Photoluminescence in Gas of Ca (Mg) -doped ZnO Nanopowders

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Abstract

ZnO is a wide-band semiconductor (E_g~3.4 eV), has a high exciton binding energy has considerable resistance to irradiation and weathering, this makes it an interesting and promising material for use in micro-, nano-, optoelectronics and gas sensors. Investigation the peculiarities of photoluminescence in different ambient of Ca and Mg doped ZnO nanopowders was carried out. The decomposition of luminescence spectra into elementary bands shows the presence of four elementary peaks. The most intense two bands in visible region which are sensitive to ambient gas, a blue-band centered at 430 nm and stronger in intensity the band around 520 nm. The influence of the impurity and the different ambient on the redistribution of elementary luminescence bands intensities was investigated. that can be used in the gas sensors [1]. The visible emissions observed may be ascribed to the intrinsic defects and oxygen vacancies. Large surface area and surface defects are the most important variables to determine the sensory properties of ZnO nanopowders and making them are the most favorable material for gas sensors.

Experimental Details

The nanopowders were obtained using pulsed laser reactive technology [2] by means of a neodymium-doped yttrium aluminium garnet (Nd:YAG) laser (λ=1.06 μm, $\tau=10^{-7}\div10^{-5}$ s, $q=10^{6}\div5\cdot10^{7}$ W/cm^2, n=14-56 Hz, d=5 mm, E_i=0.005-0.350 J). Doping was carried out by pulsed laser deposition of a thin film of impurity on nanopowders surface with further activation by laser annealing [3]. The XRD and SEM methods were used for structural and morphological characterization of obtained materials. Photoluminescence studies were performed out at room temperature at the installation using a dual monochromator DMR-4. Excitation of photoluminescence was carried out using a UV LED (λ_{max}=365 nm). The test samples were placed in a quartz cell connected to a VUP-5M vacuum unit and a multichannel SNA-2 gas inlet system, which allowed us to conduct photoluminescent studies in different gas environments at a given pressure. Signal registration was carried out using a photomultiplier FEU-27. Spectrum recording and normalization were performed automatically using specially designed software. The spectra obtained were decomposed into Gaussians using the Origin software package.

Photoluminescence in Gas Doped ZnO Nanopowders

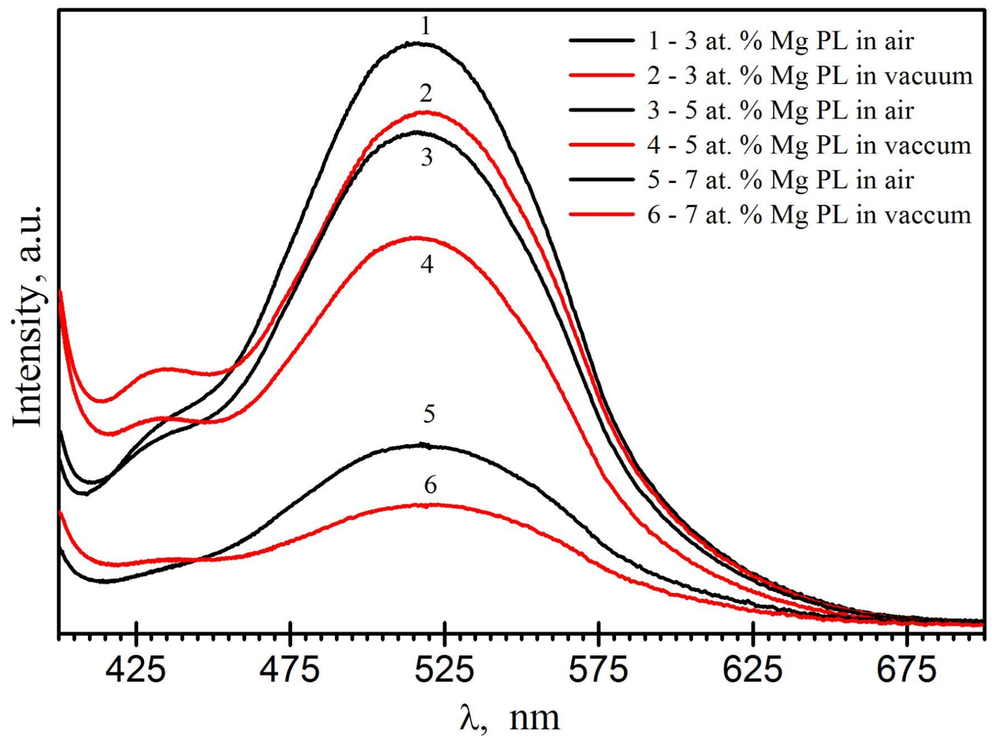

Fig 1. Photoluminescent spectra in air and vacuum (10 Pa) of *ZnO:Mg* nanopowders.

