Journal of Optoelectronics and Advanced Materials Vol. 3, No. 4, December 2001, p. 873 - 878

COMPLETE OPTICAL ANALYSIS OF AMORPHOUS As-S CHALCOGENIDE THIN FILMS BY THE COMBINED SPECTROPHOTOMETRIC METHOD

I. Ohlídal, D. Franta, M. Frumar[a], J. Jedelský[a], K. Navrátil[b]

Department of Physical Electronics, Faculty of Science, Masaryk University, 2, 611 37 Brno, Czech Republic
[a]Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, Legions Sq. 565, 532 10 Pardubice, Czech Republic
[b]Institute of Condensed Matter Physics, Faculty of Science, Masaryk University, Kotlárská 2, 611 37 Brno, Czech Republic

In this paper a combined spectrophotometric method is used to analyzed As-S chalcogenide thin films. This method is based on the simultaneous interpretation of experimental data corresponding to the reflectance from the ambient side, reflectance from the substrate side and transmittance of the chalcogenide films deposited onto the glass substrate. It is shown that this method is usable for the optical characterization of the chalcogenide films even when these films exhibit an inhomogeneity formed by a refractive index profile. Within this method our dispersion model of the optical constants of amorphous materials is used. This means that the values of the dispersion parameters determining the spectral dependences of the optical constants of the As-S chalcogenide material are evaluated. In the paper the advantages of the combined method mentioned are discussed from the practical point of view.

(Received September 12, 2001; accepted November 29, 2001)

Keywords: As-S chalcogenide films, Combined spectrophotometric method, Amorphous materials, Optical constants

1. Introduction

Amorphous As-S thin films are extensively used in practice. They are, namely employed as inorganic resists. Therefore, it is necessary to have methods enabling us to perform the analysis of these films. The optical methods belong to the efficient ones for this purpose. So far they have been employed for the analysis of the thin films mentioned in several papers (see e. g., [1-3]). From the practical point of view the methods of spectroscopic ellipsometry and spectroscopic photometry (spectrophotometry) are suitable for suitable analyzing the chalcogenide thin films. In principle the methods of spectrophotometry applied at near-normal incidence of light are simpler than the methods of spectroscopic ellipsometry (this statement is true from the experimental point of view in particular).

That is why we dealt with developing a method of near-normal spectrophotometry enabling us to perform the complete optical analysis of the chalcogenide thin films in an efficient way. This method is based on the simultaneous interpretation of experimental data corresponding to the spectral re ectance measured from the side of the ambient, the spectral reflectance measured from the side of a substrate and spectral transmittance of the sample formed by the non-absorbing substrate and chalcogenide thin film.

The method mentioned will be illustrated by means of the complete optical analysis of a chosen amorphous As-S thin film placed onto the non-absorbing substrate formed by a glass plate. Within applying this method our model of dispersion of the optical constants developed for amorphous solids will be employed [3]. It will be shown that the film under study is inhomogeneous. Further, it will be shown that the values of all the optical parameters completely characterizing this inhomogeneous As-S chalcogenide thin film will be determined with a sufficient accuracy. Practical advantages of the method will be discussed as well.

2. Preparation of the sample and experimental arrangements

The thin film studied in this work prepared by vacuum evaporation on unheated glass plate. The composition of these film was $As_{38}S_{62}$. After depositing the film was exposed to light with excitation energy greater than the band gap of its material.

The spectral dependence of the reflectance of the ambient side *R*, the spectral dependence of the reflectance of the substrate side *S* and spectral dependence of the transmittance of the substrate covered with the film analyzed were measured using a Cary 5E spectrophotometer within the spectral range 350-900 nm. The angle of incidence for measuring the spectral dependences of both the reflectances was 10 ^{o}C (of course, in the case of the reflectance *S* this angle corresponds to the incidence of light onto the rear boundary of the glass plate which is free of the film). As for the transmittance measurements the exact normal incidence was applied. Note that the spectral transmittances corresponding to the incidence of light from the ambient side and substrate side are identical [4].

3. Model of the thin film analyzed

At interpreting the experimental data of *R, S* and *T* one assumed the following physical model of the thin film system representing our sample:

1. the As-S thin film is formed by the isotropic inhomogeneous absorbing layer;
2. the substrate is formed by the isotropic homogeneous non-absorbing plan-parallel plate;
3. the boundaries of the film are ideally at and smooth;
4. the ambient is formed by air;
5. very thin native oxide layer (NOL) is respected on the upper boundary of the thin film.

