

The Luminescence Properties of ZnO:Al Nanopowders Obtained by Sol-gel, Plasma and Vaporization-condensation Methods

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Abstract: ZnO nanocrystals were synthesized and characterized by XRD and SEM methods. The luminescence spectra and decay kinetics were studied under pulsed laser excitation (266 nm, 8 ns). ZnO and ZnO:Al powders were prepared by sol-gel and plasma chemical synthesis. These powders were used as a raw material for the SPVD (Solar Physical Vapour Deposition) process. In this way, the vaporisation-condensation phenomenon (VC) led to the formation of ZnO whiskers and nanopowders. The luminescence properties of the VC nanopowders were studied and compared to those displayed by the raw material. The Al dopant, present in the raw powders as a solid solution and ZnAl₂O₄ precipitates, was only present as Al ions in the nanopowders after the SPVD. The blue luminescence intensity increased considerably after SPVD. The whiskers type microstructures showed nonlinear blue luminescence dependent on the excitation pulse density.

Introduction

ZnO is an attractive material for practical applications such as luminescent screens, varistors, lasers and optoelectronic devices. ZnO powders can be prepared by many methods (thermal oxidation of metallic zinc, sol-gel process, hydrothermal methods, plasma chemical synthesis, laser ablation, vapour condensation and others). The morphology and average size of the nanocrystal powders obtained strongly depends on the preparation method and synthesis conditions.

The luminescent method is very sensitive to the defect content, stoichiometry, impurity type and concentration, grain size and powder morphology. Therefore it is important to use X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) to study of both powders – that used for the targets as well as that obtained by SPVD process (VC) and to compare the results with the luminescence properties. The main luminescence bands were observed in the 1.8-2-4 eV spectral region (defect related luminescence) and at ~3.1-3.45 eV (excitonic states) in the ZnO crystals and the nanostructured systems at room temperature (RT). The broad luminescence peak at ~2.0 eV in 10-50 nm grain size powders was detected under high energy pulsed electron beam excitation [1]. For luminescence applications it is important to obtain material with a low defect concentration and a high level of luminescence in the blue region.

In this paper the results of investigations of the luminescence properties of sol-gel (SG), plasma (PL) raw materials and VC powders prepared by the Solar Physical Vapor Deposition method [2] from the starting raw material were described.

Experimental

Various ZnO powders were used as initial targets for the SPVD process: sol-gel (SG) and plasma (PL). The powder synthesis by PL method was described in details in [3]. Solar heat power was used for the VC process (solar flux $\sim 800 \text{ W/m}^2$). During the SPVD process the glass balloon with raw materials and the water cooled finger were placed at the focus of a solar furnace. The condensation process occur under 10 Torr air pressure. Special attention was given to the effect of Al doping on the luminescence properties. The Al doped raw material was used as a target material in the VC process. The concentration of Al in the raw material ranged between 0.8 – 5.1 at.% Al in the PL powders and 3-15 at.% Al in the SG powders.

XRD spectra were measured. The position of diffraction peaks and the peak widths were analyzed. SEM (EVO, ZEISS) images were obtained and the powder's morphology was studied. YAG:Nd laser (266 nm, 8 ns) was used for luminescence excitation. The luminescence spectra and decay kinetics were studied at RT.

Results and discussion

XRD. The PL powders were analyzed by XRD and the diffraction diagrams are shown in Fig.1a. Information was obtained about the phases present in the powders, the lattice parameters and the size of the coherent domains (called the “grain size”). The grain size of powders was deduced from the half-height width of the diffraction peaks using the Scherrer's formula. In the PL powders the ZnO phase was detected and another phase appeared. The analysis shows that this phase was ZnAl_2O_4 (Zn spinel phase). The diffraction peaks intensity of the spinel phase depended linearly on Al content (Fig.1b).

After the SPVD (vaporisation-condensation) there were no traces of the ZnAl_2O_4 phase in the XRD spectra and only a ZnO phase was detected in all Al doped VC nanopowders, possibly Al^{3+} substituting for Zn^{2+} , being in investigation.

