# The effects of post-thermal annealing on the optical parameters of indium-doped ZnO thin films*

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Indium-doped ZnO thin films are deposited on quartz glass slides by RF magnetron sputtering at ambient temperature. The as-deposited films are annealed at different temperatures from 400 °C to 800 °C in air for 1 h. Transmittance spectra are used to determine the optical parameters and the thicknesses of the films before and after annealing using a nonlinear programming method, and the effects of the annealing temperatures on the optical parameters and the thickness are investigated. The optical band gap is determined from the absorption coefficient. The calculated results show that the film thickness and optical parameters both increase first and then decrease with increasing annealing temperature from 400 °C to 800 °C. The band gap of the as-deposited ZnO:In thin film is 3.28 eV, and it decreases to 3.17 eV after annealing at 400 °C. Then the band gap increases from 3.17 eV to 3.23 eV with increasing annealing temperature from 400 °C to 800 °C.

**Keywords:** ZnO thin films, optical constants, annealing, transmittance spectra

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## 1. Introduction

Zinc oxide (ZnO) is a direct wide band-gap ($E_g \sim 3.37$ eV) semiconductor with a large exciton binding energy of 60 meV.[1] The resistivity of ZnO is not low enough for the use of transparent conductive oxide, so group III elements such as Al, Ga, and In are usually used as dopants to improve the electrical properties and stabilities of the ZnO-based materials.[1−5] Due to its suitable ionic radius (0.62 Å, 1 Å=0.1 nm) and eletronegativity (1.7),[1] indium was reported to be the most promising element as a dopant to enhance the photoelectric properties of ZnO thin films. Indium-doped ZnO (ZnO:In) thin film has a low resistivity and high transmittance in the visible region, which is suited to the fabrications of the transparent electrodes of solar cells, liquid crystal displays, heat mirrors, etc. Recently, there have been many techniques used to deposit ZnO thin films, such as chemical vapour deposition (CVD), magnetron sputtering, pulsed laser deposition (PLD), and the sol–gel method. With the advantages of low deposition temperature, simple processing, high growth rate, low-cost equipment, and suitability for large area deposition, magnetron sputtering is one of the most promising deposition techniques. Park *et al.*[6] studied the electrical and optical properties of In-doped ZnO film prepared by sputtering, and a resistivity of $1.28\times10^{-3}$ Ω·cm and a high transmittance of 80% in the visible region were obtained. Park *et al.*[7] obtained a low resistivity of $5\times10^{-3}$ Ω·cm and a high transmittance of 85% for nano-structured In-doped ZnO thin films prepared by RF magnetron sputtering. Both of these examples suggested that the sputtered In-doped ZnO thin films are suited for the use of transparent conductive oxide. For the applications in optoelectronic devices, knowledge of the optical constant, dielectric constant, and the film thickness, plays an important role in the sense that they govern device performance. In order to obtain the optical constants, the use of optical transmission spectra is one of the most attractive methods as it is easy, accurate, and nondestructive. Envelope is one of the most outstanding methods, and is suited for films with transmission spectra that display a fringe

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pattern in a highly transparent spectral region.[9,10] But for films that are not thick enough, the method is inapplicable for no fringe pattern. Recently, a nonlinear programming method of determining the optical constants and film thickness using only transmission spectra was suggested by Birgin *et al.*,[11] by which the optical constants and the film thickness of an amorphous silicon film with a thickness of less than 100 nm were successfully measured.[12] Bo *et al.*[13] similarly estimated the optical parameters of undoped ZnO thin films using this method. Thermal annealing is also a common method used to improve crystal quality and reduce the structural defects in the materials. During the annealing process, dislocations and other structural defects move in the material and adsorption/decomposition may occur in the surface, thus changing the structure and the stoichiometric ratio of the material.[14] It is obvious that the thickness and the optical constants of the film will change with annealing temperature. To date, few studies have dealt with the effect of annealing temperature on the optical parameters and thickness of ZnO:In thin films.

