

Effect of lithium on linear and nonlinear optical properties of Sn-doped zinc oxide prepared by spray pyrolysis

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Abstract. Li and Sn codoped ZnO (LTZO) thin films have been successfully deposited on heated glass substrates at 450°C using the spray pyrolysis technique, the effect of lithium of Sn-doped zinc oxide on the structural, morphological, optical and nonlinear optical properties was investigated using X-ray diffraction, transmission, the RMS average surface roughness, and third harmonic generation (THG). The value of optical band gap E_g was found to be decreased from 3.24 eV to 3.16 eV when the concentration of Li from 0 to 7%, while the concentration of Sn is fixed at 2%. The doping of ZnO films improves the nonlinear response and the highest susceptibility value $\chi^{(3)} = 13.422 \times 10^{-12}$ (esu) is found at concentration of lithium 7%.

1. Introduction

Zinc oxide (ZnO) thin films have been extensively studied and used for different domains such as microelectronic and optoelectronic applications [1], with direct band gap of 3.37 eV, high exciton binding energy of 60 meV at room temperature, is attractive for optoelectronic application in the blue and UV region, especially the data storage, which is the main work of the year, the blue emission generated to produce the new light by physics Nobel laureates [2], it can be used also at transparent conductive oxide thin films such as for application in solar cells [3]. Furthermore, the effect of ZnO doping on its nonlinear optical properties have been studied for several decades [4, 5, 6].

It was shown that the Sn doping of ZnO improves its electrical and structural properties [7], and the doping by Li was shown to be attractive for modifying the microstructure, ferroelectricity and optoelectronic properties [8] and enhance the rate of the crystal growth due to an increase of its diffusivity [9]. Furthermore, Yousefi et al [10] have reported that the crystallite and particle sizes can be increased by doping with group- I elements, reduce the oxygen vacancies in ZnO Lattice, Behera et al [11] reported that Li doping has always been in controversy, since Li ion can take up at interstitial sites, thus acting as shallow donor and compensate the acceptor action (self-compensation). Due to unequal ionic radius of lithium (0,68 Å) and zinc (0,74 Å) atoms, lithium is also expected to occupy substitution sites and thus can influence the structural and optical properties [11]. Li-Mg [12], Li-Al [13], Li-N [14], Cu-Li [8] co-doping of ZnO has also been investigated.

In this work, Li and Sn co-doped ZnO (LTZO) thin films were prepared using a spray pyrolysis technique, where the deposition temperature, the used precursors, concentration, the spray rate must be controlled [15], and its influence on the linear and non-linear optical properties is studied and discussed.



2. Experimental detail

LTZO thin films were grown on glass substrates and heated at 450°C by spray pyrolysis, experimental setup has been described elsewhere [5]. The spraying solution was 0.05M zinc chloride. The doping was achieved by adding SnCl_2 in a concentration is fixed at 2%. Different concentration of Li were used for co-doping the ZnO by adding LiClO_4 in a concentration of 3, 5 and 7 %. The spray time was 3 min with solution flow rate of 5 ml min^{-1} and the distance between the nozzle and substrate distance was fixed to be 40cm. The structural properties of thin films were investigated using X-ray diffractometry (X'Pert³ Powder PANalytical diffractometer) with Cu ($K\alpha$) radiation ($\lambda=1054\text{\AA}$). The optical transmission measurements were performed with Jasco V-570 UV/Vis/NIR spectrophotometer. Nano-surf Flex FM digital instruments operated in the tapping mode was used for the AFM images and the Third order nonlinear susceptibility was performed using third harmonic generation (THG) method [6].

3. Results and discussion

Figure 1 shows the XRD patterns of LTZO films with an atomic concentration of 2% Sn and different concentrations of Li (0, 3, 5, 7%). From the results, we can see that all films are polycrystalline with a hexagonal wurtzite structure [16].

The calculated lattice parameters a and c are summarized in the table 1. The full-width at a half maximum (FWHM) of the (002) peak are 0.13° , 0.12° , 0.11° and 0.10° and using the debay Scherrer formula, the calculated grains size are 63.142, 72.593, 76.414 and 85.404 nm, when the concentration of Li is increased from 0, 3, 5 and 7% respectively.

