ELSEVIER

Journal of Non-Crystalline Solids 222 (1997) 250–257

JOURNAL OF
NON-CRYSTALLINE SOLIDS

On the irreversible photo-bleaching phenomenon in obliquely-evaporated GeS_2 glass films

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Abstract

The photo-induced shift in the optical-absorption edge and changes in the optical constants (n,k), and their dispersion in the vicinity of the absorption edge, have been studied in obliquely-deposited thin films of the GeS_2 chalcogenide glass, prepared by vacuum thermal evaporation onto glass and silicon wafer substrates. Light exposure of the GeS_2 films in air was found to be accompanied by an irreversible bleaching. The appearance of Ge–O–Ge vibrational bands in the IR transmission spectra clearly indicates the extrinsic origin of photo-bleaching: it is most probably a result of the photo-oxidation of the layers. On the other hand, the irradiation of the GeS_2 films (deposited at an angle of incidence of $\approx 70°$) showed a decrease of thickness (and physical densification) of $\approx 8\%$. Furthermore, the dispersion of the refractive index of the as-deposited and exposed films can be described using the Wemple–DiDomenico (W–D) single-oscillator formula. Exposure-induced changes of the parameters of the W–D formula, E_0 and E_d, follow the increase of the Tauc gap and the decrease of the film thickness, respectively. © 1997 Elsevier Science B.V.

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1. Introduction

Photo-induced changes of amorphous chalcogenide layers have been the subject of extensive study from the point of view of both technological applications and also understanding of the nature of the phenomena [1–5]. As-evaporated films, when illuminated by band-gap light (photons of energy greater than the band gap), usually, exhibit a blue or a red shift of the optical gap, E_g^{opt}. This shift can be removed, for example, by thermal annealing in the case of a reversible change,

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0022-9093/97/$17.00
PII S0022-3093(97)00371-2

but it is not removed by annealing in the case of an irreversible change (which is more easily seen in obliquely-deposited films [6]). Though photo-induced changes in transmission and absorption edge of many chalcogenides have been reported in the literature [1,2,7], little is known about the quantitative behaviour of the associated optical constants. We expect examination of the optical constants (n,k) in the vicinity of the absorption edge, and their photo-induced changes, to provide information about mechanisms and conditions necessary for the occurrence of the photo-effects.

In the present paper we study the effects of light exposure of obliquely-evaporated GeS_2 glass films (prepared by vacuum thermal evaporation of bulk GeS_2 onto glass and silicon single-crystal wafer substrates) on the optical properties in the short-wavelength edge region and on the transmission in the IR-region.

2. Experimental procedure

2.1. Sample preparation and measurements

Thin-film samples were deposited by vacuum evaporation of powdered glassy material (prepared by heating an appropriate mixture of the elements in vacuum-sealed fused-silica ampoules, for about 4 h at ~ 900°C, and then air-quenched) on glass and Si wafer substrates at room temperature. The thermal evaporation process was carried out in a coating system (Edwards, model E306A) at a pressure of $\approx 10^{-4}$ Pa, from a suitable quartz crucible; the films were deposited at an angle of incidence of ≈ 70°. The deposition rate was ≈ 0.4 nm s^{-1}, and was continuously measured by a quartz-crystal monitor (Edwards, model FTM-5). Such a deposition rate produces a film composition close to that of the bulk starting material (EDAX-measurements has indicated that the film stoichiometry is correct to ± 1 at.%). The lack of crystallinity in the thin films was verified by X-ray diffraction (Philips, model PW-1830). The thickness of the a-GeS_2 films ranged between around 600 nm and 900 nm. The optical transmission spectra at normal incidence, used for calculating the optical constants and film thickness, were obtained in the 200 nm to 2500 nm range by a double-beam ratio recording UV/VIS/NIR computer-controlled spectrophotometer (Perkin–Elmer, model Lambda-19). The IR-transmission spectra were obtained in the 1000 cm^{-1} to 300 cm^{-1} range by a computer-controlled FT-IR spectrometer (Perkin–Elmer, model 2000). The thin-film samples were illuminated by a 500 W Hg arc lamp (Oriel, model 66032), through an IR-cut filter, and using a light intensity of ≈ 30 mW cm^{-2}; the samples were exposed for about 5 h in air, under normal atmospheric pressure.

