Determination of the Optical Properties of ZnSe Thin Films Using the Transfer Matrix Method

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Abstract. The transfer matrix method (TMM) is presented as a highly effective alternative in the treatment of problems of electromagnetic wave propagation through stratified media. This method allows to determine the transmission and reflection coefficients of the system. In this paper the TMM is applied to simulate the experimental transmittance spectra of ZnSe thin films prepared with high vacuum evaporation. From the simulation the spectral variation of the refractive index, the absorption coefficient and material gap of the ZnSe were obtained. The TMM was applied to a series of samples prepared at substrate temperatures between (200 and 350)^{o}C. Absorption coefficients values in the order of 10^{-3} cm^{-1} were found in the high absorption region while the refractive index was around 2.7 at $\lambda = 600$ nm. The material gap found for all the samples was about 2.65 eV.

1. Introduction

In II-VI compound semiconducting material, ZnSe is used as a window layer for the fabrication of thin film solar cells[1, 2]. It is mainly used as protective and antireflection coating for infrared-operating electrochromic thermal-control surfaces[3]. ZnSe is an important promising material for optoelectronic devices such as light-emitting diodes (it emits blue light)[4], and dielectric mirrors[5, 6]. ZnSe doped with chromium (ZnSe:Cr) has been used as an infrared laser gain medium emitting at about 2.4 μm[7]. Characterization of ZnSe thin films have been widely studied with variations such as: deposition onto transparent substrates[8], transparent substrates for specific regions of interest[9], doping with other elements, different techniques of deposition, growth and deposition temperature[10]. The variants described in the optical characterization take great importance due to the behavior of ZnSe in the regions of visible and infra-red, behaving as a dielectric with refractive index decreasing when the wavelength increases under the influence of multi-photon absorption[10].

In the characterization of thin films, some authors who analyze the transmittance or reflectance spectra have developed elaborate numerical and analytical methods[11, 12], including both the absorption of different areas as well as different angles of incidence on the sample. In the same way, the transfer matrix method (TMM) can be used for the analysis of wave propagation of quantum particles, such as electrons[13], electromagnetic[14], acoustic and elastic waves. This method is particularly effective in the analysis of transmission and reflection phenomena in layered systems, mostly in one dimension[15]. This paper proposes a model based on TMM to calculate the spectral variation of the refractive index, extinction coefficient, thickness of the samples and the gap of the material.

2. Experimental details

The samples were deposited on glass substrates, under high vacuum at a pressure of 2.5×10^{-5} $mbar$, with substrate temperatures $(100 - 350)^oC$. Evaporator temperature was held constant at 850^oC during growth of the material. ZnSe thin films were deposited by high vacuum evaporation. The samples were deposited in common glass substrates at temperatures between $(200 - 350)^oC$. The growth of the ZnSe thin film was performed using an evaporation chamber, which is formed by a coaxial oven made of graphite and a cell *Knudsen* also constructed in graphite. The material is located in the interior of the Knudsen cell, the latter one is placed inside the oven. The material is heated by radiation, passing a electrical current of about $120A$ through the oven . The material is sublimated and then released into the substrates, where the film is formed at a specific substrate temperature. During the deposition process a temperature controller mantains the substrate temperature at the desired set point with a precision of $\pm 1^oC$. Before the deposition process, the precursor material is heated at 300^oC during one hour in order to remove impurities acquired during storage. In this process, the shutter prevents the impurities released from reaching the substrates. During this process, the substrates are also heated to 100^oC and then raised to the desired temperature. After cleaning the system, the temperature is raised in the evaporator and when it reaches 850^oC the shutter is opened and the film begins to form. The deposition time were for 5 minutes in all samples. The transmittance measurements were performed by a Spectrometer Varian Cary 5000 in the spectral range of $(330 - 2500)nm$, at normal incidence to the sample surface.

