

Determination of optical constants of $Zn_xIn_{1-x}Se$ thin films deposited by evaporation

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Polycrystalline $Zn_xIn_{1-x}Se$ thin films with Se contents varying between $x=0$ (InSe) and $x=1$ (ZnSe), deposited on glass substrates, were optically characterized. These samples were grown by coevaporation of the ZnSe and In_2Se_3 compounds using a crucible constituted by two coaxial chambers. The optical constants (refractive index n , absorption coefficient α and optical gap E_g) and the film thickness d , were determined using the transmission spectrum and simple calculations based on a theoretical model including interference effect induced by multiple internal reflections in the substrate/film system. The reliability of the results was tested by comparing the experimental transmittance spectra with the theoretically ones, using values of n , α and d obtained experimentally.

Keywords: Optical properties; selenides; semiconductors; solar cells

Se caracterizaron ópticamente películas delgadas policristalinas de $Zn_xIn_{1-x}Se$ con contenidos de Se variando entre $x=0$ (InSe) y $x=1$ (ZnSe). Las películas fueron depositadas sobre substrato de vidrio. Las muestras se crecieron por coevaporación de los compuestos ZnSe e In_2Se_3 usando un crisol constituido por dos cámaras coaxiales. Las constantes ópticas (índice de refracción n , coeficiente de absorción α y brecha de energía óptica E_g) y el espesor de las películas d , se determinaron usando el espectro de transmisión y cálculos simples basados en un modelo teórico que incluye los efectos de interferencia inducidos por las múltiples reflexiones internas en el sistema sustrato/película. La confiabilidad de los resultados fue probada comparando el espectro de transmitancia experimental con el generado teóricamente, utilizando valores de n , α y d obtenidos experimentalmente.

Descriptores: Propiedades ópticas; selenuros; semiconductores; celdas solares.

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1. Introduction

Various kinds of binary, ternary and quaternary semiconductors are currently being investigated for potential photovoltaic applications. Among them, CdTe, $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) thin films have demonstrated to be promising candidates for high efficiency, low cost solar cells [1,2]. The highest efficiency have been up to now achieved using a CdS buffer layer processed in a wet chemical bath [3]. However, the chemical deposition of the CdS complicates the establishment of the in-line process to fabricate this kind of devices. Therefore, for industrial production and for environmental protection, it would be desirable to replace CdS for a less toxic buffer material deposited by a dry process. Novel materials such as In_xSe_y , ZnSe and $Zn_xIn_{1-x}Se$ are promising candidates for buffer layer, in substitution of the CdS. Efficiencies greater than 11 % have been achieved with CdTe and CIGS based solar cells fabricated using these new materials, deposited by dry processes, as buffer layer [4-6].

In this work, a description of a non conventional procedure to prepare thin films of the ternary $Zn_xIn_{1-x}Se$ compound by physical evaporation will be presented. On the other hand, values of the optical constants of thin films of In_2Se_3 , ZnSe and $Zn_xIn_{1-x}Se$, calculated using a well known procedure [7], will be reported. We want to emphasize that, despite the technological importance of these type of compounds for the development of photoconductor and

photovoltaic devices, data of their optical constants have not been previously reported. Therefore, the results of this work will be useful for researchers interested in the development of photoconductor and photovoltaic devices based on these new materials.

2. Experimental

Polycrystalline $Zn_xIn_{1-x}Se$ thin films with thicknesses between 0.1 and 3 μm were deposited on soda-lime glass substrates by co-evaporation of the precursor materials (In_2Se_3 , ZnSe). Figure 1 shows the evaporation source used for the preparation of the $Zn_xIn_{1-x}Se$ films. It consists of a cylindrical graphite crucible, which includes two coaxial chambers, from where the ZnSe and In_2Se_3 precursors are simultaneously evaporated.

The evaporation source is heated by radiation coming from a cylindrical graphite heater. Any desired chemical composition of the ternary compound can be achieved varying the diameter ϕ of the openings of the coaxial chambers and using adequate values of the substrate and evaporation temperatures.

The parameters used to prepare the samples studied, are listed in Table I. The chemical composition of the ternary compounds was determined by XRF (X-Ray Fluorescence) measurements and the transmittance measurements were done with an Oriel Spectrophotometer.

