Vacuum 114 (2015) 198-204

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Doping effects on electrical and optical properties of spin-coated ZnO thin films

N.A. Vorobyeva ^a, M.N. Rumyantseva ^a, R.B. Vasiliev ^a, V.F. Kozlovskiy ^a, Yu.M. Soshnikova ^a, D.G. Filatova ^a, V.B. Zaytsev ^b, A.V. Zaytseva ^c, A.M. Gaskov ^{a, *}

^a Chemistry Department, Moscow State University, Leninskie Gory 1-3, 119991 Moscow, Russia

^b Department of Physics, Moscow State University, Leninskie Gory 1-2, 119991 Moscow, Russia

^c Laboratory of Physicochemistry of Nanoparticles, "Novye Energeticheskie Tekhnologii", Sretensky Bul. 7/1/8-3, 107045 Moscow, Russia

ARTICLE INFO

Article history: Received 6 September 2014 Received in revised form 28 October 2014 Accepted 9 November 2014 Available online 18 November 2014

Keywords: Zinc oxide Thin films Ga-doped ZnO In-doped ZnO Ga and In co-doped ZnO Spin-coating

ABSTRACT

Undoped ZnO, as well as Ga-, In-doped and (Ga,In) co-doped ZnO thin films were deposited on glass substrates by the spin-coating technique. The effect of cation composition on the structural, morphological, optical and electrical properties of ZnO-based films was studied. Introduction of 1.0–1.3 at% of Ga in ZnO and ZnO(In) results in the enhancement of electrical and optical properties of the films. Introduction of indium leads to the decrease of resistivity. Introduction of both elements allows to improve the optical properties (the average transmittance achieves 97% in the range 400–800 nm) and to increase the conductivity up to 3.6 S/cm that is three orders of magnitude higher than the corresponding value for undoped ZnO. The effect of conductivity increase may be caused by the increase of donor elements solubility in ZnO structure for co-doped films as compared to single-doped ZnO due to the decrease of the lattice strain.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Zinc oxide is a promising functional wide-gap semiconductor with unique optical and electrical properties. ZnO-based materials belong to the group of transparent conducting oxides (TCO). For the majority of flat panel display applications crystalline Sn-doped indium oxide (indium-tin-oxide, ITO) and also amorphous In-Zn-O (IZO) films are used as transparent electrodes [1,2]. Indium-free TCO materials have attracted much attention because of high cost and future availability of indium. ZnO-based materials are promising candidates for ITO substitution. However pure ZnO is a rather resistive material and the most studied matter is the doped zinc oxide, which provides an opportunity to regulate the electrical and optical properties over a wide range. Doping of ZnO with donor impurities (Al, Ga, In) leads to the increase of the conductivity [1,2]. Co-doping of ZnO with two donor impurities provides some additional opportunities [3-5]. It was shown that co-doping allows for a higher conductivity than single-doping. For example, co-doping of ZnO with Al and In significantly improves the electrical properties

deposition for thin film transistors [5] and light emitting diodes [4]. It was found that ZnO films containing both gallium and indium show better surface morphology and electrical properties than Inor Ga-doped ZnO [4]. Search for the ZnO-based composition optimal for TCO applications with the lowest indium content remains an actual problem. Spin-coating technique has several advantages among the other methods for thin films deposition because of its simplicity, safety, low equipment cost and ease of composition control. This method was used for obtaining films based on gallium indium zinc oxides for thin film transistors, however the lowest reported concentra-

tion of indium was 20 at% [In]/([In] + [Zn]) and all films were X-ray

of ZnO films prepared by off-axis rf sputtering, the amount of indium used for these films is an order of magnitude smaller than for ITO films [3]. This effect is explained by the decrease of lattice strain

in ZnO structure for (Al,In) co-doped films (dopant size compen-

sation effect) as compared to single-doped ZnO [3]. The introduc-

tion of two dopants, having the smaller and bigger ionic radii than

that of zinc ion, leads to the compensation of cell volume

compression caused by smaller ion with the tension in volume

caused by the bigger one, so the less strain occurs in the lattice [4].

