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INFLUENCE OF COMPOSITION, EXPOSURE AND THERMAL ANNEALING ON OPTICAL PROPERTIES OF As-S CHALCOGENIDE THIN FILMS

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In this paper the influence of the composition, i.e., As concentration, UV irradiation and annealing, on the optical constants, thikness and material parameters of chalcogenide As-S thin films is studied. For determining the values of the parameters mentioned the optical method based on interpretation of experimental data consisting of spectral dependences of the transmitance measured at normal incidence and spectral dependences of the ellipsometric quantities measured for several incidence angles is used. This combined optical method is applied in multi-sample modification. Experimental data are measured in the spectral region 240-850 nm. In the frame of the interpretation of the experimental data, the structural model containing an isotropic inhomogeneous layer covered with a non-absorbing overlayer is used for representation of the films under investigation. The Jelison-Modine (Tauc-Lorentz) dispersion model is employed for expressing the spectral dependences of the optical constants of the As-S Films. It is shown that this dispersion model is suitable for interpretation of the ellipsometric data but it is insufficient for treatment of the transmittance data. Further, it is shown that the changes of composition, exposure and annealing influence markedly the material parameters and thicknesses of the As-S films.

1. Introduction

Amorphous As-S thin films are udes in various branches of practice. For example, they are employed as inorganic resists, media for recording in holography, materials in optoelectronics etc. The optical properties of the As-S films are important for these applicaions. That is why an attention has been devoted to study of the optical properties of these films (see e.g. , [1-4]). Within the optical studies mentioned the spectral dependences of the optical constants of the As-S chalcogenide films were determined. In particular the spectral dependences of the optical constants evaluated in wide spectral reions are important foi\r the practical applications. The spectral dependeces of the optical constants of the As-S thin films within the near-UV and visible regions were determined in our earlier papers [3-5]. In these papers two original dispersion models of the optical constants of amorphous materials were employed for interpreting the optical experimental data. However, both the models mentioned require numerical calculations consuming much processor time. Thus, in the studies of many samples both the dispersion models mentioned above are not efficient for quicker data processing. In our paper [3] we showed that the spectral depenences of the optical constants of the As-S thin films could be described by the Jellison-Modine (JM) dispersion model [6] in a relatively good way. Note, that in the literature this model is often called the Tauc-Lorentz model. This JM model is based on analytical calculations and therefore it is suitable for the quick data processing of many samples. This is why we have selected this model for the studies of the influence of composition, exposure and annealing on the optical properties of the As-S chalcogenide thin films. Moreover, an optical method based on the combination of variable angle spectroscopic ellipsometry (VASE) and

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spectrophotometric method has been used for studying this influence. Within the spectrophotometric method the spectral dependences of the transmittances of the films studied were measured. The spectral transmittances were used because of their strong sensitivity to small absoption of the films. This combined optical method was applied in multisensitivity to small absoption of the films. This combined optical method was applied in multisample modification for increasing the stability of the solution of the inverse task.

An efficiency of this combined method for determining the optical constants and material parameters of the As-S thin films is investigated. Further, the influence of composition, exposure and annealing on the optical constants and material parameters is presented in detail.

2. Sample preparation

The As-S films were prepared by classical thermal vacuum evapration of material on unheated BK7 glass plates in nominal thickness of 1 mm. For their preparation three targets were used. The first one was formed by glassy As_2S_3. The second and third targets were formed by As_xS_{100-s} glass, x = 38 and 42 (x = 40 corresponds to As_2S_3). Using each target the four films were prepared and studied:

1. V (virgin) – films after their deposition without any treatment
2. E (exposed) – films exposed by UV-light after their deposition (Hg high pressure lamp with IR filter, I≈14 mWcm^{-2}, 1 hour) in inert Ar atmosphere
3. A (anneled) – films annealed for 1 hour in Ar atmosphere at temperature of 160 ^{o}C) ~ 20 K bellow their transition temperature)
4. AE – films annealed and then exposed in the same conditions as in points 2 and 3.

