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MORPHOLOGY, EMISSION AND CRYSTAL STRUCTURE OF ZnO NANOCRYSTAL FILMS CO-DOPED WITH Ga AND In ELEMENTS

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Abstract. *The impact of Ga and In donor co-doping on morphology, crystal structure and photoluminescence (PL) has been studied in ZnO:Ga:In nanocrystal (NC) films. The films were deposited by ultrasonic spray pyrolysis on silicon substrates heated to 400°C. For the study of double donor doping, the group of samples was prepared, where the In content was 1 at%, but the Ga contents were varied in the range of 0.5-2.5 at.%. To stimulate crystallization of the films, all samples were annealed at 400°C for 4h in a nitrogen flow (5L/min). The obtained ZnO:Ga:1.0%In NC films are characterized by wurtzite crystal structures for all Ga concentrations. The variation non monotonous of the morphology and PL intensity of the near band edge (NBE) emission band versus Ga contents has been detected in the ZnO:Ga:1.0%In NC films. The ZnO crystal lattice parameters do not change up to the Ga content 1.0 at%, then decreases with Ga content of 1.5 at% and enlarging to ≥ 2.0-2.5 at% Ga in the films. High-quality NC films with wurtzite-type crystalline structure, planar morphology, bright NBE emission and the small intensity of defect related PL bands have been obtained for the 1.5 at% Ga. The reasons why the parameters vary non monotonic and the optimal concentrations for the Ga/In donor type doping the ZnO NC films have been analyzed and discussed.*

Keywords: *Ultrasonic spray pyrolysis, Ga and In co-doping, crystal structure, emission*

1. INTRODUCTION

Zinc oxide is a wide band gap semiconductor, which has attracted great attention over the last two decades due to its interesting optical properties, important for optoelectronic applications in blue and UV light emitting devices, solar cells and in high temperature electronics [1-4]. The high exciton binding energy (60 meV) in ZnO promising a bright exciton emission at room temperature [5, 6]. High optical transmittance in the visible spectral range and significant electrical conductivity have drawn attention to ZnO NC films as transparent conduction oxide (TCO) windows for solar cells [7, 8].

Significant effort has been addressed to the doping study of ZnO NC films. Undoped ZnO films have n-type conductivity due to the non-stoichiometry of the films and the high concentration of shallow donor defects, such as: the interstitial Zn_I clusters [9], or hydrogen atoms in oxygen sites [10]. But the conductivity of the un-doped ZnO films is not high enough to be used as TCO electrodes. To improve the electrical conductivity of the ZnO films, different donor impurities were used. The most studied impurities are the groups III (Al, Ga or In) or VII (F) dopants [11-17]. In ZnO films doped by group III atoms, electrical resistivity varying has been reported in the range from 10^{-1} to 7.9 10^{-4} Ω·cm [18- 20]. It was revealed that the resistivity is correlated with the structural and morphological characteristics of doped ZnO films.

The previous study had shown that group–III elements are important donor impurities for the TCO technology based on ZnO films. However, it was revealed that the free electron density in the Al-doped

ZnO films was limited to about 10^{19} - 10^{21} cm^{-3}. This limit in the ZnO films was approached for the Al content of 1 -4 at% [21-23] and for the In content at 2 at% [24]. The n-type doping limits in ZnO:Al [25] or ZnO:Ga [26] films, as assumed, are connected with the self-compensating effect, associated with the generation of acceptor-type defects to counteract donor doping. However, the factors that stimulate the self-compensating effect remain to be investigated.

The ionic radii of the group III elements are different and close to the ionic radius of Zn [27], which makes it possible to expect that the highest concentrations of In and Ga ions in ZnO NCs can be obtained without significant distortion of the ZnO crystal lattice. Moreover, using the co-doping by Ga and In atoms, which are characterized by lower (Ga) and higher (In) ionic radii compared to those of Zn ions, we hope to obtain the important information concerning the factors that favor to the self-compensating effect.

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The ZnO:Ga:In films, presented in this work, were grown by ultrasonic spray pyrolysis (USP) with the following annealing at 400 ° C in a nitrogen flow. The USP method is widely used for ZnO film growth due to its inexpensive technology. Actually, ZnO:Ga:In films with bright NBE emission at 300K were obtained.