Indium gallium zinc oxide films were prepared by pulsed laser





^{*} Corresponding author. Tel.: +7 495 939 54 71; fax: +7 495 939 09 98. *E-mail address*: gaskov@inorg.chem.msu.ru (A.M. Gaskov).

amorphous materials even after annealing at 600 °C [6]. As for ZnObased films, there have been some reports on ZnO(Ga) [7] and ZnO(In) [8] thin films obtained by spin-coating technique, but information on (Ga,In)-containing ZnO films was not found in the literature. In order to highlight the possible advantages of Ga and In co-doping, it is necessary to compare the optical and electrical properties of different series of films containing gallium, indium and both elements and obtained in the equal conditions. In present work we report on the synthesis of ZnO, ZnO(Ga), ZnO(In) and ZnO(Ga,In) thin films by spin-coating technique, as well as the characterization of films microstructure, electrical and optical properties.

2. Materials and methods

Thin films were deposited onto glass substrates by spin-coating method. Metal nitrates $Zn(NO_3)_2 \cdot 6H_2O$, $Ga(NO_3)_3 \cdot 8H_2O$, $In(NO_3)_3 \cdot 4.5H_2O$ were dissolved separately in 2-methoxyethanol by stirring at room temperature for 2 h. Then solutions were filtered and mixed together to obtain the composition $[M]/([M] + [Zn]) = 0 \div 5$ at%, M = Ga, In. The solutions containing both Ga and In ions were prepared analogously, the concentration of gallium was fixed at 0.74 at% [Ga]/([Ga] + [Zn]) and the concentration of indium was varied in the range $0 \div 4.7$ at% [In]/([Ga] + [In] + [Zn]). The total concentration of metal ions in all prepared solutions was 0.4 M. Throughout this paper, the composition of the films will be given as the ratio $[M]/([M] + [Zn]) \cdot 100\%$ (at%) for ZnO(M) films and $[M]/([Ga] + [In] + [Zn]) \cdot 100\%$ (at%) for ZnO(Ga,In) films, M = Ga, In.

The microscope slides were used as the glass substrates. They were cleaned in acetone and then in deionized water for 10-15 min using an ultrasonic bath and then dried at 200 °C for 10 min.

Because of the bad adhesion between the glass surface and the prepared solutions a sublayer of ZnO was deposited on substrates. The solution used for this layer contained 0.4 M $Zn(CH_3COO)_2$ and 0.4 M monoethanolamine in ethanol. This layer was deposited at 2000 rpm for 30 s using Spin-coater KW-4A and dried at 200 °C for 15 min.

Thin films from 2-methoxyethanol solutions were deposited on the glass substrates with ZnO sublayer at 2000 rpm for 30 s using Spin-coater KW-4A. After the deposition of each layer, the films were dried at 200 °C for 5 min. The procedures from coating to drying were repeated several times. Finally, all films were slowly (1.3 K/min) heated up to 500 °C, annealed at 500 °C for 6 h in the air atmosphere and then cooled with a furnace to the room temperature.

The composition of films was determined by the inductively coupled plasma mass spectrometry (ICP-MS) on a quadrupole ICP mass spectrometer (Agilent 7500c; Agilent Technologies, Waldbronn, Germany). The sample introduction system consisted of a robust Babington nebulizer with a Scott spray chamber (Agilent Technologies). The data were acquired and processed with ICP-MS ChemStation (version G1834B) software package (Agilent Technologies). ⁶⁹Ga and ⁷¹Ga, ¹¹³In and ¹¹⁵In, ⁶⁶Zn and ⁶⁸Zn isotopes were used for analytical measurements in order to control the possible interferences and matrix effects. Nitric acid (65%, Suprapur grade), used for dissolution and acidification of all standards and samples (at 1% (v/v) HNO₃), was provided by Merck (Darmstadt, Germany). High-purity water for the ICP-MS analysis was from a Milli-Q purification unit (Millipore, Bedford, USA). The ICP-MS single element standards (Ga, In and Zn; 10 mg L^{-1}) were the products of High Purity Standards (Charleston, USA). To obtain sample solutions, the films were washed off from glass substrate with 1 ml of 65% nitric acid and then diluted by water.

