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Structural, electrical and luminescent properties of ZnO:Li films fabricated by screen-printing method on sapphire substrate

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Undoped and Li-doped ZnO thick films were fabricated by a screen-printing technique on sapphire substrate. The effect of sintering temperature (T_S=800, 900 and 1000 °C) and Li content ([Li] =0.003, 0.03 and 0.3 wt%) on the photoluminescence (PL), electrical and structural properties of the films was investigated. The X-ray diffraction shows that all the films are polycrystalline with a wurtzite structure. It is found that both high sintering temperature and low Li content favour formation of the low-resistive films with an enhanced UV emission. The high Li content stimulates an appearance of semi-insulating behaviour of the films and deteriorated PL properties. It is shown that the effect of Li-doping on light-emitting properties of the films consists mainly in the modification of the film crystallinity and the engineering of the concentration of intrinsic defects.

1 Introduction Zinc oxide (ZnO) is a wide band gap (3.3 eV) semiconductor which is promising for application in light-emitting devices, solar cells and sensors [1]. ZnO shows highly efficient excitonic photoluminescence (PL) and a high exciton binding energy (60 meV) that offer the realization of light emitting devices operated in the UV spectral range at room temperature. Besides, the visible defect-related PL of ZnO creates the possibility to develop low-energy and environmentally-friendly white-light-emitting technologies [2, 3].

The bottleneck for wide ZnO application in optoelectronics is its hardly achievable p-type conductivity that has to be overcome. Generally, the realization of p-type ZnO is achieved via the doping by either the group I elements substituting the zinc sites or the group V elements substituting the oxygen-sites [4, 5]. Although the significant progress was demonstrated [6, 7], the investigation of the fundamental properties of the dopants in ZnO is still required.

Among the group I elements, lithium is considered as a promising dopant in spite of controversial discussion on stable p-type activity of Li-doped ZnO materials under equilibrium conditions. Indeed, ab-initio consideration predicted the shallow-acceptor behaviour of Li on the Zn-lattice site (Li_{Zn}) [8], whereas most of the experimental data showed the deep-acceptor nature of Li_{Zn} favoured “yellow” luminescence at 2.0–2.2 eV [4, 9, 10]. Besides, Li atoms can occupy easily the interstitial positions Li_i, acting as the donors [2]. This amphoteric behaviour together with an ability of Li_{Zn} acceptor to form neutral complexes with other defects have been suggested to be responsible for the frequently observed semi-insulating nature of ZnO material upon Li doping [8]. An introduction of Li in the ZnO can affect also its crystallinity. Specifically, it has been reported that lithium can suppress or promote the growth of ZnO particles during a synthesis [11, 12] as well as the crystal grain size in the polycrystalline ZnO films upon thermal annealing [13, 14]. At the same time, Li-doped ZnO films produced by screen-printing technique are not well considered despite the simplicity and low cost of this approach. In the present work, the effect of Li doping on the structural, electrical and luminescent properties of ZnO films fabricated by this technique was studied.

2 Experimental procedure Undoped and Li-doped ZnO films were fabricated by the screen-printing technique on the substrates of (1012) Al_2O_3 palettes with the sizes of 1×1 cm^2. The films were printed from the pastes prepared from Sigma-Aldrich ZnO powder (<5 μm particle size, 99.99%), milled with agatha balls during 125 h and then mixed with either distillate H_2O or with $LiNO_3$:H_2O solutions of different composition. As-printed films were dried at normal conditions and sintered at T_S=800–1000 °C for t_S=30 min in air atmosphere. The thickness of sintered films was about 40 μm. The Li content in the films was [Li]=0.003, 0.03 and 0.3 wt%. To investigate electrical properties of the films, stripe-like indium contacts were evaporated onto the film surface.

The emission properties of the films were studied by stationary PL spectroscopy with the use of a SDL-2 spectrometer (LOMO, St. Petersburg). The PL was excited by a 337.1 nm line of pulsed N_2-laser. The structural properties of the films were controlled by X-ray diffraction (XRD) method using X-ray powder diffractometer ARL X'TRA with the Cu Kα_1 and Cu Kα_2 radiation. The photoconductivity was measured using UV light of a 500 W Hg lamp. All the experiments were performed at room temperature.

3 Results and discussion

3.1 Structural properties The XRD patterns of the films are presented in Fig. 1. The films turn out to be polycrystalline and exhibit a hexagonal wurtzite structure. The XRD peaks were indexed using the standard JCPDS file for ZnO (JCPDS #36-1451). No extra peaks were found in the Li-doped films suggesting a uniform distribution of Li atoms without either cluster or secondary phase formation.

