

Influence of Substrate Temperature and Magnesium Content on Morphology Evolution and Luminescence of Mg-doped ZnO Films

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Results of studies by scanning electron microscopy and photoluminescence (PL) of structural features and radiative transitions of ZnO:Mg films grown by atmospheric pressure metal-organic chemical vapor deposition (APMOCVD) on silicon substrates are presented. Different ZnO:Mg microstructures from polycrystalline films with smooth morphology to columns and hexagonal rods are effectively formed in a wide temperature range 190-450 °C using two compositions of a mixture of zinc and magnesium (5 and 10 wt. %) acetylacetonates (ZnAA and MgAA, respectively) as precursors. The substrate temperatures have a drastic effect on the crystallinity and morphology of ZnO films. A column shaped ZnO microstructure is formed at a substrate temperature above 350 °C. The MgAA content in the mixture of precursors also affects the morphology of polycrystalline films. At lower substrate temperatures (200-320 °C), grown ZnO:Mg samples with MgAA content of 10 wt. % have a surface morphology characterized by enlarged grains compared to samples grown with MgAA 5 wt. %, whereas high substrate temperatures (350-450 °C) promote to form a surface morphology with rod-like structures in both cases: 5 and 10 wt. % of MgAA content. The growth rate of ZnO structures increases with increasing substrate temperatures. The PL emission spectra of samples with 10 wt. % MgAA demonstrate increased near band edge (NBE) emission and suppress defect level emission compared to samples with 5 wt. % MgAA. Therefore, we can conclude that magnesium acts as an isoelectronic impurity improving NBE PL emission due to gettering of defects. Mg also causes an increase in grain size, improving the crystalline perfection of ZnO:Mg polycrystalline films grown at low substrate temperatures, as well as helps to grow hexagonal rods at higher substrate temperatures. Thus, Mg-doped ZnO microstructures grown in the high temperature range could be an effective photocatalyst.

Keywords: Atmospheric pressure metalorganic chemical vapor deposition, Zinc acetylacetonate, Magnesium acetylacetonate, Scanning electron microscope, Photoluminescence.

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1. INTRODUCTION

Zinc oxide has a band gap of 3.37 eV at room temperature (RT), which makes it one of the most interesting candidate materials for optoelectronic devices in the ultraviolet (UV) region [1]. The large exciton binding energy of about 60 meV provides pronounced excitonic effects in the emission and absorption spectra up to RT [2]. Due to its physical properties, wide band gap zinc oxide is a promising photocatalytic material that may become a cheap alternative to existing photocatalysts based on TiO₂ for the degradation of organic pollutants in the future [3]. On the other hand, the key point of semiconductor devices is to design heterostructures that can provide the development of high electron mobility transistors and light emission diodes. It is critical to have band gap engineering in order to realize a device-based material [4]. Band gap engineering of ZnO can be realized by alloying with MgO and CdO. Theoretically, the band gap of MgZnO ternary alloys can vary from 3.37 eV (ZnO) to 7.8 eV (MgO) [5]. Nonetheless, a high MgO content leads to phase separation. For a moderate content of MgO, the alloy keeps the wurtzite crystal structure of ZnO, providing a wide range of direct band gap engineering ranging from 3.37 to 4.0 eV [6]. In addition, the exciton binding energy increases in ZnMgO/ZnO/ZnMgO quantum wells due to an increase in carrier confinement [7], thus making this heterostructure suitable for fabricating electronic LED devices.

Many techniques can be used for the preparation of ZnO films, such as molecular beam epitaxy [8], pulse laser deposition [6, 9], direct current [10] and radio frequency magnetron sputtering [11], hydrothermal [12], chemical bath deposition [13], sol-gel spin coating [14], spray pyrolysis [15] and metal organic vapor phase epitaxy (MOCVD) [16-18]. The last one allows to change the deposition parameters, respectively, to control the growth rate and morphology of ZnO structures, and to influence the photocatalytic activity [16]. The advantage of this method is the possibility to deposit coatings on large surfaces, a high deposition rate with the ability to control atomic composition for mass production. The authors of [16] discovered the formation of nanostructures with multilayer tower and rod-shaped configurations at a substrate temperature in the range from 300 to 475 °C. However, they provided information only for pure ZnO.