In the present study, ZnO:In films are prepared by radio frequency (RF) magnetron sputtering and annealed at temperatures ranging from 400 °C to 800 °C in air for 1 h, and the effect of the annealing temperatures on the optical parameters, and also the thickness of the film, are estimated from the transmission data of the samples using a nonlinear programming method.[11]

## 2. Experimental details

A powder target out of the mixed powder of high purity ZnO (99.99%) and $In_2O_3$ (99.99%) (In/(In+Zn)=5%) acted as the sputtering source material. Quartz glass (20 mm×13 mm×1 mm) was employed as the substrate, and it was pre-cleaned ultrasonically in acetone, rinsed in alcohol and then dried in hot air. ZnO:In transparent conductive thin films were deposited using 13.56 MHz RF magnetron sputtering. The distance between the target and the substrate was 70 mm. In order to avoid contaminating the film, the chamber was evacuated to a base pressure of $6.6\times10^{-4}$ Pa, and then argon gas was introduced into the chamber through a mass flow controller. The mass flow of argon gas was fixed at 24 sccm, and the sputtering pressure was 2.0 Pa. The target was pre-sputtered for 15 min to remove contaminants. The films were deposited at ambient temperature and annealed in air for 1 h in a temperature range of 400 °C–800 °C. The structure of the ZnO:In film was measured by X-ray diffraction (XRD), the surface was investigated by scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) was used to determine the composition of the film. Hall measurements were used to study the electrical properties of the film, and the transmission spectra of the film were measured by a double-beam ultraviolet/visible spectrophotometer with a wavelength range of 300 nm–800 nm, which was used to determine the optical parameters and the thickness of the film.

## 3. Theory

The problem with estimating the thickness and the optical constants of thin films using only transmission data is that is challenging because there are many local–nonglobal solutions. To solve this problem, Birgin *et al.*[11] proposed a kind of new method based on a nonlinear programming technique.

For a set of experimental data $[\lambda_{\rm i},\ T^{\rm meas}(\lambda_{\rm i})]$, $\lambda_{\min} \le \lambda_{\rm i} \le \lambda_{i+1} \le \lambda_{\max}$, for $i = 1, 2, \ldots, N$, it must hold that $T^{\rm meas}(\lambda) = T^{\rm theor}[\lambda,\ s(\lambda),\ t,\ n(\lambda),\ k(\lambda)]$, where $T^{\rm theor}$ is the calculated transmission data of the film+substrate, $n(\lambda)$ and $k(\lambda)$ are the refractive index and extinction coefficient of the films, respectively; and $s(\lambda)$ is the refractive index of the transparent substrate. For a known $t$ and given $\lambda$, this equation has two unknown variables: $n(\lambda)$ and $k(\lambda)$. And therefore the set of function $(n,\ k)$ satisfying $T^{\rm meas} = T^{\rm theor}$ for a given $t$ is infinite. Thickness $t$ can be optimized by minimizing $\sum_{{\rm all}\,i}\ [T^{\rm meas}(\lambda_i) = T^{\rm theor}\ (\lambda_i,\ s,\ t,\ n_i,\ k_i)]^2$. On the other hand, for a given thickness $t$, $n(\lambda)$, and $k(\lambda)$, there is only one corresponding $T^{\rm theor}$. If $T^{\rm theor}$ is equal to $T^{\rm meas}$, the calculated results of $n(\lambda)$ and $k(\lambda)$ are reliable.

Consequently, the absorption coefficient $(a)$, the real component $(\varepsilon_1)$, and the imaginary component $(\varepsilon_2)$ of the complex dielectric constant of the thin films are determined by:

$$\alpha(\lambda) = (2\pi k(\lambda))/\lambda, \quad \varepsilon_1(\lambda) = n(\lambda)^2 - k(\lambda)^2,$$

and $\varepsilon_2(\lambda) = 2n(\lambda)k(\lambda)$, respectively.