The phase composition and the crystal structure were determined by X-ray diffraction (XRD) measurements (DRON-3M, CoK_{α} radiation, $\lambda = 1.7903$ Å). The crystallite size (d_{XRD}) of ZnO was estimated from the broadening of the (002) XRD peak using the Scherrer equation.

The thickness of the films was determined using profilometer Talystep (Taylor-Hobson), before measuring a part of film was dissolved in dilute nitric acid to form a step "surface of film" – "glass substrate".

The surface morphology of the films was characterized by atomic force microscopy (AFM, NanoScope 3a (Digital Instruments, USA)).

The resistance of the films was determined by four point probe measurements using 302 Resistivity probe stand (Lucas Signatone Corp.) and Keithley 2400 Series SourceMeter (Keithley Instruments, Inc.). For the comparison of the electrical properties we used the resistivity, which was calculated from the sheet resistance using the thickness of the corresponding film. The use of resistivity allows us to compare the electrical properties of all the films under investigation. Optical properties were studied using UV–Vis spectrophotometer Cary 50 (Varian, Inc.). The absorbance values were calculated using the thickness of corresponding layers.

In order to choose the sufficient number of layers for receiving the good conductivity, the films with equal cation composition (1.2 at% Ga) and different number of deposition cycles were obtained. The film thickness increases and the sheet resistance R_s decreases with the number of layers deposited by spin-coating (Fig. 1). All presented data belong to the films annealed at 500 °C. The films containing more than 10 deposited layers have approximately the same resistance, so according to this data, the deposition of 10 layers was chosen for other films. The thickness of ZnO(Ga), ZnO(In), ZnO(Ga,In) films containing 10 deposited layers is within the range of 250–370 nm.

3. Results and discussion

3.1. Cation composition

The cation composition of the films annealed at 500 °C differs from the cation ratio in solution. For all of the films the increase of doping element concentration as compared to the solution composition was found. The most strongly this effect was observed for ZnO(Ga) films with high gallium concentration. The closest



Fig. 1. The dependence of sheet resistance R_s and film thickness on the number of deposited layers. Number "0" is devoted to ZnO sublayer. The inset shows the profile of film boundary obtained by profilometer.

values to initial solution composition were found for ZnO(Ga,In) codoped films. We assume that this effect is caused by the partial dissolution and removal of zinc oxide from previously deposited layers. Comparing the hydrolysis constant values of Zn^{2+} , Ga^{3+} and In^{3+} (pK = 9.0, 2.6 and 4.0, respectively [9]), one can find the decrease of pH for the solutions of the same concentration in the following order: $Zn^{2+} >> In^{3+} > Ga^{3+}$. The increase of the acidity of the solution leads to the partially dissolution of surface zinc oxide and its removal (for example, in the form of zinc ion $- Zn(H_2O)_x^{2+}$) from the substrate while rotating.

3.2. Phase composition and microstructure

The phase composition of thin films was determined by X-ray diffraction. Thin films dried at 200 °C are X-ray amorphous materials. After the annealing at 500 °C the appearance of polycrystalline ZnO (wurtzite) phase is observed for all ZnO-based films (Fig. 2). The quality of the diffraction patterns does not allow the accurate determination of ZnO unit cell parameters. The diffraction pattern of undoped ZnO film shows a small increase of relative intensity of (002) peak (growth orientation along *c*-axis) than for ZnO powder (Fig. 2b).

For ZnO(Ga), ZnO(In) and ZnO(Ga,In) thin films only the reflections of ZnO phase were observed on the XRD patterns, no gallium- or indium-containing phases were detected. In general, the increase of donor impurity content leads to the broadening of peaks indicating the decrease of ZnO grain sizes *d*_{XRD} according to Scherrer equation (Fig. 3). The influence of gallium and indium donor impurities on ZnO grain size is similar and the effect of both cations in ZnO(Ga,In) is additive. The observed dependence could be associated with the distribution of gallium and indium between volume and surface of zinc oxide grains. The decrease of $d_{XRD}(ZnO)$ with the growth of donor impurity content could be due to segregation of amorphous Ga- and In-containing phases on the surface of ZnO grains. This trend has general character and was observed for SnO₂, Fe₂O₃, MoO₃, and V₂O₅-based nanocrystalline materials in form of powders [10] and thin films [11]. The presence of impurities on the surface of the growing crystallites slows their