In this work, we present the possibilities of obtaining ZnO:Mg structures with different shapes and dimensions by means of modified MOCVD method called APMOCVD, i.e., atmospheric pressure MOCVD. By changing the temperature and composition of Zn and Mg precursors, we study the evaluation of morphology and photoluminescence behavior of ZnO:Mg structures grown by APMOCVD.

2. EXPERIMENTAL DETAILS

Mg-doped ZnO films were deposited by APMOCVD

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on silicon substrates in 190-450 °C temperature range using the mixture of zinc and magnesium acetylacetonates (ZnAA and MgAA, respectively) as precursors.

Scanning electron microscope (SEM) was chosen to investigate the morphology of Mg-doped ZnO structures depending on substrate temperatures. The microstructure of ZnO:Mg samples was studied by a Leo 1550 Gemini SEM at a primary beam acceleration potential of 5 kV.

The photoluminescence (PL) measurements were carried out at RT with a solid-state laser operating in

the UV range. The luminescence was collected and mirrored into a monochromator equipped with a Si-CCD detector (2D-matrix of 2000/800 pixels), cooled with liquid nitrogen, whose spectral resolution was around 0.1 meV.

3. RESULTS AND DISCUSSION

ZnO:Mg (ZnAA + MgAA 5 wt. %) (Fig. 1) and (ZnAA + MgAA 10 wt. %) (Fig. 2) films were grown on Si (100) substrates at temperatures from 250 to 420 °C.

