Journal of Optoelectronics and Advanced materials Vol. 7, No. 3, June 2005, p. 1305 - 1310

VERY THIN α - As –S FILMS: OPTICAL CONSTANTS AND PHOTOINDUCED RESPONSE IN VIS AND NIR

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Very thin chalcogenide films are extensively studied for the needs of emerging nanotechnologies. Presently, the knowledge of the structure of these films and their photoresponse is of theoretical interest and also of practical importance for many applications. Optical methods for thin film characterization have advantages that they are nondestructive, fast and effective. Here we report an application of recently developed spectrophotometric method for optical constants (refractive index, *n*, extinction coefficient, *k*) and physical thickness (*d*) determination to amorphous As-S films with *d* between 10 and 30 nm. Information on photoinduced changes in the films is obtained as well.

(Received April 12, 2005; accepted May 26, 2005)

Keywords: Thin chalcogenide films, Optical constants, Photoinduced changes

1. Introduction

The rapid development of nanotechnologies presents new challenges for synthesis, preparation and characterization of films with physical thickness (*d*) of few nanometers. Different experimental methods have been developed for investigations of the physical properties of nanolayers – spectrophotometric [1], ellipsometric[2], interferometric [3], holographic [4], etc. Each one of them has its advantages and shortcomings. For very thin films Abelès [5] has derived an approximate method for the calculation of optical constants (*n* – refractive index, *k* – extinction coefficient) and physical thickness. The method is based on series expansions of the thin film reflectance (*R*) and transmittance (*T*) as functions of the parameter (d/λ, λ - wavelength). Our calculations show that this method cannot be used with success for films that have significant (i.e. metals) or negligible (dielectrics) absorption. Besides, the accuracy of estimated (*n*, *k*, *d*) is not high enough. Using the Abelès formulae, we could not obtain real values for the thickness of the As-S films within the framework of the present study.

Recently, we have proposed [6] a method for (*n*, *k*, *d*) determination of very thin films (less than $\lambda/30$). In this paper, we apply this method for the investigations of vacuum deposited As-S films with *d* between 10 and 30 nm, and we present new experimental data for the optical constants and their photoinduced changes in VIS and NIR (380-1500 nm).

2. Method of determination of films' optical constants:

Here a short description of the method used for the determination of thin films (*n*, *k*, *d*) is presented. The method is only applicable when the following major assumptions are observed: a monochromatic plane wave of unit amplitude at normal incidence impinges upon a very thin optically homogeneous, isotropic film bounded by parallel surfaces. The film is supported by an optically homogeneous, isotropic semi-infinite substrate of refractive index n_s. The other semi-

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infinite half space has a refractive index of n_0 = 1. The film can be composite within the EMA models, i.e. it is considered that no scattering is present.

The optical behaviour of such a film is described by its 2 × 2 characteristics matrix [6 and Ref there cited]. The nanothickness of the film allows us to make a limited development of the matrix elements as a function of $\tilde{n}d/\lambda$, ($\tilde{n} = n - ik$ is the complex refractive index of the film) retaining the terms up to fourth order. Thus, we obtain expressions for the film transmittance (T_f), the film front reflectance (R_f) and the film back reflectance (R'_f). The use of the relations $(1 + R_f)/T_f$, $(1 - R_f)/T_f$ and $(1 - R'_f)/T_f$ leads to set of three equations, which are simpler than those for T_f, R_f, R'_f, and can be easily solved numerically for the complex permitivitty (ε) and d of the film:

$$\frac{1+R_f}{T_f}=\frac{(0.5\varepsilon_2^{\,2}+\varepsilon_1^{\,2}-\varepsilon_2^{\,2}\varepsilon_1+0.5\varepsilon_2^{\,2}n_s^{\,2}-\varepsilon_1 n_s^{\,2}+\varepsilon_1^{\,2}n_s^{\,2}+\varepsilon_1^{\,3})\omega^4 d^4}{6n_s}+ \frac{(\varepsilon_2 n_s-n_s\varepsilon_2\varepsilon_1)\omega^3 d^3}{3n_s}+\frac{[(1-\varepsilon_1)(n_s^{\,2}-\varepsilon_1)+\varepsilon_2^{\,2}]\omega^2 d^2}{2n_s}+\frac{2\omega d\varepsilon_2 n_s+(n_s^{\,2}+1)}{2n_s} \qquad (1a)$$