The peak position and full width at half maximum (FWHM) of the ZnO-related XRD peaks show a non-monotonic tendency with T_s and Li content. Table 1 shows the variation of these parameters for the (002) XRD peak. For the undoped ZnO films, the increase of T_S results in the decrease of the FWHM and the shifting of the peak position towards smaller angles. At the same time, the effect of Li doping is more complex. For example, as compared with the undoped films, the introduction of [Li]=0.003 wt% produces both the narrowing of the (002) peak and its shifting to lower angles upon the annealing at T_s=800 °C. In the films sintered at T_s=1000 °C, the doping causes the broadening of the XRD peak and its shifting towards higher angles. It means that Li doping has complicated effect on the grains' growth and interplanar spacing of ZnO lattice.

In fact, the interplanar spacing of (002) planes (d_{002}-spacing) shows somewhat variation with sintering temperature confirming the compression or expansion of lattice in comparison with relaxed ZnO (d_{002}=0.2604 nm). These changes can be caused by the incorporation of Li atoms on Zn sites and by the stresses produced by the substrate. Since the ionic radius of Li is smaller than that of Zn, the decrease of the d_{002}-spacing with Li incorporation is expected. However, it is difficult to distinguish between the effects of both factors considering that an incorporation of Li on Zn site should occur for all sintering temperatures. At the same time, the decrease of the d_{002}-spacing in the Li-doped films sintered at T_S=1000 °C can be the evidence of lattice constriction caused by the Li_{Zn} defect formation.

From the peak position and FWHM of the (002) diffraction peak a coherent scattering region (*D*) was estimated using Debye-Scherrer's equation $D=0.9\lambda/(\beta\cos\Theta)$, where Θ is the Bragg angle, λ is the incident wavelength, β is the FWHM. Obtained D values (Table 2) can be considered roughly as the size of ZnO grains in polycrystalline particles.

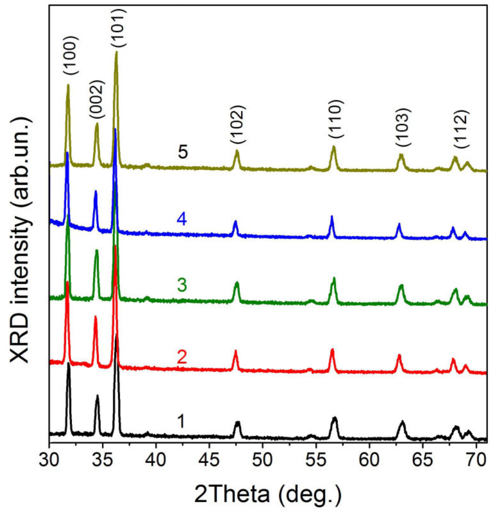

Figure 1 XRD patterns of undoped (1,4) and Li-doped ZnO (2,3,5) films with [Li]=0.003 (2) and 0.3 wt% (3,5). The films were sintered at T_S=800 °C (1–3) and 1000 °C (4,5) for t_s=30 min in air.

Table 1 Peak position (2Θ) and FWHM (β) of (002) XRD peak of undoped and Li-doped ZnO films.

[Li], wt%	T_s=800 °C		T_s=900 °C		T_s=1000 °C	
	2Θ (°)	FWHM (°)	2Θ (°)	β (°)	2Θ (°)	FWHM (°)
0	34.489	0.365	34.360	0.296	34.331	0.246
0.003	34.327	0.279	34.456	0.298	34.439	0.345
0.03	34.452	0.351	34.522	0.356	34.449	0.320
0.3	34.410	0.367	34.298	0.312	34.441	0.316

Table 2 Structural parameters of undoped and Li-doped ZnO films estimated from the XRD data.

[Li], wt%	T_s=800 °C		T_s=900 °C		T_s=1000 °C	
	D,nm	$d_{002,}$ nm	D,nm	$d_{002,}$ nm	D,nm	$d_{002,}$ nm
0	26.44	0.2598	32.59	0.2608	39.13	0.2610
0.003	34.54	0.2610	32.41	0.2601	27.99	0.2602
0.03	27.44	0.2601	27.13	0.2596	30.12	0.2601
0.3	26.29	0.2604	30.89	0.2612	30.54	0.2602

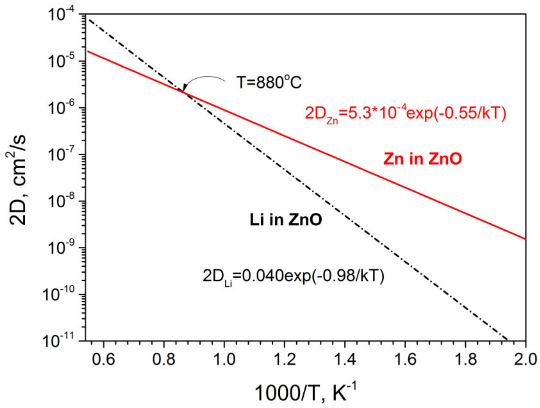

Figure 2 The diffusion coefficients of Li and Zn ions in ZnO. The dependencies were plotted using the data of Ref. [16, 17].