## 4. Results and discussion

The structure of the In-doped ZnO films was measured by X-ray diffraction, which showed that the sputtered film has a hexagonal wurtzite structure with a $c$ axis perpendicular to the substrate. The surface of the as-deposited film is smooth and compact, as shown

by SEM. The EDS indicates that the film contains approximately 5.08 at% In, which is a little higher than that in the target. The Hall measurement suggests that the In-doped ZnO film is an n-type semiconductor with a high carrier concentration ($2.5\times10^{20}$ cm$^{-3}$) and a low resistivity ($4\times10^{-3}$ Ω·cm). All these results were reported in detail elsewhere.[15–17]

Figure 1 shows the transmittance spectra of ZnO:In films at a range of 300 nm–800 nm before and after annealing at different temperatures. All the films exhibit an average transmittance of around 85% in the visible region (including the substrate) and a sharp fundamental absorption edge at about 390 nm. The calculated transmission spectrum $T^{\rm meas}$ of the film annealed at 500 °C is also given in Fig. 1 (triangles), which is consistent with the transmission measurement. This result shows that the nonlinear programming method is reliable.

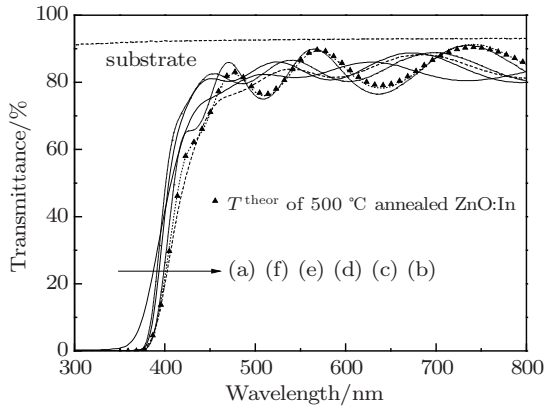



**Fig. 1.** Transmission spectra of the ZnO:In thin films before (a) and after annealing at 400 (b), 500 (c), 600 (d), 700 (e), and 800 °C (f), and the $T^{\rm thero}$ for the film annealed at 500 °C.

Figures 2 and 3 show the calculated values of refractive index ($n$) and extinction coefficient ($k$) for the ZnO:In thin films before and after annealing at different temperatures, each as a function of wavelength. It is evident that annealing temperature affects the values of $n$ and $k$ significantly. The optical constants of $n$ and $k$ both increase with increasing wavelength. The value of $n$ for the as-deposited ZnO:In thin film increases from 1.81 to 2.25 as the wavelength decreases from 800 nm to 350 nm. For a given wavelength of 500 nm, the value of $n$ increases from 1.81 to 2.11 with increasing annealing temperature from 400 °C to 600 °C, and then decreases to 1.92 when the annealing temperature increases to 800 °C. The obtained value of $n$ accords with the value for ZnO:Al thin films reported by Li *et al.*[18] using ellipsometry. The extinction coefficient $k$ reduces to zero when the wavelength is larger than 400 nm, implying little absorption in the visible range. The small absorption of the ZnO:In thin film shows high transmission of the film, which is consistent with the transmission spectra results, as shown in Fig. 1.

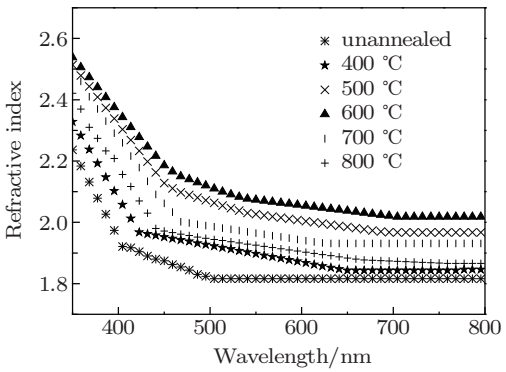



**Fig. 2.** Calculated refractive indexes of ZnO:In thin films before and after annealing, each as a function of wavelength.

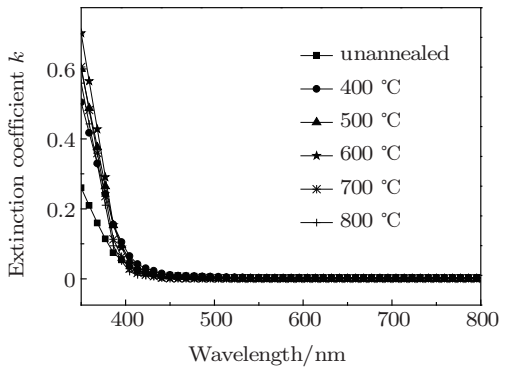



**Fig. 3.** Calculated extinction coefficients of the ZnO:In thin films before and after annealing, each as a function of the wavelength.

