

Photoluminescence Emission and Structure Diversity in ZnO:Ag Nanorods

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Abstract. The photoluminescence, its temperature dependences, as well as structural characteristics by methods of Scanning electronic microscopy (SEM) have been studied in ZnO:Ag nanorods prepared by the ultrasonic spray pyrolysis (USP). The PL spectra of the ZnO:Ag NRs over the temperature range from 10 K to 300 K are investigated. Three types of PL bands have been revealed: i) the near-band-edge (NBE) emissions, ii) defect related emission and iii) IR emissions. It is shown the IR emission corresponds to the second-order diffraction of the near-band-edge (NBE) emission bands. The study of NBE PL temperature dependences reveals that the acceptor bound exciton (ABE) and its second-order diffraction peak disappeared at the temperature higher than 200 K. The attenuation of the ABE peak intensity is ascribed to the thermal dissociation of ABE with appearing of a free exciton (FE). The PL bands, related to the LO phonon replica of FE and its second-order diffraction, dominate in the PL spectra at room temperature that testify on the high quality of the ZnO:Ag films prepared by the USP technology.

1. Introduction

Zinc oxide (ZnO) nanocrystals (NCs) with wide band gap energy (3.37 eV) have attracted great attention due to exceptional exciton properties (high exciton binding energy equal to 60 meV at 300K) and a number of deep levels that emit in the whole visible range and, hence, can provide intrinsic “white” light emission. ZnO NCs are promising candidates for the different optoelectronic applications such as light emitting diodes [2-7]. The control of the ZnO defect structure in these nanostructures is a necessary step in order to improve the device quality. Since the structural imperfection and defects generally deteriorate the exciton related recombination process, it is necessary to grow the high quality films for efficient light-emitting applications. The ultrasonic spray pyrolysis (USP) method is a simple, inexpensive, non-vacuum and a low temperature technique for the film synthesis [8]. It will be interesting to study the optical emission of the USP produced ZnO nanostructures doped with Ag versus temperature in order to identify the best regimes for obtaining bright emitting NCs and the nature of optical transitions.

2. Experimental details

ZnO:Ag thin solid films were prepared by the USP technique on the surface of soda-lime glass substrate for the substrate temperatures 400⁰ C and different deposition times of 3, 5 and 10 min.



Using this technique the nanoparticle's size can be easily controlled by changing a concentration of starting solution and the atomization parameters. The deposition system includes a piezoelectric transducer operating at variable frequencies up to 1.2 MHz and the ultrasonic power of 120 W. ZnO:Ag thin solid films were deposited from a 0.4 M solution of zinc (II) acetate [Zn(O₂CCH₃)₂] (Alfa), dissolved in a mix of deionized water, acetic acid [CH₃CO₂H] (Baker), and methanol [CH₃OH] (Baker) (100:100:800 volume proportion). Separately, a 0.2 M solution of silver nitrate [Ag(NO₃)] (Baker) dissolved in a mix of deionized water and acetic acid [CH₃CO₂H] (Baker) (1:1 volume proportion) was prepared, in order to be used as doping source. A constant [Ag]/[Zn] ratio of 2 at. % was applied at the ZnO Ag film preparation. The morphology of ZnO:Ag films has been studied using the scanning electron microscopy (SEM) Dual Beam, FEI brand, model Quanta 3D FEG with field emission gun. PL spectra were measured in the temperature range 10-300K at the excitation by a He-Cd laser with a wavelength of 325 nm and a beam power of 20 mW at 300K using a PL setup on a base of spectrometer SPEX500 described in [9-11].

3. Experimental results and discussion

SEM images of the typical ZnO:Ag nanorods (NRs) obtained at the deposition times of 3 and 10 min and the substrate temperatures 400⁰ C are presented in figure 1. It is clear that the ZnO nanorods have the hexagonal cross section and the rod orientation along the c axis. The cross section size of ZnO nanorods increases with the duration of UPS process from 50-70 nm (for the duration of 3min), 100-150 nm (at 5min) and 150-200 nm (at 10 min). PL spectra of ZnO:Ag NRs are shown in figure 2 for all studied samples.

