Materials Letters 283 (2021) 128783

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Influence of the indium on the structure and the optical properties of the ZnO thin film: Kramer kronig relation and the spectroscopic ellipsometry

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A R T I C L E I N F O

Article history:
Received 16 July 2020
Received in revised form 10 September 2020
Accepted 30 September 2020
Available online 4 October 2020

Keywords:
ITO
IZnO thin films
AFM
Optical properties
Kramer kronig relation
Spectroscopic ellipsometry

A B S T R A C T

The ZnO thin film doped indium has been fabricated by the sol–gel spin coater technique. The XRD confirmed the pristine ZnO and ZnO:In are polycrystalline phase. The optical constants (n, k) have been determined in terms of two analyses methods, **the first** was by Kramer kronig relation, and **the second** was by fitting a spectroscopic ellipsometric (SE) data (ψ, Δ) by means of the three-layer optical model. The calculated optical constants in terms of two analyses were comparable and affected by additional In at the expense of ZnO. The optical band gap reduced by the increase of the indium content at the expense of Zn from 3.1 to 2.7 eV. The atomic force microscope (AFM) was used to investigate the surface roughness, which was nearly approached with the surface roughness investigated by SE.

1. Introduction

The Zinc Oxide (ZnO) is a transparent conducting oxide (TCO) film. The ZnO has a wide direct bandgap at around 3.37 eV at the room temperature. The ZnO has several applications, for instance: optoelectronics applications[1,2], the flat panel display (FDPS), surface acoustic wave devices, gas sensors, and solar cells [3,4]. The indium titanium oxide (ITO) is the ideal material from TCO family, ITO thin films have several applications, especially utilizing as an anode in solar cells and FPDs because of its excellent work function, good conductivity, and high transparency in the visible region [5,6]. However, the cost of ITO is very high due to the lack of natural abundance and toxicity, so many researchers are looking for an alternative candidate with the same characteristics. The Zinc element has more abundance in nature and has low toxicity and high transparency in the transparent region. The ZnO is considered as the best alternative candidate for ITO and has the same characteristics. Moreover, The Zinc oxide doped with indium has much attention due to its mixed features among ZnO and ITO [7,8]. The ZnO can be used as a window layer in antireflection coatings and optical filters [9]. The nanostructures of ZnO have excellent optoelectronic characteristics as well and can be used for light-emitting diode and laser diodes, detectors for a blue and ultraviolet range of the spectrum [10–13].

In this work, The ZnO:In films have been prepared by a spin coater sol–gel technique. The optical constants (n, k) have been calculated by two methods Kramer kroing relation and spectroscopic ellipsometry.

2. Experimental process

2.1. The preparation of the ZnO:In thin films

Indium doped ZnO thin films were prepared by the sol–gel assisted spin coating on cleaned glass substrates. The Zinc acetate

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https://doi.org/10.1016/j.matlet.2020.128783
0167-577X/

and the indium chloride, which are of high quality purchased from Sigma Aldrich company, were the starting materials. Zinc acetate Zn $(CH_3COO)_2{\cdot}2H_2O$ and $InCl_3$ were dissolved in 2-Methaoxy ethanol to form the precursor solution. The monoethanolamine (MEA) was added, and it was stirred for an hour to obtain clear sol. The sol was kept aside for 48 h to form a gel. The gel has been used to coat on the substrates using a spin coater operated at 1000 rpm for 50 sec. The deposited films are thermally treated to remove any organic residues. The same procedure was repeated, and the appropriate amount of $InCl_3$ is added to obtain 2%, 4%, and 6% films. The thin films were annealed in order to increase the homogeneity of the thin films.

3. Results and discussions

Figure s1 exhibited the XRD patterns of the undoped ZnO and doped In thin films fabricated by the sol–gel spin coater technique. It is demonstrated that the films display an amorphous structure. This amorphous phase could have resulted from the interstitial or substituting location.

Our challenge to know the difference between the measured and calculated optical constants in terms of spectroscopy *ellipsometry* and *Kramer kroing* approach. The Kramer kroing relation based on the Uv–Vis spectra, so we measured the transmittance and reflectance.