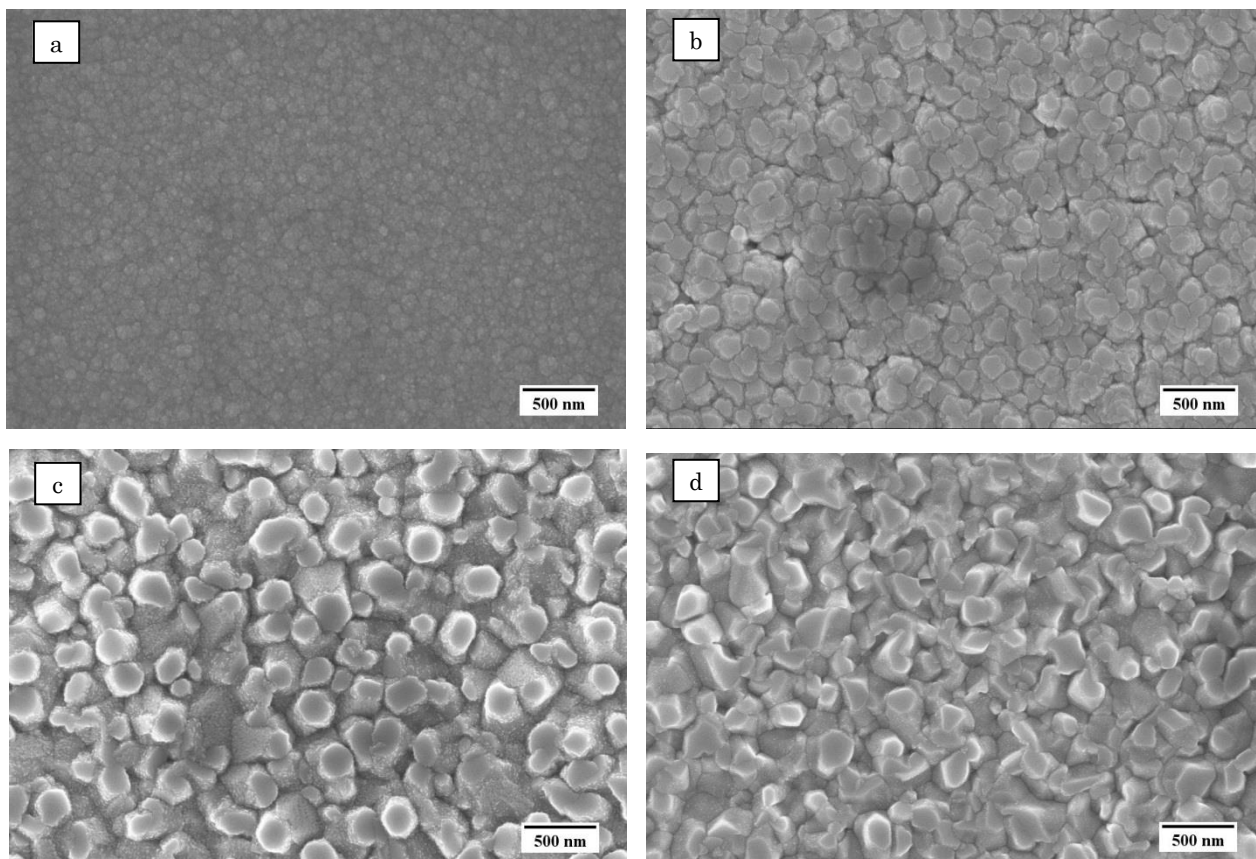


Fig. 1 – SEM images of ZnO:Mg (ZnAA + MgAA 5 wt. %) structures obtained at different deposition temperatures: (a) 250 °C, (b) 315 °C, (c) 350 °C, (d) 390 °C

As one can see, the surface morphology of ZnO:Mg structures changes with increasing substrate temperature and MgAA content in the grown samples (Fig. 1 and Fig. 2).

In the case of ZnO:Mg (ZnAA + MgAA 5 wt. %) films deposited at low substrate temperatures (250-300 °C), the mobility of adatoms is low, and the bases of ZnO wurtzite columns retain a random orientation, which together form a multigrain layer. The grain size increases with increasing substrate temperature from about 75 nm (Fig. 1a) to 100-150 nm (Fig. 1b). When the substrate temperature reaches 350-400 °C, both the mobility of adatoms and intergranular diffusion increase significantly, leading to the formation of a polycrystalline structure with a predominant orientation of crystallites in the (001) direction, i.e., perpendicular to the substrate, which is clearly visible at a substrate temperature of 350 °C (Fig. 1c) and, as can be seen, structures are formed with a clear hexagonal cut. As a

result of a further increase in temperature and intensification of the processes of diffusion and coalescence, there is a further increase in the structure with the formation of rods (Fig. 1d).

The kinetics and mechanism of the formation of self-organized structures is a complex and multi-stage process. It can be argued that their formation is a consequence of spontaneous adsorption and evaporation of adsorbate particles upon contact of the vapor phase with the surface of the solid substrate. The stage of the formation of two-dimensional clusters, their origin or nucleation is important. It is associated with a certain migration of adatoms (unattached atoms) and their coalescence. In the implementation of layered homoepitaxy by the Frank-Van der Merwe growth mechanism, the formed two-dimensional clusters grow and merge with each other forming a continuous monolayer. Volmer-Weber heteroepitaxy is associated with the formation of three-dimensional individual structures of

nuclei on the substrate surface. An intermediate link between the above two methods is the Stranski-Krastanov nucleation mechanism, which provides for the formation of the so-called wetting layer with the subsequent growth of pyramidal structures due to the removal of elastic deformations [19]. Observation of the surface demonstrates this method of forming hexagonal columns from the initial single formations of crystalline grains with a hexagonal shape of the order of 200-500 nm.

SEM images of ZnO:Mg (ZnAA + MgAA 10 wt. %) films (Fig. 2) also show the formation of large polycrystalline structures at 250 °C with grain sizes up to 800 nm, of an arbitrary (non-hexagonal) shape, which overlap and compete with each other. At temperatures

of 300-350 °C, the surface morphology of the samples takes the ordered form of hexagonal grains with a diameter of about 850 nm (Fig. 2b). In Fig. 2c, it is shown that columns already have a clear hexagonal shape. Diameters of hexagons are about 800 nm, while the tip has a size of about 200 nm. The image of the sample grown at a substrate temperature of 420 °C (Fig. 2d) shows a quasi-array of well-formed hexagonal rods with a diameter of 200-300 nm.

Comparing ZnO:Mg structures grown at different concentrations of magnesium, we can conclude that an increase in the concentration of magnesium acetylacetonate in the precursor from 5 to 10 wt. % creates conditions for the growth of ZnO-Mg rods, especially with increasing substrate temperature.