The obtained thickness of the film is very interesting. As shown in Fig. 4, the thickness of the film first increases and then decreases with increasing annealing temperature. The thickness of the as-deposited film is 512 nm, and it increases to 533 nm with the annealing temperature increasing to 500 °C. Then it decreases to 521 nm when the annealing temperature increases to 800 °C. Two reasons may account for the change in film thickness: one is that the oxygen moves into the films in the annealing process, and the stoichiometric ratio of Zn/O will decrease, which can increase the thickness of the film; the other is that the grain size becomes bigger and the film turns compact, which can reduce the thickness of the film. It may be that the first reason plays an important role at low temperature, and the second reason is dominant at high

temperature.

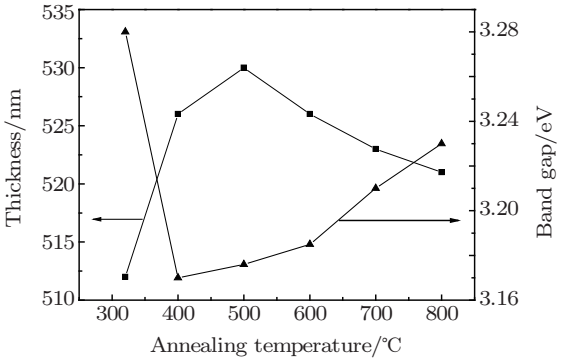



**Fig. 4.** The calculated thickness and band gap of the ZnO:In film, each as a function of annealing temperature.

As ZnO is a direct transmission semiconductor, the optical band gap can be estimated by the following equation:

$$(\alpha h\nu)^2 = A(h\nu - E_{\rm g}), \tag{1}$$

where $\alpha = 2\pi k/\lambda$, $A$, $E_{\rm g}$, and $h\nu$ are constants, optical band gap, and photo energy, respectively. The $E_{\rm g}$ can be determined by plotting the curve of $(\alpha h\nu)^2$ versus photo energy $h\nu$ and extrapolating the linear portion of the curve to the $h\nu$ axis. The obtained optical band gap of the as-deposited film is 3.28 eV, which decreases to 3.17 eV after annealing at 400 °C. And with annealing temperature increasing from 400 °C to 800 °C, it increases from 3.17 eV to 3.23 eV, as shown in Fig. 4. Li *et al.*[19] obtained a similar band gap value (3.11 eV–3.26 eV) for ZnO:In thin films deposited by DC reactive magnetron sputtering.

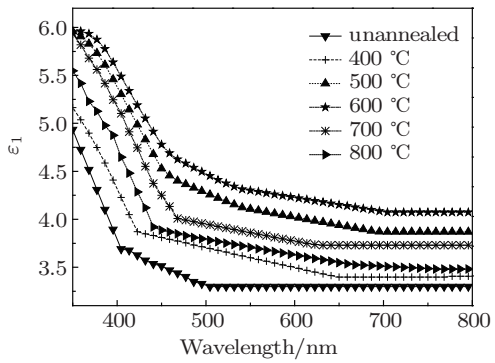



**Fig. 5.** Calculated real components of the complex dielectric constant of ZnO:In thin films before and after annealing, each as a function of the wavelength.

Figures 5 and 6 present the dependences of the dielectric constant on the wavelength of the ZnO:In thin film before and after annealing at different temperatures, each as a function of wavelength. The real part $\varepsilon_1$ and the imaginary part $\varepsilon_2$ of the dielectric constant of the film both increase with the decrease in wavelength. For a given wavelength, the real part $\varepsilon_1$ first increases and then decreases with increasing annealing temperature. The imaginary part $\varepsilon_2$ is very small in the visible range. Xue *et al.*[20] obtained the dielectric constants of ZnO thin films using their own method, and the results are in accordance with ours.

