ELSEVIER

Journal of Luminescence 87–89 (2000) 454–456

JOURNAL OF LUMINESCENCE

www.elsevier.com/locate/jlumin

The luminescence of nanocrystalline ZnO particles: the mechanism of the ultraviolet and visible emission

A. van Dijken[a,*], E.A. Meulenkamp[b], D. Vanmaekelbergh[a], A. Meijerink[a]

[a]*Debye Institute, Utrecht University, PO Box 80.000, 3508 TA Utrecht, The Netherlands*
[b]*Philips Research Laboratories Eindhoven, Prof. Holstlaan 4, 5656 AA Eindhoven, The Netherlands*

Abstract

Results of steady-state luminescence measurements performed on suspensions of nanocrystalline ZnO particles of different sizes are presented. In all cases two emission bands are observed. One is an exciton emission band in the UV and the second an intense and broad emission band in the visible, shifted by approximately 1.5 eV with respect to the absorption onset. As the size of the particles increases, the intensity of the visible emission decreases, while that of the exciton emission increases. In accordance with previous results, a model is presented in which the visible emission is assigned to the radiative recombination of an electron from a level close to the conduction band edge and a deeply trapped hole in the bulk ($V_O^{\bullet\bullet}$) of the ZnO particle. The size dependence of the intensity ratio of the visible to exciton luminescence and the kinetics are explained by a model in which the photogenerated hole is transferred from the valence band to a $V_O^{\bullet}$ level in the bulk of the particle in a two-step process. The first step of this process is an efficient surface-trapping, probably at an O^{2-} site.

Keywords: Semiconductors; Nanoparticles; Quantum size effects; ZnO

1. Introduction

ZnO has been known as a luminescent material for a century and nowadays it is used for various applications such as vacuum fluorescent displays (VFD's). However, despite numerous studies, the mechanism behind the visible luminescence has still not been established. Much of the research on the luminescence of ZnO is performed on single crystalline powders or single crystals. Two emission bands are usually found. A relatively weak and narrow UV emission band is observed around 380 nm (3.25 eV), just below the onset of absorption. This band is due to the radiative annihilation of excitons. The lifetime of this exciton emission is very short, of the order of several tens to hundreds of picoseconds [1]. A much stronger and broader emission band is situated in the green part of the visible spectrum, with a maximum between 500 and 530 nm (2.35–2.50 eV). In contrast to the exciton emission, the lifetime of the visible emission is much longer, viz. in the μs range [2]. For this report, quantum-sized ZnO particles are used.The mean particle size can be varied and its influence on the emission properties can be used to obtain information on the nature of the visible emission. The similarity of the emission properties of macrocrystalline ZnO and nanocrystalline ZnO particles suggests that the origin of the visible emission is the same for all forms of ZnO. However, the kinetics involved in the emission processes are expected to be very different for them.

2. Results and discussion

Emission spectra of suspensions in 2-propanol of nanocrystalline ZnO particles with different particle sizes are shown in Fig. 1. From the variation of the energetic position of the maximum of both the visible and UV

* Corresponding author. Tel.: + 31-30-253-2321; fax: + 31-30-253-2403.

E-mail address: a.vandijken@phys.uu.nl (A. van Dijken)

0022-2313/00/$ - see front matter
PII: S0022-2313(99)00482-2

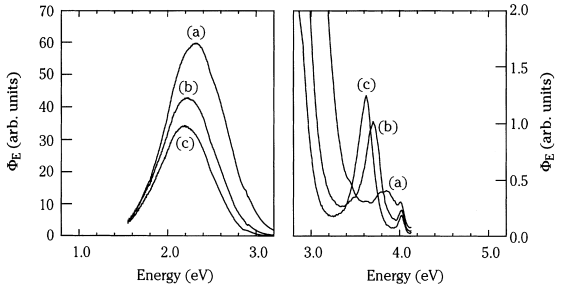

Fig. 1. Emission spectra of suspensions of nanocrystalline ZnO particles in 2-propanol taken after different periods of particle growth at room temperature: (a) 15 min, (b) 120 min, and (c) 420 min. On the left, the broad visible emission band is shown and on the right the sharp UV band is visible. The ZnO particles were excited with a light of 4.4 eV.

