Synthesis of lithium doped zinc oxide by sol gel

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Abstract. Li-doped ZnO thin films were prepared by sol-gel method and deposed on glass substrate using spin coating technique. The effects of Li on structural and optical properties were investigated. The X-ray diffraction (XRD) analysis reveals that Li incorporation leads to the great improvement of the crystalline quality of ZnO thin films. Scanning electron microscopy (SEM) images showed that nanowires are aligned nearly perpendicular to the substrate plane and are affected significantly by Li incorporation. The optical transmission of the films was higher than 80% in the visible region. It is found that the optical gap and the refractive index remain practically constant.

1. Introduction

ZnO is a very promising material for semiconductor device applications [1–2]. It has a direct and wide band gap in the near-UV spectral region [3–4], and a large free-exciton binding energy [3–4] so that excitonic emission processes can persist at, even above, room temperature [4, 5]. It is well known that ZnO crystallizes in the wurtzite structure, the same as for GaN [4]. Its properties have been studied since the early days of semiconductor electronics [6]. But the use of ZnO as a semiconductor in electronic devices has been hindered by the lack of control over its electrical conductivity. ZnO having n-type electrical conductivity, which is due to intrinsic defects such as oxygen vacancies and zinc interstitials.

There are several deposition techniques utilized to prepare ZnO thin films such as chemical vapor deposition [7], magnetron sputtering [8], electrodeposition [9-10], spray pyrolysis [11] and sol-gel [12- 13] method. Among these methods, the sol-gel method process an attractive technique for obtaining thin film, due to controllability of compositions, simple facilities, low cost, etc. In order to synthesize ZnO for several applications, can be doped with different elements (Na and K) group I for Zn sites, or (N, P and Sb) group V for oxygen sites as substitutional dopants. W. Water et al affirmed that doped Li atoms in ZnO films were involved in their substitution for Zn atom [1].

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The aim of this work is to study the influence of Li doping concentration on the structural and optical properties of zinc oxide films prepared by sol gel method. The films were deposited on glass slides with different Lithium salt concentration in the sol.

2. Experimental

The solution was prepared by zinc acetate dehydrate (Zn(CH₃COO)₂,2H₂O) and the 2-methoxy ethanol, the solution was found cloudy which became clear on addition of monoethanol amine (MEA), the molar ratio of MEA to zinc was 1/1 and the concentration of zinc acetate was 0.6mol/l, the concentration of nitrate of lithium (LiNO₃) as a dopant was of 8, 10, 12, 15 and 20 at. % Li with respect to Zn.

The solution was stirred by a magnetic stirrer at 80°C for 2h to get a clear, homogeneous and transparent sol. The solution was dropped on the glass substrate, which was rotated at 2500 rpm for 30s. After spin coating, the substrates were kept at 120°C for 20min in a tube furnace, to evaporate the solvent. This procedure was repeated 10 times to obtain the desired thickness. The thickness was measured by profilometry and ranged around 250 nm. Finally, all the films were annealed at 500 °C for 1h30min in order to eliminate the organic component in films.

X-ray diffraction (XRD) measurements were realized using a Bragg-Brentano geometry (Bruker D8 Advance, Cu Kα radiation). The morphology of the films was studied using a Field Emission Scanning Electron Microscope (FE-SEM) (JEOL J7600F). The SEM images were acquired with a fixed electron beam at low accelerating voltage (10 kV).

For optical studies, a computer-controlled UV-vis-NIR spectrometer was used in the spectral range 250–2200 nm. Blank glass substrate was used as reference for transmittance measurements.

The thickness of the electroplated LZO film was measured through a profilometer (Taylor Hobson precision Form Talysurf 50 with µltra software), with accuracy on the height of 16nm.

3. Results and discussion

3.1. Structural and morphological characterizations

Figure 1 presents XRD patterns of ZnO thin films obtained by annealing at 500°C for 90 min with different Li-doping concentration (8, 10, 15 and 20 at. % Li). All the films are polycrystalline and have three pronounced diffractive peaks (100), (002) and (101) corresponding to 2θ values of 31.60°; 34.30° and 36.13° respectively.

For the concentration of 20 at. % Li, the intensity of (002) peak was stronger than of (100) and (101) indicating that the thin films had a high preferential c-axis orientation. No other peaks were detected for all samples; indicating that all precursors were completely decomposed and no other complex product were formed. Furthermore, the X-ray diffraction patterns confirmed that the thin films synthesized in this study are ZnO with typical diffraction peaks of hexagonal (wurtzite) ZnO.
The lattice parameters $a$ and $c$ calculated using Equation (1) [14]:

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \tag{1}$$

Where (hkl) are the plans reticular, and $d$ distance between (hkl) taken from the X’pert Highscore.