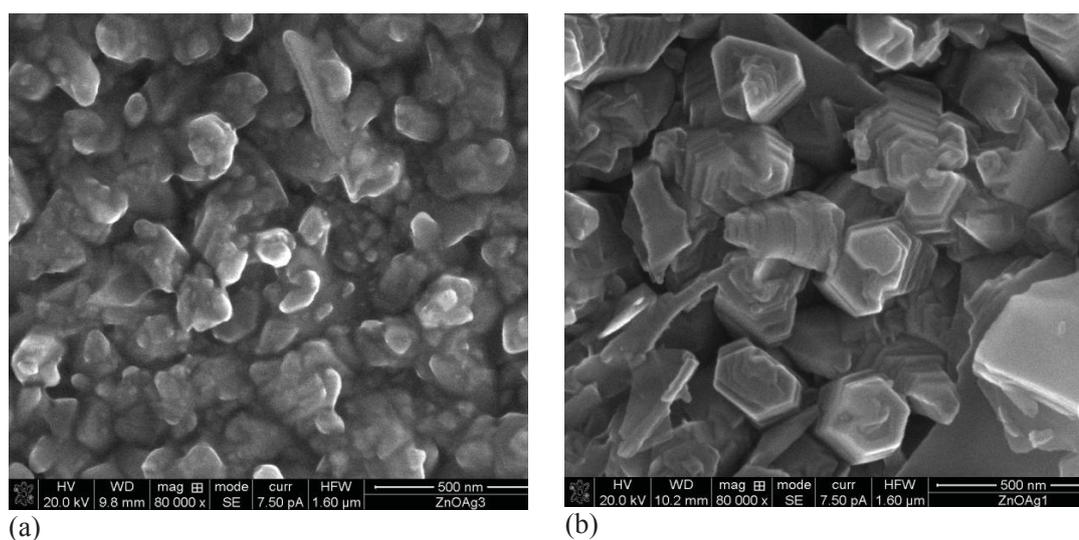


Figure 1. SEM images of the samples prepared at the substrate temperatures 400⁰ C and the durations of 3 (a) and 10 (b) min.

It is clear that the PL spectra are complex and can be represented as a superposition of elementary PL bands with the peaks in the spectral ranges: 2.90-3.25 eV (I, II), 2.00-2.50 eV (III, IV) and 1.45-1.61 eV (V,VI). The deconvolution procedure has been applied to the PL spectra with the aim to separate the elementary PL bands (Fig.3). The analysis of figures 3 permits to distinguish six elementary PL bands with the peaks at: 3.25 (1), 2.92 (2), 2.75 (3), 2.10 (4), 1.62 (5) and 1.46 (6) eV at 10K (Fig.3).

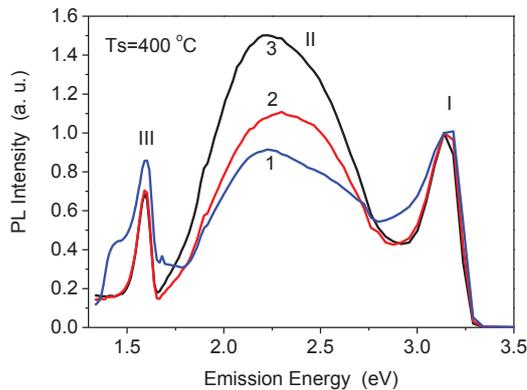


Figure 2. PL spectra of samples prepared on the substrate with $T = 400^{\circ}\text{C}$ at the deposition times: 1-3 min, 2-5 min, 3-10 min.

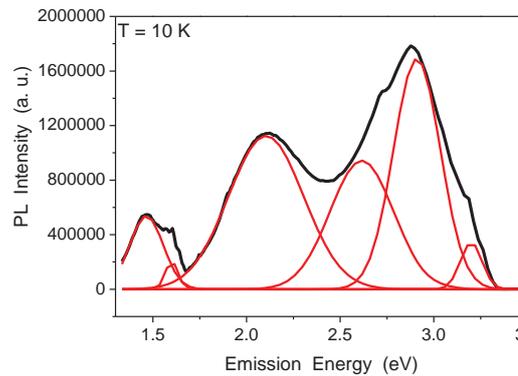


Figure 3. PL spectrum deconvolution on six elementary PL bands for the film obtained at 400°C at the duration 3 min.

It well known that the UV-visible PL bands (I) in ZnO are near-band-edge (NBE) or exciton emissions [12]. The PL band in the spectral range 2.00-2.50 eV related to the defect emission [12] and the nature of IR PL bands has to be clarified. With increasing the USP duration the intensity of defect (II) related PL bands rose mainly in comparison with the intensity of NBE PL bands (Fig.2).