This means that twelve samples of the As-S films were deposited for our investigation. The following denotation of the samples will be used to specify the individual ones: V38, V40, V42, E38, E40, E42, A38, A40, A42, AE38, AE40 and AE42, where symbol V38 denotes the 'virgin' film containing 38 at.% of As in samples, etc. The film composition mentioned above was determined using a microprobe analysis with EDAX facility.

Note that the deposition time of all the films investigated was identical (it was of ~ 15 min., ~ 1 nm sec^{-1}).

3. Experimental arrangements

The spectral dependences of the complex ellipsometric quantities $\hat{p}\left(\hat{p} = \tan\psi \exp(i\Delta)\right.$, where ψ and Δ denote the ellipsometric parameters) of the samples were measured for several angles of incidence in the spectral region 240-850 nm (the following angles of incidence was used: 55, 60, 65, 70 and 75^{o}). The spectral dependences of the transmittances T of the samples were measured in the spectral region 400-850 nm. A Jobin Yvon UVISEL spectroscopic ellipsometer and Perkin-Elmer Lambda 45 spectrophotometer were used to obtain the experimental data.

4. Model of the As-S films

For interpretation of experimental data of $\hat{p}$ and T the following structural model of the thin films representing our samples is assumed:

1. the As-S thin films are formed by the isotropic inhomogeneous absorbing layers
2. the substrates are formed by the isotropic homogeneous non-absorbing planparallel plates
3. the boundaries of the As-S films are ideally flat and smooth
4. the ambient is formed by air
5. very thin overlayers take place on the upper boundaries of the As-S films.

The spectral dependences of the optical constants of the As-S films are represented by the JM dispersion model. Within this dispersion model the imaginary part of dielectric function is given as follows [6]:

$$\varepsilon_2(E) = \frac{1}{E}\left[\frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2}\right] \quad \text{for } E > E_g \tag{1}$$

where A, E_0, C and E_g are parameters (E_g denotes the band gap). Symbol E represents photon energy. For $E > E_g$ it holds that $\varepsilon_2(E) = 0$. The real part of the dielectric function is then given by the Kramers-Kronig relation, i.e.,

$$\varepsilon_1(E) = \varepsilon_1(\infty) + \frac{2}{\pi} P\int_0^\infty \frac{s\varepsilon_2(s)}{s^2-E^2}\, ds, \tag{2}$$

where P means the principal value of the integral. Symbol $\varepsilon_2(\infty)$ is a parameter representing the value of the dielectric function in infinity. The integration in the foregoing equation can be performed in an analytical way. The corresponding expression of $\varepsilon_1(E)$ obtained with this analytical way is presented in Refs. [6,7]. The refractive index n_f and extinction coefficient k_f of the As-S films obey the following equation:

$$\hat{n}_f = n_f + ik_f = \sqrt{\hat{\varepsilon}(E)} \tag{3}$$

where $\hat{\varepsilon}(E) = \varepsilon_1(E) + i\varepsilon_2(E)$. The inhomogeneity of the As-S films is given by a profile of the complex refractive index $\hat{n}_f$ across these films. It is assumed that the refractive index profile considered coresponds to the linear profile of the dielectric function $\hat{\varepsilon}(E)$ across the As-S thin films. The linear profile of $\hat{\varepsilon}(E)$ implies certain boundary values of the refractive index, i.e., value $\hat{n}_{fL}$ (overlayer / As-S film boundary) and value $\hat{n}_{fR}$ (As-S film / glass boundary) in this way

$$\hat{n}_{fL} = \sqrt{p(\hat{n}_f^2 - 1) + 1} \text{ and } \hat{n}_{fR} = \hat{n}_f, \tag{4}$$

where p denotes the density factor. The foregoing equations express the parameterization of the refractive index profile based on only one parameter.

The refractive index profile is included in calculations of the optical quantities, i.e., in calculation of transmittance and ellipsometric quantities, using the WKBJ approximation [8,9].

The spectral dependences of the real refractive index of the overlayers n_o is fixed in the values belonging to the refractive index of amorphous SiO_2. An explanation of this concretefixation will be carried out bellow. The smoothness of the upper boundaries of the chalcogenide films is assumed since the atomic force microscopy (AFM) measurements did not indicate any roughness. Thus, the overlayers can not represent boundary roughness.

