physica status solidi

www.interscience.wiley.com

reprints

Optical properties of ZnO, Zn_{0.99}Mn_{0.01}O nanopowders

V. I. Sokolov^{*1}, A. Ye. Yermakov¹, M. A. Uimin¹, A. A. Mysik¹, V. A. Pustovarov², N. B. Gruzdev¹, and V. T. Surikov³

¹ Institute of Metal Physics UD RAS, S. Kovalevskaya Str. 18, 620041 Yekaterinburg, Russia

² Ural State Technical University, Mira Str. 19, 620002 Yekaterinburg, Russia

³ Institute of Chemistry of Solid State, UD RAS, Pervomayskaya Str. 91, 620041 Yekaterinburg, Russia

Received 18 September 2009, revised 22 November 2009, accepted 28 November 2009

Published online 6 April 2010

Keywords ZnO, ZnMnO, nanocrystals, level splitting, photoluminescence

*Corresponding author: e-mail visokolov@imp.uran.ru, Phone +7 343 378 3785, Fax: +7 343 374 5244

The photoluminescence and photoluminescence excitation spectra of Zn_{0.99}Mn_{0.01}O nanopowders are presented in this paper. Detected peaks at energies $\hbar\omega$ higher than the energy gap in the photoluminescence excitation spectra allow us to assume that the Zhang-Rice-like states

in forbidden gap due to the strong exchange coupling between 3d localized spin and valence band holes are related with valence band states perturbed by strong p-d hybridization.

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction In last years many researches of dilute magnetic semiconductors (DMS) with the ferromagnetic ordering at $T_c > 300$ K appear. The main interest is centered around the ZnO:3d materials for which the theoretical calculations show us that the increasing of T_c takes place due to the strong hybridization between the 3d localized spin and valence band holes and appearing Zhang-Rice-like (ZR) states [1–3]. It is suggested that these antibonding state is split out from the valence band top deeply into the band gap and the optical transitions from the ZR- state to the conduction band cause very strong light absorption in monocrystals and nanocrystals of Zn_{1-x}Mn_xO in the energy region of 2.2–3.0 eV [4,5]. However in photoluminescence (PL) spectra of colloidal nanocrystals of Zn_{1-x}Mn_xO the ZR-state is not observed [5]. Recently the PL-peak at the energy of 2.9 eV for Zn_{0.99}Mn_{0.01}O nanopowder, prepared by the gas phase synthesis method, was detected [6]. In the 2.9 eV photoluminescence excitation (PLE) spectrum were observed three wide peaks in the region of interband transitions at the energies of 3.9, 4.5 and 5.3 eV. In this paper the researches of the Zn_{0.99}Mn_{0.01}O system were continued in order to understand the reason of appearance of 2.9 peak in PL-spectrum and to compare with the well learned ZnMnS compound. Our results allow us to think that the Mn²⁺ ions in the Zn_{0.99}Mn_{0.01}O nanopowder induce the ad-

ditional ZR-like state. The optical transitions between this state and the ground state of the crystal create the 2.9 peak in PL-spectrum and the broad peculiarities in the PLE spectrum of this illumination at the energies of 3.9, 4.5 and 5.3 eV in the region of interband transitions.

2 Experimental detail

Nanopowder with the size of the nanocrystals of 30 nm were prepared by the method of the gas phase synthesis [7] annealed in air at 400°C during 1 hour. The manganese concentration in nanocrystals Zn_{1-x}Mn_xO before and after the annealing was determined by inductively-coupled plasma mass spectroscopy (iCAP 6000, Thermo) and $x=0.01$. Optical spectra in [6] were observed for nanocrystals Zn_{1-x}Mn_xO with $x=0.01$ also.

3 Results and discussion

Figure 1 presents the PL and PLE- spectra of Zn_{0.99}Mn_{0.01}O nanopowder before and after annealing. In both cases in PL- spectra we can see low energy peaks with the maxima at the energies of 2.1 and 2.3 eV and high energy peak at the energy of 2.9 eV. Low energy peaks were caused by deep defects in the crystals, which had been subjected to the heat treatment in oxygen atmos-

phere [8]. We assume that the quantity of oxygen vacancies decreased in result of the annealing in air. The decreasing of the peak 2.9 eV intensity, which clearly expressed in Fig. 1a, is caused probably by the following fact: this peak is formed by the complex Mn²⁺-V_O. In PLE spectra of 2.9 eV peak for as grown (i.e. without the annealing) nanopowder three peaks at the energies of 3.9, 4.5 and 5.3 eV are observed [6]. After the annealing the intensity of these peaks decreases, but the increasing of PLE spectrum with the increasing of the light quantum energy is clearly expressed, especially for the last peak 5.3 eV. Such behavior of PLE spectrum is significantly different in its character from that for the luminescence through the deep levels, when the intensity decreases along with the increasing of the excitation energy in the region $\hbar\omega > E_g$ [6].

Figure 1 a) PL spectra of as grown Zn_{0.99}Mn_{0.01}O nanocrystals (1) (excitation E = 3.64 eV, T = 86 K); and of annealed Zn_{0.99}Mn_{0.01}O nanocrystals (2) (excitation E = 3.718 eV, T = 90 K); b) PLE spectra (peak 2.9 eV) of as grown Zn_{0.99}Mn_{0.01}O nanocrystals, T = 86 K (1); and of the annealed Zn_{0.99}Mn_{0.01}O nanocrystals, T = 90 K (2); PLE spectrum (peak 2.34 eV) of the annealed Zn_{0.99}Mn_{0.01}O nanocrystals, T = 90 K (3).