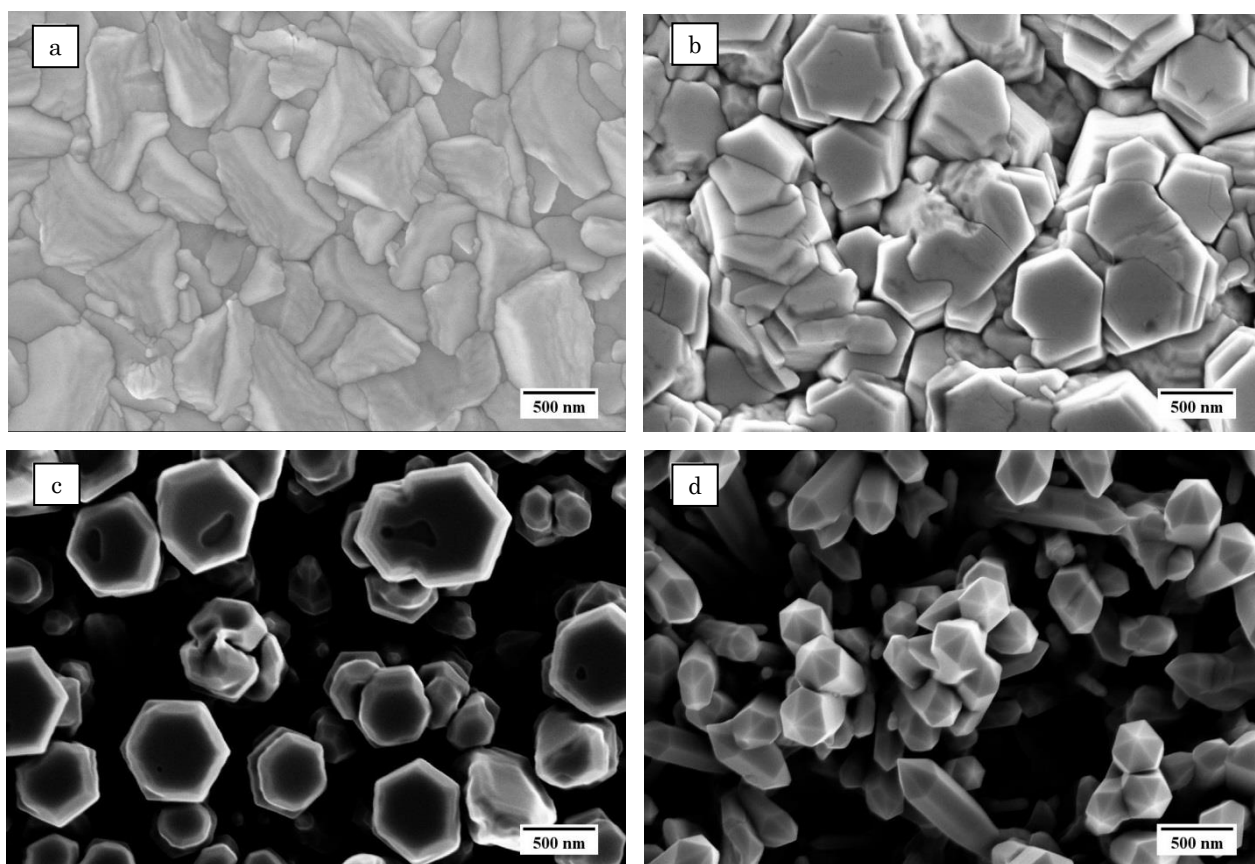


Fig. 2 – SEM images of ZnO:Mg (ZnAA + MgAA 10 wt. %) nanostructures obtained at different deposition temperatures: (a) 250 °C, (b) 315 °C, (c) 350 °C, (d) 390 °C

Fig. 3 presents SEM images of the cross section of ZnO:Mg structures. It is shown that the grain size and film thickness of ZnO:Mg increase to a certain value with increasing temperature. The reason for the formation of the film at the initial stage of the process is the low growth temperature, i.e., atoms and molecules that settle on the surface of the substrate do not have enough kinetic energy to move to the appropriate position, where they join together to form larger grains. With increasing substrate temperature to ~ 300 °C, in Fig. 3b we observe a columnar structure. The film is rough and homogeneous with a thickness of ~ 700 nm. At a substrate temperature of ~ 400 °C, the film thickness is about 1.5 μm (Fig. 3d).

As the substrate temperature increases, the for-

mation of zinc oxide molecules accelerates and the process of nucleation and crystallization of new grains decreases, as a consequence, the growth rate of separated structures increases [17].