4. Model of dispersion of the optical constants

In this work we used our empirical model of dispersion of the optical constants described in our earlier papers [5, 6]. This model is based on the model of the Lorentz oscillator which can be used to express the spectral behavior of the optical constants of the amorphous solids in the region of the interband transitions. The incorporation of the concept of the optical energy band gap into the Lorentz model is carried out using a suitable modification function of photon energy. Then the imaginary part of the dielectric function ϵ_2(E) of the amorphous solids can be expressed as follows:

$$\epsilon_2(E) = L(E)\, F(E), \tag{1}$$

where L(E) is the Lorentzian function

$$L(E) = \frac{ABE}{\left(E_0^2 - E^2\right)^2 + B^2 E^2} \tag{2}$$

and the modification function F(E) is expressed as follows:

$$F(E) = \frac{1}{\sqrt{2\pi\delta E}} \int_{-\infty}^{\infty} G(s)\, e^{-\frac{(E-s)^2}{2\delta E^2}}\, ds \tag{3}$$

where

$$G(E) = \left[f\left(\frac{|E| - E_g}{E_0 - E_g} \right) \right]^b \tag{4}$$

and

$$f(x) = \begin{cases} 0 & for \;\; x < 0 \\ 1 & for \;\; x > 1 \\ ax + (3-2a)x^2 + (a-2)x^3 & for \;\; 0 < x < 1. \end{cases} \tag{5}$$

The parameters A, B and E_0 are the strength, line-width and resonance energy of Lorentzian oscillator, respectively. Energy of the band gap Eg represents the absorption edge corresponding to the minimum of energy of the interband transitions. The function *F(E)* shapes the course of $\epsilon_2(E)$ in the vicinity of the band gap. The three parameters of the function *F(E)*, i. e., *a*, *b*, δE, correspond to the absorption edge and they have the following physical meaning: *a* and *b* determine the shape of ϵ_2(E) above the band gap; δE determines the shape of $\epsilon_2(E)$ under the band gap. It should be noted that the real part of the dielectric function $\epsilon_1(E)$ must be calculated numerically using the Kramers-Kronig relation (for details see [3, 5]). The complex refractive index of the material forming the thin film studied can be expressed in the following way:

$$n_f = n_f + ik_f = \sqrt{\varepsilon_1 + i\varepsilon_2}\,, \tag{6}$$

where n_f and/or k_f is the real refractive index and/or extinction coefficient of the thin film.

5. Theoretical background

If multiple reflections had been considered within the substrate plate the following formulae were obtained for the reflectance R and S and transmittance T:

$$R = \left|r_f\right|^2 + \left|t_f r_g^{'} t_f^{'}\right|^2 + \left|t_f r_f^{'} r_g^{'2} t_f^{'}\right|^2 + \ldots = \left|r_f\right|^2 + \frac{\left|t_f r_g^{'} t_f^{'}\right|^2}{1 - \left|r_f^{'} r_g^{'}\right|^2} \tag{7}$$

$$S = \left|r_g\right|^2 + \left|t_g r_f^{'} t_g^{'}\right|^2 + \left|t_g r_g^{'} r_f^{'2} t_g^{'}\right|^2 + \ldots = \left|r_g\right|^2 + \frac{\left|t_g r_f^{'} t_g^{'}\right|^2}{1 - \left|r_f^{'} r_g^{'}\right|^2} \tag{8}$$

and

$$T = \left|t_f t_g^{'}\right|^2 + \left|t_f r_g^{'} r_f^{'} t_g^{'}\right|^2 + \ldots = \frac{\left|t_f t_g^{'}\right|^2}{1 - \left|r_f^{'} r_g^{'}\right|^2}\,, \tag{9}$$

where r_f and/or t_f denotes the complex reflection and/or transmission Fresnel coefficient of the inhomogeneous thin film placed on the semi-infinite glass substrate, r_g and/or t_g represents the reflection and/or transmission Fresnel coefficient of the boundary between air and glass plate. The symbols $r_f^{'}, t_f^{'}, r_g^{'}$ and $t_g^{'}$ denote the same Fresnel coefficients corresponding to the opposite directions of light incidence (see Figs. 1 and 2).

