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Effect of In-doping on the optical constants of ZnO thin films

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Abstract

Highly transparent and conductive Indium-doped ZnO (ZnO:In) thin films with different In content were deposited on quartz glass slides by RF magnetron sputtering at room temperature. The thickness and the optical constants of the films were obtained by the Swanepoel method, and the effects of In concentration on the optical constants were investigated. Calculated results show that both the refractive index and optical band gap first increase then decreases with In concentration increasing in the visible region, and the variation of both ε_r and ε_i with wavelength follows the same trend as that of refractive index and extinction coefficient, respectively.

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Keywords: ZnO thin films; In doping, Magnetron sputtering, optical constants, refractive index, Swanepoel method;

1. Introduction

Transparent conducting oxides (TCOs) possess a unique position among materials owing to its fascinating physical properties and applications in commercial devices. Owing to its low resistivity, high transmittance, nontoxicity, good stability in hydrogen plasma processes and resource availability, zinc oxide (ZnO) have been considered as a potential substitution material for widly used but expensive TCO—indium tin oxide (ITO) and tin oxide (SnO_2) in many applications such as transparent electrodes [1-3], solar cells, flat panel display, ultraviolet optoelectronic devices and so on[4-6]. However, the conductivity of undoped ZnO thin films are not stable, especially at high temperatures [7], in order to enhance the stability and electrical, optical properties of ZnO-based films, doping with Group-III elements such as indium, gallium and aluminum are usually used[8-13]. It's well known that the doping efficiency depends on the difference of electronegativity and ionic radius between the dopant and host element. Compared with Al^{3+} (ionic radius: 0.39 Å, electronegativity: 1.5) and Ga^{3+} (0.47 Å, 1.6), In^{3+}(0.62 Å, 1.7) possesses a nearer ionic radius to Zn^{2+} (0.60 Å), and a larger electronegativity (1.7). The former will lead to small lattice deformation and the latter will make it less reactive and more resistive to oxidation [14]. Numerous In-doped ZnO (IZO) films preparation techniques have been employed like magnetron sputtering [15], chemical spray [8], sol-gel [16] and spray pyrolysis [9]. Because of the advantages of low deposition temperature, simple processing and inexpensive equipment, RF magnetron sputtering is an extremely reliable technique for deposition of thin films and is used in industry for large scale production.

Accurate knowledge of the optical constants (such as extinction coefficient and refractive index) of semiconductors is indispensable for the design and analysis of various optical and optoelectronic devices. Furthermore, optical constants of ZnO:In thin films is essential for comparison of samples which are produced using different methods and in different laboratories. Envelop method, improved by Swanepoel [17], is a simple and accurate method to evaluate the optical constants from transmittance and has been widely used by many researchers [18-20].

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The effects of annealing temperatures [11] and growth conditions [9] on the structure and electrical properties of In-doped ZnO thin films have been reported, but there is few reports on the effects of In doping concentration on the optical constants of ZnO:In thin films. Thus in this work, ZnO:In thin films with different indium concentration were prepared by RF sputtering method, then the optical constants of the films are calculated using Swanepoel method, and the effect of the indium concentration on the optical constants were studied and discussed.

2. Experimental

Using RF magnetron sputtering method, we prepared undoped and In-doped ZnO thin films deposited on quartz glass (20 mm × 13 mm × 1 mm) substrates which were pre-cleaned ultrasonically in acetone, rinsed in alcohol and then dried in hot air. The targets were prepared by mixing high purity ZnO (99.99%) powders and In_2O_3 (99.99%) powders with 0, 1, 3, 5, 7, 9 at.% of In. In order to avoid contaminating the films, the sputtering chamber was pumped down to 6×10^{-4} Pa by turbo molecular pump, and then, argon gas was introduced into the chamber through a mass flow controller as the working gas for sputter deposition. The working temperature was maintained at 2.0 Pa with 24 sccm Ar-flow. During sputtering, the radio power, substrate to target distance and substrate temperature were kept at 120 W, 70 mm and room temperature, respectively. Pre-sputtering for 20 minutes was done before deposition in order to remove contaminants and also keep stability during the sputtering.