The spectral dependences of the refractive index of the glass substrates are represented with the Cauchy formula:

$$n_s = A_s + B_s / \lambda^2, \tag{5}$$

where A_s and B_s denote the material parameters and wavelength λ is connected with photon energy E through the following equation:

$$E = \frac{hc}{\lambda} \tag{6}$$

where h is the Planck's constant and c is light velocity.

5. Data processing

At first experimental data corresponding to all the samples studied have been treated simultaneously. This means that the spectral dependences of the ellipsometric quantities measured for the selected incidence angles θ_0 and the spectral dependences of the normal transmittance of all the individual As-S films have been processed using the least-squares method (LSM) simultaneously. Thus, the minimum of the following merit function $S(\vec{X})$ has been searched:

$$S(\vec{X}) = \sum_i \left| \hat{p}_i^{\exp} - \hat{p}(\vec{X}, \lambda_i, \theta_{0,i}) \right|^2 w_i + \sum_j \left[T_j^{\exp} - T(\vec{X}, \lambda_j) \right]^2 w_j, \qquad (7)$$

where vector $\vec{X}$ has the components identical with the parameters sought. Symbols i and j correspond to the summation over experimental values of $\hat{p}_i^{\exp}$ and $T_j^{\exp}$, respectively. Symbols w_i and w_j denote the weights of the individual experimental values. The weights are given by the standard deviations of the individual measurements. The LSM employed has been based on the Marquardt-Levenberg altgorithm [10].

One can define the following quantity:

$$\chi = \sqrt{\frac{S}{N - p}} \qquad (8)$$

where S is the residual sum of the squares corresponding to the minimum of the merit function $S(\vec{X})$ and N and/or p represents the number of the measurements and/or the number of the parameters sought. The quantity χ allows to perform a comparison of the quality of the individual fits. If the value of χ is close to unity the corresponding fit can be considered to be optimum, i.e., the differences between the experimental and theoretical data adree with the estimated errors.

Within the data treatment it has been assumed that the thickness of the overlayers and the refractive index of the glass substrates have been identical for all the samples. Thus, the three parameters characterize all overlayers and all substrates, i.e., the thickness of the overlayers d_o and the two parameters A_S and B_S corresponding to the Cauchy's formula of the substrate. Each As-S film is characterized with the eight parameters: d_{fT} (thickness corresponding to the transmittance data), d_{fE} (thickness corresponding to the ellipsometric data), p (density factor) and A, E_0, C, E_g, ε_1 (∞) (dispersion parameters). Note that the two parameters representing the thickness of each As-S film are taken into account because in principle it is necessary to assume different thicknesses for ellipsometric data and transmittance data. This is implied by the fact that a slight thickness non-uniformity can take place along the As-S films and that the light spots corresponding to the ellipsometric measurements on the one hand and the transmittance measurements on the other hand are different. From the foregoing it is seen that by means of the LSM the values of 99 parameters ($3 + 12 \times 8$) have been evaluated for all the twelve samples.

Thus, the method used to characterize the As-S films corresponds to the multi-sample modification of the combined optical method based on simultaneous treatment of both the ellipsometric and transmittance data. The multi-sample modification employs the fact that both the substrates and overlayers of all the samples studied are identical. Of course, in principle one can employ the single-sample modification for characterizing the individual As-S films. However, by using the multi-sample modification one can reduce the influence of the systematic errors associated with the optical measurements and model of the films under investigation. In other words, this multi-sample modification increases the stability of the solution of the inverse task in principle.

6. Results

Using the multi-sample modification of the combined optical method a satisfactory agreement between the experimental and theoretical data has not been obtained (the theoretical data have been calculated by the matrix formalism using the values of the parameters found at the treatment of the experimental data). The value of χ has been found in value of 14.5. The poor agreement of both data is also seen in Fig. 1. Because of this poor agreement the values of the parameters characterizing the As-S films studied are not presented here. The corresponding values of the parameters characterizing both the overlayer and substrate have been found as follows: d_o = 2.68 nm, and A_S = 1.331 and B_S = 75300 nm^2. Note that the accuracy of the parameter values determined is indicated by the last numbers, i.e., the errors are in the last numbers of the values (e.g. d_o = (2.68 ± 0.04) nm). While the value of the overlayer thickness is appearing to be correct the spectral dependence of the glass substrate refractive index given by A_S and B_S values is not realistic.