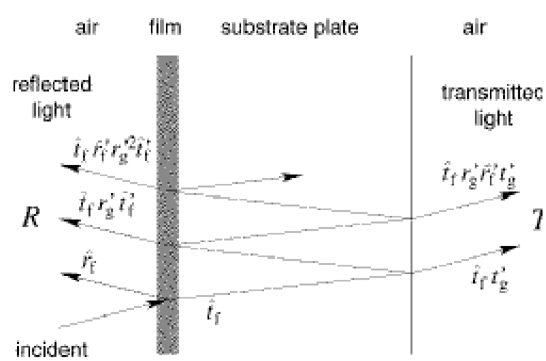

Fig. 1. Schematic diagram of the interaction of light with the system formed by a non-absorbing substrate plate and thin film when light falls onto the system from the ambient side.

The Fresnel coefficients of the inhomogeneous thin film, i. e., r_f , t_f , $r_f^{'}$ and $t_f^{'}$, were calulated using the matrix formalism developed in our recent papers [7, 8]. It was assumed that the gradient of the optical constants of the inhomogeneous chalcogenide thin films was relatively small across this film. Then it was possible to use the Wentzel-Kramers-Brillouin-Jeffries (WKBJ) approximation. Of course, within this matrix formalism multiple reflections were respected inside the thin film (i. e., coherent superposition of amplitudes of the individual reflected waves was taken into account inside of the thin film). Note that these Fresnel coefficients of the film are functions of the thickness and optical constants of the film studied. They are also dependent on the refractive index of the glass substrate. It should be pointed out that the Fresnel coefficients r_f, t_f, $r_f^{'}$ and $t_f^{'}$, depend on the thickness and optical constants of the NOL if this layer is considered.

The foregoing equations (7)-(9) are true for normal incidence of light onto the system plotted in Figs. 1 and 2. However, in the case of the reflectances measured the oblique incidence is actually realized (strictly speaking the near-normal incidence corresponding to 10^o was realized). One must therefore calculate the reflectances R_p, R_s and S_p, S_s corresponding to the p- and s-polarization for the incidence angle mentioned, respectively. The measured reflectances R and S must be then interpreted using the formulae corresponding to the mean reflectances belonging to the both polarizations because incident light is natural one ($R = (R_p + R_s) / 2$ and $S = (S_p + S_s) / 2$).

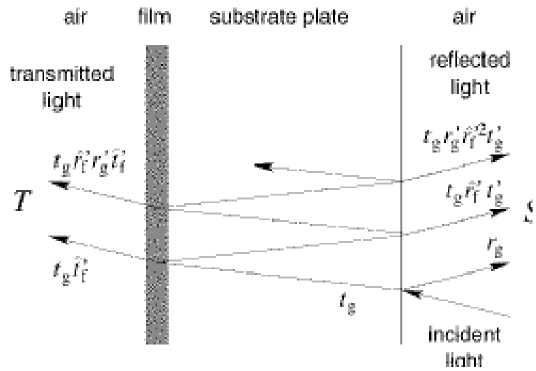

Fig. 2. Schematic diagram of the interaction of light with the system formed by a non-absorbing substrate plate and thin film when light falls onto the system from the substrate side.

6. Data treatment

The spectral dependences of R, S and T measured were treated simultaneously using the least-squares method (LSM). The following merit function has been constructed within the LSM:

$$Q\left(\vec{X}\right)=\sum_i\left(R\left(\vec{X},\lambda_i\right)-R_i^{\exp}\right)^2+\sum_j\left(S\left(\vec{X},\lambda_j\right)-S_j^{\exp}\right)^2+\sum_k\left(T\left(\vec{X},\lambda_k\right)-T_k^{\exp}\right)^2 \qquad (10)$$

where $\vec{X}$ denotes the vector whose components are identical with the parameters sought and $R_i^{\exp}, S_j^{\exp}$ and $T_k^{\exp}$ are the experimental values. The symbol λ denotes the wavelength of incident light. The symbols $R\left(\vec{X},\lambda_i\right)$, $S\left(\vec{X},\lambda_j\right)$ and $T\left(\vec{X},\lambda_k\right)$ represent the theoretical values the reflectances and transmittance calculated using Eqs. (7)-(9).