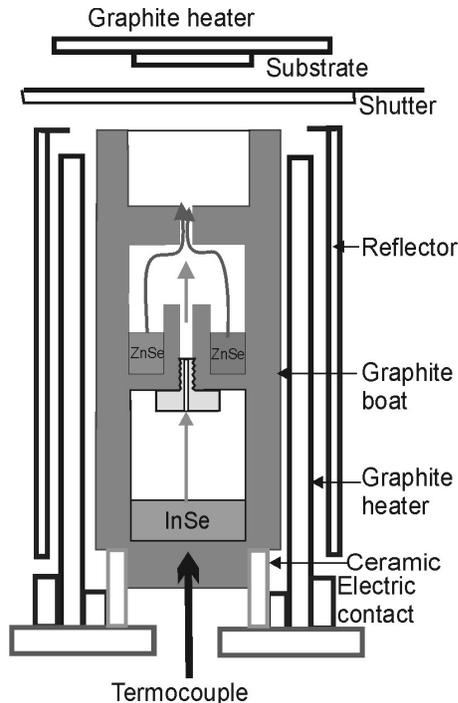


FIGURE 1. Coaxial source for the deposition of $Zn_xIn_{1-x}Se$ thin films with chemical composition varying in a wide range.

TABLE I. Ranges of variation of the parameters used for the deposition of the In_xSe_y , ZnSe and $Zn_xIn_{1-x}Se$ thin films studied in this work.

PARAMETERS	In_xSe_y	ZnSe	$Zn_xIn_{1-x}Se$
Base pressure (mbar)	8×10^{-6}	8×10^{-6}	8×10^{-6}
Substrate temperature ($^{\circ}C$)	250 – 450	250	250
Evaporation temperature ($^{\circ}C$)	850	900	850 – 950
ϕ_{ZnSe} (mm)	-	6	6
ϕ_{InSe} (mm)	2.5	-	0.8 – 2.5
Chemical Composition x	-	-	0 – 1

3. Results and discussion

The refractive index and absorption coefficient are usually determined by elaborated computer iteration procedures [8,9] using both, the transmission and reflection spectra. In this work, we used a procedure developed by Swanepoel [7] to determine $n(\lambda)$ and $\alpha(\lambda)$ by simple straightforward calculations using the transmission spectrum alone. The film thickness was determined from the interference fringes of the transmission spectrum.

3.1. Spectral transmittance measurements

It was found from XRD (x-Ray diffraction) measurements, performed in previous works [10,11], that the phase and crystalline structure in which the In_xSe_y and ZnSe films grow, depend on the evaporation and substrate temperatures. However, the samples studied in this work (deposited under the

parameters listed in Table I) grow in the In_2Se_3 and ZnSe phases, respectively. The In_2Se_3 films grow with hexagonal structure, whereas the ZnSe films grow with cubic structure. On the other hand, it was found that, independently of the phase or structure in which the In_xSe_y and ZnSe films grow, their wavelength cutoff is significantly influenced by the film thickness.

Figure 2 shows typical transmittance spectra of In_2Se_3 and ZnSe films with different thicknesses, determined using the procedure described in Sec. 3.2. It is observed a shift of the transmittance curves toward the region of lower values of λ when their thickness decreases. We have not found a definitive explanation of this behavior. However, we consider that the shift of the wavelength cutoff observed when the thickness of the InSe and ZnSe samples increases from values less than 100 nm in which the films are in the coalescence stage, up to values of the order of μm s in which a continuous film is formed, could be associated to changes in the band structure, induced by changes in the different interaction processes which take place during the different growth stages of the thin films. In particular, the superposition degree of electron clouds of neighboring atoms, which affect the band width, is feasible to increase by increasing the film thickness. It was also found that for thicknesses greater than $1 \mu m$, the optical gap of the $Zn_xIn_{1-x}Se$ thin films keeps constant. Therefore, to prevent the effect of the thickness on the determination of the optical gap, samples with thicknesses greater than $1 \mu m$ will be selected from now on.

