

High transparency of ZnO:In coated glass substrates

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Abstract

Undoped and heavily indium doped ZnO were deposited by dip-coating sol-gel method on glass substrates. When undoped ZnO was deposited the maximum value of transmittance decreases from 91% for bare substrate to less than 86%. However for ZnO:In coated substrate an unexpected high transmittance of 93.5% was obtained, exceeding that of bare glass substrate. To understand this particular behavior a theoretical model based on the propagation of electromagnetic waves in thin films was adapted to the studied samples and the measured transmittance spectra were perfectly fitted. The optical analysis of the two types of samples showed that the deposited films are dense inside the film while their refractive index decreases for the surface layers. Besides, it was noted that even if the preparation conditions are strictly identical, the heavily doped ZnO films is thicker and less dense than that of undoped ZnO. These results agree with AFM and SEM observations. The particular optical behavior described in this paper could be very beneficial for optical, optoelectronic and solar applications.

Keywords: ZnO:In; transmittance; simulation; nanostructure.

1. Introduction

In optical, optoelectronic or photovoltaic components, the problem of light transmission is omnipresent. Antireflective coatings are often applied to surfaces to improve their transmittance [1]. The materials used for antireflective coatings must have lower refractive indices than coated substrates (less than 1.5 for glass coating) [2]. Chemically stable materials like MgF_2 or CaF_2 , with such characteristics are rare [3-4]. For certain applications, a graded porosity is created on the surface of the glass by chemical etching making it possible to obtain a decreasing optical index from the substrate to the air [5]. In optoelectronic and photovoltaic, the development of new efficient and inexpensive transparent and conductive oxides (TCOs) to replace ITO (indium tin oxide, the most used TCO), is focused on ZnO doped by trivalent elements such as Al, In or Ga [6]. In the majority of published works, the transmittance decreases after coating glass substrates with doped ZnO [7-8]. This decrease is generally due to the poor surface quality and the losses due to light scattering. However, in recent years, the mastery of nanotechnologies and the control of the surface state made it possible to obtain very high transmittances when depositing ZnO doped with indium or gallium on glass substrates [9-12]. In certain articles, unexpected transmittances of more than 100% are reported [13-14]. This may seem absurd, but knowing that most researchers prefer measuring relative transmittance (by taking the glass

substrate as a reference), this simply highlights the antireflective effect of the deposited layer. Normally, ZnO has a higher refractive index than that of the generally used glass substrates and then the transmittance recorded after coating should be lower than that of the glass substrates [15]. In the best cases (homogeneous films and smooth surface), the transmittance exhibits maxima which approach without exceeding the transmittance spectrum of the glass substrate [16-17]. Exceptionally, in the case of ZnO doped with trivalent elements, some transmittances are reported to be higher than that of used glass substrates, but the authors do not bother explain clearly this behavior [13-14; 18].

In this work, thin films of ZnO highly doped with indium (IZO) were deposited on glass substrates to highlight this phenomenon and a mathematical model is proposed to calculate the transmittance of these films and to explain this particular optical behavior.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), indium nitrate trihydrate ($\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$), absolute Ethanol ($\text{C}_2\text{H}_5\text{OH}$), and Monoethanolamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$) pure products of Sigma-Aldrich were used to prepare undoped and In-doped ZnO thin films.

2.2. Preparation of ZnO and IZO thin films

ZnO and IZO thin films were prepared by the sol-gel dip-coating method using zinc acetate dihydrate and Indium nitrate trihydrate as starting materials. These materials were dissolved in absolute ethanol to obtain a total molarity of 0.2. Monoethanolamine (MEA) was added to the mixture as stabilizer. The molar ratio of MEA to metals precursors was maintained at 1. To obtain a clear and homogeneous solution, the mixture was stirred at 60°C for 2h. The glass substrates were cleaned in an ultrasonic bath in acetone, ethanol and distilled water successively. The layers were deposited by immersing a substrate in the solution for 2 min (Dip-coater KSVDCX2), and then dried at high temperature 300°C for 4 min in an electric furnace (Nabertherm B-180). The procedure from immersing to drying was repeated 20 times, the films were then annealed at 500°C for 2h. To investigate the effect of high In doping concentration on the physical properties of ZnO, 11 at% indium is added to the solution used for depositing IZO thin films.