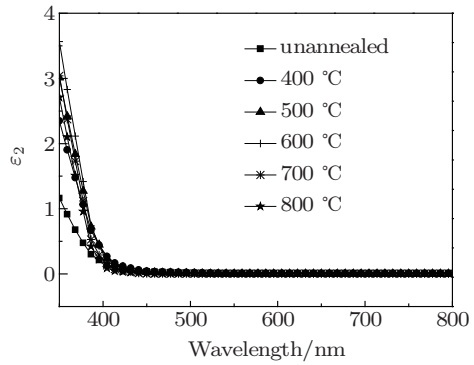



**Fig. 6.** Calculated imaginary components of the complex dielectric constants of ZnO:In thin films before and after annealing, each as a function of the wavelength.

## 5. Conclusions

A nonlinear programming method suggested by Birgin *et al.* is used to determine the optical parameters and thickness of ZnO:In films before and after annealing, and the effect of annealing temperature ranging from 400 °C to 800 °C in air ambient on the optical parameters and film thickness are investigated. It is found that the thickness of the film increases when the annealing temperature is lower than 500 °C, and then decreases with increasing annealing temperature. At low annealing temperatures, oxygen moves into the film, which can increase the thickness of the film; and the grain size of the film becomes bigger and more compact at high annealing temperatures, which reduces the thickness. The obtained optical band gap of the as-deposited film is 3.28 eV, and it decreases to 3.17 eV after annealing at 400 °C. The refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ both decrease with increasing wavelength in the visible range. For a given wavelength, the refractive index increases when the annealing temperature is lower than 600 °C, and then decreases with an increase in temperature. The obtained optical parameters of the ZnO:In thin films accord with the results calculated by other methods, which suggests that the nonlinear programming method is reliable for the calculation of optical parameters from transmittance data only.

# References


[1] Pearson S J, Orton D P N, Ip K, Hoe Y W and Steiner T 2005 *Prog. Mater. Sci.* **50** 293

[2] Yao Z G, Zhang X Q, Shang H K, Teng X Y, Wang Y S and Huang S H 2005 *Chin. Phys.* **14** 120

[3] Park J H, Ahn K J, Na S I and Kim H K 2011 *Sol. Energy Mater. Sol. Cells* **95** 657.

[4] Zhang H F, Liu R J, Liu H F, Lei C X, Feng D T and Yuan C K 2010 *Matter. Lett.* **64** 2112

[5] Xue S W, Zu X T, Su H Q, Xiang X, Deng H and Yang C Y 2007 *Chin. Phys.* **16** 1119

[6] Park J B, Park S H and Sang P K 2010 *J. Phys. Chem. Solids* **71** 669

[7] Park Y R, Kim E K, Jung D, Park T S and Kim Y S 2008 *Appl. Phys. Sci.* **254** 2250

[8] Chambouleyron I, Martinez J M, Moretti A C and Mulato M 1998 *Thin Solid Films* **317** 133

[9] Swanepoel R 1983 *J. Phys.* E **16** 1214

[10] Swanepoel R 1984 *J. Phys.* E **17** 896

[11] Birgin E G, Chambouleyron I and Martinez J M 1999 *J. Comp. Physiol.* **151** 862

[12] Mulato M, Chambouleyron I, Birgin E G and Martinez J M 2000 *Appl. Phys. Lett.* **77** 2133

[13] Huang B, Li J, Wu Y B, Guo D H and Wu S T 2008 *Mater. Lett.* **62** 1316

[14] Yang J H, Gao M, Zhang Y J, Yang L L, Lang J H, Liu Y Q and Fan H G 2008 *Superlattice Microst.* **44** 137

[15] Peng L P, Fang L, Yang X F and Huang Q L 2009 *J. Alloys. Compd.* **484** 575

[16] Peng L P, Fang L, Yang X F, Ruan H B, Huang Q L and Wu F *Int. J. Mod. Phys.* B in press

[17] Peng L P, Fang L, Yang X F, Ruan H B and Li Y J 2009 *Physica* E **41** 1819

[18] Li Q H, Zhu D L, Liu W J, Liu Y and Ma X C 2008 *Appl. Surf. Sci.* **254** 2922

[19] Li H, Xie E Q, Qiao M, Pan X J and Zhang Y Z 2007 *J. Electron. Mater.* **36** 1219

[20] Xue S W, Zu X T, Zhou W L, Deng H X, Xiang X, Zhang L and Deng H 2008 *J. Alloys Compd.* **448** 21