LUMINESCENT PROPERTIES OF LOW-DIMENSIONAL ZnO:Ag POWDERS OBTAINED BY CHEMICAL DEPOSITION FROM AQUEOUS SOLUTION

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Abstract

Photoluminescence (PL) spectra of ZnO:Ag highly dispersed powders obtained by chemical deposition from aqueous solution are investigated in the wavelength range between 360 and 750 nm at room temperature under excitation between 250 and 350 nm. Before starting the synthesis, the Ag dopant was introduced into the initial solution in the form of $AgNO_3$ silver nitrate in the amount of 12, 102, and 252 mg. The PL spectra consist of an ultraviolet emission (380 nm) attributed to Ag_{Zn} acceptor-bound exciton, a short-wavelength violet emission (400 – 450 nm) and a wide long-wavelength yellow-orange emission (560 – 600 nm). With decreasing excitation energy, the violet emission decreases in intensity, while the yellow-orange emission increases. This is caused by the phenomenon of self-absorption of the short-wavelength emission and energy transmission to the centers of the long-wavelength emission. A rapid decrease in intensity of all the PL bands is found for the sample with maximum Ag concentration. This fact is due to the appearance of the second phase in the form of silver oxide and, consequently, a decrease in the concentration of Ag_{Zn} point defects responsible for the bands.

Keywords: ZnO, highly dispersed powders, photoluminescence, self-absorption, Ag impurity.

Rezumat

În intervalul de lungimi de undă între 360 și 750 nm, la temperatura camerei, prin excitare cu o radiație din regiunea (250 – 350) nm, sunt investigate spectrele de fotoluminescență (FL) a nanopulberilor de ZnO:Ag obținute prin metoda de depunere chimică din soluția acvatică. Impuritatea de Ag a fost introdusă în soluția inițială sub formă de azotat de argint $AgNO_3$ în cantitate de 12, 102 și 252 mg. Spectrele de PL conțin benzile de emisie ultravioletă (380 nm), atribuită excitonului legat de acceptor de Ag_{Zn}, emisie violetă (400 – 450 nm) și emisie galbenă-oranjă (560 – 600 nm). Odată cu scăderea energiei de excitare, intensitatea emisiei violete descrește, în timp ce intensitatea emisiei galbene-oranje crește. Acest fapt este cauzat de

fenomenul de autoabsorbție a emisiei din regiunea undelor scurte și transmitere de energie către centrele de emisie din regiunea undelor lungi. O descreștere rapidă a intensității tuturor benzilor de PL se observă pentru proba cu concentrația maximă de Ag. Acest fapt este stiplulat de apariția celei de-a două faze sub formă de oxid de argint și, ca rezultat, de scăderea concentrației defectelor punctiforme de Ag_{Zn} responsabile de aceste benzi.

Cuvinte cheie: ZnO, nanopulberi, fotoluminescența, autoabsorbție, impuritate de Ag.

1. Introduction

Wide band-gap ZnO semiconductor (E_g(300K) = 3.37 eV) is of great interest both for investigation of radiative properties and applications in optoelectronics and solar energy [1]. Being optically transparent in a wide wavelength range, zinc oxide is used for high-performance light-emitting devices operating in the ultraviolet (UV) and blue regions of the spectrum, UV filters, solar cells, thin-film transistors, sensor devices, etc. [1-3].

It is well known that PL spectra of ZnO samples consist of near-band-edge emission at (370 – 390 nm), violet emission at (396 – 410 nm), and three wide bands of visible emission: "green" (500 – 530 nm), "yellow-orange" (590 – 620 nm) and "red" (700 – 780 nm) [4]. The predominance of one or another PL bands essentially depends on the impurity-defect composition of the samples.

PL study of ZnO thin films obtained by magnetron sputtering and doped with the group I acceptor impurities (Cu, Ag, and Au) has showed the predominance of the "green" emission attributed to donor-acceptor (DA) pairs with intrinsic oxygen vacancies as the donors and introduced doping impurities as the acceptors [5]. At the same time, after oxygen enrichment during the growth and impurity doping of ZnO:Cu and ZnO:Ag films by electron-beam deposition, PL spectra consist of near-band-edge and exciton emission lines in the violet spectral region [6]. Introduction of dopants into zinc oxide nanocrystals allows modifying the functional properties of ZnO, thereby expanding their applications [7–9].

In the present paper, the evolution of PL spectra of low-dimensional ZnO:Ag powders with increasing dopant concentration and excitation wavelength is analyzed.