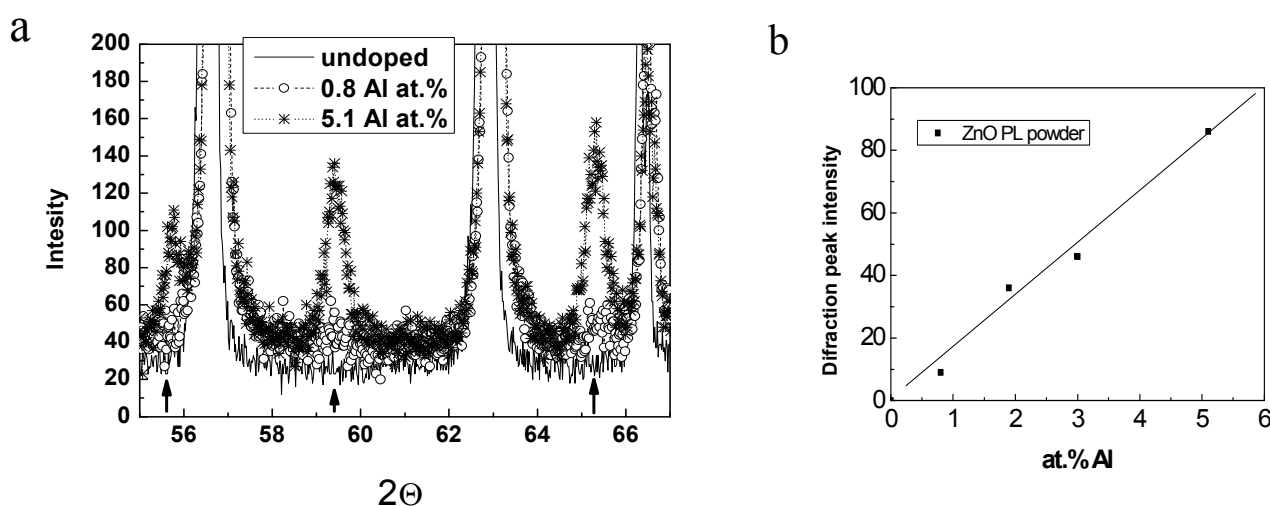


Fig.1. a - XRD diagrams of undoped and Al doped ZnO initial plasma powders (PL). The arrow marked diffraction peaks correspond to a ZnAl_2O_4 phase; b - dependence on Al content of ZnAl_2O_4 peak intensity at $2\theta = 59.5^\circ$.

The analysis of the XRD diagrams shows that the substructure “grain size” reduces after the SPVD process (VC nanopowders) : along $hkl = 100$ (or 200) and at low Al content : the grain size ranged between 60-90 nm for the initial PL powders and is between 30-50 nm after SPVD. This effect was observed up to approximately 2 at.% Al concentration.

SEM. The microstructure of the powders before and after SPVD was studied. The SEM images (Fig.2) shows the “tetra pods” type structure for the PL powders whereas the VC powders display a “whiskers” type structure (often tetrahedral arranged). The same microstructural changes were observed for the SG ZnO:Bi and ZnO:Al hydrothermal powders [4]. For these powders the morphology changed from spherical particles to whiskers $\sim 1\text{-}3\text{ }\mu\text{m}$ long and $\sim 2\text{-}20\text{ nm}$ thick.