3. Transfer matrix method TMM

From the requirements of the continuity of the tangential components of the electric $\mathbf{E}$ and the magnetic $\mathbf{H}$ fields, the transfer matrix M_{1-2} is derived from a single interface between two media. Its elements determine the transmission and reflection amplitudes for both the electric and the magnetic fields. The boundary conditions on the tangent components of the field vectors $\vec{E}$ and $\vec{H}$ hold that they are the same on both sides of the interface. Thus the relation between the electric fields on opposite sides of the interface can be expressed as:

$$\begin{pmatrix} E_2^+ \\ E_2^- \end{pmatrix} = M_{(1-2)} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix}; \qquad M_{(1-2)} = \frac{1}{2} \begin{pmatrix} 1 + \frac{\mu_2}{\mu_1}\frac{k_{1z}}{k_{2z}} & 1 - \frac{\mu_2}{\mu_1}\frac{k_{1z}}{k_{2z}} \\ 1 - \frac{\mu_2}{\mu_1}\frac{k_{1z}}{k_{2z}} & 1 + \frac{\mu_2}{\mu_1}\frac{k_{1z}}{k_{2z}} \end{pmatrix} \tag{1}$$

$M_{(1-2)}$ corresponds to the ***transfer matrix*** for a single interface, where for normal incidence $k_{(iz)} = (\omega\hat{N}/c)\cos(\theta)$ will be $k_{(i)} = (\omega/c)(n_i + \imath\kappa_i)$ (for the general case). The transfer matrix $\mathbf{M}_{(i-j)}$ is defined for the general case having the electromagnetic waves coming from the left and the right of the interface. The transmission $t_{(1-2)}$ and the reflection $r_{(1-2)}$amplitudes are defined from the matrix transfer as:

$$t_{(1-2)} = \frac{detM_{(1-2)}}{M_{22\,(1-2)}} = \frac{2\mu_2 k_{1z}}{\mu_1 k_{2z} + \mu_2 k_{1z}}; \qquad r_{(1-2)} = -\frac{M_{21\,(1-2)}}{M_{22\,(1-2)}} = \frac{\mu_2 k_{1z} - \mu_1 k_{1z}}{\mu_1 k_{2z} + \mu_2 k_{1z}} \tag{2}$$

where 2 are the familiar *Fresnel* relations for a single interface. For multilayer systems, it is possible to determine a simple method of analysis. First of all is important recognize that the last matrix transfer found in the previous section corresponds to the matrix transfer for a single interface $\mathbf{M}_{(1-2)}$, and it is always useful that the electromagnetic wave changes the media. Thus, for two slab $Fig.1$ we will need three of these matrixes $\mathbf{M}_{(1-2)}$ from the media 1 to 2, $\mathbf{M}_{(2-3)}$ from the media 2 to 3 and $\mathbf{M}_{(3-4)}$ so on. However it is necessary to introduce a new matrix called the *propagation matrix* $\mathbf{M}^{(P)}$ which describes the wave propagation within the thin film (ϵ_2, μ_2) and the substrate (ϵ_3, μ_3). This matrix can be deduced following the last treatment.

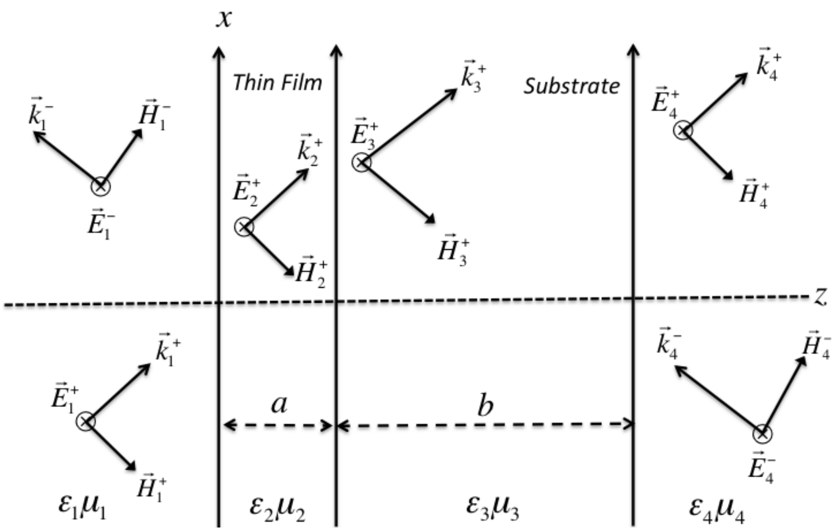

Figure 1. Transmission of an electromagnetic wave through a thin film deposited on a substrate with width a and b respectively.