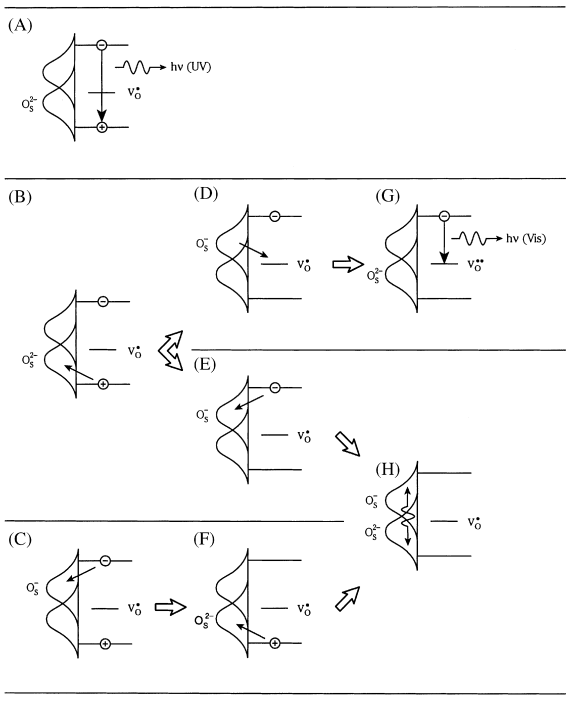

Fig. 2. A schematic overview of the relaxation processes that take place upon photoexcitation of a ZnO particle. The band edges as well as a deep trap level in the bulk of the particle are shown. At the surface of the particle, an energy distribution of a O^{2-}/O^{-} system is shown. It is assumed that non-radiative recombination occurs only at the particle surface. (A–C). Three competing relaxation processes for the exciton: exciton emission and trapping of one of the charge carriers at the surface. (D–E) possible processes following surface trapping of a hole. (G) Visible emission, following the tunneling of the surface-trapped hole back into the particle. (H) Non-radiative recombination, which can be the result of either of the two different processes: trapping of a hole at the surface followed by trapping of an electron at the surface (B and E) or vice versa (C and F).

emission band as a function of particle size, it has been shown that the visible emission from nanocrystalline ZnO particles is due to a transition of a photogenerated electron from the conduction band to a deeply trapped hole [3]. From Fig. 1 it is also clear that the intensity of the visible emission band is much higher than that of the exciton emission band. As both emission processes compete with each other this means that the visible emission process must involve a step in which the photogenerated hole is trapped efficiently somewhere in the particle. The rate of this hole trapping must be much faster than the radiative recombination rate of the exciton emission. Because of the large surface-to-volume ratio of our ZnO particles, efficient and fast trapping of photogenerated holes at surface sites can be expected. A probable candidate for the trapping of holes are O^{2-} ions at the surface [4]. Trapping of a photogenerated hole at the surface is also in agreement with the size-dependence of the emission intensities. The rate for a surface trapping process decreases as the particle size increases since the surface-to-bulk ratio decreases. The transition rate of the exciton recombination will not be influenced strongly by the particle size and thus the intensity of the exciton emission will increase with increasing particle size, as shown in Fig. 1.

With respect to the nature of the deep trap involved in the visible emission process, the defect chemistry of ZnO has to be considered. The presence of $V_O^{\bullet}$ centers as the predominant paramagnetic defects has been established by EPR measurements [5]. These defects are represented by a level approximately 2 eV below the conduction band edge [6] and in some publications $V_O^{\bullet}$ is assumed to be the recombination center for the visible emission. After such a recombination, the effectively neutral V_O^{x} center will be formed, which has an energy very close to the conduction band edge (due to the correlation energy of the two electrons). A transition of an electron from the conduction band to a $V_O^{\bullet}$ level can therefore never yield photons with an energy of 2 eV; as such a transition effectively takes place between the conduction band edge and the V_O^{x} level. However, recombination of a conduction band electron with a $V_O^{\bullet\bullet}$ center can yield photons with an energy of about 2 eV. Such a center can be created when a $V_O^{\bullet}$ center traps a hole.