2. Experimental details

Thin films of ZnO:Ga:In were grown by ultrasonic spray pyrolysis on 2-inch, (100) oriented silicon substrates heated to 400°C [28]. The methanol, water, and acetic acid solution in the 80:10:10 ration with 0.2M zinc acetate (C4 H6 O4 Zn·xH2O) was applied as the Zn precursor. In acetate hydrate ((CH3CO2)3In xH2O) or Ga acetate hydrate ((CH3CO2)3Ga xH2O) in different contents were used as precursors of In or Ga. The content of the In atom in the solution were chosen to obtain of 1.0 at% In in all films. But the Ga concentrations were varied in the range of 0.5-2.5 at% Ga in the ZnO films. The crystallization of the films was carried out at 400°C for 4h in a constant flow of nitrogen (5L/min).

A scanning electronic microscope (SEM), model JSM7800F-JEOL was used to monitor the film morphology [29]. A diffractometer, Model XPERT MRD with Pixel detector, three-axis goniometry, parallel collimator, and X-ray beam of the Cu source (line Ka1 1.5406Å) was used to study the XRD patterns. PL spectra were detected on a SPEX 500 spectrometer with a Hamamatsu photomultiplier [30]. The light excitation source was a He-Cd laser (model KIMMON: IK3102R-G) with a power of 50 mW and an excitation light wavelength of 325 nm.

3. Experimental results and discussion

The SEM images of ZnO:Ga:In films are shown in figure 1 for the In content 1.0at% and Ga contents of 0.5, 1.5, and 2.5 at%.

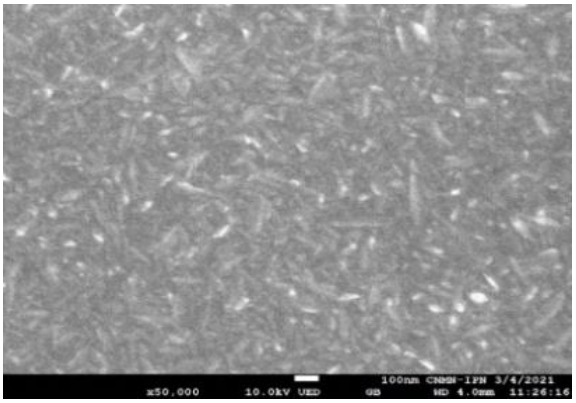
At a small Ga content (≤1.0 at%) and a high Ga content (≥2.0at%), the grains are in the form of nanosheets with a size of 100-200 nm distributed randomly on the surface of the ZnO films (Fig.1a, c). The grain shape changes in the ZnO:Ga:In film with 1.5at% Ga. The nanosheet shape changes to nanorod with the size of hexagonal cross sections 50-100 nm typical for the wurtzite ZnO crystal structure (Fig.1b). Simultaneously, the nanorod density increases and the surface roughness decreases (Fig.1b). The surface of the ZnO:1.5%Ga:1.0% In film is characterized by a flat morphology suitable for device applications. Thus we have seen that the surface morphology of ZnO:Ga:In films varies non-monotonic and nanograins with the typical hexagonal cross section of wurtzite ZnO crystals can be obtained for the ZnO:1.5%Ga:In films.

In Figure 2, the XRD patterns of the ZnO thin films doped with In, and co-doped with In and Ga are shown.

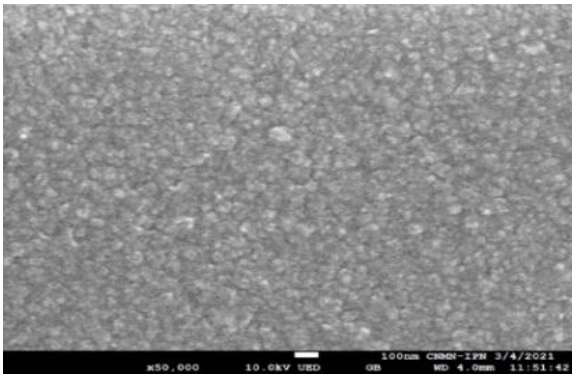
The XRD pattern of the In-doped ZnO film includes the peaks 2Θ = 34.37°, 47.33° and 62.73° related to diffraction on the (002), (102) and (103) crystal planes in the wurtzite ZnO crystal structure (JCPDS file no. 003-0888) with the preferential (002) plane orientation in the film (Fig.2). Note that the XRD peak positions in ZnO :1.0%In films are smaller, than the corresponding positions 2Θ = 34.44°, 47.56° and 62.83° detected in un-doped ZnO films (JCPDS file no. 003-0888), owing to the increase of the ZnO crystal lattice parameters at In doping. The latter is related to the higher ionic radius of the In^{3+} ions (0.80Å) compared to those for the Zn^{2+}(0.74 Å) ions [31].