The surface morphology of the films were investigated by SEM. The optical transmittance data of the films were obtained from a double-beam UV-visible spectrophotometer in a wavelength range of 300–1200 nm and the optical band gaps were determined from the transmission spectra.

3. Results and discussion

3.1. Morphological properties

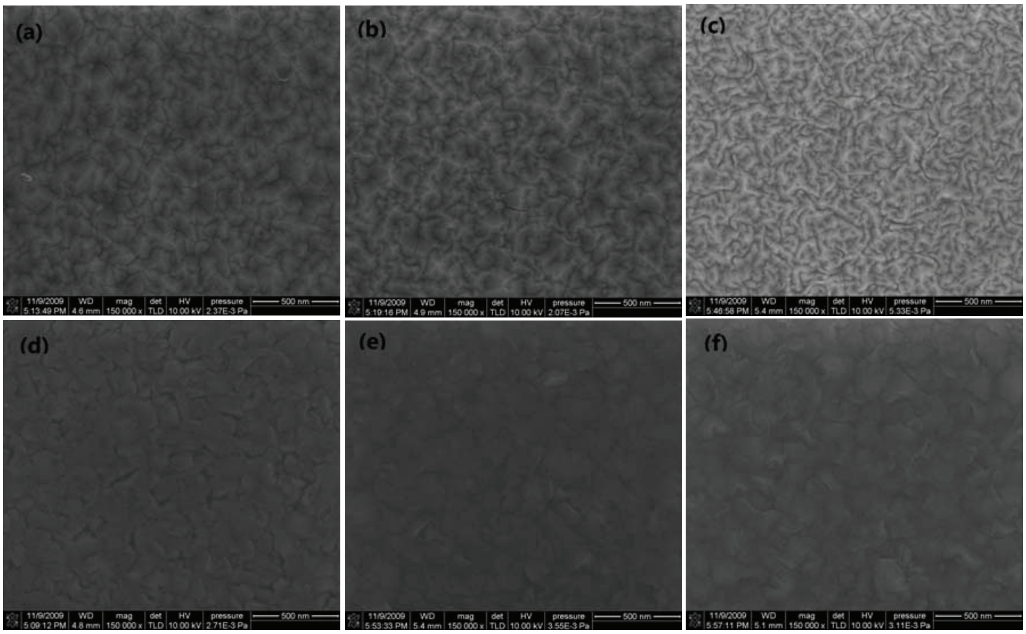


Fig. 1 SEM micrographs of the undoped and In-doped ZnO films: (a) undoped (b) 1 at.% (c) 3 at.% (d) 5 at.% (e) 7 at.% (f) 9 at.%

SEM micrographs for the ZnO films with different In concentrations are shown in Fig. 1. It suggests that the In concentration has great influence on the crystallinity and grain size. When the doping concentration is no more than 3at.%, the films surface is smooth and the grain are uniformly and compactly stacked up, but as the doping concentration further increases, the grains begin to grow loosely, typically the surface of the 9at.% In-doped ZnO thin films is as loose as some tree leaves pack up.

3.2. Transmittance of the films

The transmittance spectrum of thin film samples (substrate included) in the wavelength range of 300-1200 nm are plotted in Fig. 2. For the sake of comparison, the transmittance spectrum of the bare substrate is given too. The fringes associated with interference effects confirm the optical homogeneity and the excellent surface quality of deposited thin films, otherwise, the fringes should have been destroyed and shown as some smooth transmittance curves [21]. The films exhibit good transparency in the visible range (>85% if excluding the glass substrate) and a sharp fundamental absorption edge around a wavelength of 400nm wavelength, but a difference has observed in the near-IR region. The IR transmission of In-doped films drops beyond 800 nm wavelength and is progressively lowered as the wavelength increases. Ma et al. [22] reported the same decrease for ZnO:Ga thin films by DC reactive magnetron sputtering. They attributed this behavior to the high reflectance, which originates from the plasma resulting from the high electron concentration according to the classical Drude theory. Besides, we can observe that In concentration slightly affects the transmittance of the films in the visible range.