$$\frac{1-R_f}{T_f}=\frac{\varepsilon_2^{\,2}\omega^4 d^4}{6}+\frac{(\varepsilon_2 n_s^{\,2}-\varepsilon_2\varepsilon_1)\omega^3 d^3}{3n_s}+\frac{\omega d\varepsilon_2+n_s}{n_s}; \qquad (1b)$$

$$\frac{1-R'_f}{T_f}=\frac{\varepsilon_2^{\,2}\omega^4 d^4}{6}+\frac{(\varepsilon_2-\varepsilon_2\varepsilon_1)\omega^3 d^3}{3}+\omega d\varepsilon_2+1, \qquad (1c)$$

where $\varepsilon = \varepsilon_1 - i\varepsilon_2 = \tilde{n}^2$, $\omega = 2\pi/\lambda$ is the wave number.

To calculate (ε_1, ε_2, d) we use the Levenberg – Marquart optimization approach [7]. The method, described above, is very fast and effective for evaluation of optical constants from spectrophotometric measurements at normal incidence of light.

3. Results and discussion

The investigated As–S films were obtained by a method described elsewhere [3]. Films optical transmission and reflection were measured with Cary 5E spectrophotometer at normal incidence in the range 380 to 1500 nm with accuracy of 0.5% and 1%, respectively. After spectrometric measurements, the films were irradiated with low-pressure mercury lamp HBO-200 (intensity = 20 mW/cm^2, distance to sample = 30 cm, IR (cut–off filter present) for 30 minutes.

3.1. Influence of the substrate:

The equations (1) are valid in case when we consider the substrate infinite. In order to analyze the influence of the finite slightly absorbing substrate (multiple intensity reflections in the substrate) we must know its optical constants (n_s, k_s, d_s). For substrate with small absorption ($k_s \ll 1$), its reflectance and transmittance are [8]:

$$T_s = T_{a,s}a_s/\{1 - R_{a,s}a_s^2\}; \quad R_s = R_{s,a} + T_{a,s}^2R_{a,s}a_s^2/\{1 - R_{a,s}a_s^2\}, \qquad (2)$$

with $a_s = exp(- 4\pi k_s d_s/\lambda)$; $R_{s,a} = R_{a,s} = (n_s - 1)^2/(n_s + 1)^2$ and $T_{s,a} = T_{a,s} = 4n_s/(n_s + 1)^2$. R_s and T_s are, in fact, energetic coefficients and are measurable quantities. Usually we do not know the values (n_s, k_s), but we can evaluate them from spectrophotometric data by solving numerically the equation set (T_s, R_s) for the unknown ($n_s(\lambda)$, $a_s(\lambda)$). The dispersion of n_s for the substrates used in our experiments (pre-cleaned Ca-Na silicate plates) is presented in Fig. 1.

For the system (film – finite substrate) we must consider 3 measurable quantities: transmittance T_{exp}, front reflectance R_{exp} for film facing the incident light and back reflectance R'_{exp} for the substrate facing the incident light [8].

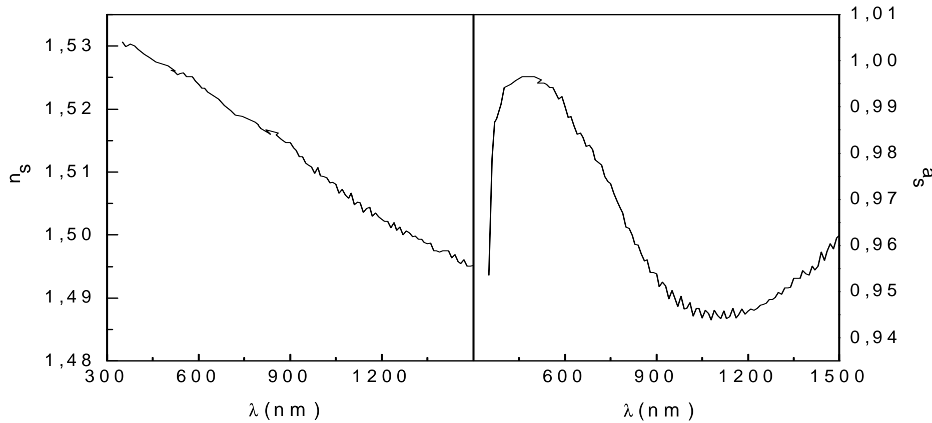

Fig. 1a. Spectral dependence of n_s. Fig. 1b. Spectral dependence of a_s.