2. Experimental techniques

Highly dispersed zinc oxide powders were synthesized by chemical deposition from aqueous solution. The solutions of 0.05M zinc nitrate hexahydrate and urotropine (hexamethylenetetramine, HMTA) in a molar ratio of 1:1 were used as the main components of the synthesis. ZnO is formed in the solution that contains zinc nitrate as a Zn^{2+} precursor and urotropine due to the following chemical reactions between $Zn(NO_3)_2$ and HMTA [10]:

$$(CH_2)_6N_4 + 6\ H_2O \leftrightarrow 6\ HCHO + 4\ NH_3 \quad (1)$$

$$NH_3 + H_2O \leftrightarrow NH_4 + OH^- \quad (2)$$

$$2\ OH^- + Zn^{2+} \rightarrow ZnO + H_2O \quad (3)$$

Hydroxide ions appearing during the decomposition of HMTA react with Zn^{2+} and form zinc oxide.

The doping impurity of Ag was introduced into the solution before the synthesis in the

form of a salt of nitric acid ($AgNO_3$) in the amount of 12, 102, and 252 mg. Chemical deposition of zinc oxide was carried out with continuous stirring using a magnetic stirrer in a two-stage heating mode. At the first stage, the temperature of the reaction mixture reached (48 – 50) °C, the duration was 1 hour. At the second stage, the temperature was increased to (78 – 80) °C, and, under these conditions, the synthesis continued for 2 hours. After completing the synthesis, a sediment of zinc oxide settled at the bottom of reaction cell was cooled, washed many times in a distilled water, and dried. The obtained powders were gray in color and the color intensity increased with increasing Ag concentration in the powder.

PL spectra and PL excitation spectra of ZnO:Ag powders were measured at room temperature between 360 and 750 nm under excitation with UV radiation between 250 and 350 nm. The spectra were registered using a standard synchronous detection system with Fluorolog-3 (HORIBA) fluorospectrometer. A xenon lamp of 500 W was used as an excitation source. A two-monochromator system was used for the lamp radiation decomposition into individual wavelengths and registration of emission spectra of the samples. PL spectra were recorded in an automatic mode at every 10 nm of the excitation radiation wavelength.

3. Experimental results and discussion

Fig. 1 shows the evolution of PL spectra with excitation radiation wavelength for ZnO:Ag samples with various concentrations of Ag. The spectra consist of two bands in the short-wavelength (400 – 450 nm) and long-wavelength (560 – 600 nm) regions.

The short-wavelength violet emission in the range between 390 nm (3.179 eV) and 420 nm (2.952 eV) was previously observed at room temperature in the spectra for ZnO thin layers grown under an excess of oxygen, regardless of the growth method [11-17]. The nature of emission centers and mechanism of violet emission were analyzed in detail in [4]. The violet PL band in the spectra for ZnO crystals and thin films was attributed to the recombination of non-equilibrium charge carriers within DA pairs. The defects, such as the group III elements as substitutional defects (Al_{Zn}, Ga_{Zn}, In_{Zn}) and Li_i, Zn_i interstitial atoms, may be the donors. Zinc vacancies (V_{Zn}) or ($Al_{Zn}V_{Zn,}$), ($Ga_{Zn}V_{Zn}$), ($In_{Zn}V_{Zn}$) associates may be the acceptors [12]. In our ZnO:Ag nanopowders, the Ag_{Zn} point substitutional defects may be the acceptors. It was previously established [6] that the monovalent silver atoms were incorporated into ZnO in the form of Ag_{Zn} substitutional defects with $3d^{10}$ electron configuration.

The long-wavelength yellow-orange emission is due to Li and Na background impurities, which take part in the formation of DA pairs [18]. Transitions of electrons to these centers from the conduction band or shallow donors localized close to these centers are responsible for the PL bands at 575 nm (2.157 eV) (Na-DA pairs) and 615 nm (2.016 eV) (Li-DA pairs) [18, 19]. However, in later works [20-23], the yellow-orange emission in PL spectra of low-dimensional ZnO was attributed to interstitial oxygen atoms or oxygen-based complexes. The authors note that this PL band is more often observed for zinc oxide grown from an aqueous solution at relatively low temperatures and, therefore, enriched with oxygen, which corresponds to our case.