In the case of increasing the concentration of the initial precursor of MgAA to 10 wt. % in a relatively high temperature range (350-400 °C), nanostructures grow in the form of rods with a hexagonal pointed pyramidal top (Fig. 3h). In addition, the thickness of these films is greater and is more than 2 μm.

The morphology analysis of the formed films and structures allows us to conclude that the formation of the film and the growth of structures depend on the mass of the precursor, which slowly evaporates. The greater the mass of the precursor or the closer the sub-

strate is to the evaporation zone of the precursor, the greater the film thickness. Structures are formed mainly by the Stranski-Krastanov mechanism, but when the vapor pressure above the substrate decreases and at a

temperature sufficient to activate the diffusion mechanism, the structures grow according to the Volmer-Weber mechanism.

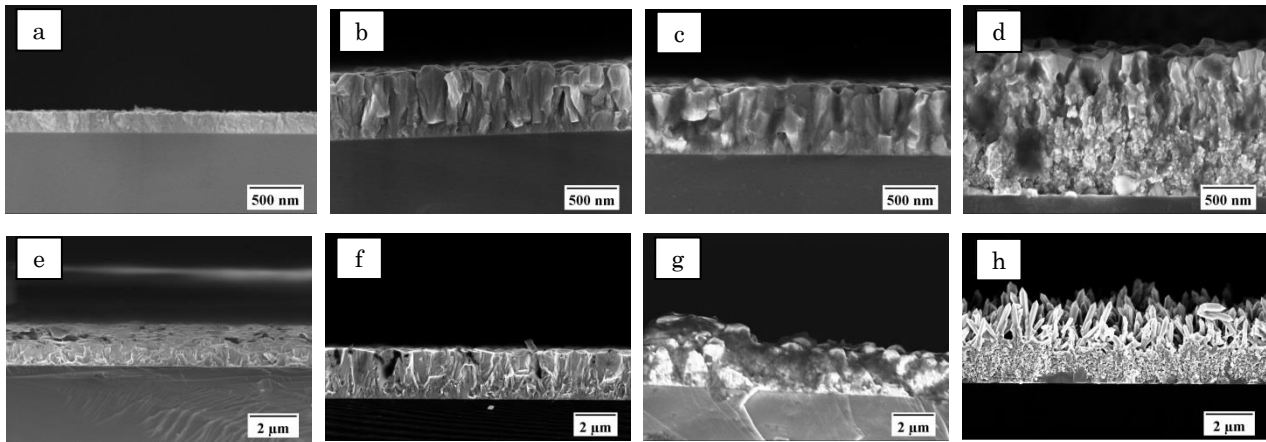


Fig. 3 – Cross-section view of ZnO:Mg structures obtained at different deposition temperatures: a-d (ZnAA + MgAA 5 wt. %) (a) 250 °C, (b) 315 °C, (c) 350 °C, (d) 390 °C; e-h (ZnAA + MgAA 10 wt. %) (e) 250 °C, (f) 320 °C, (g) 350 °C, (h) 420 °C

The main characterization technique to be used for ZnO structures is PL spectroscopy. In this technique, a UV laser (325 nm) is used to excite the sample. As a result, the photon emission with different wavelengths, the so-called near band edge (NBE) emission and deep level emission (DLE), is observed (Fig. 4).

Fig. 4 shows the measured at RT PL spectra of ZnO:Mg (ZnAA + MgAA 5 wt. %) samples grown on silicon substrates in the temperature range 190-450 °C. The spectra show a sharp peak at 377 nm, which is attributed to the NBE emission of ZnO originated from free exciton recombination. The radiation band in the visible wavelength range (peak at ~ 470 nm) occurs due to radiative recombination (DLE) due to point defects in the ZnO lattice, such as oxygen vacancy, zinc vacancy, oxygen and zinc interstitials [4, 20]. However, the identification of recombination centers and mechanisms responsible for the luminescent properties is still controversial. It should be noted that Mg does not have a significant effect on the PL spectrum (there is no significant blue shift of the emission maximum). This may indicate that Mg is not fully incorporated (5 wt. % of MgAA in the precursor mixture) in the cationic sublattice of Zn.