Figure 3 shows typical transmittance spectra of $Zn_xIn_{1-x}Se$ Se films with chemical compositions varying between $x=0$ (In_2Se_3) and $x=1$ (ZnSe). The results of Fig. 3 show that the slope of the transmittance curve of the In_2Se_3 film is quite smaller than those of the $Zn_xIn_{1-x}Se$ Se films with lower content of In. This indicates that in the In_2Se_3 films, the contribution of photon absorption via states within the energy band gap (probably caused by mechanical defects and/or tail band) is greater than in the $Zn_xIn_{1-x}Se$ Se films with lower content

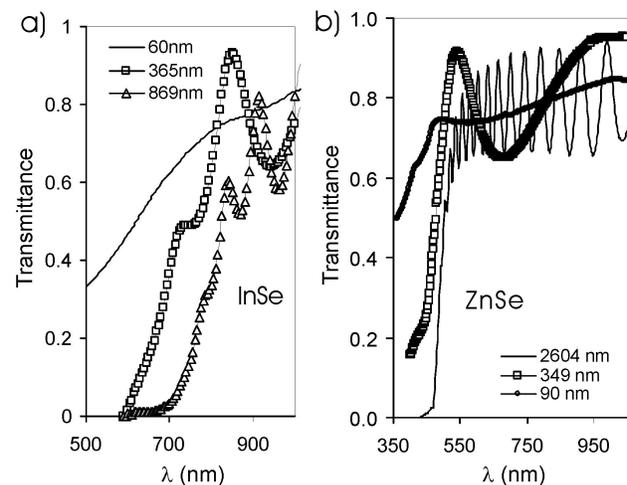


FIGURE 2. Influence of the film thickness on the transmittance of In_2Se_3 and ZnSe thin films deposited by evaporation.

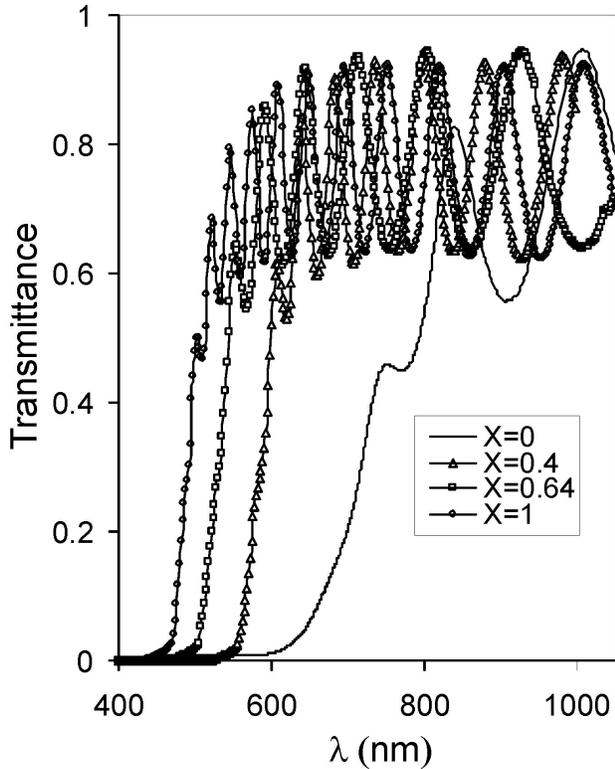


FIGURE 3. Transmittance spectra of $Zn_xIn_{1-x}Se$ thin films deposited by co-evaporation of the In_2Se_3 and $ZnSe$ compounds, with Se content of $x=0$, $x=0.4$, $x=0.65$ and $x=1$ respectively.

of In. The shift of the transmittance curves toward the region of lower λ values when the Se content increases, indicates that the optical gap of the Zn_xIn_{1-x} films increases with the Se content.

3.2. Determination of the optical constants

This section presents results corresponding to the calculation of the thickness and optical constants of the $Zn_xIn_{1-x}Se$ thin films depicted in Fig. 3. These were obtained using the transmittance spectrum and calculations based on a procedure described in detail in Ref. [7]. This consists basically in the following:

- Initially the thickness d and complex refractive index $n^* = n - ik$ are determined by simple straightforward calculations using the transmission spectrum alone. k is the extinction coefficient which can be expressed in terms of the absorption coefficient α ($k = \alpha\lambda/4\pi$).
- Subsequently, the optical gap E_g is determined through the relation: $(\alpha h\nu) = A(h\nu - E_g)^{1/2}$, which is valid for direct band gap semiconductors, like those studied in this work.