ZnO films co-doped with Ga and In atoms are also characterized by the wurtzite ZnO crystal structure (Fig.2). The XRD patterns of these ZnO films include the five XRD peaks 2Θ = 31.63°, 34.38°, 36.14°, 47.37° and 56.54° related to diffraction on the (100), (002), (101), (102) and (110) crystal planes (JCPDS file no. 003-0888).

a) ZnO:0.5%Ga:1.0%In



b) ZnO:1.5%Ga:1.0%In



c) ZnO: 2.5%Ga:1.0%In

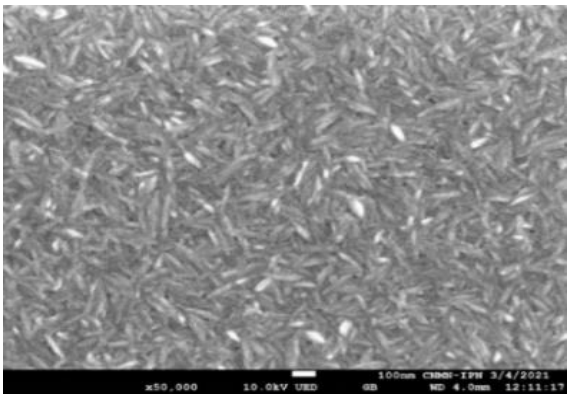


Figure 1. SEM images of studied ZnO films doped with 1.0at%In and different contents of Ga atoms: 0.5at% (a), 1.5at% (b), and 2.5at%(c).

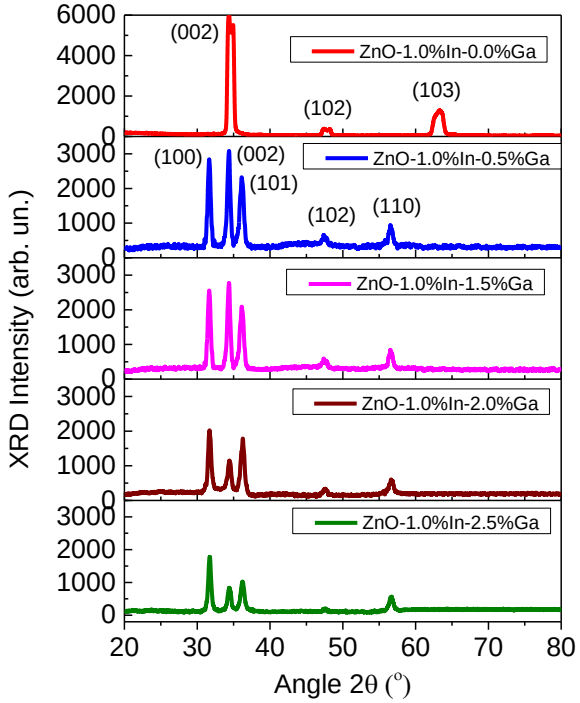


Figure 2. XRD patterns of the ZnO:Ga:In films with different Ga contents mentioned on the figures

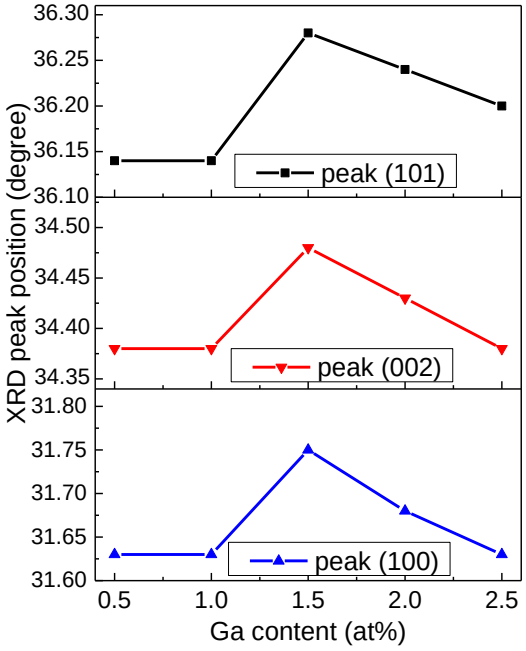


Figure 3. The shift of XRD peak positions versus Ga contents

With the increase in Ga concentrations in the range 0.5-1.5 at%, the intensities of the (100), (002), (101), (102) and (110) peaks decrease insignificantly (Fig.2), and the XRD peak positions do not change up to 1.0 at% (Fig.3). However, with the higher Ga content of 1.5 at% the XRD peaks shift to higher angles (Fig.3). However, at the Ga contents (≥2.0-2.5at%), the intensities of the mentioned XRD peaks move downward (Fig.2). Simultaneously, the positions of the XRD peaks are shifted towards the lower 2Θ angles (Fig.3). The last effect is related to the increase in the ZnO crystal lattice parameters at higher Ga contents due to the formation some native defects. The different reasons can stimulate the decrease of the crystallinity of ZnO:In films with higher Ga doping, such as: the increase of the ZnO grain density accompanied by some disorder of the ZnO NCs and loss of the preferential (002) ZnO plane orientation, or the formation of complex defects related to the Ga ions in the ZnO crystal lattice.