Fig. 1 displays an optical transmittance $T(\lambda)$ of ZnO and In doped ZnO thin film in a wavelength (λ) ranged from 290 to 900 nm. Indium substitution affects the transmittance in the visible region. Notably, the observed transmittance spectra of pure ZnO thin film is the lowest compared with the In doped ZnO meanwhile, the transmittance increases by increasing the concentration of In. The behavior of the reflectance spectra is the same entirely to that of the transmittance spectra, as demonstrated in Fig. 1. The comparative analysis of the transmission spectra of pure and doped films does not show any noticeable spectral alterations excepting small change at concentration 1%. Fig. 1 displays the reflection spectra for undoped ZnO thin film and doped with various indium concentrations, where the peak broads around 360 nm, for pristine ZnO thin film. For all doping films, a small red-shifted was displayed in the transmission spectrum. Furthermore, the reflective intensity decreases due to the increasing of In concentration and due to light dispersion on the raw surfaces of the doped ZnO nanostructures.

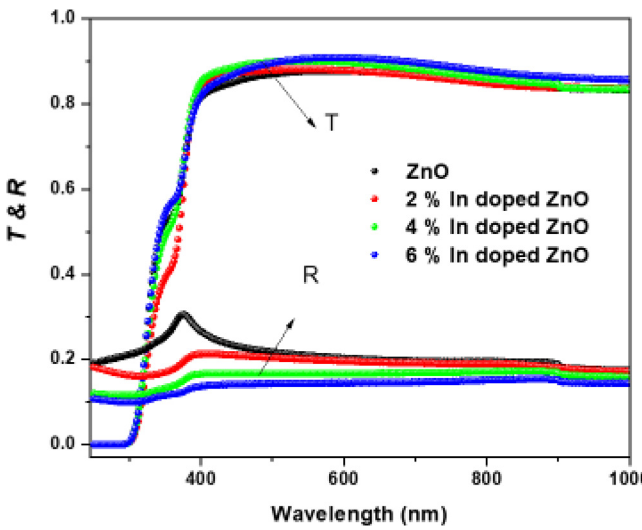

Fig. 1. The Spectra of the Transmittance, T, and Reflectance, R, for pure ZnO and doped indium thin films.

3.1. Optical constants in terms of the Kramer-Kronig relationship and spectroscopic ellipsometry

The Kramer-Kronig approach is the best solution for the accurately optical constant calculations without relying on film thickness. Due to the importance of optical applications and electronics, the optical constants are very important to determine by an accurate method. All calculated methods of optical constant based on the thin film thickness, and it is considered a significant issue since there is no accurate device to measure the thickness.

Spectroscopic ellipsometry (SE) is a powerful method with high accuracy for measuring the optical properties; meanwhile, it is based on the change in the polarization state of the light during the reflection for the surface characterization, interfaces, thin films, and nanostructure materials. Concerning the thin film samples analysis, the ratio of amplitude changes Psi (ψ) and the difference in phase change Delta (ψ) for the p- (in the plane of incidence), and the s- (perpendicular to the plane of incidence) polarized components were deduced from the spectroscopic ellipsometry. The ratio of complex reflectance can be determined by the following relation based on the measurables Psi (ψ) and Delta (Δ) as a function in the wavelength.

$$\rho = \frac{r_p}{r_s} = \tan\psi \, \exp(i\Delta) \tag{7}$$

where r_s and r_p are the complex Fresnel reflection coefficients of the sample for *p*- and *s*- polarized light, respectively [14,15].

The optical constants (n, k) pure and ZnO:In films have been calculated by spectroscopic ellipsometry (SE) using three optical layer model ((Cauchy layer of substrate/ B-Spline layer of ZnO:In film/-surface roughness layer.), see Fig. 2 and also calculated by K-K relation [16]. Fig. 3(a, b). illustrates the comparable values of *n* and *k* that calculates by the two methods (SE and K-K).Also, The surface roughnesses of pure ZnO and ZnO:In were investigated by SE, and Atomic force microscope (AFM), the calculated mean surface roughness by the two methods nearly approached. The refractive index for the undoped ZnO, exhibits values ranging between 2.2 and 2.4 with main peak feature appearing at the beginning of the visible region by both methods a seen in Fig. 3a, as the In concentrations were increased by 2, 4, and 6%, *n* decreased slightly in the visible region. Fig. 3b shows the extinction coefficient (k) spectra for the films decrease with increasing *In* concentration, particularly in the visible region.