In order to obtain the thickness and the values of n and α from the transmission spectra, it is necessary to analyze them as follow:

3.2.1. Interference zone

Assuming that the interferences are fully coherent, the location of the interference maxima and minima are related to the

real part of the refractive index n , through the expression:

$$2nd = m\lambda \tag{1}$$

where the interference order m is an integer for maxima and half integer for minima. There is no way of obtaining information on either n or d separately using Eq. (1); however, these parameters can be determined as follows:

In the transparent region (far below the band gap energy) where $\alpha = 0$, the n value at a minimum is given by the following relation [7]:

$$n = \left[M + (M^2 - s^2)^{1/2} \right]^{1/2}, \tag{2}$$

with $M = 2s/T_{min} - (s^2 + 1)/2$, where T_{min} is the transmittance at λ values corresponding to the minima and s the refractive index of the substrate. The refractive index in two consecutive minima can be obtained solving Eq. (2). These values are subsequently used to determine the film thickness through the following relation [7]:

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

where n_1, n_2 are the refractive indexes in two consecutive minima and λ_1, λ_2 the corresponding wave lengths. Using this method, the thickness of the samples depicted in Fig. 3 was determined; the thickness calculated for the samples with chemical compositions corresponding to $x=0$, $x=0.4$, $x=0.64$ and $x=1$ were 0.8, 1.6, 1.2 and 1.7 μm respectively.

The values of n and d calculated previously from Eqs. (2) and (3), allows determining the interference order m . The values of n in the whole of the interference region can be calculated substituting the values of m and d in Eq. (1).

Finally, the absorption coefficient in the low absorption region of the interference zone can be calculated using the following relation [7]:

$$\alpha = -\frac{1}{d} \left\{ \ln \left[\frac{E_M - \left[\frac{E_m^2 - (n^2 - 1)^3 (n^2 - s^4)}{(n-1)^3 (n-s^2)} \right]^{1/2}}{E_M - (n^2 - 1)(n^2 - s^2)} \right] \right\}; \tag{4}$$

3.2.2. Interference free zone

In this region, the refractive index is determined by extrapolating the curve of n vs λ obtained previously at λ values within the interference zone. For that, the n vs λ curve is fitted to a polynomial equation of the form $n = A + B/\lambda^2$ (Cauchy equation).

The absorption coefficient in the high absorption region of the interference free zone is calculated using the following Eq. (7):

$$\alpha = -\frac{1}{d} \left\{ \ln \left[\frac{(n+1)^3 (n+s^2) T}{16n^2 s} \right] \right\}. \tag{5}$$

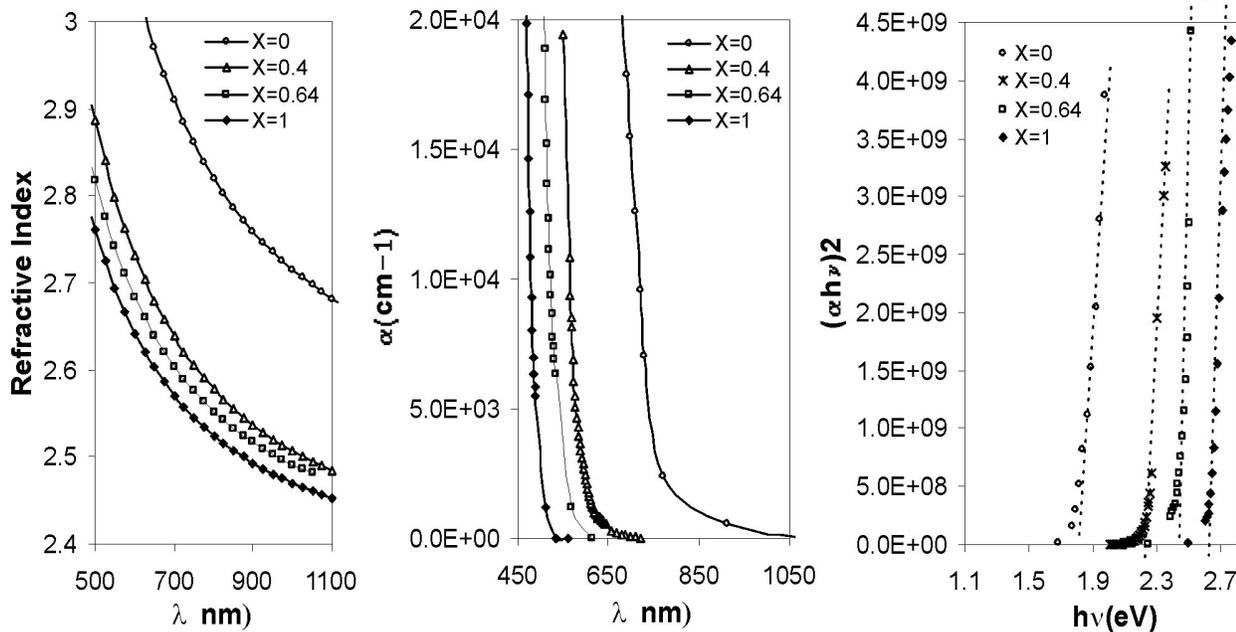


FIGURE 4. Curves of n vs λ , α vs λ and $(\alpha h\nu)^2$ vs $h\nu$, corresponding to $\text{Zn}_x\text{In}_{1-x}\text{Se}$ thin films deposited by evaporation with Se contents of $x=0$, $x=0.4$, $x=0.65$ and $x=1$ respectively.