2.3. Analysis techniques

The surface morphology was studied using A100 atomic force microscope of APEResearch with Gwyddion 2.34 software. The samples cross-section images were performed with a Tescan Lyra3 FEG-SEM combining high resolution and high-performance Ga focused ion beam (FIB). The optical properties were investigated using a spectrophotometer UV-Vis (Jasko V-630).

3. Results

3.1. Morphological properties

Fig. 1 shows the AFM micrographs of ZnO and IZO thin films prepared by the sol-gel dip-coating method. For undoped ZnO, rounded columns oriented upwards are observed in accord with the (002) preferred growth frequently observed in ZnO films [19-20]. The statistic calculations using Gwyddion software indicate that the average grain size is around 140 nm while the root mean square RMS roughness is 3.14 nm indicating a very smooth surface. However, for heavily In doped ZnO, the topography changed from a rounded columnar structure to a fine wires structure. The grain size significantly decreases to 17.1 nm. Lim et al observed by SEM a similar morphology in the form of nanowires (NWs) of hexagonal sections typical of (002) oriented ZnO [21]. This comportment can be attributed to a competitive growth between indium and Zinc oxide, probably because of the high amount of indium introduced segregating in grain boundaries. The decrease of grains size and RMS roughness indicates an improvement in the surface quality required for optical applications.

The samples cross-sections, properly obtained by Ga source FIB, were observed by FEG-SEM (Fig. 2). The thickness of the two films is homogenous and surfaces are very smooth. In the two samples, similar rough interfaces between the film and the substrate are observed. However the ZnO thin film appears to be denser and thinner than that of IZO. The deposited films present more porosity near the surface. The texture of the film cross-section is finer for IZO.

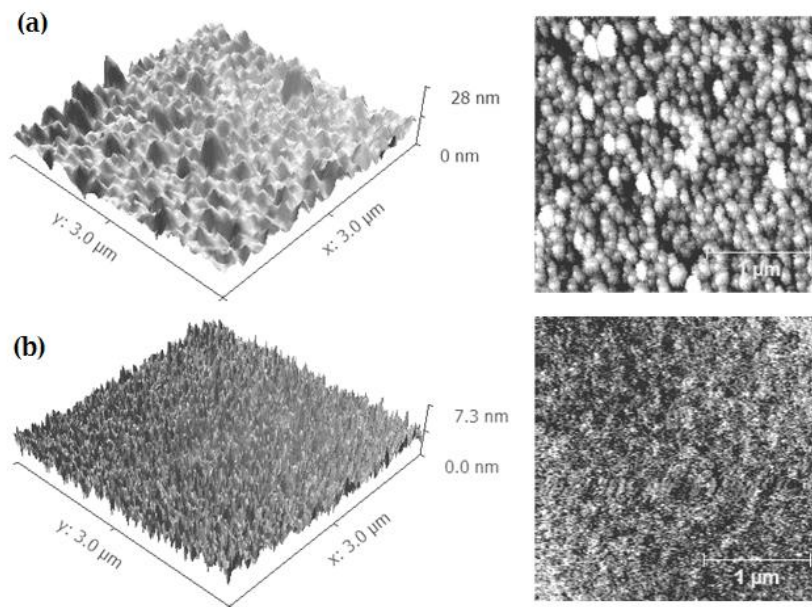


Figure 1. AFM micrographs of undoped ZnO (a) and IZO thin films (b).

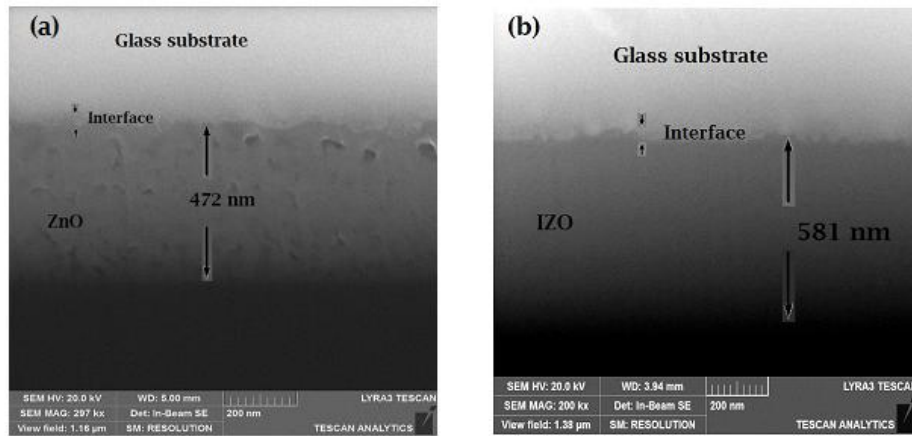


Figure 2. Cross-sections images of undoped ZnO (a) and IZO thin films (b) performed by FEG-SEM.