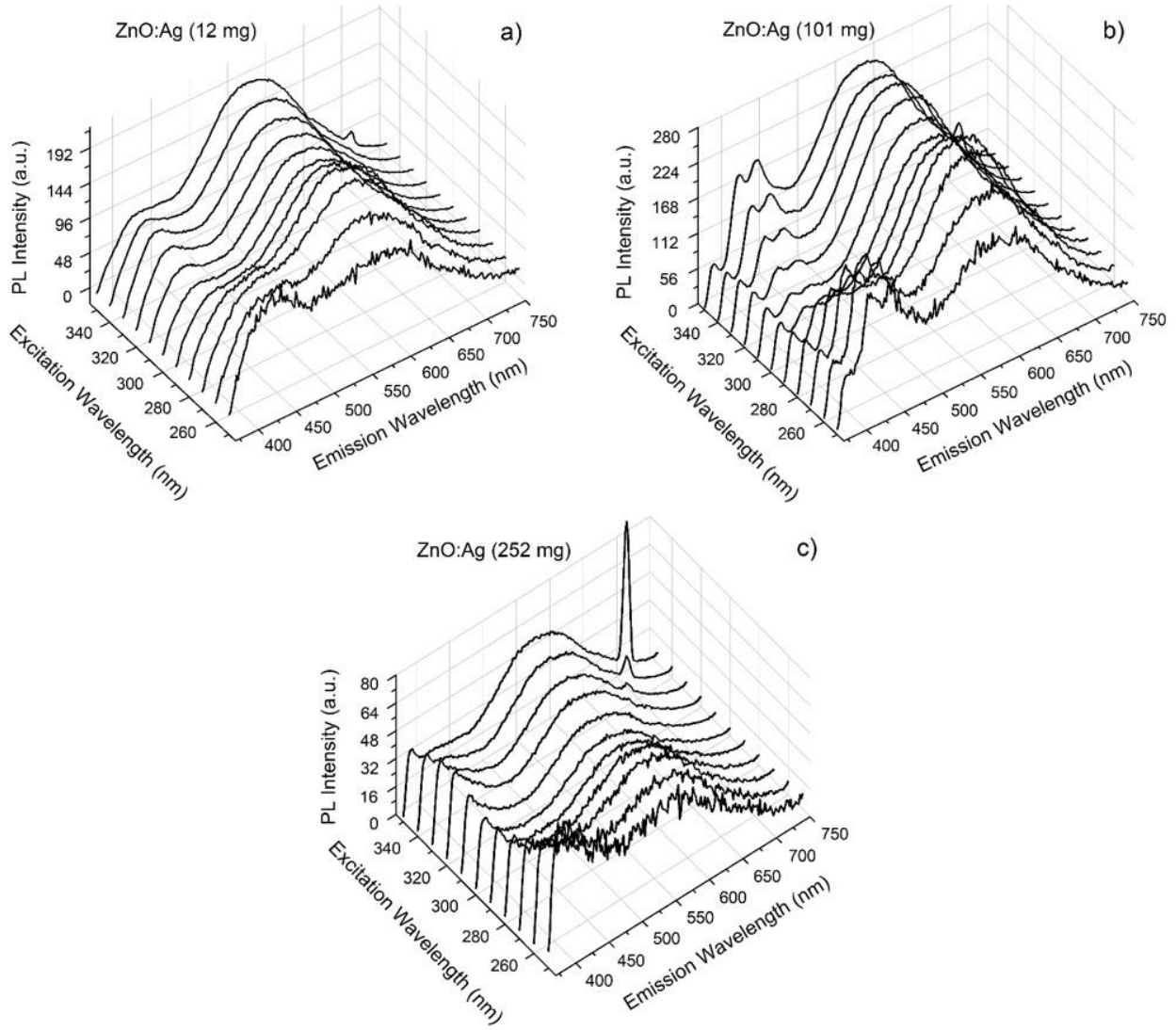


Fig. 1. PL spectra of ZnO:Ag powders with Ag content in aqueous solution of 12 mg (a), 102 mg (b), 252 mg (c). λ_{exc} = (250 – 350) nm. T = 300 K.

It is worth to note that the intensity ratio at the maximum of the long-wavelength emission to that of the short-wavelength one depends on the excitation radiation energy (Fig. 2). At high excitation radiation energy, the short-wavelength emission is predominant in intensity (Fig. 2 a), while at lower excitation radiation energy, the long-wavelength emission becomes predominant (Fig. 2 b). This modification is due to a self-absorption effect that was observed in thin ZnO films [12]. With decreasing excitation radiation energy, generation of quanta of the short-wavelength emission occurs at higher depth of the sample. As a result, the energy of this emission is partially absorbed in the material, and the centers of the long-wavelength emission are excited.

