ON THE PARAMETRIC MODELING OF OPTICAL FUNCTIONS OF AMORPHOUS/POLYCRYSTALLINE SEMICONDUCTORS

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1. Introduction

For photonic applications of amorphous or polycrystalline semiconductors and dielectrics knowledge of basic optical properties, mainly the refractive index and absorption related constants is a meaningful issue reflecting differences in growth conditions and/or post-deposition processing. In general different metrologies based on the parametrization, i.e. on dispersion models offering information on wavelength depending refractive indices and absorption including the optical band gap is always a current point [1-3]. Dispersion relations are necessary to obtain optical properties of a system indirectly from measured data gathered by spectrophotometric or ellipsometric measurements.

For amorphous semiconductors and dielectrics a well-known Forouhi-Bloomer model was developed and later used also for crystalline solids [4]. This model yields satisfactory results only in a limited range therefore several modifications have been suggested later. Nowadays the models mainly used in the optical data inversion of semiconductors are the Tauc-Lorentz and Cody-Lorentz parametrizations that become to the most realistic [2,5,6,7]. The Cody-Lorentz parametrization is frequently used for the data inversion and the film thickness determination from ellipsometric measurements. There are still many debates on the parametrization and some improvements of the Tauc-Lorentz and Cody-Lorentz models have been published recently [8-10]. A review of the parametrization devoted to semiconductor nanocrystals is given in [11].

In this paper the parametric models of Tauc-Lorentz and Cody-Lorentz are theoretically described and used to present the optical data inversion of multiphase Zn-Ti-O ternary oxides as three featured examples. From transmittance spectra the wavelength-dependent refractive indices and extinction coefficients are determined and compared. Discussions to the observed differences are presented.

2. Theoretical background

Amorphous or polycrystalline materials can be described as a collection of non-interacting oscillators, which is the key idea of the so-called Lorentz oscillator model. The imaginary part $\varepsilon_2(E)$ of the dielectric function $(\varepsilon_1, \varepsilon_2)$ versus the photon energy E regarding this model is given by [3]

$$\varepsilon_2(E) = \begin{cases} \dfrac{E_1}{E} exp\left\{\dfrac{E - E_t}{E_u}\right\}; & 0 \le E \le E_t \qquad (1a) \\ G(E)L(E) = G(E)\dfrac{AE_0 \Gamma E}{[(E^2 - E_0^2)^2 + \Gamma^2 E^2]}; & E > E_t \qquad (1b) \end{cases}$$

where E_u is the Urbach transition energy representing the widths of the tail states with an exponential energy distribution caused by the disorder in amorphous/polycrystalline semiconductors. E_t is the boundary energy between the Urbach and the band-to-band transitions. A, E_0 and Γ denote the Lorentz oscillator amplitude, the Lorentz oscillator peak energy and the oscillator width, respectively.

Eq. (1a) formulates the Urbach exponential absorption for $0 \leq E \leq E_t$ neglecting the dependence of ε_1 on E over this interval. Eq. (1b) for $E > E_t$ includes the Lorentzian function $L(E)$ and its product with the variable band edge function $G(E)$. $G(E)$ comprises the tendency of $\varepsilon_2(E)$ to express the energy dependence of absorption just above the optical band gap E_g. E_1 provides the continuity of $\varepsilon_2(E)$ at $E = E_t$ thus $E_1 = E_t L(E_t) G(E_t)$.

As usual the real part $\varepsilon_1(E)$ obeys the Kramers-Kronig transformation that takes the Urbach tail and the Lorentz oscillator integrals into account [3]

$$\begin{aligned}\varepsilon_1(E) &= \varepsilon_{1\infty} + I_U(E) + I_L(E)\\ &= \varepsilon_{1\infty} + \frac{2E_1}{\pi} P \int_0^{E_t} \frac{\exp\,[(E'-E_t)/E_u]}{E'^2-E^2}\, dE' \\ &\quad + \frac{2}{\pi} P \int_{E_t}^{\infty} \frac{E'G(E')L(E')}{E'^2-E^2}\, dE'\end{aligned} \tag{3}$$

where $\varepsilon_{1\infty}$ is the constant contribution to the real part of dielectric function. P denotes the principal value of the integrals, $I_U(E)$ is the Urbach tail integral and $I_L(E)$ is the Lorentz oscillator integral [1]. Functional descriptions of the calculations of integrals in Eq. (3) are given e.g. in [1], [3].