Table 1. AFM and photometry results: Grain size (D), Roughness (RMS), total thickness (d) and Forouhi-Bloomer parameters, for the three strata numbered from air to substrate.

Samples	D (nm)	RMS (nm)	d (nm)	Strata thicknesses		A	B	C	N_{inf}	E_g (eV)
ZnO	140	3.14	495	1 st	95 nm	0.0678	5.6236	0.1891	1.83	2.51
				2 nd	318 nm	0.3115	6.6440	0.2622	1.87	3.44
				3 rd	82 nm	0.3714	6.6942	0.0363	1.56	3.03
IZO	33	1.59	571	1 st	280 nm	0.0582	5.6610	0.1073	1.73	3.14
				2 nd	228 nm	0.1859	5.8624	0.0458	1.84	3.27
				3 rd	63 nm	0.3772	6.5971	0.0545	1.52	2.82

3.2. Optical properties

Fig. 3-a shows the optical transmission spectra of undoped ZnO and IZO thin films compared to that of glass substrate. The transmittance spectrum of the substrate is typical of an ordinary microscope slide (soda-lime slide) having an absorption edge around 300 nm and a maximum transmittance of 91%. For the substrate coated with undoped ZnO, the transmittance decreased to less than 86%. Compared to many published results [7-8; 22] this value is relatively high because of the good quality of the surface mentioned above. Contrary to this, for IZO sample, a very high transparency (93.5%) is observed in the visible region. The transmittance of IZO exceeds that of the bare substrate. For a better understanding the relative transmittances (taking the glass substrate as reference) are plotted in Fig. 3-b; the relative transmittance is then greater than 100%. This singular behavior deserves absolutely to be clarified. It seems obvious that the high In doping has a important effect on the optical properties of IZO. The vertical growth of IZO (NWs evoked in morphological analysis) facilitates the transmission of photons flow and the smooth surface minimizes the light scattering. Few authors were interested in interpreting this singular optical behavior. Tikhonravov et al [23] then Basu et al [24] studied theoretically the effect of small inhomogeneities in optical films on the variation of the transmittance and reflectance extrema.

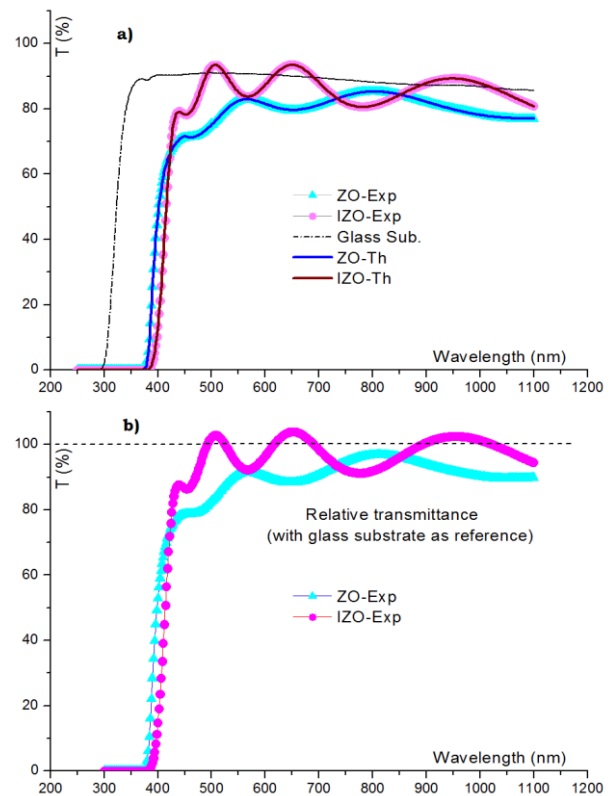


Figure 3. Transmittance spectra of undoped ZnO and IZO thin films: a) Air as reference; b) glass substrate as reference.