Fig. 5 shows the RT PL spectra of ZnO:Mg (ZnAA + MgAA 10 wt. %) samples deposited on silicon substrates in the temperature range 190-450 °C. The results are similar to those described above. However, it should be noted that the use of 10 wt. % MgAA in the precursors mixture (instead of 5 wt. %) leads to an increase in the intensity of the marginal emission in the UV region of the spectrum and the suppression of defective emission in the blue-green region of the spectrum. It is also seen that the highest intensity of the marginal emission is demonstrated by samples deposited at 420-450 °C. This may be due to the optimal quantum constraint associated with the geometry and size of nanorods (see Fig. 2d and Fig. 3h). The high and sharp maximum is located approximately at a wavelength of 378 nm ($E = 4.135 \times 10^{-15}$ eV·s).

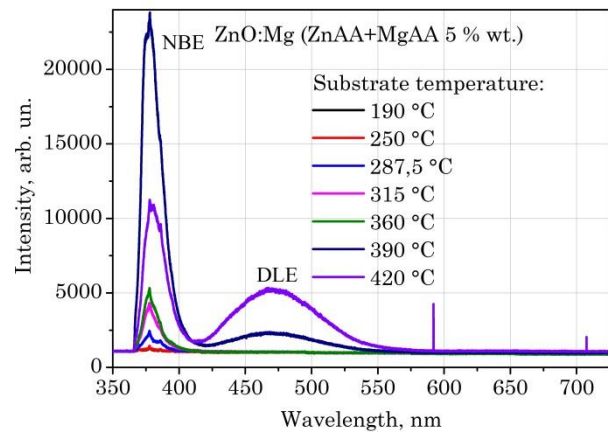


Fig. 4 – PL spectra of ZnO:Mg (ZnAA + MgAA 5 wt. %) films obtained in the temperature range 190-420 °C

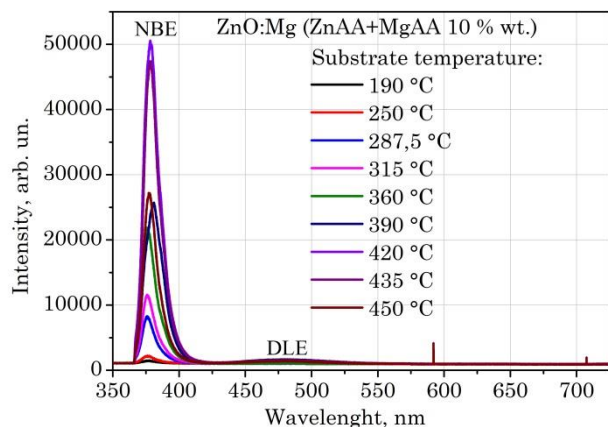


Fig. 5 – PL spectra of ZnO:Mg (ZnAA + MgAA 10 wt. %) films obtained in the temperature range 190-450 °C

We reconstruct one of the ZnO:Mg (ZnAA + MgAA 10 wt. %) PL spectra in the coordinates of the semi-logarithmic dependence of the emission intensity on energy (Fig. 6). Only the dominant peak of marginal

emission can be clearly observed in our sample, while the blurred maximum of the defective emission is still visible, for clarity it is depicted with a 10-fold increase in intensity (green curve in Fig. 6). The obtained film is considered to have high quality crystallites.

With the introduction of ~ 10 wt. % Mg, the band gap can be increased by ~ 0.1-0.2 eV, and this should cause a blue shift of the maximum peak of NBE (see Fig. 6) when measuring PL at low temperatures [5]. It is known that the marginal emission depends on the temperature and can decrease from ~ 3.36 eV at 4 K to 3.28 eV at RT for undoped zinc oxide [21]. It was initially expected that doping with 10 wt. % Mg would cause a significant blue shift of the edge emission band in the PL spectra. However, we have a blue shift of marginal emission of only 0.02 eV. It should be noted that a small size of nanostructures can cause a red shift of the maximum edge emission, compensating for the effect of magnesium [21]. Moreover, phonon replicas of free excitons are also responsible for the red shift of the main peak position.