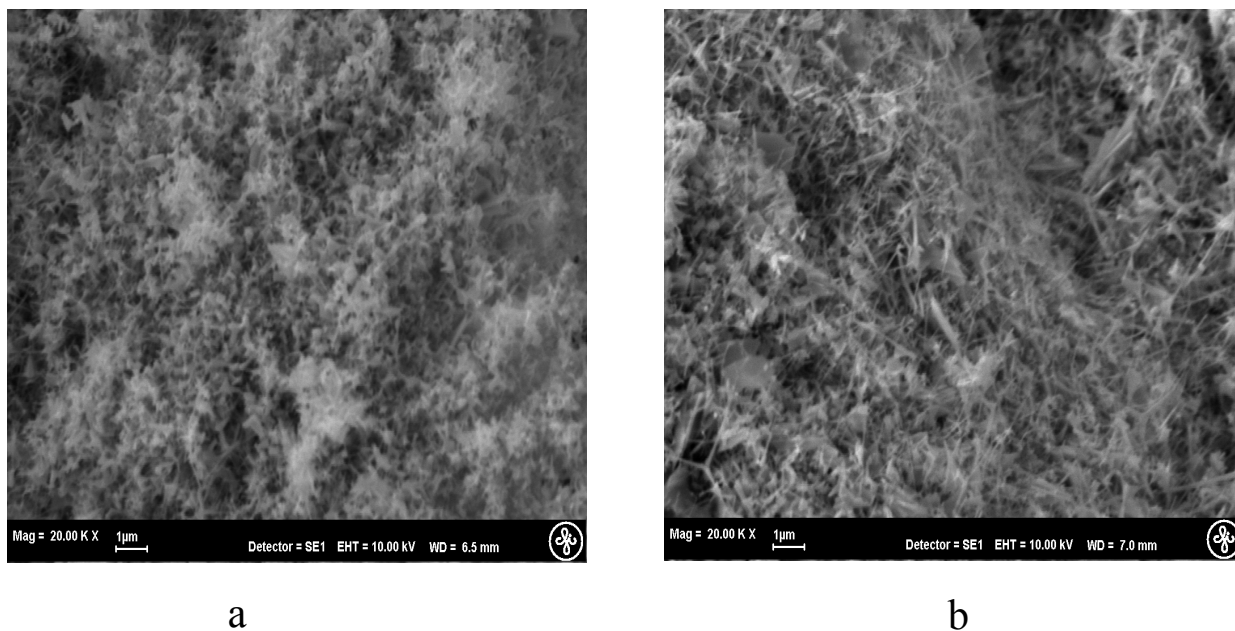


Fig.2. SEM images of ZnO:Al (5.1 at.%Al) PL powders:

(a) initial powder; (b) after the SPVD process (VC)

The whiskers are filamentary type crystals and it is well known that this kind of crystal has unique behaviour: a dislocation free structure, giving high mechanical strength, and a low concentration of native defects. This behaviour is due to a specific whiskers growth process along a dislocation. High Resolution Electron Microscopy (HRTEM) images show very characteristic and different boundaries for spherical nanoparticles and whiskers. For the spherical particles the distorted surface area is significantly larger than that in whiskers. When the whiskers thickness is smaller than 10 nm, quantum effects are expected. The thickness of ZnO whiskers observed by HRTEM images is close to 2 nm.

Luminescence. The typical luminescence spectra at RT of nanopowders consists of three bands - the wide composite exciton type band and two defect bands in the yellow-red (1.8-2.0 eV) and green (2.45 eV) spectral region. The exciton band decays within some hundred picoseconds whereas the defect bands decay time is in microseconds.

The spectrum of undoped PL powders shows the yellow-green and blue luminescence, whereas the green luminescence band and blue luminescence was observed for the nanopowders prepared by VC. The same defect band evolution was observed for undoped ZnO and all Al doped samples (Fig.3). Moreover, the yellow band disappearance and the green band growth were observed in SG powders after SPVD. Another very important effect was observed after VC for ZnO:Al powders:

the intensity of the blue luminescence increased. The result of the blue luminescence testing is shown in Fig.4. The effect of excitonic luminescence quenching with Al content in PL samples is due to the Zn spinel phase mentioned above.