PL spectra of ZnO:Ag NRs measured at different temperature in the range of 10-300K are shown in Fig.4. The same rates of the variation of PL peak intensities versus temperature have been revealed for the PL bands 1 and 7, as well as for the emission bands 2 and 8 (Fig.4). This fact, as well as the PL peak positions, permits to assign the IR PL bands 7 and 8 to the second order diffraction of the NBE PL bands 1 and 2, respectively [13].

A great variety of luminescence bands in the UV and visible spectral ranges have been detected in ZnO crystals [12]. The near-band-edge (NBE) emission at 3.0-3.37 eV is attributed to the free (FE) or bound (BE) excitons, their LO phonon replicas, such as FE-1LO or FE-2LO, to optical transition between the free to bound states, such as the shallow donor and valence band, or to donor-acceptor pairs [14]. However, the position of the near-band-edge emission at room temperature can vary significantly due to the variation of relative contributions of free exciton emission and phonon replicas [15].

The defect related green PL band in the spectral range 2.40-2.70 eV in ZnO is assigned ordinary to oxygen vacancies [16], Cu impurities [17] or surface defects [18]. The orange PL band with the peak at 2.02-2.10 eV was attributed earlier to oxygen interstitial atoms (2.02 eV) [19] or to the hydroxyl group (2.10eV) [20, 21]. Taking into account that the PL intensity of this PL band increased with raising the USP duration (Fig.2) the assumption that the corresponding defects are related to oxygen interstitial atoms (or to the hydroxyl group) looks very reliable.

Finally, we need to discuss the nature of the near-band-edge PL bands at 2.92 and 3.25 eV. Studied ZnO films were doped by Ag and, therefore, have the acceptor type defects, Ag_{Zn} , which were formed when the Ag atoms substitute Zn atoms in the ZnO crystal lattice. The intensity of 2.92 eV PL band decreases essentially with temperature and this PL band and its IR second-order diffraction peak (1.46eV) disappeared completely at 200K (Fig.4).

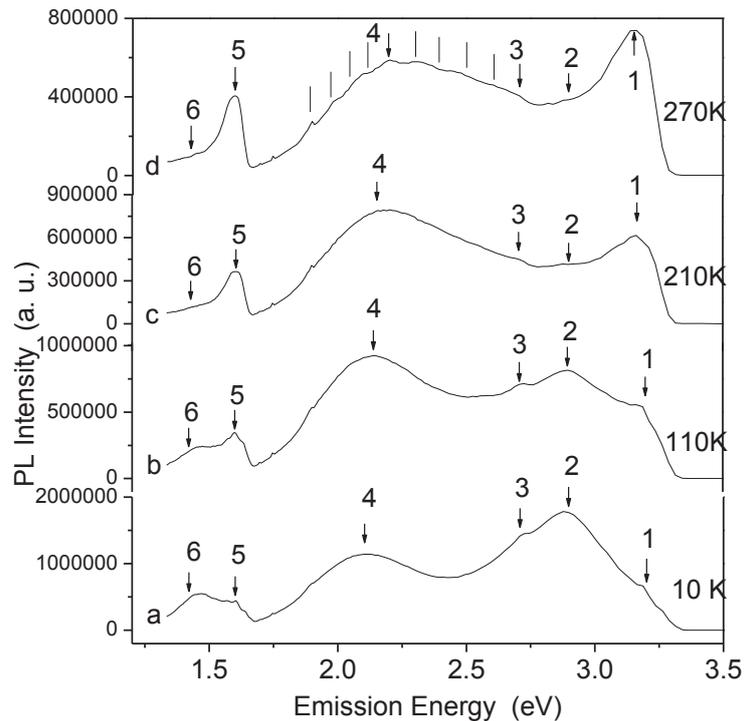


Figure 4. PL spectrum variation with temperature for the sample prepared at the duration 5 min.

Thus it is possible to assume that this PL band (2.92 eV) owes to emission of the acceptor bound excitons (ABE), involving the acceptor Ag_{Zn} , or its complexes such as donor-acceptor pairs, in the ZnO:Ag nanorods. The thermal decay of the 2.92 eV PL intensity is assigned to the thermal dissociation of ABE to free exciton. In this case the 3.25 eV PL band, which dominates in the room temperature PL spectrum (Fig.4) can be attributed to the LO phonon replica of FE emission.