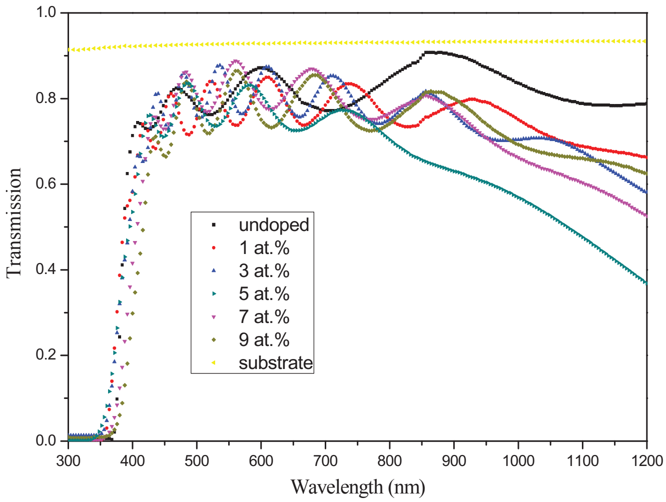


Fig. 2 Plot of transmission versus wavelength (nm) for the undoped and In-doped ZnO thin films

According to the principle of Swanepoel's method, which is based on the idea of Manificier et al. [23], the optical constants of thin films can be evaluated from transmittance data by creating upper and lower envelopes of the transmission spectrum. The applicability of this method is limited to the situation that a thin homogeneous film deposited onto a transparent substrate whose absorption index $\alpha_s = 0$ and the thickness of the substrate is several orders of magnitude larger than the film thickness d. Our films meet the above conditions, so Swanepoel's method can be used to obtain the corresponding optical constants. Following this method, as a first step, the maximum $T_M(\lambda)$ and the minimum $T_m(\lambda)$ envelope curves were determined using peaks and valleys of the transmission spectrum. Fig. 3 is a typical result for the undoped and 1 at.% In-doped ZnO thin films.

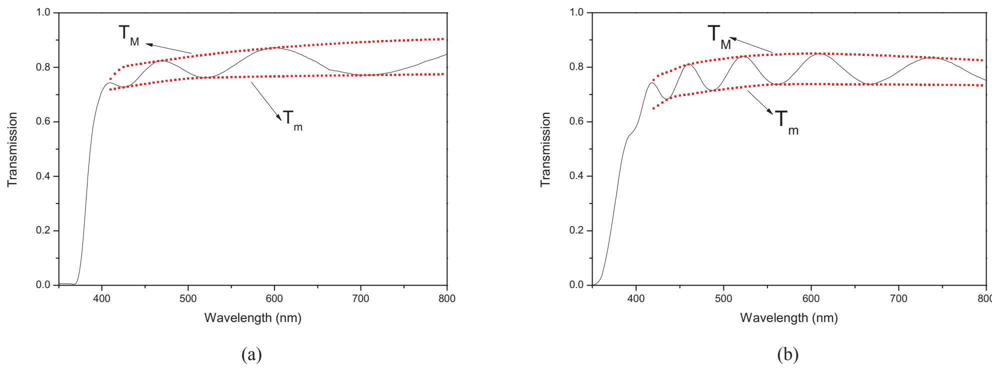


Fig. 3 The maximum $T_M(\lambda)$ and the minimum $T_m(\lambda)$ envelope curves (dotted lines) of the (a) undoped, (b) 1 at.% In-doped ZnO thin films