Based on the discussion presented above, a model for the relaxation of a photoexcited ZnO particle can be derived. A photoexcited ZnO particle can return to the ground state via three different processes: (1) exciton emission, (2) trap emission, and (3) non-radiative recombination. The latter can occur at the surface or at quenching centers in the particle. In view of the large surface area of the ZnO particles, only non-radiative recombination at the surface is considered. To derive a more detailed model, the possible processes are evaluated step by

step. Upon photoexcitation of a ZnO particle, an exciton is formed. The competing processes on the excitonic level are (1) radiative recombination (exciton emission), (2) trapping of the hole at the surface, and (3) trapping of the electron at the surface. The latter step will result in non-radiative recombination after subsequent surface trapping of a hole. After surface trapping of the hole, there are two possible steps. One possibility is that a photogenerated electron – which is still in the conduction band – gets trapped at the surface and recombines non-radiatively with the surface-trapped hole. The other is that the surface-trapped hole tunnels back into the particle to recombine with an electron in a deep trap ($V_O^{\bullet}$ center). This step results in the creation of the recombination center for the visible emission ($V_O^{\bullet\bullet}$ center)

In Fig. 2, a schematic overview of the relaxation processes of a photoexcited ZnO particle is presented as described above. In this figure, the band edges as well as a deep trap level ($V_O^{\bullet}/V_O^{\bullet\bullet}$) and the energy distribution of a O^{2-}/O^{-} surface system are shown. The tunneling rate of a surface-trapped hole to a $V_O^{\bullet}$ center as well as the trapping rate of a conduction band electron at the surface decrease with increasing particle size. The tunneling rate decreases more strongly since tunneling takes place between two localized states while the surface trapping of the conduction band electron (leading to non-radiative relaxation) involves a delocalized state. As a result, the intensity of the trap emission decreases with increasing particle size in agreement with the experimental results shown in Fig. 1.

3. Conclusion

Steady-state luminescence measurements were performed on suspensions in 2-propanol of nanocrystalline ZnO particles of different sizes. All suspensions show two emission bands: a relatively weak and sharp exciton emission band and a more intense and broad trap emission band in the visible part of the spectrum. A model for the kinetics of the radiative and non-radiative processes in nanocrystalline ZnO particles is proposed, based on the assignment of the visible emission to a recombination of a shallowly trapped electron with a deeply trapped hole. From the particle size dependence of the emission properties it is concluded that the photogenerated hole is trapped at a surface system (probably O^{2-}/O^{-}). The surface-trapped hole can tunnel back into the particle where it recombines with an electron in an oxygen vacancy ($V_O^{\bullet}$) resulting in the creation of a $V_O^{\bullet\bullet}$ center, the recombination center for the visible emission. The probability of dependence for this tunneling process on particle size is much stronger than that of the non-radiative processes. This results in an increase of the visible emission intensity as the size of the ZnO particles decreases.

References

[1] V.V. Travnikov, A. Freiberg, S.F. Savikhin, J. Lumin. 47 (1990) 107.
[2] M. Anpo, Y. Kubokawa, J. Phys. Chem. 88 (1984) 5556.
[3] A. van Dijken, E.A. Meulenkamp, D. Vanmaekelbergh, A. Meijerink, J. Lumin, in press.
[4] G.H. Schoenmakers, D. Vanmaekelbergh, J.J. Kelly, J. Phys. Chem. 100 (1996) 3215.
[5] K. Vanheusden, W.L. Warren, C.H. Seager, D.R. Tallant, J.A. Voigt, B.E. Gnade, J. Appl. Phys. 79 (1) (1996) 7983.
[6] F.A. Kröger, The Chemistry of Imperfect Crystals, North-Holland, Amsterdam, 1964, p. 691.