For the undoped ZnO films, the enlargement of ZnO grains from *D*=26±1 nm for T_S=800 °C up to *D*=39±1 nm for T_S=1000 °C is found. This is a typical behavior of polycrystalline films which undergoes a grain growth during high temperature annealing because the mobility of grain boundary is strongly temperature-dependent [15].

The effect of Li doping on the grains' formation depends on the Li content, i.e. low Li content favors formation of ZnO grains whereas the high Li content suppresses grain growth (Table 2). The former effect is observed for the lowest sintering temperature of T_S=800 °C, while the latter is found for all the sintering temperatures. It should be noted that a similar non-monotonic dependence of the grain size on Li concentration had been observed for Li-doped ZnO films prepared by a sol-gel method and thermally annealed at 700 °C [8]. The effect of Li doping on the grain size can be explained taking into account the diffusion coefficients of Li (D_{Li}) [16] and Zn (D_{Zn}) [17] in ZnO crystal. As one can see from Fig. 2, both ions have comparable diffusion coefficients at T_S≈880 °C.

When the films are sintered at lower T_S, i.e. T_S=800 °C, the D_{Zn} value exceeds the D_{Li} one. This means that at this temperature the diffusion of Zn ions will dominate and the formation of larger ZnO grains becomes possible. At higher doping level and higher temperatures the Li ions can be effectively gathered at the grain boundaries. As a rule, the impurities segregated to grain boundaries exert a drag force on boundary motion and suppress grain growth [13]. It worth to note that for the films grown at T_S=900 °C both Li and Zn diffusion will compete and the formation of ZnO grains will depend mainly on the Li content.

3.2 Conductivity The increase of grain size implies the decrease of the density of grain boundaries. The latter act as the sinks for point defects, in particular for oxygen ions. In the polycrystalline ZnO films, the negatively charged oxygen ions chemisorbed at the film surface and at the grain boundaries are known to be the origin of low dark conductivity [18]. Therefore, one can expect higher dark conductivity in the films with larger grain sizes.

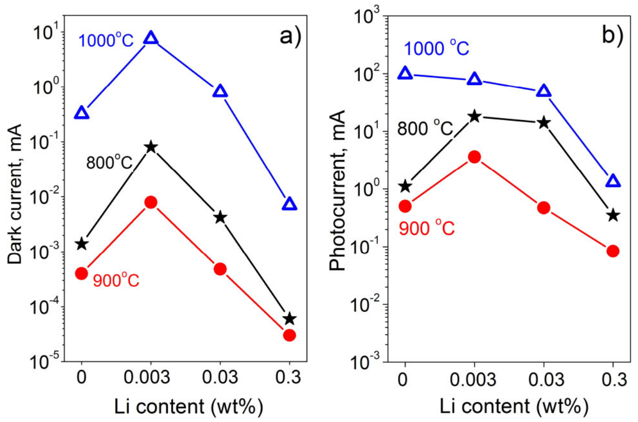

Figure 3 Dark (a) and photo- (b) conductivities of undoped and Li-doped ZnO films sintered at T_S=800 (★), 900 (●) and 1000 °C (△) versus [Li] content. U_{sample}=9 V.

The results on the electrical characterization of the films are summarized in Fig. 3. In fact, the dark conductivity of the films sintered at T_S=800 °C and 900 °C is much lower than those of the films sintered at T_S=1000 °C (Fig. 3a). The films with [Li]=0.3 wt% show a hundred-fold lower conductivity than their undoped or doped counterparts annealed at the same temperature.

It should be noted that the electrical properties of the Li-doped films are determined not only by the effect of Li on the ZnO grain growth, but also by the appearance of Li_{Zn} acceptors and Li_i donors. Thus, the competition of these two factors determines electrical characteristics of the doped films.

3.3 PL properties The PL spectra of the films are shown in Fig. 4. In the spectra, an UV PL band (I_{UV}) and a wide defect-related PL band (I_{DEF}) in the green-orange spectral range are observed. The parameters of each PL band depend significantly on the sintering conditions and Li content.

Undoped ZnO films sintered at T_S=800 °C and 900 °C show lower UV PL intensity contrary to the films sintered at T_S=1000 °C. Doping with the lowest Li concentration (0.003 wt%) strongly enhanced an UV emission for the films sintered at low T_S (Fig. 4a). At the same time, irrespectively of T_S value, the highly doped films ([Li]=0.3 wt%) do not demonstrate any UV emission, and the defect-related PL band is decreased too. This indicates the increase of concentration of the centers of non-radiative recombination in highly doped films.