This is a linear set of equations for (R_f, R_f', T_f), which enter in the analytical expressions for the film optical constants in equation (1). They are easily obtained:

$$R_f = R_{exp} - T^2_{exp}R_{s,a}/(R_{s,a}R'_{exp} + T_{s,a} - R_{s,a});$$
$$R_f' = (R'_{exp} - R_{s,a})/\{a_s^2(R_{s,a}R'_{exp} + T_{s,a} - R_{s,a})\}; \quad (3)$$
$$T_f = (T_{s,a}T_{exp})/a(R_{s,a}R'_{exp} + T_{s,a} - R_{s,a}).$$

In such way the finite substrate, multiple reflections in it and its optical performance (for instance in small spectral absorption) are taken into account.

3.2. Optical characteristics of very thin As-S films:

We have studied three films: F1, F2 and F3. Solving equations (1), we obtained for their thickness F1: d=15.1 nm, F2: d=20.4 nm and F3: d=24.2 nm. The results for n and k dispersion are shown in Fig. 2a and Fig. 2b respectively. There is a pronounced dependence of n and k on the film thickness: $n(\lambda)$ and $k(\lambda)$ decrease with decrease of d.

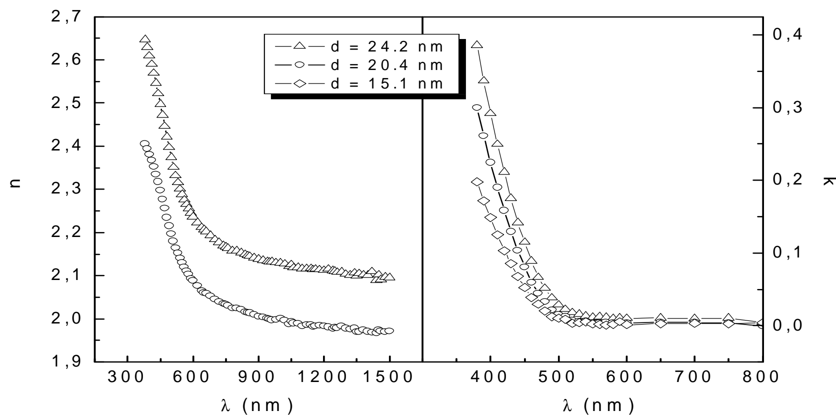

Fig. 2a. Dispersion of n for As-S film. Fig. 2b. Dispersion of k for As-S film.

As a measure of the accuracy of the estimated (*n*, *k*, *d*) we use the differences $\Delta T = T_{cal} - T_f$ and $\Delta R = R_{cal} - R_f$, where T_{cal} and R_{cal} are the transmittance and front reflectance of the films, calculated with obtained (*n*, *k*, *d*) by the help of exact thin film formulae; T_f and R_f are the experimental data (after taking into account the finite thickness of the substrate). In Fig. 3a and 3b the dispersions of ΔT and ΔR are presented respectively. The differences are less that maximal uncertainty of the Cary 5E for the films with *d* = 15.1 nm and *d* = 20.4 nm (in the whole spectral range) and for the films with *d* = 24.2 nm (for λ>480 nm).