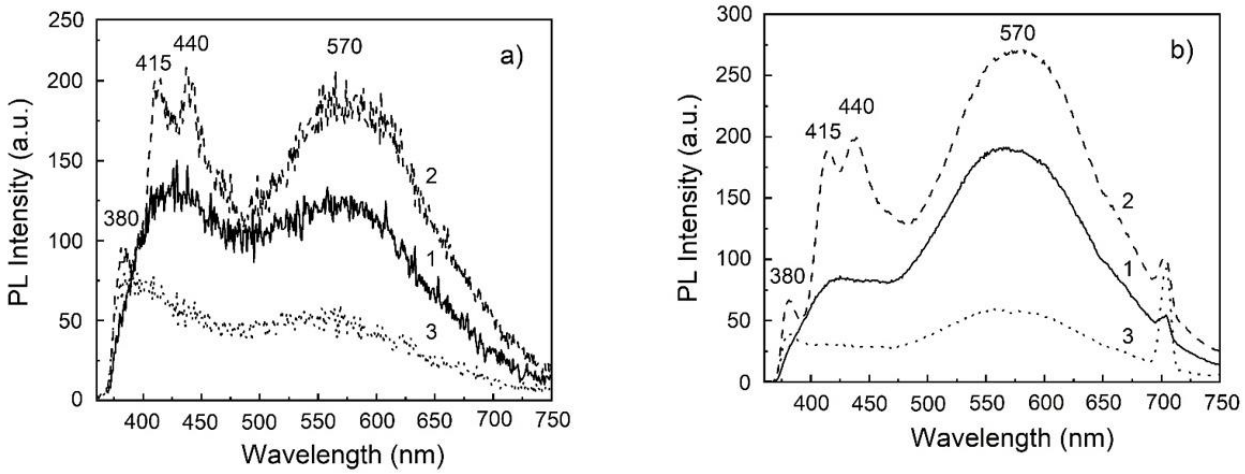


Fig. 2. PL spectra of ZnO:Ag powders under excitation radiation wavelength of 250 nm (a) and 350 nm (b). Ag content in aqueous solution, mg: 1 – 12; 2 – 102; 3 – 252. T = 300 K.

In addition to these PL bands, the short-wavelength band of exciton emission is observed at 380 nm (3.263 eV) in the PL spectrum of ZnO:Ag sample with medium doping level (102 mg Ag) (Fig. 2, curve 2). Increasing doping concentration decreases this PL band intensity (Fig. 2, curve 3). For the sample with minimum doping impurity concentration (12 mg Ag), this PL band is absent both at low and high excitation radiation energy (Fig. 2, curve 1). The spectral position of the exciton PL band is in good agreement with localization of (A^0X) acceptor-bound exciton (ABE) PL band at 381 nm (3.255 eV) at room temperature that was observed earlier for ZnO nanocrystals [24]. According to the empirical Haynes rule [25], the ionization energy of Ag_{Zn} acceptor, which is responsible for this ABE, is equal to:

$$\Delta E_A\left(Ag_{Zn}\right) = 10 \cdot \left(3.293 - 3.263\right) \text{ eV} = 0.300 \text{ eV}, \quad (4)$$

where 3.293 eV is the energy of free exciton emission in ZnO at 300 K [24], 3.263 eV is the energy of ABE emission at 300 K (Fig. 2). The value of 0.20 eV as the ionization energy of Ag_{Zn} acceptor is reported in [6] for ZnO:Ag thin films.

The structure of PL spectra of ZnO:Ag powders is slightly changed, mainly in the short-wavelength range, with increasing doping impurity concentration (Fig. 2). As Ag concentration increases, intensity of all the PL bands first increases and then decreases. A similar behavior for ZnO:Ag thin films was explained by the appearance of the second phase in the form of silver oxide at high concentration of Ag impurity [6]. A higher value of ionic radius for Ag (0.113 nm) relative to that for Zn^{2+} (0.083 nm) [26] induces a lattice strain during the doping process, and this strain is compensated by the second phase appearance. As a result, the concentration of Ag_{Zn} point defects decreases, and the PL intensity decreases too (Fig. 2).

Fig. 3 shows PL excitation spectra for the short-wavelength violet emission (380 nm) (Fig. 3 a) and long-wavelength yellow-orange emission (570 nm) (Fig. 3 b) for ZnO:Ag samples with various concentrations of doping impurity. Spectral position of the maxima of PL and PL excitation spectra is shown in Table 1.