The PL spectra of ZnO:In NC films, obtained by ultrasonic spray pyrolysis with different In contents, were investigated early by us [32]. It was shown that at small In contents (0.5-1.0 at%) the PL bands: orange (O) centered at 2.2 eV and green (G) peaked at 2.5 eV, related to the native host defects, decreased and then they disappeared completely at 2.5 at% In [32]. Simultaneously, the PL intensity of the near band edge (NBE) emission increased significantly in PL spectra of the films with 0.50-1.0 at% In and its maximum shifted to 3.14 -3.15eV (Fig.4a). The last fact is connected with the increase of the parameters of the ZnO crystal lattice at In doping, which is accompanied by the decrease of the ZnO:In energy band gap compared to its value in undoped ZnO NCs [32, 33].

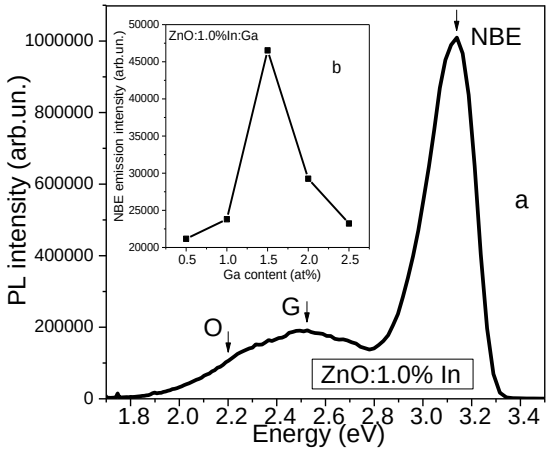


Figure 4. The PL spectrum of ZnO:I,0%In film (a) and the dependence of the NBE emission intensity (b) in the ZnO1.0%In:Ga films versus Ga contents

It was shown [32], that NBE emission band (centered at 3.14 -3.15 eV) was related to the LO phonon replicas of the free exciton emission. It should be noted that the high intensity of NBE emission testifies to a high quality of the studied ZnO:1.0%In films. This is one of the reasons why the In content of 1.0 at% was used in the ZnO films in the work presented.

The variation of the Ga contents in the ZnO:1.0%In films stimulate the non-monotonic changes of the PL intensity of NBE emission bands (Fig.4b). The NBE emission intensity increases for the Ga content range of 0.5-1.5 at% in ZnO:1.0%In films (Fig.4b). But for the higher Ga concentrations from the range 1.5-2.5 at% Ga, the PL intensity of the NBE emission bands decreases significantly (Fig.4b).

The non-monotonic changes in film morphology correlates with the non-monotonic change in PL intensity of the NBE emission band. It was mentioned earlier that the Ga^{3+} ionic radius (0.62 Å) is smaller and In^{3+} ionic radius (0.80 Å) is greater than that of Zn^{2+} (0.74 Å). In the ZnO:In films with a small Ga contents (0.5-1.0 at%), the compression stresses, which appear due to the In doping (1.0 at%), prevent the effective

oxidation and the formation of hexagonal ZnO nanorods at the ZnO film crystallization (Fig.1a). The doping with 1.5at% Ga makes it possible to partially compensate of compressive stresses in the films. This effect is favored by the effective ZnO oxidation, as well as by the dissolution of Ga and In ions in the ZnO films in thermal annealing. Simultaneously, the typical hexagonal ZnO nanorods growth at the crystallization (Fig.1b) and high quality ZnO NC films have been produced with the bright NBE emission band (Fig.4).

The further increase in Ga contents to 2.0-2.5at% leads to significant distortion of the ZnO crystal lattice which again prevents efficient crystallization of the ZnO films (Fig.1c). Simultaneously, the intensity of XRD peaks falls (Fig.2) and the XRD peak positions move towards the lower 2Θ values (Fig.3). The last effect attests to the significant dissolution of Ga ions in the ZnO crystal lattice, which is accompanied by the generation of native host defects and the decrease in the PL intensity of the NBE emission band (Fig.4b). The obtained results, as expected, will be useful for further improvement of the doping process in the ZnO:Ga:In films.

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