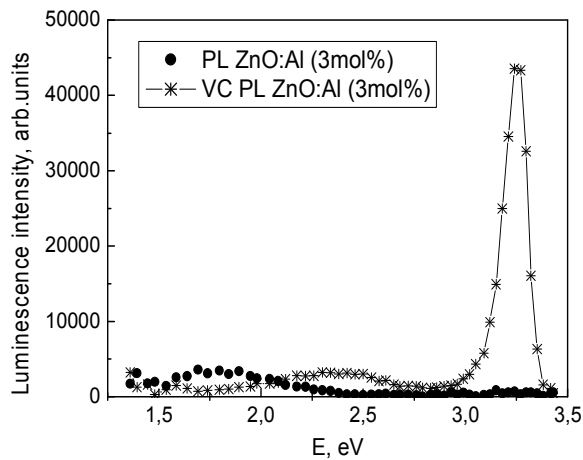


Fig.3. Luminescence spectra for ZnO:Al powders before and after the SPVD process

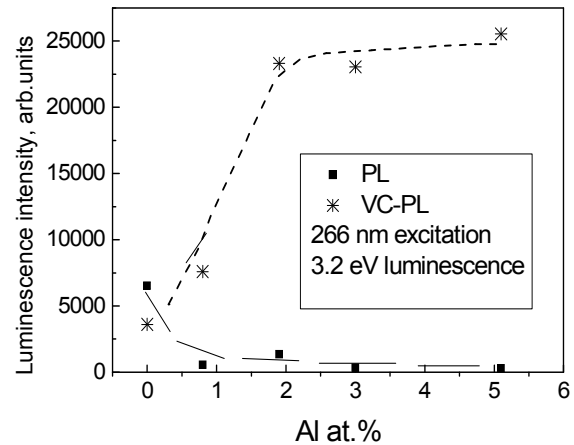


Fig.4. The blue luminescence dependence on Al concentration

The luminescence of Al doped SG powders increased with the Al content of the yellow, the green and the blue luminescence intensities (Fig.5). After VC the yellow-red luminescence disappears and the main luminescence band is blue. In the VC SG samples the intensity of blue luminescence exceeds by twenty times the intensity of the green luminescence. The blue luminescence band was also dominant in nanopowders obtained by the SPVD process from PL powders. Thus the blue band intensity has been enhanced by the SPVD independent of the raw material (PL or SG) used.

It is known that under band-to-band excitation the electron-hole pairs were created. During relaxation process the carriers have been captured at defect states or create excitons. The excitons transfer the excitation to defect states since the excitons are mobile. The concept that the efficiency of the energy transfer process in ZnO does not depend on defect concentration and that the creation of defect excited states is proportional to defect concentration is supported. So, two competitive process occur under excitation: excitation of the defect state (defect luminescence) and the creation and annihilation of the excitons. It was observed the increase of blue luminescence - under excitation of the excitons annihilation (blue luminescence) is more effective than the defect state luminescence. The green luminescence (2.45 eV) is caused by the radiative recombination of holes with a singly ionized oxygen vacancy [5] and it is well known for ZnO:Zn samples. These experimental results demonstrate directly that the concentration of defect states is considerably smaller if VC samples are compared with PL or SG samples. The reason for the observed effects is in the whiskers growth process. Whiskers correspond to filaments and it is known that the concentration of dislocation, native and boundary defects is very low in such crystals. In summary, for the VC powders whiskers structure with a low defect concentration was produced and the luminescence due to excitonic states dominated in these samples.

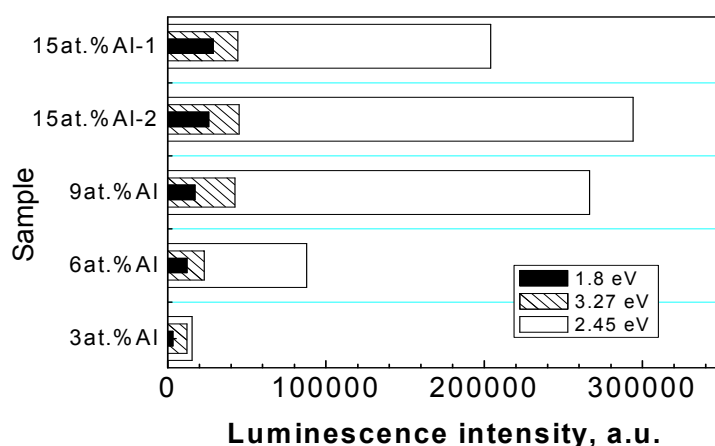


Fig.5. The luminescence band intensities for SG ZnO:Al powders

ZnO has been investigated as a material for blue-light emitting displays and laser diodes. UV lasing in ZnO epitaxially grown films [6] and nanowires [7] was recently reported. The lasing effect is not clear to date; the difference in the threshold intensities has been estimated for samples with different film thickness or morphology. It is clear that the lasing was observed from the different type of excitons in ZnO. The processes under high density excitation for nanostructure systems are poorly investigated and only a few studies have been devoted to the excitonic properties in ZnO [8]. The luminescence intensity versus excitation density was studied for VC and SG powders are shown in Fig.6a and b.

