photoelectric properties were done on an automated installation based on a monochromator MDR-41 (Lomo JSC). When studying the photoconductivity spectra, the powder was placed in a sandwich-type cell consisting of two quartz glasses with transparent antimony doped tin dioxide electrodes applied. The thickness of the active layer was controlled by fluoroplastic liners and was around 100 μm. Prior to the measurements, the cell with the sample had been kept in the dark for 12 hours.

3. Results and discussion

Figure 1 shows the outcomes of studying the structural features of zinc oxide based nanoparticles obtained via the sol-gel method.

![Figure 1](image_url)

**Figure 1.** XRD patterns of ZnO samples annealed at different temperatures (a) and an electron microscopic image of a ZnO sample subjected to thermal treatment at a temperature of 400 °C (b).

As can be seen from figure 1, the diffractograms of ZnO samples subjected to thermal treatment at different temperatures, display peaks typical of zinc oxide in wurtzite-type structure (JCPDS card no. 36-1451). Besides, as the calcination temperature increases, the intensity and narrowing of the peaks in the diffractograms do up, which is associated with an increase in ZnO nanoparticles dimensions due to particles aggregation during sintering and improved crystallinity of the resulting samples. The
estimates of the crystallite size, performed using the Debye-Scherrer formula for the (101) plane, yielded the values of 12, 30 and 38 nm for samples 1, 2 and 3, respectively.

As the results of the analysis of electron-microscopic images showed, the obtained zinc oxide nanoparticles have a shape that is close to spherical, figure 1, (b).

The optical band gap ($\Delta E_g$) of nano-sized ZnO was evaluated through studying the diffuse reflection spectra employing the Kubelka-Munk function following the method described in [17], figure 2. The results of the evaluation numerical values can be seen in Table 1.

Table 1. Major features of nano-sized ZnO obtained through sol-gel method.

| # of sample | $T_{\text{ samp }}$, C | $\Delta E_g$, eV | The average particle size, nm |
|-------------|-----------------------|-----------------|------------------------------|
| Sample 1    | 175                   | 3.45            | 12                           |
| Sample 2    | 270                   | 3.29            | 30                           |
| Sample 3    | 400                   | 3.27            | 38                           |

The displacement of the absorption edge into the region of lower energies (observed from diffuse reflection spectra), and hence the width of the band gap, along with increasing processing temperature is associated with an increase in the size of the ZnO nanoparticles [18,19].

The luminescence spectra were measured at excitation into the fundamental absorption region with 3.96 eV quanta (the band excreted by a monochromator from the spectrum of a high-pressure mercury lamp was used as the source of excitation).

All the samples had luminescence in two non-overlapping ultraviolet and visible spectral regions. In the ultraviolet region, this was the edge luminescence (figure 2, curves b), where the presence of ZnO is explained by radiative recombination of free excitons [5,11]. Note to be made that the position of the luminescence maximum peak basically coincides with the values of $\Delta E_g$ obtained when analyzing the diffuse reflection spectra.

The maximum of the edge luminescence spectrum shifts to the long-wave region along with an increase in the processing temperature, which also indicates a decrease in the width of the band gap. The increase in the intensity of this luminescence at increasing temperature can be attributed to improved crystallinity of the samples.

Figure 2. Tauc plots ($(F(R)h\nu)^2$) and spectra of edge photoluminescence (PL) of nanoparticles ZnO.
The visible luminescence spectra in figure 3 have a non-elementary form and can be decomposed into separate Gaussian components. For all the samples, the luminescence spectra consist of two elementary bands (in figure 3 they are shown as 1 and 2, respectively), whereas there is a change in the contribution magnitude and the maximum position of these bands along with an increase in the processing temperature.

![Figure 3. Photoluminescence spectra of nanoparticles ZnO (λ_ex=365 nm).](image)

The maximum of luminescent band 1 is located at a wavelength of 530 nm, while its contribution goes up along with an increase in the processing temperature. For band 2, when the sample processing temperature is increased, the maximum is shifted to the long-wave region (for sample 1 the value obtained was 587 nm; for sample 2 – 635 nm; for sample 3 – 642 nm), whereas its contribution to the visible light intensity decreases.

To determine the luminescence and photoconductivity centers, measurements of the photoconductivity spectral features were carried out (figure 4, curves a) and photoexcitation (figure 4, curves b) of nano-sized ZnO. The photoexcitation spectra were measured by recording the radiation at the luminescence maximum.

![Figure 4. Spectra of photoconductivity and photoexcitation (λ_em=530 nm) of nanoparticles ZnO.](image)
At the present time, two reasons have been described for the disturbed current transmission during photoexcitation of powder structures based on zinc oxide. The first reason is due to deep capture levels the presence in ZnO [20], while the second one is related to the effect that adsorbed oxygen has on the conductivity mechanisms [21]. At the same time, we believe that the nature of the current transmission does not have a significant effect on the position of the local maxima in the photoconductivity spectrum.