They demonstrated that a graded refractive index decreasing from substrate to ambient results in an increase in transmittance maxima. In the transparent area of the spectra, interference fringes due to multiple reflections on the different interfaces are observed indicating that the deposited films (in accordance with SEM observations) are smooth and uniform [25]. The number of interference fringes increased following the introduction of indium, indicating an increase in the optical thickness. High indium doping leads to a vertical growth of low-density films with more thickness (the lateral growth limited by indium oxide). One can also evoke the expansion of the crystal structure of ZnO by the incorporation of indium atoms having an ionic radius greater than that of zinc. The total thicknesses of the deposited films are reported in Table 1. The values obtained by fitting the transmittance experimental spectra using the theoretical model described below correspond perfectly to the SEM observations. Fig. 3a shows a perfect concordance between theoretical and experimental spectra. On another side, the shift of the absorption edge towards lower energies indicates that indium atoms were correctly incorporated into the ZnO structure. The decrease of the band gap energy related to this shift is mainly due to the distortions in the crystal structure caused by the incorporation of the doping atoms [26].

4. Discussion

Starting from the conclusions of Basu et al [24], a theoretical model describing the transmission of light through a thin film deposited on both sides of the glass substrate by dip-coating method is proposed. The deposited thin film is represented by multilayer systems with a graded refractive index decreasing from the substrate to the air according to the SEM observations. The optical indices N and K of the layers are defined for each photon energy ($E=hc/\lambda$) by five parameters (A, B, C, N_{inf} and E_g) in the following Forouhi-Bloomer relations [27-28]:

$$\tilde{N} = N - iK \quad (1)$$

$$K(E) = \frac{A(E - E_g)^2}{E^2 - B.E + C} \quad (2)$$

$$N(E) = N_{inf} + \frac{B_0 E + C_0}{E^2 - B.E + C} \quad (4)$$

$$B_0 = \frac{2A}{\sqrt{4C - B^2}} \left(-\frac{B^2}{2} + E_g.B - E_g^2 + C \right) \quad (5)$$

$$C_0 = \frac{2A}{\sqrt{4C - B^2}} \left(\frac{B}{2}(E_g^2 + C) - 2E_g.C \right) \quad (6)$$

Hayfield and White's method [29-30] gives a simple description of the light transmission through the sample with a system of (2x2) matrixes where L_m , L_s and $L_{m-1,m}$ matrixes represent the M layers, the substrate and their interfaces respectively:

$$\begin{bmatrix} E_i \\ E_r \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} = I_{01} \cdot L_1 \cdot I_{12} \cdots I_{m-1,m} \cdot L_m \cdot I_{m,m+1} \cdots L_M \cdot I_{MS} \cdot L_S \cdot I_{SM} \cdot L_M \cdots I_{m+1,m} \cdot L_m \cdot I_{m,m-1} \cdots I_{21} \cdot L_1 \cdot I_{10} \begin{bmatrix} E_i \\ 0 \end{bmatrix} \quad (7)$$

E_i , E_r and E_t represent the incident, reflected and transmitted electric fields.

For each interface between two successive strata of the optical system:

$$I_{m-1,m} = \frac{1}{t_{m-1,m}} \begin{bmatrix} 1 & r_{m-1,m} \\ r_{m-1,m} & 1 \end{bmatrix} \quad (8)$$

$r_{m-1,m}$ and $t_{m-1,m}$ are the Fresnel coefficients at the different interfaces :

$$r_{m-1,m} = \frac{\tilde{N}_{m-1} - \tilde{N}_m}{\tilde{N}_{m-1} + \tilde{N}_m} \quad (9)$$

$$t_{m-1,m} = \frac{2\tilde{N}_{m-1}}{\tilde{N}_{m-1} + \tilde{N}_m} \quad (10)$$

For each layer ($1 < m < M$) of the optical system:

$$L_m = \begin{bmatrix} \exp(-i\delta_m) & 0 \\ 0 & \exp(i\delta_m) \end{bmatrix} \quad (11)$$

$$\delta_m = \frac{2\pi}{\lambda} \tilde{N}_m d_m \quad (12)$$

For thick substrates the interferences are incoherent, the substrate matrix is then written:

$$L_s = \begin{bmatrix} \exp(-\alpha_s d_s) & 0 \\ 0 & \exp(\alpha_s d_s) \end{bmatrix} \quad (13)$$

where $\alpha_s = 4\pi K_s / \lambda$ is the absorption coefficient of the substrate and d_s its thickness.