7. Results and their discussion

Within the LSM treatment the values of the following parameters characterizing the optical parameters of the inhomogeneous chalcogenide film studied corresponding to the upper boundary (the boundary between air and the film) and the lower boundary (the boundary between the film and substrate) were searched: E_{0L}, A_L, B_L, E_{gL}, δE_L, a_L, b_L, E_{0R}, A_R, B_R, E_{gR}, δE_R, a_R, b_R (index L and/or R denotes the parameters belonging to the upper (left) and/or lower (right) boundary). Further the values of the three thicknesses d_r, d_s and d_t of this film were also searched (the indices r, s and t correspond to the reflectance R, reflectance S and transmittance T, respectively). Namely, it has been assumed that the thickness of the chalcogenide film is different for the reflectance R, reflectance S and transmittance T. This assumption includes the possibility of a slight thickness non-uniformity of the film analyzed. It is not possible to ensure the identical place for measuring the photometric quantities mentioned above and therefore under assumption of the slight thickness non-uniformity one must take into account the different thicknesses for the experimental data corresponding to the reflectance R, reflectance S and transmittance T. Moreover, the values of the refractive index of the glass plate have been determined. It has been supposed that the spectral dependence of the glass refractive index is expressed by the Cauchy formula containing two terms, i. e.,

$$n_s = A_s + \frac{B_s}{\lambda^2} \tag{11}$$

Thus, the values of the parameters A_s and B_s have been searched together with the values of the parameters of the film introduced above.

The values of the fourteen parameters corresponding to the spectral dependences of the optical constants of the inhomogeneous chalcogenide film found using the optical method described are summarized in Table 1. The values of the remaining five parameters have been determined as follows: d_r = (935.5 ± 0.5) nm, d_s = (935.1 ± 0.5) nm, d_t = (929.4 ± 0.5) nm, A_s = 1.5155 ± 0.0027 and B_s = (6210 ± 940) nm^2. Thus, the nineteen parameters describe the optical properties of the chalcogenide film and glass substrate in an unambiguous way. The spectral dependences of the optical constants characterizing this film corresponding to the parameter values determined are plotted in Fig. 4. Note that the refractive index and thickness of the NOL have been fixed in the values determined in our recent paper [3]. In Fig. 3 both the experimental and theoretical data of *R, S* and *T* are presented (the theoretical data have been calculated using the values of the parameters found by means of the LSM). One can see that there is a relatively good agreement between both the theoretical and experimental data for all the spectrophotometric quantities which supports a correctness of our results achieved in the way specified above.

Table 1. The values of the dispersion parameters corresponding to the upper and lower boundaries of the As-S chalcogenide thin film studied.

parameter	upper boundary (L)	lower boundary (R)
E_0 [eV]	5.378 ± 0.034	5.67 ± 1.23
A [eV^2]	277.0 ± 3.8	301 ± 85
B [eV]	6.138 ± 0.091	7.06 ± 2.36
E_g [eV]	2.363 ± 0.014	2.559 ± 0.010
δE [eV]	0.070 ± 0.010	0.028 ± 0.009
a	2.88 ± 0.12	2.75 ± 3.867
b	1.922 ± 0.067	1.25 ± 0.10

It is should be emphasized that similar results have been obtained for the other As-S chalcogenide thin films under investigation. Within the spectrophotometric method presented it was impossible to determine the values of the optical parameters of the NOL together with the optical parameters of the film and substrate. If we want to determine the optical parameters of the NOL it is necessary to combine the method described here with an ellipsometric method (for details see our earlier paper [3]).

From the foregoing one can see that the combined spectrophotometric method described is suitable for the complete optical analysis of the chalcogenide films. This method is relatively simple from the experimental point of view in particular. Simultaneously this method provides the maximum optical information about the system studied within the spectrophotometry. The main advantage of the method is represented by the fact that it is very sensitive to weak absorption within the film. Namely, if the film is strictly non-absorbing, the following relations must be fulfilled for each wavelength:

$$R + T = S + T = 1 \quad \text{hence} \quad R = S. \tag{12}$$

If the film is absorbing the foregoing equations must be replaced by the following ones:

$$R + T + A = S + T + A' = 1 \quad \text{hence} \quad R \neq S, \tag{13}$$

where A and/or A' denotes the absorption in the film in the case when light is incident on the film from the side of the ambient and/or substrate. The further important advantage of the method is given by the fact that it is sensitive to the inhomogeneity of the film studied corresponding to the refractive index profile within the spectral region at which the film is not transparent. This is caused by measuring the reflectance from both the sides of the sample. The method discussed is efficiently utilized when the substrate is transparent within the entire spectral region of interest. Thus, it is evident that the results presented above can be improved by using the substrate formed by fused silica instead of the glass substrate employed in this work. In this way the correlation between some parameters sought will be reduced which will imply the higher accuracy in determining these parameters correlated (i. e., parameters E_{0R}, A_R, B_R and a_R, see Table 1).