The unsatisfactory results corresponding to the multi-sample modification of the combined optical method have induced the necessity of changing the strategy of the treatment of the experimental data. Therefore in the latter step of our analysis we have tried to treat the ellipsometric and transmittance data separately. If we only treated the ellipsometric data in multi-sample modification we achieved a relatively satisfactory results. In this case χ has been found in the value of 3.65. The improved agreement between theoretical and experimental data is also evident from Fig. 1. The values of the overlayer thicknesses and dispersion parameters of the substrates have been found as follows: d_o = 2.94 nm, and A_S = 1.476 and B_S = 35200 nm^2. These values A_S and B_S are also incorrect. However, they are closer to the true ones presented for BK7 glass in the literature. For BK7 glass the true values of the dispersion parameters are namely as follows: A_S = 1.5043, B_S = 4250 nm^2 (Schott catalogue). The spectral dependences of the refractive index and extinction coefficient of the annealed As-S thin films calculated on the basis of the values of the material parameters found is plotted in Fig. 2 (samples A38, A40, A42). The spectral dependences of the optical constants of all the As-S films studied are mutually rather close. Therefore, it is reasonable to observe the differences among the As-S films by means of the values of the material parameters taking place in JM dispersion model. For clarity the values of the material parameters of all twelve As-S thin films studied are only presented in a graphical form in Figs. 3-7. The values of the density factors of the As-S films determined are plotted in Fig. 8. The values of their thicknesses are presented in Fig. 9.

When the multi-sample modification has only been applied to the transmittance data no improvement was found in comparison with the combined optical method. Moreover, it has been proved that the multi-sample transmission data do not give a sufficient information for determining the values of all the 99 parameters characterizing the films under investigation.

7. Discussion

The first aim of this paper has been to examine whether the simple and very frequently employed JM dispersion model can be used to characterize the chalcogenide thin films within the wide spectral region instead of the more complicated dispersion models presented in the last years [3,5,11]. From the results presented in the foregoing section it is evident that this dispersion model is not usable for the optical characterization of the As-S films if the transmittance experimental data are used. If the ellipsometric data are only employed one obtains relatively reasonable values of the parameters characterizing the films studied and, moreover, the relatively good agreement between the theoretical and experimental data. The foregoing conclusions are mainly caused by the fact that the JM dispersion model does not include the Urbach tail expressing the weak absorption of amorphous solids corresponding to the existence of the localized electron states taking place in the band gap. It is known that transmittance of relatively thick amorphous films are relatively sensitive to the existence of this Urbach tail on the contrary of the ellipsometric quantities measured in reflection that are less sensitive to the week absorption for the below-band gap region. On the other hand, the ellipsometric measurements are sensitive to the absorption corresponding to the interband transitions in above-band gap region where the thick films are not transparent. In the above-band gap region the transmittance of these films equals zero and therefore the transmittance can not be employed for the optical characterization within this region.

As mentioned above the latter aim of this paper has consisted in the study of the influence of the composition, exposure and annealing on the optical constants and material parameters characterizing the As-S films. Such studies are important for potential applications. We found that the influence of the As content, annealing and UV exposure on the values of the material parameters of these films was relevant. For example, the values of the band gap decrease from ~ 2.42 to ~ 2.32 eV with the increasing of As concentration from 38 to 42 at.%. Further, it is interesting that all the films studied have exhibited the refractive index profile in such a way that the refractive indices at the overlayer / As-S boundary $\hat{n}_{fL}$ have been lower than those $\hat{n}_{fR}$ corresponding to the As-S / glass boundary. This refractive index profile has been more pronounced for the films with the higher As concentration without annealing (see Fig. 8). This fact is probably connected with an As diffusion across the As-S films during annealing. Detailed mechanism explaining the dependences of the optical constants and material parameters of the As-S films the As concentration, exposure and annealing have not been presented so far.