In the Tauc theory parabolic edges of the valence and the conduction band are proposed based on a constant momentum matrix element. Jellison and Modine [1] named the combination of the Lorentz oscillator and the Tauc model of the density of states as the Tauc-Lorentz (T-L) model. In this model $G(E)$ in Eq. (1b) has the form [3]

$$G(E) = \frac{(E-E_g)^2}{E^2} \tag{2}$$

where E_g is the Tauc optical band gap.

G.D. Cody proposed to favour a constant dipole matrix element rather than a constant momentum matrix element. This assumption reflected in the parametrization is known as the Cody-Lorentz (C-L) model. $G(E)$ in this model has the following form

$$G(E) = \frac{(E-E_g)^2}{(E-E_g)^2 + E_p^2} \tag{4}$$

E_p denotes the transition energy separating photon energies belonging to the absorption onset ($E < E_p + E_g$) and the Lorentz oscillator behaviour ($E > E_p + E_g$).

Once we obtain $\varepsilon_2(E)$ and $\varepsilon_1(E)$ the refractive index and the extinction coefficient can be established from the well-known expressions corresponding to the refractive index n and the extinction coefficient k as the real and imaginary part of the complex refractive index

$$n = \left\{\left[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} + \varepsilon_1\right]/2\right\}^{1/2} \tag{5}$$

$$k = \left\{\left[(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1\right]/2\right\}^{1/2} \tag{6}$$

The absorption coefficient α is related to the extinction coefficient as $\alpha = 4\pi k/\lambda$ where λ is the wavelength of light ($E = hc/\lambda$, c is the speed of light and h Planck's constant).

3. Featured results and discussion

Ternary oxides of Zn-Ti-O are transparent in the visible and near IR spectral region and therefore well suited for applications in solar cells, LEDs, displays, and also in imaging and photocatalytic applications. Three Zn-Ti-O thin films were applied here as featured samples deposited by reactive magnetron co-sputtering with different atomic percentage content of titanium on clean Corning Eagle 2000 glass substrates. Details of the deposition and structure are given in [12]. For this study three samples of the different titanium content were selected: 0 at.%, 6.7 at.% and 8.7 at.%. All samples are polycrystalline. With the increasing atomic percentage of the titanium content the phase composition evolved from ZnO to $Zn_xTi_{1-x}O_y$ with bimodal distribution of crystallites. In the sample of 0 at.% of titanium content (002) ZnO orientation prevails. In spite of the fact that this sample is ZnO we refer to it as Zn-Ti-O with 0 at.% of titanium content as it is a member of a series. Optical transmittances recorded in wide spectral range of (250 – 1100) nm by Specord 210 spectrophotometer with air blank reference channel are in Fig.1.

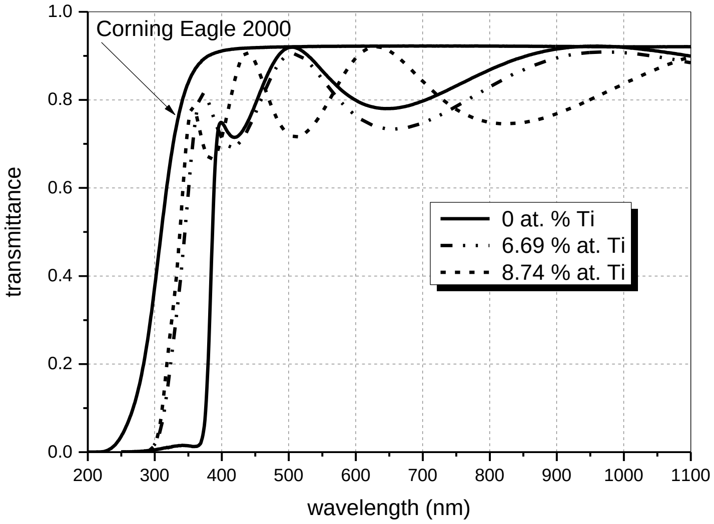

Fig.1: *Optical transmittances of Zn-Ti-O thin films deposited at different at.% of titanium content. The transmittance of Corning Eagle glass substrate is included.*