X-ray diffractometry, scanning and transmission electron microscopy investigation were conducted to determine the structure, shape, and size of the nanoparticles. The X-ray diffraction patterns have peaks characteristic of the hexagonal wurtzite structure, peaks corresponding to other oxides or compounds were not detected. Fig.1 shows the room temperature PL spectra of ZnO nanoparticles doped by different Mg concentration. The conducted decomposition showed the presence in the photoluminescence spectra of ZnO nanopowder four luminescence bands with maxima of 430, 480, 520 and 555 nm. Studies have shown an increase the concentration of Mg leads to an decrease the emission intensity. Changing the ambient leads to a significant change in the intensity of the PL spectra and its deformation, that can be used in the gas sensors [1]. The emission band in the region from 410 to 440 nm (λ_{max}~430 nm) is the most sensitive to the ambient atmosphere and may be caused by electron transitions from the Zn_i energy level, located at 0.22 eV below the conduction band, to the valence band.

Fig.2 shows the photoluminescence spectra of Ca-doped ZnO nanopowders in air and vacuum. The nature of the photoluminescence of ZnO:Ca is similar to ZnO:Mg. However, with increasing Ca concentration, there is a increase the integral luminescence intensity. Studies have shown an increase the concentration of Ca up to 5% leads to an increase the emission intensity, with a further increase the concentration up to 7% there is a decrease the intensity. Emission (λ_{max}~520 nm) is associated with oxygen defects such as interstitials (O_i) and vacancies (V_O). The large number of defects and models proposed in the literature illustrates the differences regarding the origin of this emission band. For this peak the intensity in air is greater than the intensity in vacuum, this can be explained by the fact that excess oxygen is adsorbed on the surface, while oxygen is lacking deficient in vacuum.

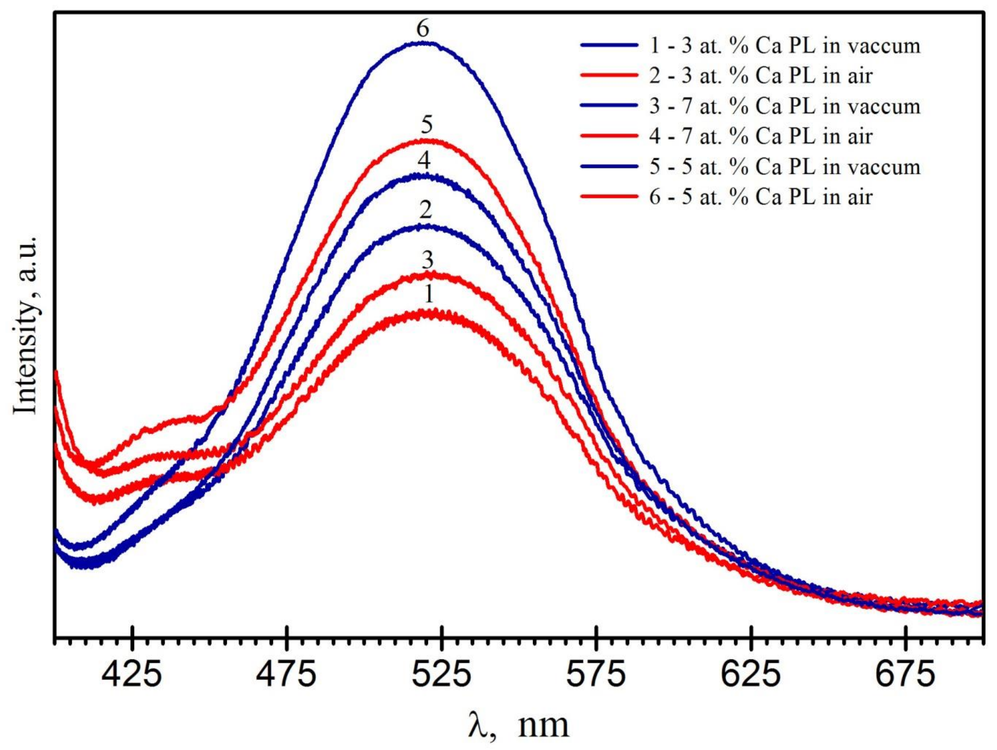

Fig 2. Photoluminescent spectra in air and vacuum (10 Pa) of *ZnO:Ca* nanopowders.

Conclusion

Have been studied the peculiarities of photoluminescence in different ambient Mg and Ca doped ZnO nanopowders. The decomposition of luminescence spectra into elementary bands shows the presence of four elementary peaks of 430, 480, 520 and 555 nm. The influence of the impurity on the redistribution of elementary luminescence bands was investigated. Changing the ambient leads to a significant change in the intensity of the photoluminescence spectra and its deformation. Obviously, this is a result of the redistribution of existing luminescence centers and the emergence of new luminescence adsorption centers on the nanopowders surface. The investigated nanopowders can be effectively used as sensitive materials for the construction of gas sensor systems.

Reference

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2. Gafiychuk V.V., Ostafiychuk B.K., Popovych D.I., Popovych I.D., Serednytski A.S. *ZnO nanoparticles produced by reactive laser ablation* // Applied Surface Science -2011. -257(20). -P.8396–8401.