Fig. 3. The dependence on ZnO grain size d_{XRD} calculated from the broadening of the (002) XRD peak on donor impurity content. The dash line indicates the approximation of experimental data by power-law dependence (equation (1)).

growth under the isothermal annealing due to the so-called Smith–Zener diffusion inhibition (Zener pinning) [12], according to which the maximum size of the crystal grain D_m is determined by the volume fraction f and the size r_s of the particles, segregated on the surface of the growing crystallites:

$$D_m = a \frac{r_s}{f^b}.$$
 (1)

It was shown by Monte-Carlo simulations, that for the twophase nanocrystalline/amorphous films, the increase of the amorphous phase volume fraction should lead to a significant reduction in the size of nanocrystalline particles at fixed temperature and duration of isothermal annealing. The reducing of the crystallite size with the volume fraction of the amorphous phase segregated on their surface is described by a power law [13].



Fig. 2. XRD patterns of (a) – ZnO film; (b) – ICDD [75–576] data for ZnO powder; films obtained from the solutions with the following cation ratio: (c) – ZnO(Ga) – (1) 0.7 at%, (2) 1.0 at%, (3) 3.0 at% Ga; (d) – ZnO(In) – (4) 0.5 at%, (5) 1.0 at%, (6) 3.0 at% In; (e) – ZnO(Ga,In) – 0.7 at% Ga and (7) 0 at%, (8) 0.5 at%, (9) 1.0 at%, (10) 4.7 at% In.

The XRD patterns of the films (Fig. 2) show a preferred growth orientation along *c*-axis, other orientations are also presented with comparatively low intensities. It can be assumed that the segregation of the impurity-containing amorphous phases leads to the crystal growth in the direction [002] which is more kinetically favored [14]. Also different crystallite orientation in the ZnO-based films may be caused by the difference in the precursor chemistry [14]: pH of the solution; viscosity; the presence of different concentrations of cations (Zn²⁺, Ga³⁺, In³⁺) and anions (OH⁻, NO₃⁻) which can adsorb on the surface of grains and regulate the oriented growth.

AFM images for ZnO, ZnO(Ga), ZnO(In) and ZnO(Ga,In) films after annealing at 500 °C are shown in Fig. 4. All the films have granular structure. In all cases the introduction of donor element leads to the decrease of particle size as compared to undoped ZnO film. The mean surface roughness changes non-monotonously with the impurity content. The introduction of small amount of donor impurities (about 1 at%) leads to the decrease of this parameter from 100–150 nm down to 20–50 nm. Further increase of dopant concentration results in a slight increase of the surface roughness. This growth may be caused by the increased agglomeration



Fig. 4. AFM images of ZnO, ZnO(Ga) (from top to bottom: 0.7, 1.0, 3.0, 5.0 at% Ga in the initial solution), ZnO(In) (from top to bottom: 0.5, 3.0, 5.0 at% In in the initial solution) and ZnO(Ga,In) (0.7 at% Ga; from top to bottom: 0.5, 2.9, 4.7 at% In in the initial solution) films. The size of each image is 2.0 × 2.0 μm.

between the smaller grains, which possess the larger free surface energy and, consequently, the higher tendency toward agglomeration. The lowest values of surface roughness were obtained for codoped samples: this parameter increased from 20 to 30 nm with the indium content.