From the optical indices and the thicknesses of the different strata of the defined optical system, the transmittance for each wavelength can be determined by:

$$T = \left| \frac{1}{S_{11}} \right|^2 \quad (14)$$

Then the theoretical spectrum is adjusted to the experimental measurements in order to determine the thickness and optical indices of the system by minimizing the error function:

$$\chi^2 = \frac{1}{P} \sum_{j=1}^P (T_{Exp} - T_{Th})^2 \quad (15)$$

P is the number of measurements in the transmittance spectrum.

It is clear that the adjustment is all the more difficult to obtain as the system is complex, the calculation time is longer but the result is usually better.

Fig. 3a shows an example of a successful fit with a three-layer system ($\chi^2 < 10^{-5}$). Minima of error function χ^2 resulting from the fittings of the transmittance spectra, for a

variable number of layers in the theoretical model, are represented in Fig. 4. The variation of the error function with the increasing number of strata follows the same decreasing form for the two samples. However, in the case of IZO, χ^2 is slightly lower regardless of the number of strata. This is probably due to imperfections in the experimental spectrum measured on ZnO sample. It is noticed that the fit is first improved by increasing the number of strata and then it stabilizes beyond three layers. In the case of a continuously graded index film, the quadratic error would have continued to decrease with the number of strata. However for the present work a three-layer system seems to be more appropriate. This system comprises an interfacial layer (glass/ZnO), a low density layer at the surface (ZnO/Air) and a thicker intermediate layer (ZnO or IZO); which corresponds perfectly to the SEM observations. The adjustment results of the obtained using a three strata system are reported in Table 1.

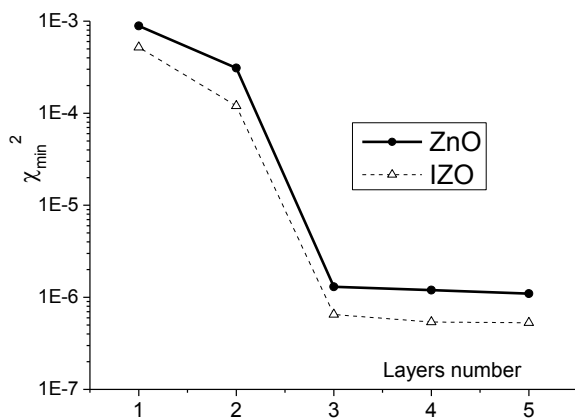


Figure 4. Minima of error function resulting from the transmittance spectra fitting.

The N_{int} Forouhi-Bloomer parameter representing the minimum refractive index is a good indicator of the deposited film density [27]. Interfacial layers of small thicknesses for the two samples present an index slightly greater than that of glass substrate; it represents the imperfection of slide surface observed by SEM. For ZnO sample, N_{int} varies from 1.87 for internal layer to 1.83 on the external surface indicating that this thin film is slightly porous; its total thickness estimated at 495 nm corresponds very well to that observed by SEM. For IZO sample, the deposited film is thicker (571 nm) but less dense with lower refractive index (N_{int} ranging from 1.84 inside the film to 1.73 at the surface) in accordance with SEM observations. This difference is probably due to the growth in the form of nanowires described above but difficult to discern on SEM cross-section images. The outer stratum (less dense) is thicker for IZO (280nm), which implies a more efficient antireflection effect. Finally the high transparency of IZO coated glass can be explained by the particular nanostructure of the film leading to a low refractive index with a more pronounced gradient.

5. Conclusion

Glass substrates coated on both sides with heavily indium doped ZnO, using dip-coating sol-gel method, exhibited a particularly high transparency. Their transmittance increased to 93.5% after IZO coating, exceeding the 91% maximum value of bare glass substrate. To explain this singular behavior a theoretical model based on the propagation of electromagnetic waves in thin stratified films was adapted to the studied samples and the measured transmittance spectra were perfectly fitted. The analysis of optical measurements showed that IZO films are thicker and less dense than that of undoped ZnO. Besides, IZO films presents a more pronounced refractive index gradient decreasing from the inner to the outer strata. These results perfectly agree with AFM and SEM observations. The smooth surface and the fine nanostructure of IZO leading to a low refractive index with a more pronounced gradient are probably at the origin of the very high obtained transparency.

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