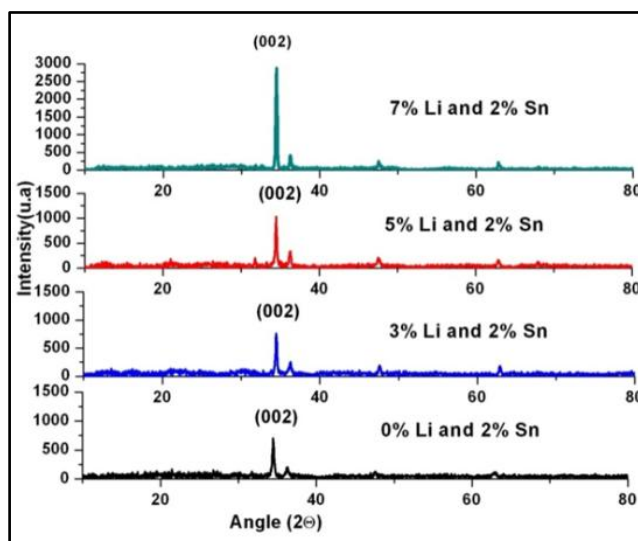


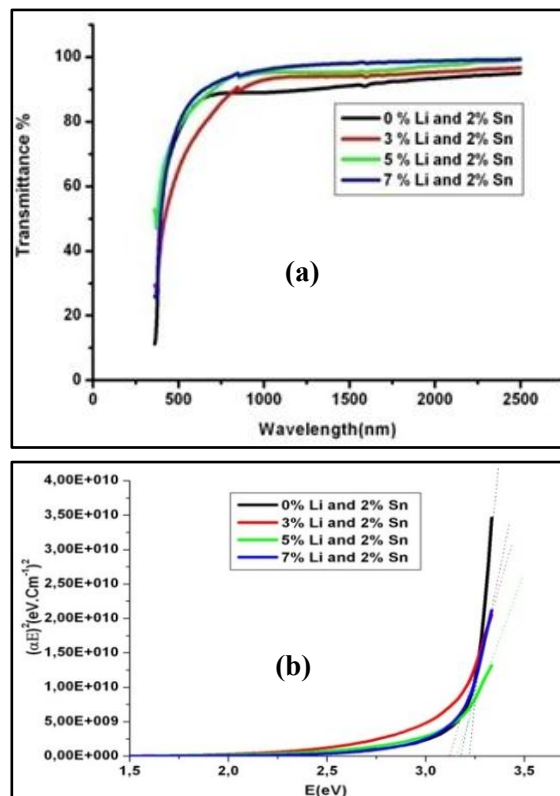
Figure 1. XRD patterns of LTZO films with various doping concentration. All films were grown at 450 [16]

Table 1. Lattice parameters, FWHMs and average crystal size obtained from XRD patterns

Films	a (Å)	c (Å)	FWHM β (deg)	Average crystal size (D)
0% Li and 2% Sn	3.2491	5.2005	0.13	63.142
3% Li and 2% Sn	3.2517	5.1984	0.12	72.593
5% Li and 2% Sn	3.2491	5.2000	0.11	76.414
7% Li and 2% Sn	3.2529	5.2003	0.10	85.404

Figure 2(a). Depicts the optical transmission spectra of LTZO thin films. All films exhibit an average optical transparency exceeding 85% in the visible region, the average transmittance was increased after Li/Sn codoping, reaching the maximum for Li and Sn concentration of 7% and 2% respectively. In effect Fellahi et al [17] reported that, the light scattering decreases with the improvement of the crystallinity of the ITO films. In fact the crystallinity probably affects the light scattering on the transparency of the LTZO films.

Figure 2(b) illustrates a plot of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ for the LTZO films. The extrapolation of the slopes of the curves, gives the optical band gap E_g . The values of optical band gaps decreases from 3.24 to 3.16 eV with increasing Li concentration from 0 to 7% .It has been reported that the increased concentration of Li in a Li/Al co-doped ZnO can induce a resonance structure in the density of state, which split off the band [13].