3.3. Electrical properties

The dependence of ZnO(Ga) resistivity on gallium content has non-monotonous character (Fig. 5). The introduction of small amount of gallium (up to 1.2 at%) leads to the decrease of the resistivity. Gallium acts as a donor impurity in zinc oxide and occupies cation sites in the ZnO lattice that leads to the increase of free charge carriers concentration according to the quasi-chemical reaction (Kröger–Vink notation of point defects is used) [1]:

$$M_2O_3 \rightarrow 2M_{Zn}^{\bullet} + 2O_0^X + 2e' + \frac{1}{2}O_{2(gas)}, \quad M = Ga, In.$$
 (2)

Further increase of gallium content results in the increase of resistivity. The non-monotonous change of the resistivity may indicate that Ga total concentration >1.2 at% exceeds the gallium solubility limit in zinc oxide. At high gallium concentration the formation of some kinds of neutral defects containing gallium atoms may occur, resulting in the decrease of the free electron density [15]. Also the increase of gallium concentration in the films results in the decrease of films crystallinity (Fig. 2c), which can influence on the conductivity. It was shown for amorphous ZnO(Ga) and ZnO(Ga,In) films obtained by pulsed laser deposition [16] and amorphous gallium indium zinc oxide films (In:Zn = 1:1) obtained by spin-coating technique [6] that the increase of gallium concentration leads to the decrease of electron mobility, and this effect may predominate over the increase of electron concentration at high gallium content. Moreover the decrease of conductivity with gallium content for films containing more than 1.2 at% Ga may be caused by the segregation of gallium-containing phases with relative high values of band-gap energy ($E_g(Ga_2O_3) = 4.9-5.0$ eV; $E_g(\text{ZnGa}_2\text{O}_4) = 4.4-4.7 \text{ eV}$ [17]. The analogous dependence of conductivity change with gallium content was obtained for nanocrystalline ZnO(Ga) powders [18].

The electrical resistivity of ZnO(In) films decreases monotonously with the indium content (Fig. 5). The introduction of indium



Fig. 5. The dependence of resistivity of films as a function of donor impurity content for (1) - ZnO(Ga), (2) - ZnO(In), (3) - ZnO(Ga,In) films.

leads to the increase of electron concentration as for gallium (reaction (2)). However, contrary to the gallium doping, the increase of indium concentration in amorphous indium gallium zinc oxide films (obtained by pulsed laser deposition) [16] and in ZnO(In) films (obtained by spin-coating technique and containing 0–10 at% of indium) [19], results in the increase of the electron mobility. The possible segregation of indium-containing phases (Zn₅In₂O₈, Zn₃In₂O₆) on zinc oxide grains does not lead to the increase of resistivity because of relative high conductivity of these phases comparing to ZnO [19].

The introduction of both gallium and indium in ZnO films leads to the more pronounced decrease of the resistivity values compared to Ga- or In-doped films (Fig. 5). The simultaneous introduction of both elements in ZnO structure may result in the dopant size compensation, which allows to achieve higher dopant solubility while retaining ZnO structure. It was shown for ZnO(Al,In) films that the dopant size compensation effect leads to the decrease of cell volume change and to the improved electron mobility as compared to single-doping [3]. Assuming that Ga and In occupy regular Zn sites in ZnO lattice (reaction (2)), their coordination number would be 4 (wurtzite structure). The effective ionic radii of Zn^{2+} , Ga^{3+} and In^{3+} for this coordination number are 0.60, 0.47 and 0.62 Å, respectively [20], the mismatches to Zn^{2+} radius are -22% for Ga³⁺ and +3% for In³⁺. So in the case of indium the higher solubility in zinc oxide could be expected as compared to gallium. However it was shown that gallium could substitute Zn states in the octahedral interstitials [21]. The Frenkel-type defects in ZnO leads to the formation of neutral (Zn_i^X) and ionized (Zn_i^{\bullet}) zinc interstitials. Since oxygen octahedral coordination is observed for Ga₂O₃ and In₂O₃ oxides, it may be more preferred for substitution than tetrahedral coordination in ZnO regular sites. The effective ionic radii for these ions for coordination number 6 (interstitial state in ZnO lattice) are 0.74, 0.62 and 0.80 Å for Zn²⁺, Ga^{3+} and In^{3+} , respectively [20], the mismatches to Zn^{2+} radius are -16% for Ga³⁺ and +8% for In³⁺. The difference of ionic radii comparing to Zn²⁺ radius leads to the large strain in the lattice for single-doped ZnO. For both coordination numbers the effective ionic radius for zinc ion is located between Ga³⁺ and In³⁺ values, so the effect of dopant size compensation may result in the increase of donor impurity solubility, which leads to the enhancement of morphology of ZnO-based films (ZnO(Ga,In) films have the most smooth surfaces as compared for single-doped films) or crystal quality of ZnO-doped particles.