The determination of both the refractive index and thickness of the overlayers has not been possible using the method employed. This fact is given by a correlation between the overlayer parameters searched using the LSM. The correlation causes that only one of the overlayers parameters can be determined. The refractive index values of the overlayers and the As-S thin films are not known. Therefore we have fixed values of the refractive index of the overlayers in those of amorphous SiO_2 as mentioned above and the value of the thickness of these overlayers have been searched. Of course, the fixation of the overlayer refractive index in the values of amorphous SiO_2 must be understood as the reasonable first approximation of this quantity. This approximation had to be adopted because the influence of the overlayers on the interpretation of the experimental data can not be neglected. On the basis of the results obtained for similar thin films with overlayers one can expect that the fixation of the overlayer refractive index in values of the SiO_2 refractive index does not influence the values of the parameters of the As-S films found in an appreciate way. Thus, it is not too important in which values the refractive index of the overlayers is fixed.

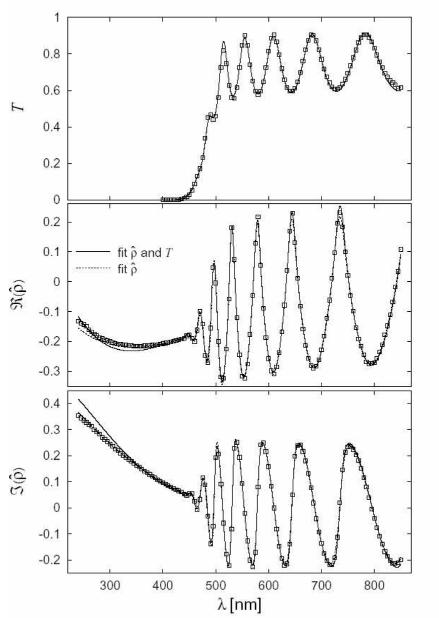

Fig. 1. The spectral dependences of the transmittance T and real part $\Re$ and imaginary part $\Im$ of the ellipsometric ratio $\hat{\rho}$ for sample V38: points denote experimental values and lines represent the calculated values using the parameter values found by LSM.

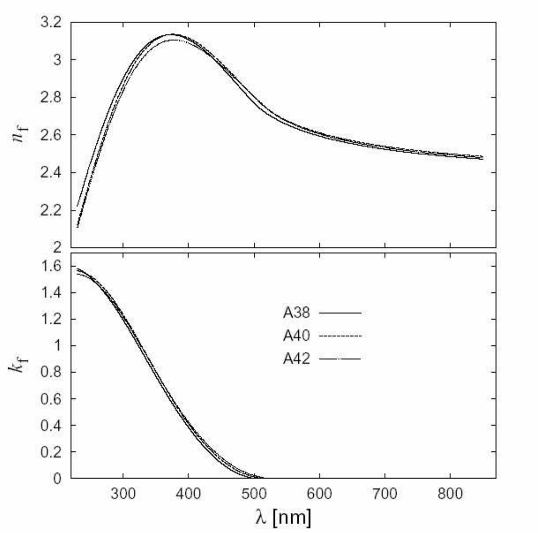

Fig. 2. The spectral dependences of the refractive index n_f and extinction coefficient k_f calculated on the basis of the material parameters found for the annealed samples.

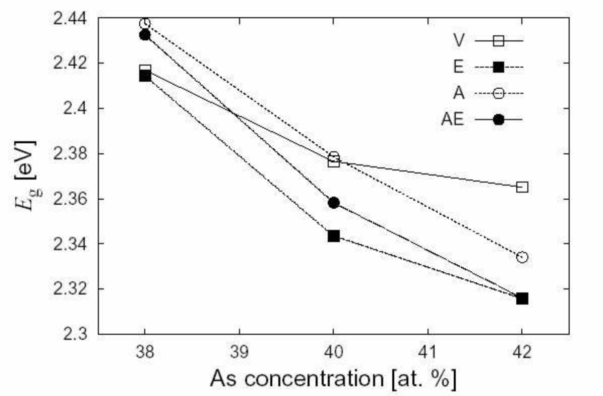

Fig. 3. The dependences of the band gap E_g on the As concentration.