**Figure 2.** Optical properties of LTZO films. (a) Transmittance spectra and (b) Plots of $(\alpha h\nu)^2$ vs. $h\nu$.

The transparency of ZnO at 1064 nm, which is the laser excitation wavelength, makes it a good candidate for nonlinear optical applications [18]. Figure 3 shows the THG spectra of LTZO films. The third-order optical nonlinearities of Li-Sn codoped ZnO (LTZO) films were investigated by THG technique in order to study the effect of lithium on nonlinear optical properties of Sn-doped zinc oxide thin films, Figure 3 exhibit Maker-fringes obtained by rotating the samples through the range from $\pm 60^\circ$ to the normal.

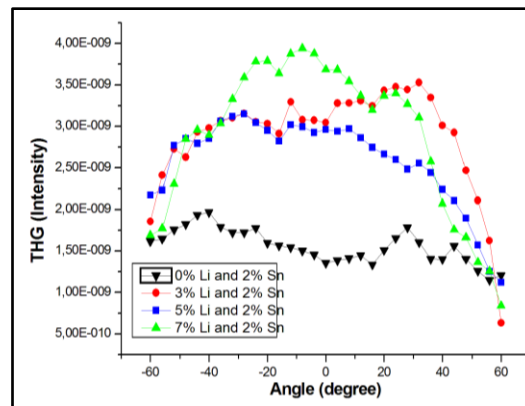


Figure3.The THG spectra of LTZO films deposited on glass substrates

The $\chi^{(3)}$ can be expressed as [19]

$$\chi^{(3)} = \chi_s^{(3)} \left(\frac{2}{\pi} \right) \left(\frac{L_{c,s}}{l} \right) \left(\frac{I_{3\omega}}{I_{3\omega,s}} \right)^{1/2} \quad (1)$$

Where the $I_{3\omega}$ is the THG intensity, the suffix s refers to the reference material, as silica. $L_{c,s}$ is the coherence length of microscope slide which is around $18\mu\text{m}$. The value of the nonlinear susceptibility is about: $\chi_s^{(3)} = 5.7841 \times 10^{-12} (\text{esu})$.

The values of $\chi^{(3)}$ calculated using the formula (1) are summarized in the table (2) it can be seen that the Li-Sn co-doping of zinc oxide thin films improves the nonlinear response, and the highest susceptibility value $\chi^{(3)} = 13.422 \times 10^{-12} (\text{esu})$ was found at concentration of lithium (7%), which can be explained by the fact that the surface smoothed by the Li doping as shown in the table (2), so the light diffusion is reduced, this agrees with the increase of the transmission of the films when the Li concentration is increased as shown in the figure 2.a. Moreover, as we showed in previous work [16] the scattering of light is strongly affected by the roughness and the structural properties of the films, while it can be deduced that the smoothing of the surface reduces the scattering of light and generates the highest nonlinear optical response. Same behaviour was reported by Addou et al [20].

Table 2. Third order nonlinear susceptibility $\chi^{(3)}$, the RMS average surface roughness of LTZO films with different concentrations of Li.

Films	RMS(nm)	$(\chi^{(3)}) \times 10^{-12} (\text{esu})$
0% Li and 2% Sn	26.950	10.916
3% Li and 2% Sn	25.558	12.772
5% Li and 2% Sn	19.587	11.424
7% Li and 2% Sn	13.678	13.422

4. Conclusion

LTZO thin films have been deposited by spray pyrolysis technique. the films were polycrystalline with an hexagonal wurtzite structure, with an average optical transparency exceeding 85% in the visible range .The optical band gap E_g was found to decrease from 3,24 to 3,16 eV with increasing Li concentration from 0 to 7% .It was found that the codoping of ZnO thin films improves the nonlinear response .The highest susceptibility value $\chi^{(3)} = 13,422 \times 10^{-12}$ (esu) was found for the highest concentration of lithium (7%), which indicates the correlation between the structural, optical and morphological properties of co-doped ZnO thin films with the nonlinear optical properties .

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