3.4. Optical properties

Optical absorbance spectra of ZnO(Ga) and ZnO(In) films annealed at 500 °C are shown in Fig. 6. The appearance of well distinguishable peak at 3.42 eV on absorbance spectrum of undoped ZnO film (Fig. 6a, line 1) may be attributed to the exciton band. The existence of exciton emission in ZnO even at room temperature is due to relatively high exciton binding energy of ~60 meV (for bulk ZnO), which is 2.4 times larger than the room-temperature thermal energy ($k_{\rm B}T = 25$ meV, $k_{\rm B}$ – Boltzmann constant) [1,2]. Only one peak is found because of close lying and thermally broadened exciton transitions. With the increasing of donor impurity centers concentration the exciton peak becomes broader and then disappears for the samples with high gallium or indium content. The introduction of donor impurity and, correspondingly, the increase of electron concentration, lead to the screening of the Coulomb interaction of electron and hole in the exciton. The influence of donor impurity concentration on the ZnO absorbance spectra could be determined by intraband screening and Pauli blocking [22]. The presence of the exciton peak leads to the difficulties in the bandgap calculation. The use of the extrapolation of linear portion in the



Fig. 6. Absorbance spectra of (*a*) ZnO(Ga) films prepared from the solutions containing (1) - 0 at%, (2) - 0.25 at%, (3) - 1.0 at%, (4) - 3.0 at%, (5) - 5.0 at% Ga and (*b*) ZnO(In) films prepared from the solutions containing (1) - 0.25 at%, (2) - 0.5 at%, (3) - 1.0 at%, (4) - 3.0 at%, (5) - 5.0 at% Ga and (*b*) ZnO(In) films prepared from the solutions containing (1) - 0.25 at%, (2) - 0.5 at%, (3) - 1.0 at%, (5) - 5.0 at% Ga and (*b*) ZnO(In) films prepared from the solutions containing (1) - 0.25 at%, (2) - 0.5 at%, (3) - 1.0 at%, (5) - 5.0 at% Ga and (*b*) ZnO(In) films prepared from the solutions containing (1) - 0.25 at%, (2) - 0.5 at%, (3) - 1.0 at%, (4) - 3.0 at%, (5) - 5.0 at% Ga and (*b*) ZnO(In) films prepared from the solutions containing (1) - 0.25 at%, (2) - 0.5 at%, (3) - 1.0 at%, (4) - 3.0 at%, (5) - 5.0 at% In.

plot of $(Abs^*hv)^2$ against (hv) is not correct because of the overlap of the exciton peak and the band-gap edge. These effects are close enough and it is impossible to resolve the overlapping and to separate the effects carefully. The shift of exciton peak position on absorbance spectra with gallium and indium content (Fig. 7) may be attributed to the decrease of the exciton binding energy due to screening of the Coulomb energy. Also introduction of gallium and indium causes the decrease of grain size (as was seen from XRD and AFM data) that may lead to the increase of band-gap energy (quantum confinement effect). For ZnO(Ga,In) thin films the exciton peak is not observed because of relatively high total concentration of donor impurities.

Transmission values are determined by the composition and the thickness of film. The effect of film thickness is smaller than that caused by the film composition: no strong correlation was observed for the transmission and thickness changes for films with different cation ratio. This fact allows us to consider the change of transmittance as a function of cation ratio.

Fig. 8 shows the transmittance spectra of ZnO and ZnO(Ga) thin films in the range of 320–800 nm. ZnO(Ga) films are transparent in the visible region. The change of transmittance values at 400–800 nm are shown in the inset of Fig. 8. The average transmittance for ZnO film is about 89% in this range. Introduction of

gallium leads to the increase of minimum transmittance values. However for high gallium concentration the highest value of the transmittance in the range 400–800 nm decreases. Introduction of 0.6–1.2 at% Ga leads to the increase of average transmittance up to 95%, further increase of gallium content results in the decrease of average transmission.