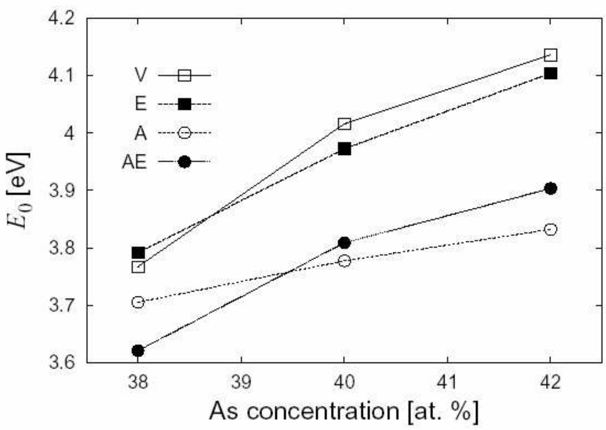

Fig. 4. The dependences of parameter E_0 on the As concentration.

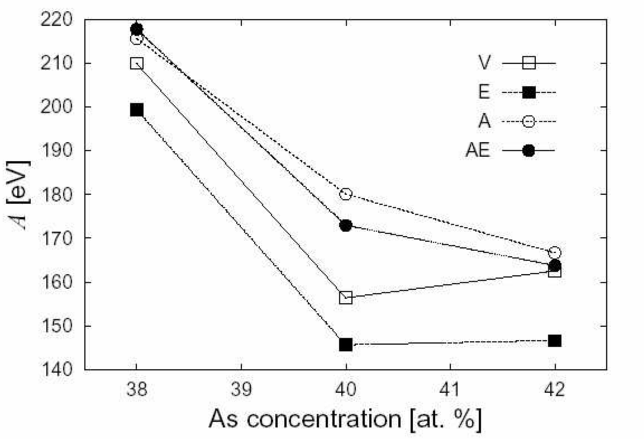

Fig. 5. The dependences of parameter *A* on the As concentration.

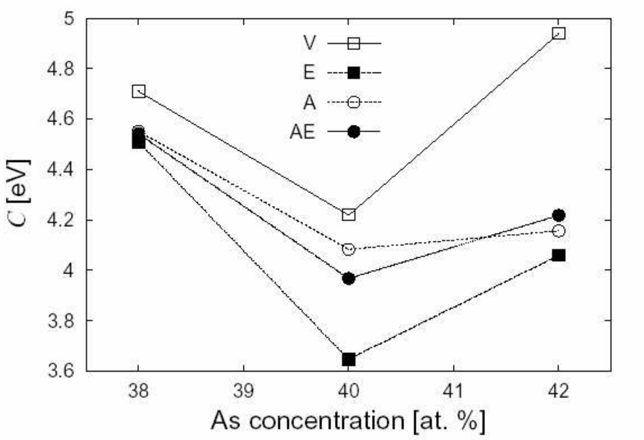

Fig. 6. The dependences of parameter *C* on the As concentration.

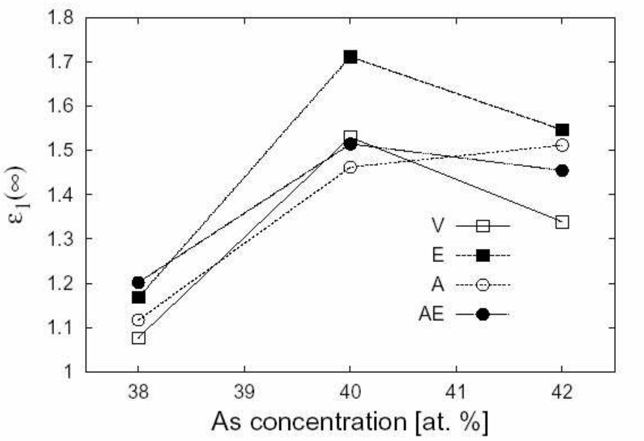

Fig. 7. The dependences of parameter $\boldsymbol{\varepsilon}_1$ (∞) on the As concentration.