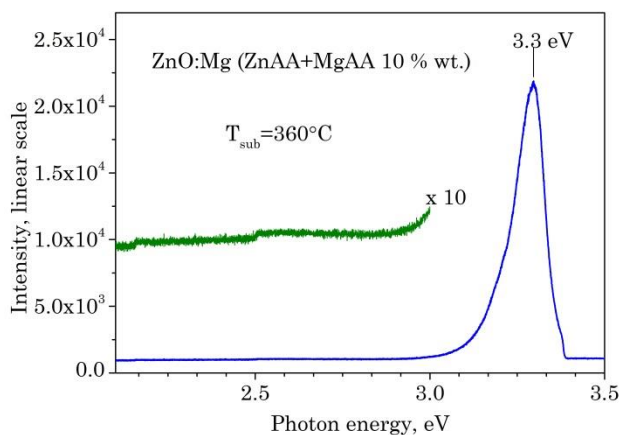


Fig. 6 – PL spectrum of ZnO:Mg (ZnAA + MgAA 10 wt. %)

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Briefly, the high-intensity NBE peak at ~ 376 nm caused by free exciton recombination has the peak full width at half maximum of about 14.41 nm. The emission band in the visible wavelength range (peak at ~ 470 nm) arises from radiative recombination through point defects in the ZnO lattice. The ratio of the peaks of NBE and DLE spectral integral intensity emission (figure of merit) was about 6, confirming that ZnO:Mg nanostructures are suitable for LED applications.

4. CONCLUSIONS

The method of atmospheric pressure chemical vapor deposition for obtaining nanostructures of zinc oxide of different morphology is presented. From SEM images, we can conclude that in order to synthesize quasi aligned ZnO nanorods via APMOCVD on Si substrates, a substrate temperature between 400 and 500 °C is required. Lower Si substrate temperatures result in amorphous or polycrystalline thin films.

From the PL spectra, it is revealed that the use of 10 wt. % MgAA (instead of 5 wt. %) leads to an increase in the NBE intensity and suppression of DLE in the luminescence of ZnO nanostructures.

Magnesium acts as an isoelectronic impurity and leads to an increase in grain size (improving crystalline perfection) and improvement in NBE PL emission due to gettering of defects.

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Вплив температури підкладки і вмісту магнію на розвиток морфології та люмінесценцію плівок ZnO:Mg

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У роботі наведено результати досліджень методами сканувальної електронної мікроскопії і фотолюмінесценції (ФЛ) особливостей мікроструктури та випромінювальних переходів плівок ZnO:Mg, отриманих методом хімічного осадження з парової фази металорганічних сполук при атмосферному тиску на підкладки кремнію. Різноманітні мікроструктури ZnO від полікристалічних плівок з гладкою морфологією до стовпців та гексагональних стержнів ефективно утворюються в широкому діапазоні температур 190-450 °C з використанням двох композицій суміші ацетилацетонатів цинку і магнію (ZnAA та MgAA) (5 та 10 ваг. %) в якості прекурсорів. Температура підкладки має суттєвий вплив на кристалічність та морфологію плівок ZnO. Структури ZnO у формі колон утворюються при температурах вище 350 °C. Вміст MgAA у суміші прекурсорів також впливає на морфологію частинок. При вмісті MgAA 10 ваг. %, при низьких температурах підкладки (200-320 °C) утворюються зерна більших розмірів порівняно з ростом зерен у плівках при MgAA 5 ваг. %, тоді як при вищих температурах підкладок (350-450 °C) утворюються стержнеподібні структури. Швидкість росту структур ZnO зростає із збільшенням температури підкладки. У спектрах емісії ФЛ зразків з 10 ваг. % MgAA (у порівнянні з 5 ваг. %) спостерігається ріст інтенсивності крайової смуги та пригнічується випромінювання дефектних рівнів люмінесценції структур ZnO. Тому можна зробити висновок, що магній діє як ізоелектронна домішка і приводить до покращення крайової емісії люмінесценції за рахунок гетерування дефектів. Магній також спричиняє збільшення розміру зерен, покращуючи досконалість кристалітів полікристалічних плівок ZnO:Mg, вирощених при низькій температурі підкладки, а також сприяє росту гексагональних стержнів при більш високих температурах підкладки. Структури оксиду цинку, леговані магнієм, можуть виступати як ефективні фотокаталізатори.

Ключові слова: Метод хімічного осадження з парової фази металорганічних сполук при атмосферному тиску, Ацетилацетонат цинку, Ацетилацетонат магнію, Скануюча електронна мікроскопія, Фотолюмінесценція.