The same tendency in the change of average transmittance is observed for ZnO(In) films (Fig. 9), although the values are smaller comparing to ZnO(Ga). The maximum average transmittance was found for ZnO(In) film containing 0.3 at% In. Introduction of 10 at% of indium leads to the decrease of average transmittance down to about 80%. The highest value of the transmittance at 400–800 nm decreases with indium content. The films with high indium and gallium concentration look slightly white probably because of light scattering at the interfaces and grains.

ZnO(Ga,In) co-doped film (1.3 at% Ga, 0.7 at% In) is the most transparent and its average transmittance achieves 97% in the range 400–800 nm (Fig. 10). Comparing to ZnO(In) films, introduction of small amount of gallium in ZnO(Ga,In) films leads to the significant increase of transmittance for the films with approximately equal indium content. Introduction of both gallium and indium leads to the increase of maximum and minimum values of films transmittance at 400–800 nm. This fact may be explained by



Fig. 7. The dependence of exciton peak position (E_{peak}) on concentration of Ga (1) and In (2) in zinc oxide films.



Fig. 8. Transmittance spectra of ZnO(Ga) thin films prepared from the solutions containing (1) - 0 at%, (2) - 0.25 at%, (3) - 0.7 at%, (4) - 1.0 at%, (5) - 3.0 at%, (6) - 5.0 at% Ga. The inset shows maximum (*a*), average (*b*) and minimum (*c*) values of transmittance at 400–800 nm depending on the films composition.



Fig. 9. Transmittance spectra of ZnO(In) thin films prepared from the solutions containing (1) - 0 at%, (2) - 0.25 at%, (3) - 0.5 at%, (4) - 1.0 at%, (5) - 3.0 at%, (6) - 5.0 at% In. The inset shows maximum (*a*), average (*b*) and minimum (*c*) values of transmittance at 400–800 nm depending on the films composition.



Fig. 10. Transmittance spectra of ZnO(Ga,In) thin films prepared from the solutions containing 0.7 at% Ga and (1) - 0 at%, (2) - 0.5 at%, (3) - 1.0 at%, (4) - 2.9 at%, (5) - 4.7 at% In. The inset shows maximum (*a*), average (*b*) and minimum (*c*) values of transmittance at 400–800 nm depending on the films composition.

the formation of more perfect crystal structure for ZnO(Ga,In) films due to the decrease of lattice strain. The changes of the surface roughness may influence on the transmittance values: the increase of the roughness leads to the optical scattering of light. The presence of X-ray amorphous impurities at the grain boundaries of highly-doped films (>1.5 at% of donor elements) also leads to the light scattering.

4. Conclusions

ZnO(Ga), ZnO(In), ZnO(Ga,In) films were prepared on glass substrates using spin-coating technique with further annealing at 500 °C. Only ZnO (wurtzite) phase was observed for all films. The structural, morphological, electrical and optical characteristics of thin films were studied. The increase of gallium and indium content leads to the decrease of crystallite size of ZnO. Introduction of 1.0–1.3 at% of gallium in ZnO and ZnO(In) results in the enhancement of electrical and optical properties of ZnO(Ga) and ZnO(Ga,In) films as compared to undoped ZnO. Introduction of indium in ZnO and ZnO(Ga) films leads to the monotonous decrease of resistivity. The highest average transmittance in the range of 400–800 nm was obtained for co-doped ZnO film containing 1.3 at% of Ga and 0.7 at% of In. So, to sum up, co-doping of ZnO with gallium and indium is preferable to single-doping. Introduction of both gallium and indium allows to increase conductivity by 3 orders of magnitude as compared to ZnO for films with rather low concentrations of indium. This effect may be caused by the decrease of lattice strain in ZnO structure for co-doped films as compared to single-doped (effect of dopant size compensation) and, consequently, the increase of solubility of donor elements in ZnO structure.

Acknowledgments

This work was supported by RFBR grants 12-03-00481 and 12-03-00804.