It was found that, when the concentration was 15 at. % Li, the lattice parameters decrease with increasing of Li content (Figure 2). A decrease in the lattice parameters can be expected when Zn$^{2+}$ ions are replaced by Li$^+$ ions because of the smaller radius of Li$^+$ ions (0.06 nm) than Zn$^{2+}$ ions (0.074 nm). It is well known that the doping of semiconductors with electrically active atoms can cause in change of lattice constant could be attributed to Li incorporation and is the indicative of defect evolution in the lattice. This decrease in the lattice parameter for Li-doped ZnO was previously reported by water et al [1].
The structural parameters such as D size of grains and the texture coefficient $T_C(hkl)$ were listed in Table 1. The size of grains was determined first from XRD spectra, using Scherrer relation (2) [15]:

$$D = \frac{(0.9 \times \lambda)}{(\beta \times \cos \theta)}$$  \hspace{1cm} (2)

Where $\lambda$ is the wavelength, FWHM is the full width at half maximum of the peak and $\theta$ is the Bragg angle. Table 1 shows the variation of sol-grain size. Note that the Li increases is associated to an increase of the crystallite size.

We have studied the influence of Li on the film texture of the plane (002) by systematically calculating the texture coefficient (TC) for different pH according the following formula [16] (3):

$$Tc(002) = \frac{I(002)}{I_0(002)} \frac{N^{-1}}{N} \sum I(hkl) \frac{I_0(hkl)}{I(hkl)}$$ \hspace{1cm} (3)

Where $I(hkl)$ is the measured relative intensity of a plane (hkl), $I_0(hkl)$ is the standard intensity of the plane (hkl) taken from the JCPDS data (36-1451), $n$ is the reflection number and $N$ is the number of diffraction peaks.

Table 1 shows that the maximum intensity occurs at 20 at. % Li for (002) peak intensity. This is strengthened by the highest value of TC value obtained for the same sample.
Table 1. TC (hkl) values and D size of grain of Li doped ZnO films deposited on glass substrate by sol gel.

|        | 8at.%Li | 10at.%Li | 15at.%Li | 20at.%Li |
|--------|---------|----------|----------|----------|
| $T_c(100)$ | 1.48    | 1.42     | 3.99     | 0.41     |
| $T_c(002)$ | 1.41    | 1.64     | 1.86     | 4.05     |
| $T_c(101)$ | 1.88    | 1.92     | 0.33     | 1.95     |
| $D$(nm)  | 52.84   | 62.22    | 60.39    | 64.24    |

Figure 3 shows, a SEM micrograph of the ZnO nanowires grown. It can be seen that the nanowires are aligned nearly perpendicular to the substrate plane. The nanowires are between 20 and 50 nm in diameter and 100 nm in length. According to the figure 1, the high intensity of the ZnO (002) peak at $2\Theta=34.3$° for Li doped ZnO at 20% is due to the strong preferred orientation of the nanorods.

3.2. Optical properties

The optical transmittance is an important optical parameter for transparent conducting oxides. Optical transmittance spectra of ZnO thin films with different concentration of Li showed that all films are transparent in the visible regions (Figure 4). All films exhibit a high average transmittance (80%) and show a sharp fundamental absorption edge at about 380 nm. One can see that Li-ZnO prepared at 15 and 20 at. % Li show better transmittance than the other ones, in good agreement with what has preceded above.
The energy band gap ($E_g$) could be estimated by assuming a direct transition between the valence band ($E_v$) and the conduction band ($E_c$) by using the following equation [17]:

$$\alpha h\nu = A (h\nu - E_g)^{1/2} \tag{4}$$

Where $A$ is a constant. The optical band gaps were obtained by extrapolating the linear part of curves ($\alpha h\nu$)$^2$ as a function of incident photon energy $h\nu$ to intercept the energy axis.

The optical band gaps determined from these curves are listed in table 2. The founded values range around 3.20 eV which is in good agreement with literature [18]. The $E_g$ values seem to be none affected by the Li values. This can be explained by the dependence of lattice parameter on the ZnO doped Li.

Refractive indexes of the produced ZnO thin films were calculated using equation (5) [19].

$$n^2 = \frac{3}{\sqrt{E_g/20}} - 2 \tag{5}$$

Where $n$ is the refractive index of the ZnO thin films and $E_g$ is the band gap energies of the ZnO thin films. Refractive index practically constant values 2.3 table (2).
Table 2: Refractive index and band gap energies of Li doped ZnO films deposited on glass substrate by sol gel.

| Li (at.%) | Eg(eV) | n    |
|----------|--------|------|
| 8         | 3.182  | 2.35 |
| 10        | 3.271  | 2.32 |
| 15        | 3.218  | 2.34 |
| 20        | 3.220  | 2.34 |

4. Conclusion
ZnO doped Li thin films were prepared on glass substrates by the sol gel method, the effects of Li doped ZnO on the structural and optical properties were analysed: The structural and morphological studies revealed that the crystallinity was improved with increasing the Li, the high intensity exhibited strong (002) peak with preferred c-axis orientation, the nanowires are between 20 and 50nm in diameter. The transmittance in the visible is over 80% and the band gap energy is 3.2eV. The most ideal property is obtained at 20 at. %Li.

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5. References
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