In the optical transmittance spectra (Fig.1) apparent interference fringes are present due to weak absorption of light above the absorption edge. The shift of the transparency onset of Zn-Ti-O of 6.7 and 8.7 at.% of titanium in comparison with the sample of 0% is obvious. The transmittance of a homogeneous thin film with parallel interfaces deposited on a thick substrate is a nonlinear function of the wavelength, the film thickness and the complex refractive indices of the film and the substrate. Spectral refractive indices *n* (Eq. (5)) and extinction coefficients *k* (Eq.(6)) of the films were extracted from the measured transmittance spectra using a global optimization procedure based on genetic algorithm minimizing differences between the experimental and the theoretical transmittance in the broad spectral region including the region in the vicinity of the absorption edge. The theoretical transmittance was calculated using the theory in [13] and applying both the T-L and C-L dispersion models for the refractive index and the extinction coefficient and compared with the experimental transmittance. The differences were taken into account.

The results of both parametrizations to be compared are in Fig. 2 – 4 and all are physically meaningful. From the comparison of the implementation of the T-L and C-L model in optical data inversion for the featured samples it implies:

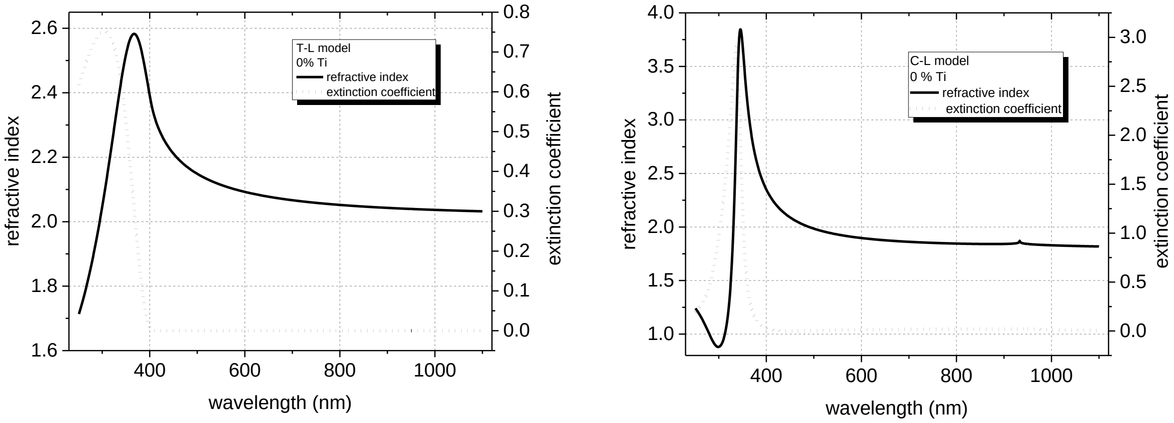

Fig.2: *Optical parameters of Zn-Ti-O of 0 at.% of titanium content determined by the T-L (left) and the C-L (right) parametrization.*