Since the matrix transfer for the entire structure will be obtained from the multiplication of five matrixes, three for the interfaces and two for the propagation in the media.

$$\begin{pmatrix} E_4^+ \\ E_4^- \end{pmatrix} = M_{(12)} \cdot M^{(P_2)} \cdot M_{(23)} \cdot M^{(P_3)} \cdot M_{(34)} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} \tag{3}$$

where the matrices $M_{(ij)}$ are given by the equations 1, and the diagonal matrix $\mathbf{M}^{(P_j)}$

$$\begin{pmatrix} e^{ik_{jz}l} & 0 \\ 0 & e^{-ik_{jz}l} \end{pmatrix} \tag{4}$$

Correspond to the matrix propagation for a homogeneous media (ϵ_j, μ_j). Having solved this matrix system, the *matrix transfer* is therefore obtained.

$$\begin{pmatrix} E_4^+ \\ E_4^- \end{pmatrix} = M^{System} \begin{pmatrix} E_1^+ \\ E_1^- \end{pmatrix} \tag{5}$$

In order to find the transmission and reflection amplitudes, these are calculated in the same way than for a single interface with the equations 2 respectively.

$$t_s = \frac{detM^s}{M_{22}^s} \quad and \quad r_s = -\frac{M_{21}^s}{M_{22}^s} \tag{6}$$

and for the transmission coefficient we have

$$T_s = \frac{\mu_1}{\mu_4}\frac{Rek_{4z}}{Rek_{1z}}|t_s|^2 \tag{7}$$

Finally for the system embedded in a homogeneous medium $(k_4 = k_1)$, $(\mu_4 = \mu_1 \approx 1)$ and for a thin film that presents absorption $\left(\alpha = \frac{4\pi}{\lambda}\kappa\right)$.

$$T_s = \frac{1}{A + B + C + D + E + F + G + H} \tag{8}$$

where

$$
\begin{aligned}
A &= \frac{\cos^2(\gamma)}{2}\left[\cos(\alpha)+\cosh(\beta)\right] & C &= \frac{\cos(\gamma)\sin(\gamma)}{2}\left[o\sinh(\beta)-p\sin(\alpha)\right]\\
B &= \frac{\cos^2(\gamma)}{2}\left[h\sinh(\beta)-m\sin(\alpha)\right] & D &= \frac{\cosh(\beta)-\cos(\alpha)}{8}\left[q\sin^2(\gamma)+r\cos^2(\gamma)\right]\\
G &= \frac{k_{13}\sin^2(\gamma)}{4}\left[p\sinh(\beta)+o\sin(\alpha)\right] & E &= \frac{k_{13}}{4}\cos(\gamma)\sin(\gamma)\left[h\sin(\alpha)+m\sinh(\beta)\right]\\
H &= \frac{k_{13}^2}{8}\sin^2(\gamma)\left[\cosh(\beta)+\cos(\alpha)\right] & F &= \frac{\cos(\gamma)\sin(\gamma)}{2}\left[\cosh(\beta)-\cos(\alpha)\right]\,u
\end{aligned}
$$