The ratio of the intensities of the UV to defect-related PL band (I_{UV}/I_{DEF}), shown in Fig. 5a, can be used for the estimation of the structural performance of ZnO films. The best PL properties are observed for the films doped with [Li]=0.003 wt% whereas the highly doped films are the worst. The improvement of crystalline quality of the films occurred at higher annealing temperature and upon the doping with the lowest Li concentration is in agreement with the results of structural and electrical characterization.

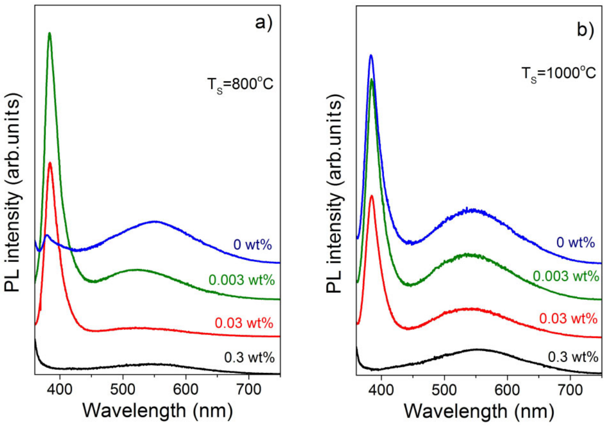

Figure 4 PL spectra of undoped and Li-doped ZnO films with different content of Li (0, 0.003, 0.03 and 0.3 wt %) which were sintered at T_S=800°C (a) and 1000°C (b) for t_s=30 min in air.

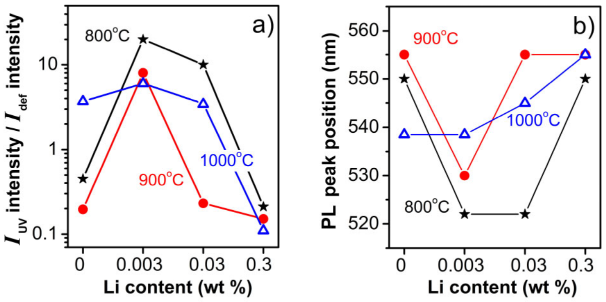

Figure 5 Ratio of integrated intensities of the I_{UV} to the I_{DEF} band (a) and spectral position of the I_{DEF} band (b) versus Li content in the ZnO films sintered at different temperatures.

It should be noted, that in the undoped and Li-doped films, the spectral position of the UV band shifts from 378 nm in the films with low UV emission to 384 nm in the films with strongly enhanced UV PL. In turn, the peak position of the I_{DEF} band varied in the range of 522–555 nm in different samples and showed the shortest wavelength position for the Li-doped films with [Li]=0.003 and 0.03 wt % and sintered at T_S= 800 °C (Fig. 5b). This indicates that the defect-related PL band is complex and composes of at least two overlapping PL bands peaked at 520 nm (“green”) and 590 nm (“orange”).

In the undoped ZnO, these PL bands are usually ascribed to intrinsic defects, such as the Zn vacancy (V_{Zn}), interstitial zinc (Zn_i), the O vacancy (V_O), oxygen antisite (O_{Zn}), etc. [1, 2]. In spite of the fact that the “orange” band is often ascribed to Li_{Zn} acceptor we cannot exclude that in the Li-doped films this band originates from the intrinsic defects of ZnO whose concentration depends on crystallization process. This is because we do not observe a pronounced increase in the intensity of the “orange” band upon the Li-doping. Moreover, the peak position of the I_{DEF} band is found to be shifted to the orange spectral range both in the undoped ZnO films sintered at low T_S and in highly Li-doped ZnO films.

4 Conclusions The undoped and Li-doped polycrystalline ZnO films of wurtzite structure were successfully fabricated by a screen-printing method. The effect of sintering and doping conditions on the films crystallinity was observed. The increase of sintering temperature results in the enlargement of ZnO grain sizes in the undoped films. At the same time, similar grain sizes can be achieved for the films sintered at lower temperatures via their doping with [Li]=0.003 wt%. These data demonstrate the possibility to produce the films with high UV emission, reduced concentration of crystalline defects, high dark and photoconductivities with lower thermal budget for film production. At the same time, the introduction of high Li concentration ([Li]=0.3 wt%) suppresses the grain growth even at 1000 °C and introduces a large amount of crystalline defects in the films. This leads to the semi-insulating nature of the highly doped film with no excitonic emission. It is supposed that the effect of Li doping on the PL of polycrystalline ZnO film is determined mainly by the effect of Li on the internal crystalline defects.

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