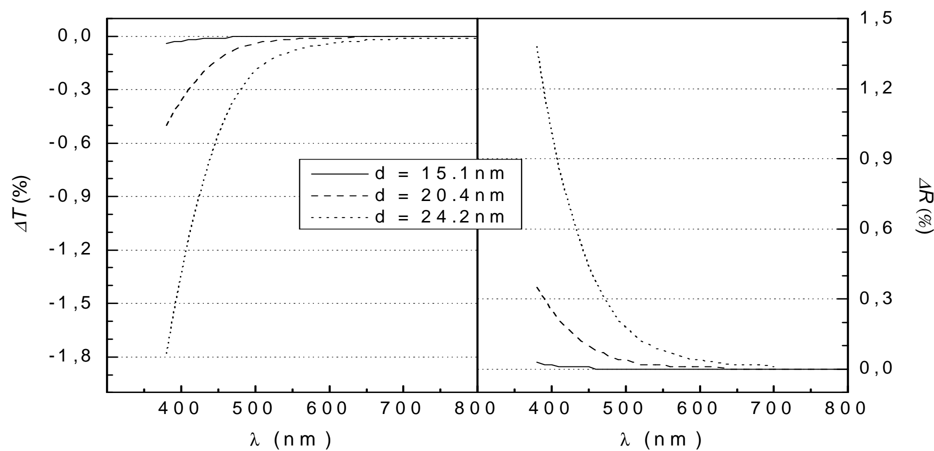

Fig. 3a Dispersion of ΔT for As-S film. Fig. 3b. Dispersion of ΔR for As-S film.

An approximate estimation of the joint confidence region can be calculated by treating *(n, k, d)* as independent random variables (no covariance terms). For λ below the As - S absorption edge (λ = 500 nm) we obtain confidence intervals for the thickness $\delta d = \pm 1$ nm (F1), $\delta d = 0.45$ nm (F2) and $\delta d = \pm 0.35$ nm (F3). The intervals for *n* vary from $\delta n = \pm 0.04$ for the thinnest layer, to $\delta n = \pm 0.01$ for the film with *d* = 24.2. For λ = 600 nm (above the absorption edge), the confidence intervals δd are nearly doubled, but the δn are practically the same.

From the estimated $k(\lambda)$ values, the optical gap E_{gap} has been evaluated using the relation: $\sqrt{\alpha E} = \left(E - E_{gap}\right)$, where $\alpha = 4\pi k/\lambda$. The obtained data for the three samples is as fallows: for F1: $E_{gap} = 2.37$ eV, F2: $E_{gap} = 2.36$ eV and F3: $E_{gap} = 2.32$ eV. The film F1 (*d* = 15.1 nm) is included as well, because we consider that in the range 400 – 600 nm the obtained values of $k(\lambda)$ are fairly consistent with the F2 and F3 data. The gaps are very close to the value of 2.38 eV [11].

The refractive index dispersion of films F2 and F3 is shown in Fig. 2a. The F1 sample has $n(\lambda)$ essentially lower than those of F2 and F3 and is not presented in the figure. In order to obtain a plausible interpretation of the refractive index dependence on film thickness, we have tried to treat the samples as composite materials with air inclusions. We have applied different EMA models (Newton, Maxell-Garnett and Bruggeman mixing rules) with $n(\lambda)$ being the effective refractive index. However, the estimated filling factors were unacceptably high (0.3 to 0.5). Therefore, we assume that F2 and F3 samples are not nanocomposite films and F1 reveals island structure.

The refractive index data is studied within the frame of the Wemple-DiDomenico model [9]. We apply the relation:

$$n(E)^2 = 1 + E_d E_0 / \{ E_0^2 - (E)^2 \}, \quad (5)$$

where E is the photon energy and E_d and E_0 are single oscillator fitting constants, which measure the oscillator energy and strength respectively. By plotting $(n^2 - 1)$ against $(E)^2$ and fitting a straight line, E_d and E_0 are determined. It has been pointed out [9] that the dispersion energy E_d obeys a simple

empirical relation: $E_d = \beta N_c Z_a N_e$, where β is a constant, which value in covalent crystalline and amorphous materials is estimated to be 0.37 ± 0.04 eV; N_c, is the coordination number of the cation nearest neighbor to the anion; Z_a is the formal chemical valence of the anion and N_e is the total number of the valence electrons per anion. The results are presented in Table 1. The obtained values are not consistent with data from other publications [2] on thicker As-S films. For such films the estimated As coordination number is greater than the theoretical value of 3. The nearest-neighbor values of our samples are much lower than the effective crystalline or amorphous glass values because of the low single oscillator strength E_d .This can be due to the lower mass density of our samples, compared to the well annealed evaporated or glass layers If we assume that As octahedra bond layers to form 3D structure, it is not the case of our samples, which are of much greater disorder. On the other hand, the estimated values of the single oscillator energy E_o agree fairly well with the published data. This correlates to the estimated optical gap, as the two parameters are related. In general, the validity of Wemple - DiDomenico model for nanolayers should be further investigated.