The optical gap E_g was determined using the relation $\alpha(h\nu) = A(h\nu - E_g)^{1/2}$. The intercept with the $h\nu$ axis of the α^2 vs $h\nu$ curve gives the value of E_g .

Figure 4 shows the influence of the chemical composition on the curves of n vs λ , α vs λ and $(\alpha h\nu)^2$ vs $h\nu$ which were obtained for the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ samples depicted in Fig. 3.

From the results shown in Fig. 4, the following facts can be remarked:

- The refractive index of the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ thin films increases with the Se content, being the refractive index of the In_2Se_3 films significantly greater than that of the ZnSe films. This behavior seems to be basically caused by an increase of both the conductivity under illumination and the photo-conductivity of $\text{Zn}_x\text{In}_{1-x}\text{Se}$ films when their In content increases, taking into account that the refractive index can be expressed by the relation, $n = 4\pi\sigma/c\alpha$ [12] and that the absorption coefficient α of both materials are similar. Under an illumination of 80 mW/cm^2 , the In_2Se_3 and ZnSe films present conductivities σ of about $10^{-5} (\Omega\text{cm})^{-1}$ and $5 \times 10^{-8} (\Omega\text{cm})^{-1}$, respectively.
- The n vs λ curves of all the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ samples studied, fitted quite well to a polynomial expression of the form $n = A + B/\lambda^2$ (Cauchy equation), indicating that, in the range of wavelengths studied, the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ films present normal dispersion.
- The linear behavior of the $(\alpha h\nu)^2$ vs $h\nu$ curves indicates that the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ thin films have a direct energy band gap. Using the relation $\alpha^2 = A(E_g - h\nu)$, which is valid for this type of materials, E_g values varying between 1.85 and 2.65 eV were found, when the Se con-

tent of the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ thin films varied between $x=0$ and $x=1$. These values are similar to those reported in the literature [5,13]

Since, in general, the film thickness does not significantly affect the optical constants of samples with thicknesses varying between 0.8 and $2 \mu\text{m}$, its effect was not included in the calculations of the n and α values reported in this work.

3.3. Theoretical calculation of the transmittance

In order to verify the reliability of the values of the thickness and optical constants determined previously, the transmittance of the same samples whose spectra are depicted in Fig. 3 was theoretically calculated as a function of the wavelength. For that, we used Eq. (1) which was developed by other authors [7] to calculate the transmission spectrum of thin films presenting interference fringes:

$$T = \frac{Az}{B - Cz \cos(\varphi) + D^2}, \quad (6)$$

with

$$A=16z^2; \quad B=(n+1)^3(n+s); \quad C=2(n^2-1)(n^2-s^2); \\ D=(n+1)^3(n-s^2); \quad \phi=4\pi nd/\lambda; \quad g=\exp(-\alpha d).$$

Being n and α the refractive index and absorption coefficient of the $\text{Zn}_x\text{In}_{1-x}\text{Se}$ films, s the refractive index of the substrate, and d the film thickness.

Figure 5 compares the theoretical and experimental transmittance spectra of the mentioned $\text{Zn}_x\text{In}_{1-x}\text{Se}$ samples. The T vs λ curves were obtained using Eq. (6) and experimental