3.3. Optical constants

The refractive index n is an important parameter for optical materials and applications. From $T_M(\lambda)$ and $T_m(\lambda)$, n of the film in the spectral region of weak and medium absorption can be calculated by the expression[17]:

$$n = \sqrt{2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2}{2} + [(2s\frac{T_M - T_m}{T_M T_m} + \frac{s^2+1}{2})^2 - s^2]^{1/2}} \quad (1)$$

where s was obtained using the below relation [17] from transmission spectrum of glass substrate T_s, which is almost a constant (~ 0.93 in our case) when λ >300 nm. As a result, s =1.47 in this study.

$$s = \frac{1}{T_s} + \left(\frac{1}{T_s^2} - 1\right)^{1/2} \quad (2)$$

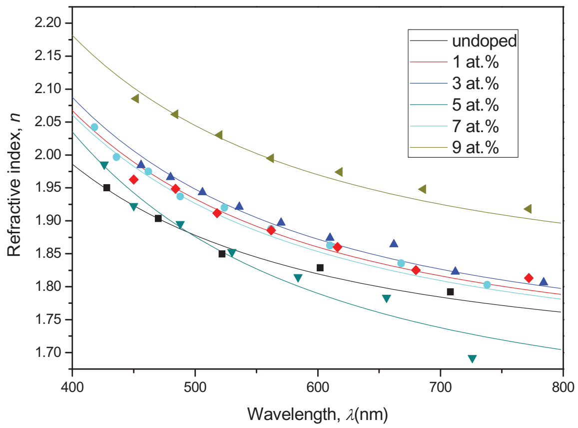


Fig. 4 Spectral dependences of refractive index (n) of the undoped and In-doped ZnO thin films: scatters, the calculated results and lines the fitted results

The calculated refractive indices at different wavelength are shown in Fig. 4. It's clear that the refractive index n is in the range of 1.7-2.2 in the visible region decreases with the increase of the wavelength, similar trend has been reported by in ZnO:In thin films deposited using spray pyrolysis method by Benouis et al. [24]. This behavior is due to increase in transmission and decrease of absorption coefficient with wavelength [25]. Now, the values of n can be fitted to a reasonable function such as the two-term Cauchy dispersion relationship [26], $n(\lambda) = A+B/\lambda^2$, which can be used to extrapolate the wavelength dependence beyond the range of measurement. The least squares fit of A and B for the different samples are listed in Table 1. It's also evident from Fig.4 that In doping can improve the refractive index, and with the increase of In content, n first increases then decreases. The increase in the refractive index with In doping is attributed to the increased polarizability of the larger In atomic radius 2.0 Å compared with the Zn atomic radius 1.53 Å [27], Benouis et al. [24] also reported this trend. They investigated ZnO:In thin films with indium concentration below 5%. However, when In concentration is up to 5 at.%, the refractive index decreases, probably due to the looser surface or the presence of In_2O_3 phase, but this has not been clear by now and future studies are needed to elucidate this point. With continuing increase of In doping, the increase of n maybe attribute to the degradation of crystallinity, which could change the structure and bonding arrangement.

Following Swanepoel's method, the film thickness was calculated using the expression [17]:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (3)$$

where n_1 and n_2 are refractive indices of two adjacent maxima or two minima at wavelength λ_1 and λ_2. Table 1 shows the thicknesses of the undoped and In-doped ZnO films by this equation. Our results are consistent with those calculated with PUMA method, which is proposed by Birgin et al. at 1999 [28].

Table 1 Values of A, B, thickness and optical band gap (E_g) for the undoped and In-doped ZnO thin films

Film	A	B	Thickness (nm)		E_g (eV)
			Swenepoel	PUMA	
ZnO	1.69	4.8×10^4	494	475	3.29
ZnO:In 1 at.%	1.69	6.1×10^4	819	901	3.39
ZnO:In 3 at.%	1.70	6.2×10^4	977	1043	3.40
ZnO:In 5 at.%	1.60	7.1×10^4	643	715	3.46
ZnO:In 7 at.%	1.69	6.0×10^4	745	671	3.32
ZnO:In 9 at.%	1.80	6.1×10^4	704	651	3.21