whit the constants

$$
\begin{aligned}
\alpha &= \frac{2n_2\omega a}{c} & k_{13} &= \left(\frac{k_1}{k_3}+\frac{k_3}{k_1}\right) & m &= \frac{n_2(\kappa^2+n_2^2+n_1^2)}{n_1(n_2^2+\kappa^2)}\\
\beta &= \frac{2\kappa\omega a}{c} & u &= \frac{\kappa(n_2\kappa(n_3^2-n_1^2)}{n_1n_3(n_2^2+\kappa^2)} & o &= \frac{\kappa(\kappa^2+n_2^2-n_3^2)}{n_3(n_2^2+\kappa^2)}\\
\gamma &= \frac{k_3b}{c} & h &= \frac{\kappa(\kappa^2+n_2^2-n_1^2)}{n_1(n_2^2+\kappa^2)} & p &= \frac{n_2(\kappa^2+n_2^2+n_3^2)}{n_3(n_2^2+\kappa^2)}
\end{aligned}
$$

$$
q = \frac{n_3^4+2n_3^2(n_2^2-\kappa^2)+(n_2^2+\kappa^2)^2}{n_3(n_2^2+\kappa^2)} \qquad r = \frac{n_1^4+2n_1^2(n_2^2-\kappa^2)+(n_2^2+\kappa^2)^2}{n_1(n_2^2+\kappa^2)}
$$

4. Results and discussion

The Figure 2 shows a typical transmission spectrum of ZnSe thin film (solid black line) deposited by evaporation, which was obtained by using a spectrophotometer PERKIN-ELMER Lambda 9 and theoretical fitting by the TMM (dashed red line). Transmittance experimental spectra were simulated theoretically by equation 8 to determine the optical properties of the material, the spectral variation of the real part of the refractive index n_ω and absorption coefficient α. Using the model proposed by *Wemple and DiDomenico*[16], which consists of fitting the n_2 data, obtaining the following expression for the medium and weak regions of absorption.

$$n^2 - 1 = \frac{(E_0E_d)}{E_0^2 - (\hbar\omega)^2} \tag{9}$$

such expression was deduced using the model of a single-effective-oscillator; where $\hbar\omega$ is the photon energy, E_0 is the single oscillator energy and E_d is the dispersion energy.

Figure 3 shows the theoretical results by TMM for the refractive index of a ZnSe sample. The full line corresponds to the fitting according to the W-D model. TMM method allowed us to obtain the values for the refractive index n_2, absorption coefficient κ and thickness a reported in (Table I), by adjusting the spectrum in all of range of wavelength according to the experimental data. Figure 4 shows the variation of the refractive index as a function of the photon energy for substrate temperatures corresponding to $(200, 250, 300\, and\, 350)^oC$ with values of $(2, 54)$, $(2, 71)$, $(2, 79)$ and $(2, 86)$ respectively at $600nm$ of wavelength. Similar results have been reported by Lakshmikumar and Rastogi [18] and [17]. The figure 4 shows similarly, as well how the refractive index increases with the temperature of the substrate, which is attributed to an improvement in the crystallinity of the deposited films of ZnSe[8, 17].

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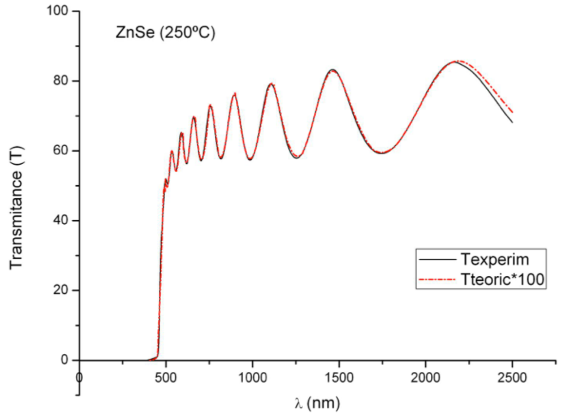

Figure 2. Typical transmission spectrum of a ZnSe thin Film (solid line) deposited by evaporation (substratum temperature 250^{o}C) and theoretic curve fit (dashed line)