For comparison we demonstrate the PL and PLE spectra for Zn_{0.995}Mn_{0.005}S (Fig. 2). Luminescence with the energy of 2.12 eV caused by the intracentral transitions of Mn²⁺ ion (⁴T₁-⁶A₁). The PLE spectrum exhibits intensive peaks due to the transitions to high-energy states of Mn²⁺ ion (⁴T₂ and ⁴A₂, ⁴E), whereas in the interband transition region we can see the maximum near the E_g and smooth decreasing of intensity at $\hbar\omega > E_g$. Similar decreasing of

excitation intensity at $\hbar\omega > E_g$ takes place for the luminescence peaks 2.34 eV (Fig. 1-b3) and 2.12 eV [6] due to the transitions through the deep states.

Figure 2 a) PL spectra of the Zn_{0.995}Mn_{0.005}S monocrystal, excitation E = 3,230 eV (1) and 4.78 eV (2); b) PLE spectrum of the Zn_{0.995}Mn_{0.005}S monocrystal, emission E = 2,12 eV

We can see that the PLE spectrum for Zn_{0.99}Mn_{0.01}O nanopowders (emission 2.9 eV, Fig. 1) significantly distinguishes from that for luminescence of 2.1 eV of Zn_{0.995}Mn_{0.005}S monocrystals (Fig. 2) and emission 2.34 eV of the Zn_{0.99}Mn_{0.01}O nanocrystals (Fig. 1). On the other hand some resemblance exists. This similarity consists in the fact that the luminescence and its excitation in Zn_{0.99}Mn_{0.01}O and Zn_{0.995}Mn_{0.005}S take place through the series of some states connected with one another. In the case of Zn_{0.995}Mn_{0.005}S it is the intracentral states of Mn²⁺ ion d⁵ shell. In the case of Zn_{0.99}Mn_{0.01}O a situation is not so simple. A small band length in Zn_{1-x}Mn_xO results in a strong hybridization between d and p states Zn_{1-x}Mn_xO. For this case the ZR-like states due to the strong exchange coupling between 3d localized spin and valence band holes were predicted for description of the intensive absorption band [1]. Really in Zn_{1-x}Mn_xO the ZR-like states are more complicated due to Γ_7 , Γ_9 and Γ_7 sub-bands at the valence band top and to possible influence of oxygen vacancies in a Mn²⁺ environment. So, we have some reasons to consider that there is the ZR-like state providing the 2.9 eV lumi-

nescence band. This state is schematically presented on Fig. 3. The transition from this state to the ground state forms the 2.9 eV PL peak. But the excitation of this peak takes place through higher valence band states perturbed by a strong hybridization between d and p states $\text{Zn}_{1-x}\text{Mn}_x\text{O}$. They are denoted as V_1 , V_2 and V_3 and displayed at the energies higher than E_g in Fig. 3.

Figure 3 Left panel: schematic presentation of Mn^{2+} energy levels in $\text{Zn}_{1-x}\text{Mn}_x\text{S}$ monocrystal, transition $4T_1 \rightarrow 6A_1$ forms the 2.1 eV emission and transitions to higher intracentral states which form peaks of PLE spectrum (Fig. 2b); right panel: the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ Zhang-Rice-like state and valence band V_1 , V_2 , V_3 states and transitions forming the 2.9 eV PL peak and the V_2 and V_3 PLE peaks are shown.

So we can assume some relation between ZR-like states and V_1 , V_2 and V_3 bands.

4 Conclusion In our paper for the first time the experimental PL and PLE spectra are interpreted in terms of the theoretical descriptions of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ strong d-p hybridization [1-3]. We think it to be interesting to further investigate these states in the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ semiconductors in particular to understand better the role of the oxygen vacancies.

Acknowledgements The authors express their gratitude to T. Dietl, V.I. Anisimov and A.V. Lukoyanov for the discussion of the localized ZR states in $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ system. The paper was performed with the partial support of Russian Foundation for Basic Research (grants No. 07-02-00910 a and No. 08-08-99080 r-ofi) and Russian Federal Agency for Science and Innovations (grant No. 02. 740.11.0217).

References

- [1] T. Dietl, Phys. Rev. B **77**, 085208 (2008).
- [2] T. Dietl, Abstracts of 14 Internat. Conf. on II-VI Compounds, St. Petersburg, August 23-28, 2009, p. 273, report Mo3-1.
- [3] T. Chanier, F. Viot, and R. Hayn, Phys. Rev. B **79**, 205204 (2009).
- [4] F.W. Kleinlein and R. Helbig, Z. Physik **266**, 201 (1974).
- [5] R. Beaulac, P.I. Archer, and D.R. Gamelin, J. Solid State Chem. **181**, 1582 (2008).
- [6] V.I. Sokolov, A.Ye. Yermakov, M.A. Uimin, A.A. Mysik, V.A. Pustovarov, M.V. Chukichev, and N.B. Gruzdev, J. Lumin. **129**, 1771 (2009).
- [7] V.I. Sokolov, A.Ye. Yermakov, M.A. Uimin, A.A. Mysik, V.B. Vykhodets, T.E. Kurennykh, V.S. Gaviko, N.N. Schegoleva, and N.B. Gruzdev, J. Exper. Theor. Phys. **105**, 65 (2007).
- [8] I.P. Kuzmina and V.A. Nikitenko, Zinc Oxide. Growth and Optical Properties (Science, Moscow, 1984) (in Russian).