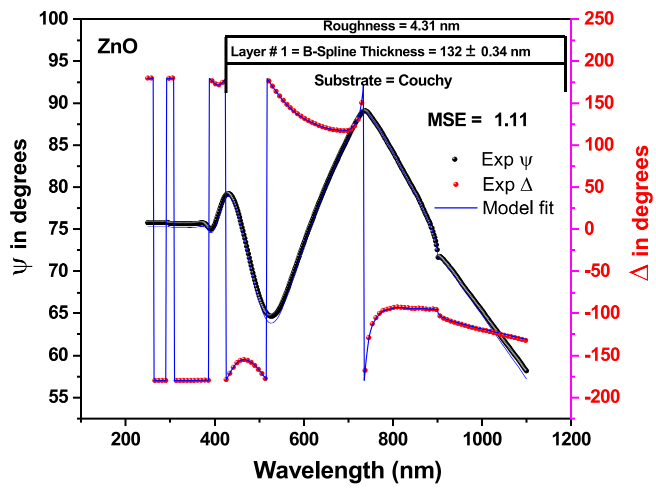

Fig. 2. The ellipsometric measured data (black and blue symbols) and the model fit (red line) for parameters Psi (ψ) and Delta (Δ) for pure ZnO and doped indium thin films. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

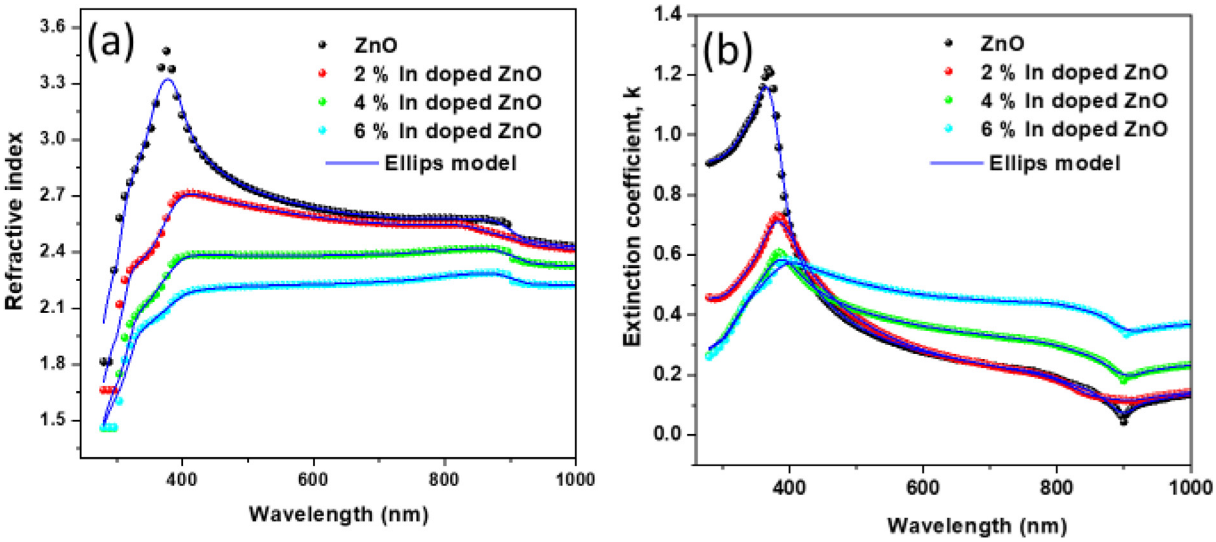

Fig. 3. (a) The spectra of the refractive index, n (b) The spectra of the extinction coefficient, k in terms of Kramer-Kroning relation, and ellipsometry for pure ZnO and doped indium thin film.

4. Conclusion

The sol–gel spin coater technique synthesized the pristine ZnO thin films and doped by indium. The XRD confirmed that the ZnO: In thin films have a polycrystalline phase. The optical constant studied with two methods Kramer kroing and fitting a spectroscopic ellipsometric data (ψ, Δ) using three optical models layed, the result exhibited the optical constants (n, k) that calculated by the two methods were comparable. The energy gap of ZnO:In decreased by increasing the ratio of indium. The thin films of the ZnO:In make a competitive semiconductor for many optoelectronic applications with the selective band stop filter, and optical limiting characteristics.

CRediT authorship contribution statement

Abdelaziz M. Aboraia: Calculation and solving of Kramers-Kronig relations and writting the manuscript. **Mohammed Ezzeldien:** Writing- Original draft preparation and editing. **H. Elhosiny Ali:** Validation, Software, Writing - review & editing. **I.S. Yahia:** Supervision, Conceptualization. **Yasmin Khairy:** Validation, Software. **V. Ganesh:** Methodology, Data curation, Writing- Original draft preparation and editing. **Alexander V. Soldatov:** Investigation, Writing- Original draft preparation. **E. R. Shaaban:** the spectroscopic ellipsometry measurments and Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P. 2/50/40.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2020.128783.

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