4. Conclusions

ZnO:Ag nanorods with hexagonal structures have been successfully synthesized by the USP method. The PL spectra of the ZnO:Ag NRs over the temperature range from 10 K to 300 K have been investigated. Temperature-dependent PL spectra show that the IR emissions correspond to the second-order diffraction of the NBE emissions. The study of NBE PL temperature dependences reveals that ABE and its second-order diffraction peak disappeared when the temperature higher than 200 K. The attenuation of the ABE peak intensity is ascribed to the thermal dissociation of ABE to free exciton. The PL bands, related to the LO phonon replica of free exciton and its second-order diffraction, dominate in the PL spectra at room temperature that testifies on the high quality of the ZnO:Ag films prepared by USP.

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References

- [1] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner 2005 Prog. Mater. Sci. **50**, 293
- [2] M.H. Koch, P.Y. Timbreil, R.N. Lamb 1995 Semicond. Sci. Technol. **10**.
- [3] K. Vanheusden, C.H. Seager, W.L. Wareen, D.R. Tallant, J. Caruso, M.J. Hampden-Smith, T.T.

- Kodas, J. *Lumin.* 1997 **75** 11
- [4] R. Scheer, T. Walter, H.W. Schock, M.L. Fearheiley, H.J. Lewerenz 1997 *Appl. Phys* **63** 3294
- [5] Y. Chen, D.M. Baghall, H. Koh, K. Park, K. Hiraga, Z. Zhu, T. Yao, J.1998 *Appl. Phys.* **84** 3912
- [6] Y.B. Li, Y. Bando, D. Golberg, 2004 *Appl. Phys.* **84** 3603
- [7] J. Ding, T.J. McAvoy, R.E. Cavicchi, S. Semancik 2001 *Sens. Actuat.* **77** 597
- [8] W. Tang, D.C. Cameron 1994 *Thin Solid Films* **238** 83
- [9] M. Dybic, S. Ostapenko, T.V. Torchynska, E. Velazquez Lozada 2004 *Appl. Phys.* **84** 5165
- [10] T. V. Torchynska, A.I. Diaz Cano, M. Dybic, S. Ostapenko, M. Mynbaeva, *Physica B*, 2006 *Condensed Matter* 376-377
- [11] T.V. Torchynska, J. Palacios Gomez, G.P. Polupan, F.G. Becerril Espinoza, A. Garcia Borquez, N.E. Korsunskaya, L.Yu. Khomenkova 2000 *Appl. Surf. Science* **167** 197-204
- [12] A. B. Djuris, A.M.C. Ng, X.Y. Chen. 2010 *Progress in Quantum Electronics* **34** 191-259
- [13] J. Lv, Ch. Liu, W. Gong, Zh. Zi, X. Chen, K. Huang, T. Wang, G. He, Sh. Shi, X. Song, Zh. Sun, 2012 *Optical Materials* **34**
- [14] T. Mahalingam, K.M. Lee, K.H. Park, S. Lee, Y. Ahn, J.Y. Park, K.H. Koh, 2007 *Nanotechnology* **18**
- [15] T. Voss, C. Bekeny, L. Wischmeier, H. Gafsi, S. Borner, W. Schade, A.C. Mofor, A. Bakin and A. Waag 2006 *Appl. Phys.* **89**
- [16] M.K. Patra, K. Manzoor, M. Manoth, S.P. Vadera, N. Kumar, *J. Lumin.* 2008
- [17] N.Y. Garces, L. Wang, L. Bai, N.C. Giles, L.E. Halliburton, G. Cantwell, *Appl. Phys.* 2002 **81**
- [18] A.B. Djurišić, W.C.H. Choy, V.A.L. Roy, Y.H. Leung, C.Y. Kwong, K.W. Cheah, T.K. Gundu Rao, W.K. Chan, H.F. Lui, C. Surya, 2004 *Adv. Funct. Mater*
- [19] X. Liu, X. Wu, H. Cao, R.P.H. Chang, J. 2004 *Appl. Phys.* **95**
- [20] J. Qiu, X. Li, W. He, S.-J. Park, H.-K. Kim, Y.-H. Hwang, J.-H. Lee, Y.-D. Kim, 2009 *Nanotechnology* **20**
- [21] T.V. Torchinskaya, N.E. Korsunskaya, B. Dzumaev, B.M. Bulakh, O.D. Smiyan, A.L. Kapitanchuk, S.O. Antonov, 1996 *Semiconductors* **30**