References

- Ellmer K. Transparent conductive zinc oxide and its derivatives. In: Ginley DS, Hosono H, Paine DC, editors. Handbook of transparent conductors. New York: Springer; 2010. p. 193–263.
- [2] Özgür Ü, Alivov Yal, Liu C, Teke A, Reshchikov MA, Doğan S, et al. A comprehensive review of ZnO materials and devices. J Appl Phys 2005;98: 041301.
- [3] Kirby SD, van Dover RB. Improved conductivity of ZnO through codoping with in and Al. Thin Solid Films 2009;517:1958–60.
- [4] Chirakkara S, Krupanidhi SB. Gallium and indium co-doped ZnO thin films for white light emitting diodes. Phys Status Solidi RRL 2012;6:34–6.
- [5] Suresh A, Wellenius P, Dhawan A, Muth J. Room temperature pulsed laser deposited indium gallium zinc oxide channel based transparent thin film transistors. Appl Phys Lett 2007;90:123512.
- [6] Kim D, Koo CY, Song K, Jeong Y, Moon J. Compositional influence on sol-gelderived amorphous oxide semiconductor thin film transistors. Appl Phys Lett 2009;95:103501.
- [7] Tsay C-Y, Wu C-W, Lei C-M, Chen F-S, Lin C-K. Microstructural and optical properties of Ga-doped ZnO semiconductor thin films prepared by sol–gel process. Thin Solid Films 2010;519:1516–20.
- [8] Chen KJ, Hung FY, Chang SJ, Hu ZS. Microstructures, optical and electrical properties of In-doped ZnO thin films prepared by sol-gel method. Appl Surf Sci 2009;255:6308–12.
- [9] Wulfsberg G. Principles of descriptive inorganic chemistry. Sausalito: University Science Books; 1991.
- [10] Rumyantseva MN, Gaskov AM. Chemical modification of nanocrystalline metal oxides: effect of the real structure and surface chemistry on the sensor properties. Russ Chem Bull 2008;57:1086–105.
- [11] Rumyantseva MN, Safonova OV, Boulova MN, Ryabova LI, Gaskov AM. Dopants in nanocrystalline tin dioxide. Russ Chem Bull Int Ed 2003;52:1217–38.
- [12] Miodownik M, Holm EA, Hassold GN. Highly parallel computer simulation of particle pinning: zener vindicated. Scr Mater 2000;42:1173–7.
- [13] Liu Z-J, Shen YG. Effects of amorphous matrix on the grain growth kinetics in two-phase nanostructured films: a Monte Carlo study. Acta Mater 2004;52: 729–36.
- [14] Znaidi L. Sol-gel-deposited ZnO thin films: a review. Mater Sci Eng B 2010;174:18–30.
- [15] Hu J, Gordon RG. Atmospheric pressure chemical vapor deposition of gallium doped zinc oxide thin films from diethyl zinc, water, and triethyl gallium. J Appl Phys 1992;72:5381–92.
- [16] Hosono H. Ionic amorphous oxide semiconductors: material design, carrier transport, and device application. J Non-Cryst Solids 2006;352:851–8.
- [17] Robbins JJ, Fry C, Wolden CA. An interrogation of the zinc oxide—gallium oxide phase space by plasma enhanced chemical vapor deposition. J Cryst Growth 2004;263:283–90.
- [18] Vorobyeva NA, Rumyantseva MN, Forsh PA, Gaskov AM. Conductivity of nanocrystalline ZnO(Ga). Semiconductors 2013;47:650–4.
- [19] Kurz A, Aegerter MA. Novel transparent conducting sol-gel oxide coatings. Thin Solid Films 2008;516:4513-8.
- [20] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst 1976;A32:751–67.
- [21] Kaul AR, Gorbenko OYu, Botev AN, Burova LI. MOCVD of pure and Ga-doped epitaxial ZnO. Superlattices Microstruct 2005;38:272–82.
- [22] Schleife A, Rödl C, Fuchs F, Hannewald K, Bechstedt F. Optical absorption in degenerately doped semiconductors: Mott transition or Mahan excitons? Phys Rev Lett 2011;107:236405.