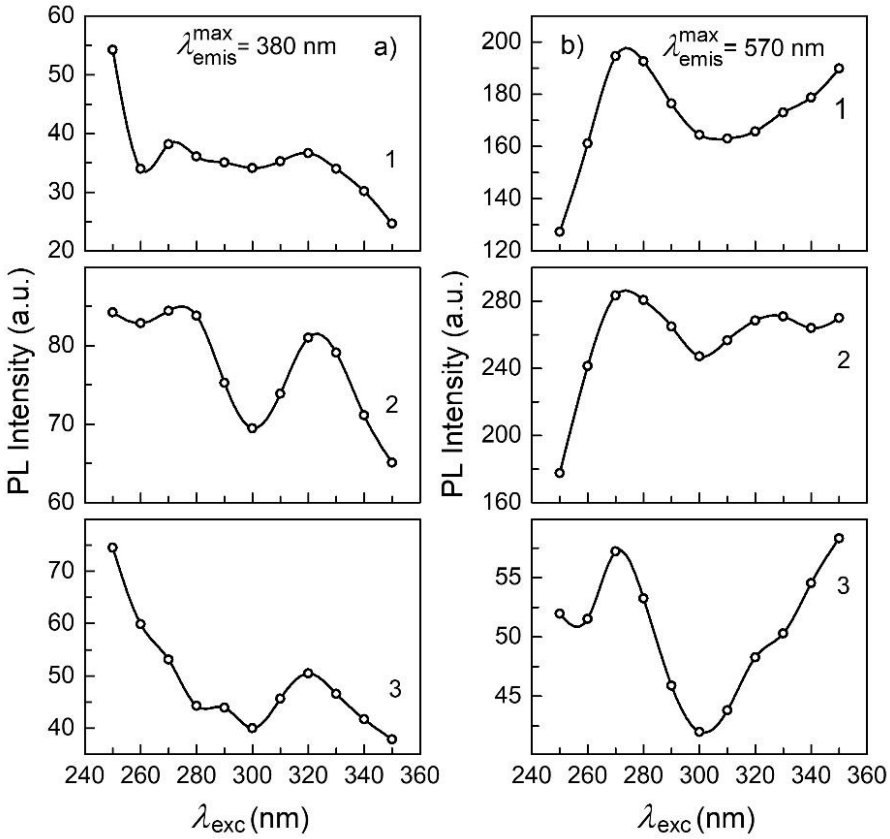


Fig. 3. PL excitation spectra for the short-wavelength violet emission (a) and long-wavelength yellow-orange emission (b). Ag content in aqueous solution, mg: 1 – 12; 2 – 102; 3 – 252. T = 300 K. Lines are guide to the eye.

Table 1

Maxima for PL and PL excitation spectra of ZnO:Ag nanopowders

	Ag content in aqueous solution, mg		
	12	102	252
λ_{emis}^{max}, nm	λ_{exc}^{max}, nm		
380	272 320	275 323	290 320
415	270 330	260	323
440	270 337	260	320 340
570	274 330	274 328	272 320

With increasing excitation radiation wavelength above 320 nm, the exciton PL band (380 nm) decreases in intensity (Fig. 3 a), while the impurity PL band (570 nm) increases (Fig. 3 b). For the short-wavelength emission, a maximum of low intensity is observed at 290 nm for the sample with maximum Ag content (252 mg) (Fig. 3 a, curve 3). This maximum is probably stipulated by the appearance of the second phase in the form of silver oxide, as it was mentioned above. For the long-wavelength emission, this maximum is not observed (Fig. 3 b, curve 3), since Ag impurity, apparently, is not a part of the luminescence center responsible for this emission (570 nm). A lack of pronounced maximum at (270-275) nm in the excitation spectrum of exciton emission (Fig. 3 a, curve 3) is also the evidence of structural modifications caused by the appearance of the second phase in ZnO:Ag powders with maximum Ag concentration.

5. Conclusions

The synthesis of ZnO low-dimensional powders by chemical deposition from aqueous solution accompanied by Ag impurity doping is realized in this work. A series of ZnO:Ag powders with various concentrations of doping impurity is obtained. It is found that monovalent silver atoms introducing into ZnO as Ag_{Zn} substitutional defects of acceptor type with the ionization energy of ~ 300 meV form emission centers, and namely, acceptor-bound excitons and donor-acceptor pairs, which are responsible for the ultraviolet (380 nm) and violet (415-440 nm) emissions respectively.

All the observed PL bands are decreased in intensity for the sample with maximum Ag concentration (252 mg in initial aqueous solution). This fact is due to the appearance of the second phase in the form of silver oxide and, as a result, a decrease in the concentration of Ag_{Zn} point defects responsible for the bands. It is shown that, with increasing excitation radiation wavelength, the violet emission decreases in intensity, while the yellow-orange emission (570 nm) increases. This behavior is caused by the phenomenon of self-absorption of the short-wavelength emission and energy transmission to the centers of the long-wavelength emission.

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