The figure show that in the photoconductivity and photoexcitation spectra, all the samples reveal typical peaks indicated as $E_g$ and $E_1$; besides, the photoconductivity spectra for samples 2 and 3 reveal a peak in the 470-490 nm region, which is indicated as $E_2$.

The $E_g$ peak in its position (Table 2) can be linked to electronic interband transitions. The photoconductivity in the visible region is apparently associated with point defects in zinc oxide, which is also mentioned in [22]. Along with increasing processing temperature, the position of these peaks shifts to the long-wave region; this is well associated with a change in the band gap size. An increase in photoconductivity observed along with an increase in the annealing temperature may be due to the hydroxyl groups desorption from the zinc oxide nanoparticles surface.

| # of sample | $E_g$ (nm) | $E_1$ (nm) | $E_2$ (eV) | Relative photoconductivity value |
|-------------|----------|----------|---------|-------------------------------|
| Sample 1    | 361      | 387      | –       | 0.17                          |
| Sample 2    | 375      | 407      | 479     | 2.58                          |
| Sample 3    | 377      | 410      | 484     | 2.56                          | 1                              |

When assessing a defective situation, it can be assumed that defects with a low formation energy should prevail. Such defects are vacancies of zinc $V_{Zn}$ and oxygen $V_O$ [19, 24], while at processing temperatures above 200 °C other defects [23, 24] should be expected, such as interstitial oxygen atoms $O_i$, Zinc in the Zn interstitium, as well as atoms in anti-structural positions of $O_{Zn}$, $Zn_O$. Of all the defects listed above, under abundance of oxygen, $Zn_O$ reveals a very high formation energy [24], so it is unlikely to have a significant effect on zinc oxide photoluminescence and photoconductivity. Zinc in the interstitial $Zn_i$, as is described in [23], has a very low activation energy for migration, and hence its concentration should be minimal. Therefore, the following defects should be responsible for luminescence and photoconductivity in the obtained samples – zinc $V_{Zn}$ oxygen $V_O$ vacancies and interstitial oxygen atoms $O_i$, oxygen in the anti-structural position of $O_{Zn}$.

Since in our case the thermal treatment was carried out in the air atmosphere, the concentration of oxygen vacancies should decrease along with an increase in the temperature due to vacant oxygen sites being filled with adsorbed oxygen atoms. At the same time, the concentration of zinc vacancies should go up due to the release of metal ions to the oxide surface, which in some cases leads to the formation of a metallic phase that delivers the powders gray color.

Given the considerations above, the luminescence band 1, whose intensity increases along with an increasing temperature, can be related to the transition of an electron from the conduction band to the zinc vacancy. A similar energy position was calculated in [25] for the free levels of $V_{Zn}$ and $V_{Zn}$. The luminescence band 2, whose intensity goes down as the annealing temperature increases, can be related to the transition of an electron from the oxygen vacancy to the valence band. The energy position of the free level $V_O$, theoretically calculated in [25], correlates well with the experimental data that we obtained for ZnO sample annealed at temperature of 175 °C.

The shift in the second band luminescence maximum is probably associated with a change in the radiative recombination path. As the processing temperature rises, the concentration of oxygen vacancies decreases, while the concentration of defects of another type increases simultaneously, which may be $O_i$, whose recombination, involving the free level, can give red luminescence [26].
An increase in the thermal treatment temperature leads to a significant increase in the contribution that the $E_1$ peak has to the photoconductivity, and apparently, it can be related to zinc vacancies. In its energy position [25], it coincides with the transition of electrons from the occupied level $V_{Zn}^{-1}$ to the conduction band.

The photoconductivity peak $E_2$, which can be seen in samples annealed at above 270 °C, can be associated with defects of $O_i$, $O_{Zn}$. The concentration of interstitial oxygen and zinc atoms in an anti-structural position should go up along with increasing temperature under conditions rich in oxygen, since they perform a compensating role, similar to zinc vacancies [24]. The $O_i$ and $O_{Zn}$ defects are deep acceptors and the photoconductivity peak $E_2$ is associated with electron transition from the $O_i$, $O_{Zn}$ level to the conduction band. Mention to be made that the position of the occupied $O_i^{-2}$ level calculated in [27] fits the data obtained in the data we obtained through our study.

4. Conclusion

The study was aimed at investigating the spectral features of the luminescence and photoconductivity of nano-sized ZnO obtained by the sol-gel method. The outcomes show along with an increase in the processing temperature, the optical width of the band gap decreases, which is probably due to an increase in the crystallite size of zinc oxide nanostructures. The obtained zinc oxide samples proved to have luminescence in the near ultraviolet and visible regions. The luminescence in the ultraviolet region is explained with the appearance of free excitons radiative recombination. The luminescence in the visible region is associated with the recombination of photoexcited charge carriers involving the levels of intrinsic point defects of zinc oxide. Zinc oxide nanostructures were revealed to possess photoconductivity where three characteristic peaks can be distinguished, of which the first one is associated with the interband mechanism of nonequilibrium charge carriers emergence, whereas the second and third ones – with intrinsic defects involved in increasing conductivity upon visible radiation absorption.