Then, the obtained values of the layer thickness and the refractive index were used to calculate the spectral dependence of the absorption coefficient α by the following expression [17]:

$$\alpha = -\frac{1}{d}\ln\frac{E_M - \sqrt{E_M{}^2 - (n^2-2)^3(n^2-s^4)}}{(n^2-1)^3(n-s^2)} \tag{4}$$

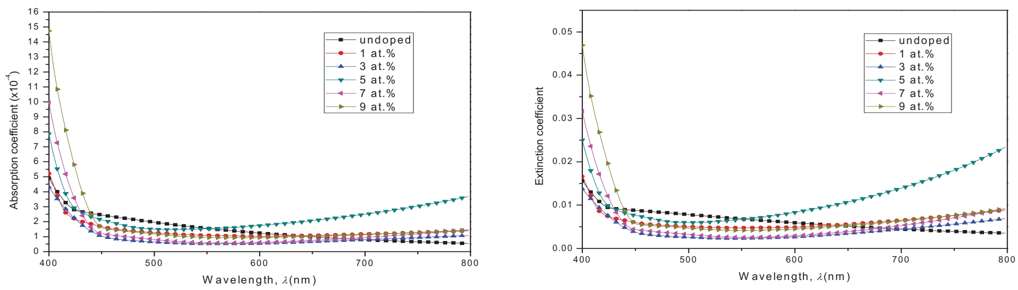
where

$$E_M = \frac{8n^2 s}{T_M} + (n^2-1)(n^2-s^2).$$

And the extinction coefficient k was determined through the relation:

$$k = \frac{\alpha\lambda}{4\pi} \tag{5}$$

The wavelength dependence of α and k values of undoped and In-doped ZnO thin films are given in Fig. 5 (a) and (b), respectively. It can be noted that α and k exhibit the same trend in the visible region: both show a steeper decrease with increasing wavelength initially, then a short shoulder, finally a tendency to increase again except the undoped sample, which is corresponding with the transmission spectrum. Clearly, the decrease is due to the existence of an absorption band located at $\lambda <$ 400 nm, which is caused by interband transitions. The shoulder is believed to be attributed to electronic transition to the impurity levels, and the increase of doped ZnO films maybe the results of high reflectance, as was explained above. Furthermore, with different In concentrations, the absorption coefficient and extinction coefficient changes a little.



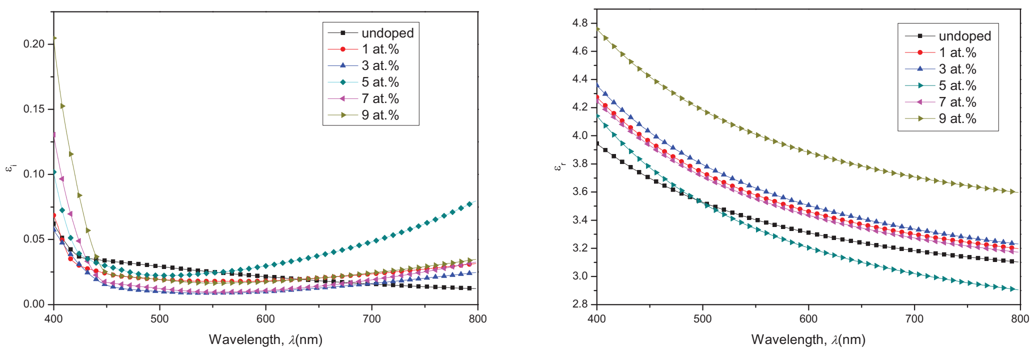
(a) (b)

Fig. 5 Dependence of α (a) and k (b) on wavelength for different samples of thin film

The fundamental excitation spectrum of the film was described by means of a frequency dependence of the complex electronic dielectric constant. The dielectric constant is defined as $\boldsymbol{\varepsilon}=\varepsilon_r+i\varepsilon_i$, and the real part ε_r and imaginary parts ε_i are related to the n and k by the following formulas:

$$\begin{aligned}\varepsilon_r &= n^2 - k^2 \\ \varepsilon_i &= 2nk\end{aligned} \tag{6}$$

As shown in Fig. 6, both ε_r and ε_i show a steeper decrease with increasing wavelength initially, then a short shoulder, finally a tendency to increase again except the undoped sample, whose relationship with wavelength are same as that of refractive index and extinction coefficient, respectively. However, the ε_r values are larger than ε_i.