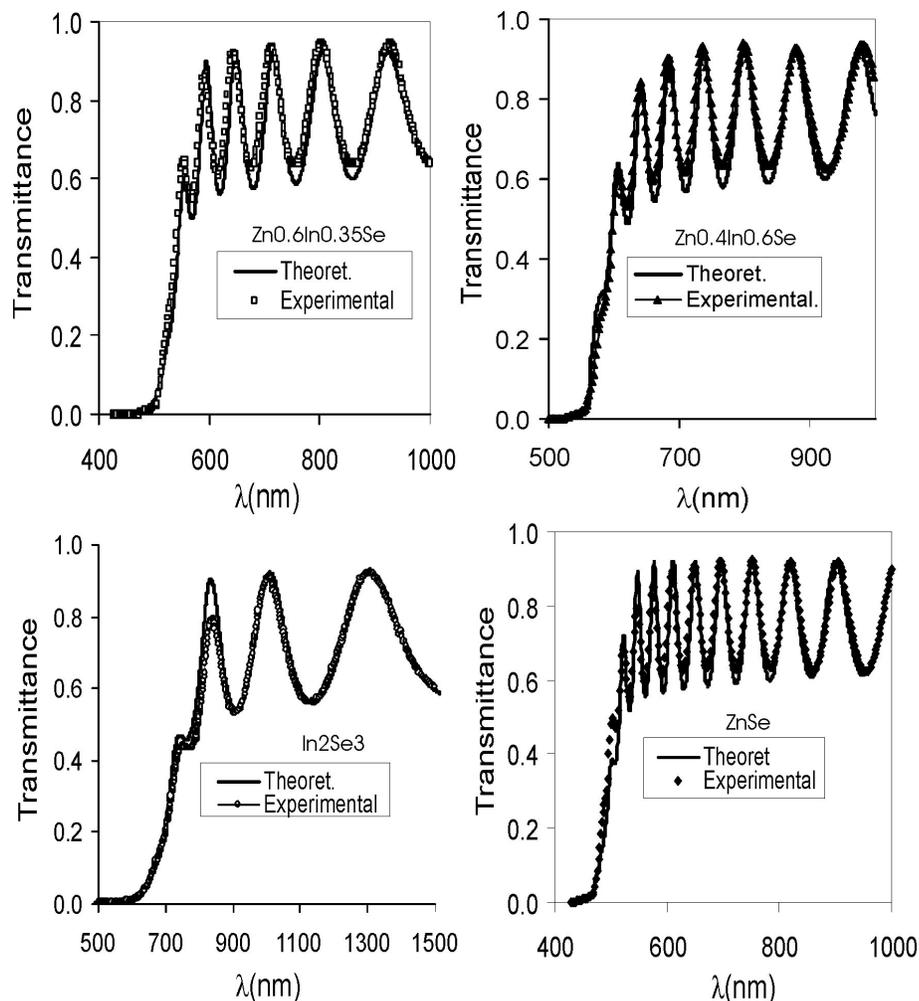


FIGURE 5. Comparison of the experimental transmittance spectra of the $Zn_xIn_{1-x}Se$ samples showed in Fig.3 with those obtained theoretically.

values of d , n and α obtained. The results show that the theoretical T vs λg curve fits quite well the experimental one, indicating that the values of thickness and optical constants of the $Zn_xIn_{1-x}Se$ films are reliable. The differences observed when comparing the experimental transmittance spectra with the theoretical one, could be caused by effects of surface roughness and inhomogeneities in film thickness, which were not taken into account in the model used to get Eq. (6).

4. Conclusions

The optical constants (refractive index n , absorption coefficient α , and optical gap E_g) of $Zn_xIn_{1-x}Se$ thin films, deposited by coevaporation of the $ZnSe$ and In_2Se_3 compounds, were determined by simple straightforward calculations using only the transmission spectrum. Values of α in the range of 10^4cm^{-1} were found for all the samples studied (for $h\nu$ greater than E_g); for the optical gap, values ranging from 1.85 eV to 2.65 eV were found, when the Se content of the $Zn_xIn_{1-x}Se$ films varied between $x=0$ and $x=1$.

The refractive index of the $Zn_xIn_{1-x}Se$ thin films increases by increasing their In content. This behavior seems to be associated to an increase of both the conductivity under illumination and the photo-conductivity of $Zn_xIn_{1-x}Se$ films when their In content increases. Values of n ranging between 2.45 to 3 were found. In the studied spectral range, the refractive index of the $Zn_xIn_{1-x}Se$ films changes as a function of λ according to an expression of the form $n=A+B/\lambda^2$, indicating that these type of samples present normal dispersion.

Theoretical calculation of the transmission spectra, carried out using experimental values of the thickness and optical constants, fitted quite well those obtained experimentally, indicating that, in the studied spectral range, the values obtained for the optical constants of the $Zn_xIn_{1-x}Se$ films with Se content varying between $x=0$ and $x=1$, are reliable.

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