Given the results of the impact that the thermal treatment temperature has on the photoluminescence and photoconductivity spectra, possible transitions of charge carriers involving defects levels and allowed bands, were analyzed. Based on this, visible luminescence is associated with electrons transition from the conduction band to the $V_{Zn}^0$ and $V_{Zn}^{-1}$ (band 1) vacancies, and from the $V_{O_i}^{-1}$ oxygen vacancies to the valence band (band 2). At the same time, an increase in the thermal treatment temperature results in a shift of the 2-band maximum to the long-wave region, associated with the occurrence of recombination involving $O_i^{-1}$ defects. Photoconductivity in the visible region is associated with the occurrence of nonequilibrium charge carriers due to electron transition from the occupied levels of $V_{Zn}^{-1}$ (band $E_1$) and $O_i^{-2}$, $O_{Zn}$ (band $E_2$) to the conduction band.

References

[1] Raghupathi K R, Koodali R T and Manna A C 2011 Langmuir 27 4020-28
[2] Shu Z, Zhang Y, Yang Q and Yang H 2017 Nanoscale Res. Lett. 12:135
[3] Hoffmann M R, Martin S T, Choi W and Bahnemann D W 1995 Chem. Rev. 95(1) 69–96
[4] Hsua C-L, Chenb K-C, Tsaic Y and Hsueh T-J 2013 Sens. and Actuators B:Chemical 182 190-196
[5] Özgür Ü, Alivov Y I, Liu C, Teke A, Reshechikov M A, Doğan S, Avrutin V, Cho S-J and Morkoç H 2005 J. of Appl. Phys. 98 041301
[6] Lim J W, Hwang D K, Lim K Y, Kang M, Shin S-C, Kim H-S, Choi W K and Shim J W 2017 Solar Energy Materials and Solar Cells 169 28–32
[7] Fang J, Fan H, Tian H, Dong G 2015 Mater. Charact. 108 51–7
[8] Jung S-H, Oh E, Lee K-H, Yang Y, Park C G, Park W and Jeong S-H 2008 Cryst. Growth Des. 8 26–9
[9] Hayat K, Gondal M A, Khaleed M M, Ahmed S and Shemsi A M 2011 Appl. Catal. A: General 393 122–9
[10] Baruwaiti B, Kumar D K and Manorama S V 2006 Sensors and Actuators B: Chemical 119 676–
[11] Djurisic A B, Ng A M C and Chen X Y 2010 Progress in Quantum Electronics 34 191–259
[12] Zhang L, Yin L, Wang C, Lun N, Qi Y and Xiang D 2010 J. Phys. Chem. C 114 9651–8
[13] Li M, Xing G, Xing G, Wu B, Wu T, Zhang X and Sum T C 2013 Phys. Rev. B 87 115309
[14] Kawabata K, Nanai Y, Kimura S and Okuno T 2012 Appl Phys. A 107 213–20
[15] Camarda P, Messina F, Vaccaro L, Agnello S, Buscarino G, Schneider R, Gerthsen D, Lorenzi R, Gelardi F M and Cannas M 2016 Phys. Chem. Chem. Phys. 18 16237–44
[16] Han N, Wu X, Chai L, Liu H, Chen Y 2010 Sens. and Actuators B 150 230–8
[17] Stone F S 1983 UV-visible diffuse reflectance spectroscopy applied to bulk and surface properties of oxides and related solids Surface Properties and Catalysis by Non-Metals ed by J P Bonnelle, B Delmon, E G Derouane (Dordrecht: Springer), chapter 8 pp 237-272
[18] Chithira P R and John T T, 2017 J. of Luminescence 185 212–8
[19] Koao L F, Dejene F B and Swart H C 2014 Materials Sci. in Semiconductors Process. 27 33–40
[20] Nayak J, Kasuya J, Watanabe A and Nozaki S 2008 J. Phys.: Condens. Matter. 20 195222
[21] Prades J D, Hernandez-Ramirez F, Jimenez-Diaz R, Manzanares M, Andreu T, Cirera A, Romano-Rodriguez A and Morante J R 2008 Nanotechnology 19 465501
[22] Mishra S K, Srivastava R K and Prakash S G 2012 J. Alloys and Comp. 539 1–6
[23] Janotti A and Van de Walle C G 2009 Rep. Prog. Phys. 72 126501
[24] Vidya R, Ravindran P, Fjellvag H, Svensson B G, Monakhov E, Ganchenkova M and Niemen R M 2011 Phys. Rev. B 83 045206
[25] Patterson C H 2006 Phys. Rev. B 74 144432
[26] Lee C T 2010 Materials 3 2218–59
[27] Hu J and Pana B C 2008 J. Chem. Phys. 129 154706