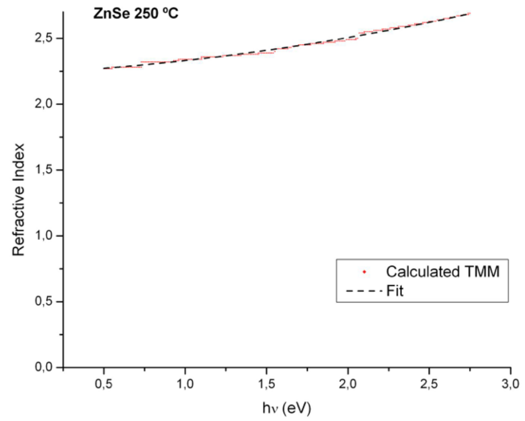

Figure 3. Variation of the refractive index of a ZnSe sample, calculated using TMM.

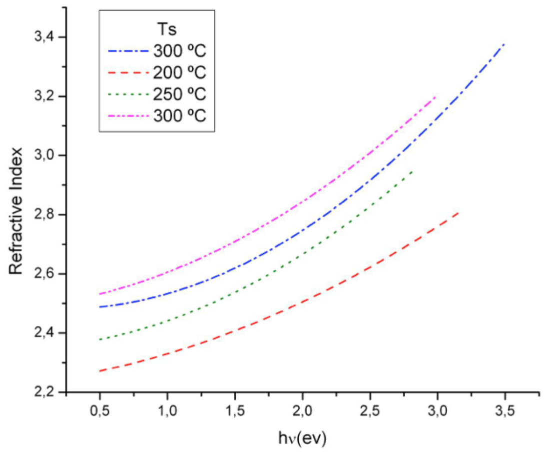

Figure 4. Variation of the refractive index n as a function of the photon energy for ZnSe thin films with four different substratum temperatures.

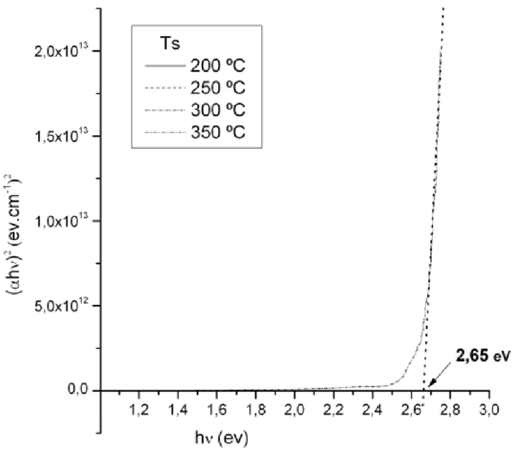

Figure 5. Curves of $(\alpha h\nu)^2$ Vs hν corresponding to ZnSe thin films with four different subtratum temperatures.

Figure 5 shows the curves of $(h\nu\alpha)^2$ vs $h\nu$ corresponding to the four samples of (ZnSe) before mentioned. The optical gaps E_g of the four samples were determined from the intercepts of the $(h\nu)$ axis with the straight lines which fit the $(h\nu\alpha)^2$ and $h\nu$ curves in the region of strong absorption, considering here that these semiconductors are direct band gap type. The opticals gaps obtained for the four samples were $2,65\,eV$.
Since the results presented in this work are in agreement with those reported in the literature for ZnSe thin films [8, 12, 17], it can be concluded that the practical method proposed in this article permits the determination with good reliability of the optical constants (n, α) thickness and the optical gap of ZnSe thin film prepared by evaporation.

Table 1. Values parameters refraction index n_ω and thickness a for ZnSe thin films, deposited at different substrate temperatures.

Temperature ($^\circ C$)	Refraction $n_{(\omega)}$	Thickness a (nm)
200	2,54	900
250	2,71	1000
300	2,79	650
350	2,86	450

5. Conclusions

it was used the transfer matrix method to theoretically simulate the transmittance spectra of ZnSe thin films. From the simulation the spectral variation of the refractive index and the extinction coefficient were extracted and the thickness of the samples and the material gap was found as well. The optical values obtained were comparable with those found in the literature [8, 17].

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