Table 1. Single oscillator fitting constants.

d [nm]	N_0	E_0 [eV]	E_d [eV]	N_c
20.4	1.95	5.13	14.41	2.09
24.2	2.07	5.05	16.72	2.42
29.9 (exp)	1.86	4.49	11.07	1.60

We have irradiated the samples in order to study the photoinduced changes in the optical characteristics of very thin As-S films. It was found that light scattering from the samples has significantly increased. Only spectrophotometric data for the film with d=24.2 nm was successfully processed by the equations (1). We believe that, due to irradiation, the homogeniosity of the films is strongly affected. After exposure the thickness of the F3 sample was evaluated to be d = 29.9 nm. Thus rather strong expansion of about 20% is obtained. In Fig. 4 we present the refractive index and extinction coefficient dispersions before and after exposure. The refractive index of the exposed film is lower than that of unexposed. This contradicts the usual behavior of As–S films and will be studied in the future. Results from the interpretation of the single oscillator model for the F3 irradiated sample are included in Table 1 just for the record.

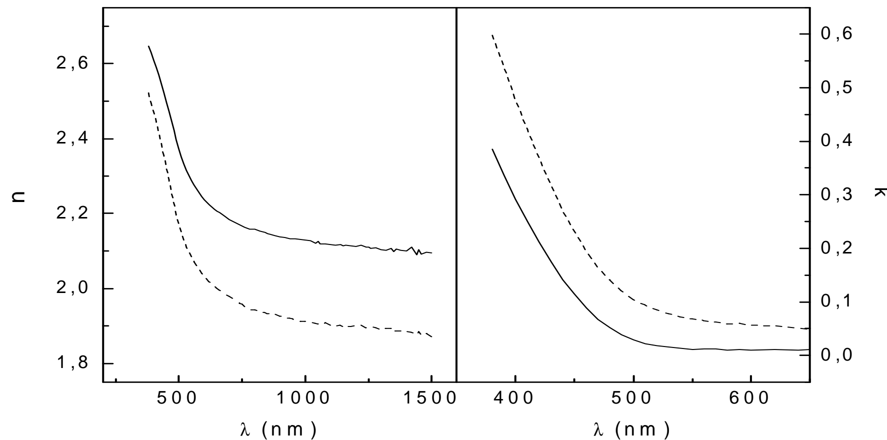

Fig. 4. Dispersion of n and k for As-S film with d = 24.2 nm before (—) and with d = 29.9 nm after (---) exposition.

On the other hand, the well known photodarkening (red shift of the absorption edge) of the nanofilm is observed. The E_{gap} of the exposed film is found to be 2.20 eV compared to 2.32 eV of the unexposed film. Tanaka [10] has not obtained any photoresponse in annealed As_2S_3 films with d ~ 50 nm, and he has not studied thinner samples. Obviously, the photoinduced phenomena in very thin films must be thoroughly investigated.

4. Conclusion

By the help of a simple method for determination of optical constants we have investigated the optical properties of very thin arsenic sulfide films in VIS and NIR. We have obtained new data for the dispersion of the complex refractive index between 380 and 1500 nm, and the optical gap for As-S nanolayers. Our results show that evaporated films with thickness up to ~25 nm have structures that differ from that of the crystalline, glassy or thermally deposited thick samples. This correlates with the observed dependence of the complex refractive index on physical thickness. Irradiation of such very thin layers leads to photoinduced changes (photodarkening), but in the same time, under exposure conditions described above, it ‘blows up’ the surface continuity. Films entity is broken and its structure, most probably, becomes island in form with strong nonhomogeneities.

Acknowledgements

We thank Dr J. Dikova for supplying of As-S samples.

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