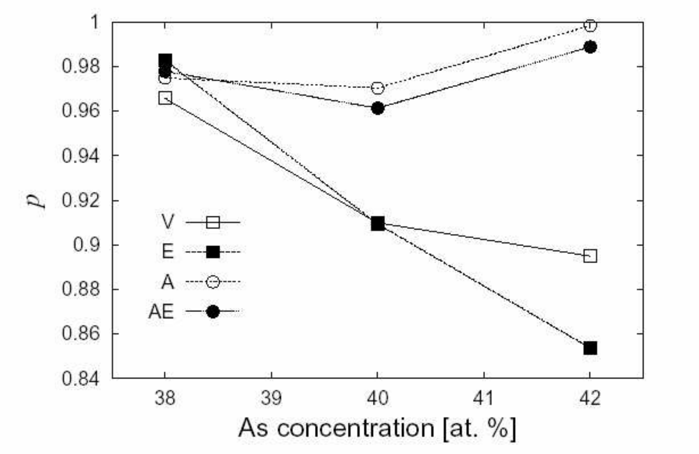

Fig. 8. The dependences of the density factor p on the As concentration.

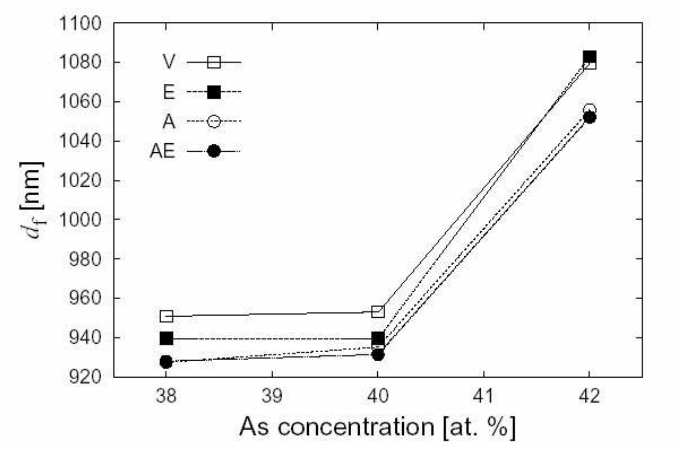

Fig. 9. The dependences of the thickness d_f on the As concentration.

Within the combined optical method presented here, the good agreement ($\chi \sim 1$) between the theoretical and experimental data is expected if the Urbach tail is included into the dispersion model of the optical constants of the chalcogenide films. The including of the Urbach tail can be carried out with the improved dispersion models presented recently [3,5,11]. Moreover, using these improved models the true values of the glass substrates can also be obtained. The results achieved using the improved dispersion models for the As-S films will be presented in our forthcoming paper.

8. Conclusion

In this paper the optical properties of the chalcogenides As-S films have been studied using the JM dispersion model. Using this dispersion model the experimental data corresponding to the combined optical method based on the VASE and transmittance data on the one hand and VASE on the other hand have been treated. It has been found that the JM model can not be used to treat the data of the combined optical method in the satisfactory way. This fact has been evidently caused by the absence of the Urbach tail in this dispersion model. In particular this absence have negatively been manifested in the transmittance data. If these transmittance data have been omitted from the data treatment, i.e., if only VASE data have been employed, the satisfactory results have been achieved. Thus, VASE has been usable for the study of the optical constants, material parameters and thicknesses of the As-S films. Therefore, the only ellipsometric data have been utilized for investigating the influence of the composition, exposure and annealing on the values of the optical constants, materials parameters and thicknesses characterizing these films.

It has been shown that the changes of the composition, exposure and annealing (see Section 2) have influenced the thickness and material parameters markedly, which is in accordance with [12]. It is interesting that all the As-S film studied have exhibited certain optical inhomogenity corresponding to the refractive index profile. Further, it should be emphasized that the existence of the overlayers taking place on the upper boundaries of the As-S films had to be respected when experimental data are treated.

A comparison of the results of the optical characterization of the As-S films presented in this paper with those found using the improved dispersion models will be carried out in our forthcoming paper.

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