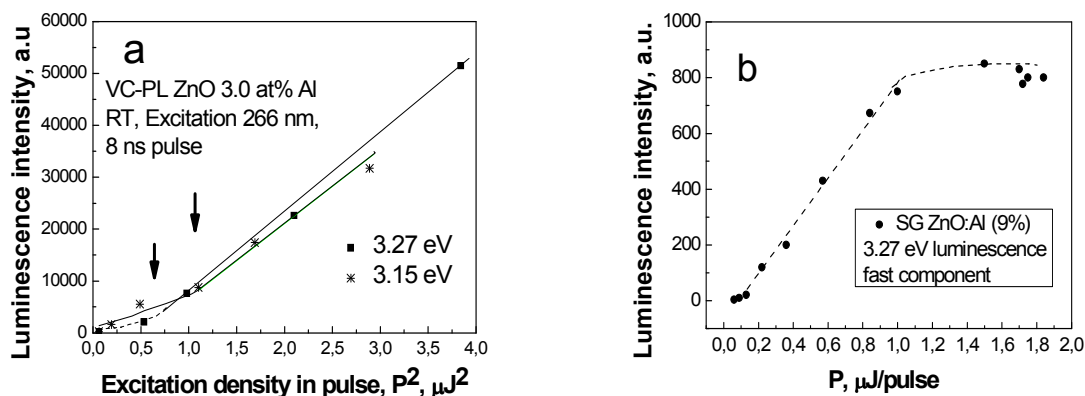


Fig.6. Luminescence intensity dependence on excitation pulse density: a – quadratic dependence for VC samples (arrow shows the threshold from linear to superlinear behavior), b – linear dependence with saturation for SG sample.

It was found that for VC powders the superlinear intensity growth was observed, whereas for SG powders the linear dependence with saturation at high density excitation was detected. The SG powders were doped with Al and the additional near-edge luminescence due to donor-acceptor luminescence is known. These aspects clarify the observed luminescence intensity linearity and saturation with excitation density.

The increase of luminescence proportional to the square of the excitation density for the VC samples was suggested as being due to exciton molecule creation. The different exciton states were

involved and the different threshold was observed (Fig. 6a). The efficiency of excitonic molecule creation is high in nanostructures – the creation of two close (within a short distance) excitons is more probably. From this point of view the whiskers structure is successful for excitonic molecule observation. The role of the confinement effect to exciton creation and annihilation is under investigation.

Summary

ZnO and ZnO:Al nanopowders with different morphologies were studied. In VC samples the Al concentration is lower than in raw material and the incorporation efficiency depends on the SPVD conditions, oxygen partial pressure and solar flux, and it is very important to control the Al content in the raw SG and PL powders and in the VC powders. In PL ZnO:Al powders the ZnAl_2O_4 phase was detected. ZnAl_2O_4 phase powders were not detected in the nanopowders obtained by the SPVD process (VC). The morphology of nanopowders was changed by the SPVD process – whiskers microstructure was detected by means of the SEM and TEM techniques. The luminescence band due to defects changes from the yellow-red to the green spectral range after VC. The main luminescence band in VC nanopowders is in the blue (excitonic) spectral region. The blue luminescence intensity increases with Al concentration. A superlinear blue luminescence intensity dependence on the luminescence excitation density was observed in VC powders.

Acknowledgements

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References

- [1] D.Millers, L.Grigorjeva, W.Lojkowski, T.Strachowski: Radiation Measurements Vol.38 (2004), p. 589
- [2] B.Martinez, F.Sandiumenge, L.I. Balcells, J.Arbiol, F.Sibieude, C.Monty: Phys.Rev.B Vol.72 (2005), p.165202
- [3] J.Grabis, Dz.Jankovica, M.Berzins, L.Chera, I.Zalite: J.European Ceramic Society Vol.24 (2004), p.179
- [4] R.R.Piticescu, R.M.Piticescu, C.J.Monty: J. of the European Ceramic Society Vol.26 (2006), p. 2979
- [5] K.Vanheusden, W.L.Warren, C.H.Seager, D.R.Tallant, J.A.Voigt, B.E.Ganade: J.Appl.Phys. Vol.79 (1996), p.7983
- [6] S.W.Jung, W.I.Par, H.D.Cheong, Gyu-Chul Yi, Hyun M.Jang, S.Hong, T.Joo: Appl.Phys.Lett. Vol.80 (2002), p.1924
- [7] M.H.Huang, S.Mao, H.Feick, H.Yan, Y.Wu, H.Kind, E.Weber, R.Russo, P.Yang: Science Vol.292 (2001), p.1897
- [8] Y.M.Lu, H.W.Liang, D.Z.Shen, Z.Z.Zhang, J.Y.Zhang, D.X.Zhao, Y.C.Liu, X.W.Fan: Journal of Luminescence Vol.119-120 (2006), p.228.