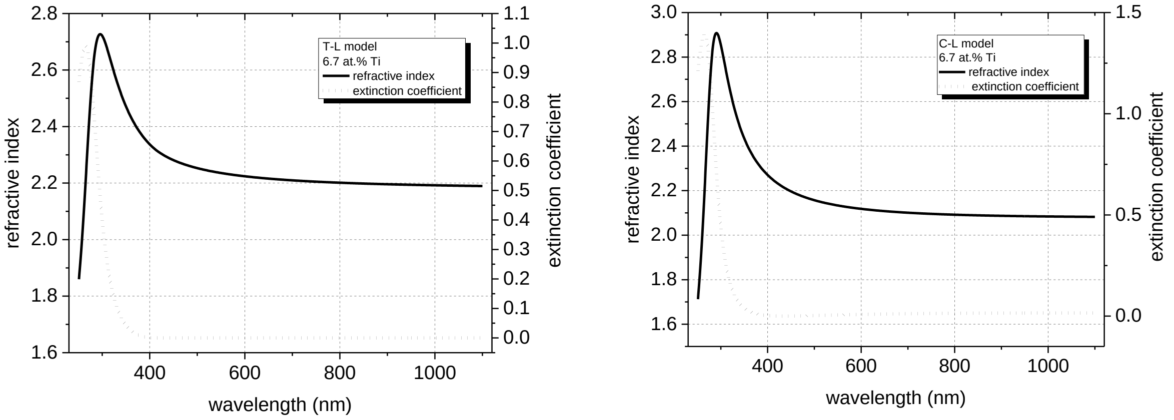

Fig.3: *Optical parameters of Zn-Ti-O of 6.7 at.% of titanium content determined by the T-L (left) and the C-L (right) parametrization.*

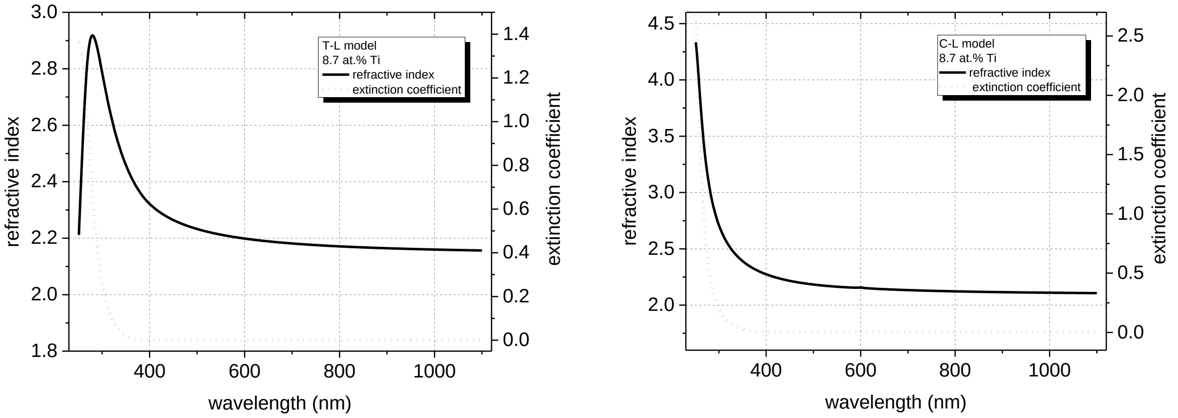

Fig.4: *Optical parameters of Zn-Ti-O of 8.7 at.% of titanium content determined by the T-L (left) and the C-L (right) parametrization.*

- In the spectral region far from the absorption edge the differences are minimal although the C-L model returns slightly lower values of the refractive index *n* and higher values of *k*. The shift of *n* to lower values is often observed for the data inversed from ellipsometric measurements using the C-L model. It is obvious that differences do not originate from the experiment but from the parametrization.

- Apparently the main differences are in the vicinity of the absorption edge. A systematic absorption increase is obtained from the C-L model. However better fitting around the absorption edge was obtained with the T-L model. Therefore the T-L results related to optical absorption seem to be more realistic. The corrections of the C-L model proposed in [8] could improve the absorption region metrology.

Conclusions

We conclude that the optical inversion results using both models are similar in the transparent spectral region and physically reasonably represent the materials. However the refractive indices obtained from using the C-L model are slightly shifted to lower values. This is a frequent observation for optical data inversion from ellipsometric measurements using mostly commercial C-L-based software. Therefore the differences are caused by the parametrization model not by the experiment. For this reason when reporting results from the optical data inversion it is always necessary to comment on the model used for the parametrization. In the vicinity of the absorption edge the C-L model returns quite higher values of the extinction coefficient but based on worse fitting. Therefore we recommend favouring the absorption data obtained from the T-L model.

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