(a) (b)

Fig. 6 Dependence of ε_i (a) and ε_r (b) on wavelength for different samples of thin film.

The optical band gap can be calculated from the fundamental absorption edge of the films which corresponds to electron transitions from valence band to conduction band. In the direct transition materials such as ZnO, the absorption coefficient (α) can be expressed by [29]:

$$\alpha(h\upsilon) = A(h\upsilon - E_g)^{1/2} \tag{7}$$

where A is a dimensional constant, E_g the optical band gap. As shown in Fig.7, the value of E_g is determined by a linear extrapolation of the plot of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis. The obtained optical energy gap of the undoped and In-doped ZnO thin films are listed in table 1. It is shown that the band gap of the undoped ZnO film is 3.29eV, and that of In-doped films increases with In doping up to 3.46 eV at 5 at.%, then decrease with the increase of In concentration. The doped ZnO has a larger band gap than that of undoped ZnO is thought to be due to the increase of carrier concentration by doping, similar results were obtained by Benouis et al. [24] and Gupta et al. [30]. This band gap widening may be explained by the Burstein-Moss shift [31], while the reduction of the band gap is usually caused by a shift in energy of the valence and conduction bands resulting from some known effect such as electron–impurity and electron-electron scattering [32]. These two contradictory effects together decide the change of E_g. In present work, E_g values decreased as the concentration higher than 5 at.%, it can be regarded that the shrinkage effect was dominant over the widening or Moss–Burstein effect.

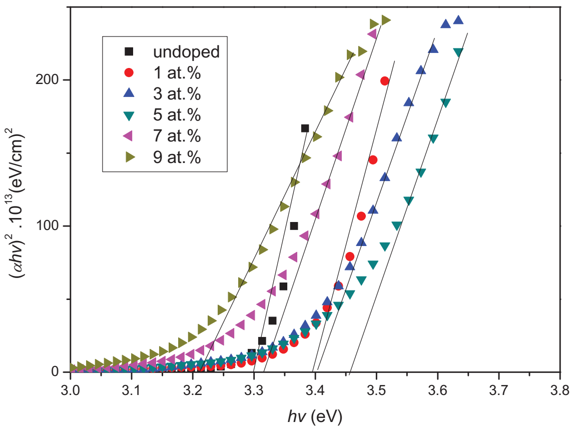


Fig. 7 Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for the undoped and In-doped ZnO thin films

4. Conclusions

Undoped and In-doped ZnO films were deposited by RF magnetron sputtering method. The optical properties of these films were investigated. All the films exhibit good transparency in the visible range. The film thickness and optical constants (refractive index n, extinction coefficient k, absorption coefficient α and dielectric constant $\boldsymbol{\varepsilon}$) were calculated in the visible range using Swanepoel's method. The refractive index n is in the range of 1.7-2.2 in the visible region, and decreases with the wavelength, and n first increases then decreases with the increase of In content. α and k exhibit a steeper decrease with increasing wavelength initially, then a short shoulder, finally a tendency to increase, and In concentration affects them slightly. The wavelength dependence of ε_r and ε_i were found to follow the similar trend as that of refractive index and extinction coefficent, respectively. The optical band gap, E_g, increased from 3.29 eV to 3.46 eV as In concentration increased from 0 to 5 at.%, then it decreased to 3.21 eV when In concentration increased to 9 at.%.

Acknowledgments

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