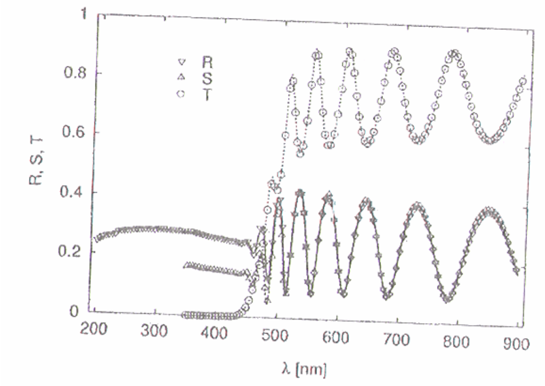

Fig. 3. Spectral dependences of the reflectance R, reflectance S and transmittance T for the film studied: points denote the experimental values and curves represent the theoretical ones.

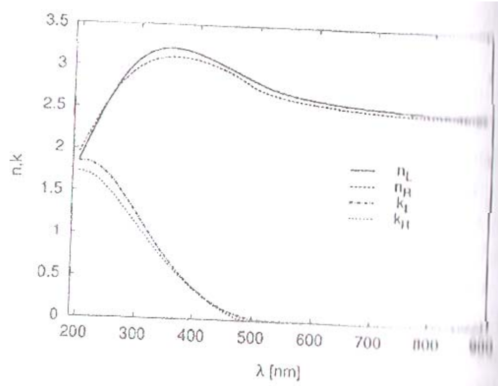

Fig. 4. Spectral dependences of the optical constants of the inhomogeneous As-S chalcogenide thin film corresponding to the upper boundary (n_L, k_L) and lower boundary (n_R, k_R).

8. Conclusions

In this paper the optical method based on combining the interpretation of the reflectance data measured from the ambient, reflectance data measured from the side of the substrate and transmittance data used for analyzing the chalcogenide films is presented. It is shown that using this method one can perform the complete optical analysis of the films mentioned even when these films exhibit the inhomogeneity formed by the refractive index profile. Further, it is shown that by means of the dispersion model of the optical constants of the chalcogenide thin films it is possible to evaluate the values of the parameters characterizing the optical properties of the materials forming these films (i. e., the band gap, resonance energy etc.). It has been found that the chalcogenide films studied exhibit a slight thickness non-uniformity. It should be pointed out that the method employed is relatively simple in comparison with the other optical method (e. g., ellipsometric methods). It is evident that the method described here can serve as an efficient tool for investigating the influence of the technological conditions on the optical properties of the chalcogenide thin films. Of course, the combined spectrophotometric method presented can be used to analyze the other absorbing homogeneous or inhomogeneous thin films. This method is especially useful if the substrates of the films analyzed are transparent within the entire spectral region of interest (of course these transparent substrates have to be formed by plan-parallel plates).

Acknowledgement

This work was supported by the Grant Agency of Czech Republic under contract no. 203/00/0085. The majority of the numerical computations was performed using computers of the Supercomputing Center Brno.

References

[1] F. Lukeš, K. Navrátil, Z. Cimpl, F. Kosek, phys. stat. sol. (a) 124, K 145 (1991).
[2] E. Márquez, J. M. González-Leal, R. Prieto-Alcón, M. Vlček, A. Stronski, T. Wagner, D. Minkov, Appl. Phys. **A 67**, 371 (1998).
[3] D. Franta, I. Ohlídal, M. Frumar, J. Jedelský, Appl. Surface Sci. 175-176, 555 (2001).
[4] Z. Knittl, Optics of Thin Films, Wiley, London p. 193 (1976).
[5] D. Franta, I. Ohlídal, D. Munzar, Acta Phys. Slov. **48**, 451 (1998).
[6] D. Franta, I. Ohlídal, D. Munzar, J. Hora, K. Navrátil, C. Manfredotti, F. Fizzotti, E. Vittone, Thin Solid Films 343-344, 295 (1999).
[7] I. Ohlídal, D. Franta, Ellipsometry of Thin Film Systems, in: Progress in Optics, Vol. 41 (ed. Wolf E.), North-Holland, Amsterdam, pp. 181-282 (2000).
[8] I. Ohlídal, D. Franta, Acta Phys. Slov. **50**, 489 (2000).