2.2. Optical method

The optical system under consideration corresponds to homogeneous and uniform thin films, deposited on thick, transparent substrates. The thermally-evaporated films have thickness, d, and complex refractive index, $n_c = n - ik$, where n is the refractive index and k the extinction coefficient, which can be expressed in terms of the absorption coefficient α, by the equation $k = \alpha\lambda/4\pi$; the thickness of the substrate is several orders of magnitude larger than d, and its refractive index is symbolized by s. On the other hand, the optical transmission, T, is a very complex function [8], which can be simplified by neglecting the extinction coefficient k, an approximation that is valid over most of the spectrum. Thus, the expression for T is

$$T = \frac{Ax_a}{B - Cx_a\cos\phi + Dx_a^2} \tag{1}$$

where $A = 16\,n^2 s$, $B = (n+1)^3(n+s^2)$, $C = 2(n^2 - 1)(n^2 - s^2)$, $D = (n-1)^3(n-s^2)$, $\phi = 4\pi nd/\lambda$ and $x_a = \exp(-\alpha d)$. The values of transmission at the extrema of the interference fringes (present in the spectra) can be obtained from Eq. (1), by setting the interference conditions $\cos\phi = 1$ and $\cos\phi = -1$ for maxima, T_M, and minima, T_m, respectively.

According to Swanepoel's method [9], which is based on Manifacier et al.'s idea [10] of creating the envelopes of the interference maxima and minima, a first approximation of the refractive index, n_1, in the region of the transmission spectrum of medium and weak absorption, is given by

$$n_1 = \left[N + (N^2 - s^2)^{1/2}\right]^{1/2}, \tag{2}$$

where

$$N = 2s\frac{T_\mathrm{M} - T_\mathrm{m}}{T_\mathrm{M}T_\mathrm{m}} + \frac{s^2 + 1}{2}.$$

In addition, s at each λ was obtained by independently measuring the transmittance of the substrate alone [9]. Next, the n_1s can be employed to determine the film thickness and also to increase the accuracy of the refractive indices from the basic equation for the interference fringes, $2nd = m\lambda$ (where the order number m is an integer for maxima and half-integer for minima), as described in detail in our previous works [11–14].

Furthermore, in the region of the transmission spectrum of medium and weak absorption the x_as are determined, following Swanepoel's method, from the equation

$$x_\mathrm{a} = \frac{E_\mathrm{M} - \left[E_\mathrm{M}^2 - (n^2 - 1)^3(n^2 - s^4)\right]^{1/2}}{(n - 1)^3(n - s^2)}, \tag{3}$$

where

$$E_\mathrm{M} = \frac{8n^2 s}{T_\mathrm{M}} + (n^2 - 1)(n^2 - s^2).$$

In the region of strong absorption the interference fringes disappear and, then Eq. (1) can be written (for $x_\mathrm{a} \ll 1$) as

$$T_0 \approx A x_\mathrm{a}/B$$

or

$$x_\mathrm{a} \approx \frac{(n + 1)^2(n + s^2)}{16n^2 s}T_0. \tag{4}$$

3. Results

3.1. Ultraviolet / visible / near-infrared spectroscopy

In Fig. 1 some typical optical transmission spectra of amorphous $\mathrm{GeS_2}$ films are shown in the region of the short-wavelength edge (SWE). One can see that exposure of the samples leads to a very strong bleaching. Next, we examine the optical dispersion of the unexposed and exposed films: from the spectral dependence of transmission in the SWE region we calculated, using the method of the envelope curves (see Fig. 1), the spectral dependence of the refractive index of the films. The results are summarised in Fig. 2 in the form $(n^2 - 1)^{-1}$ against $(\hbar\omega)^2$ (and also in the form n vs. λ), according to the Wemple–DiDomenico single-oscillator formula [15,16]

$$n^2(\omega) - 1 = \frac{E_0 E_\mathrm{d}}{E_0^2 - (\hbar\omega)^2}, \tag{5}$$

where E_0 is the single-oscillator energy and E_d the dispersion energy. In Table 1 are listed the values of E_0, E_d, $n(\omega \to 0)$ and the optical frequency dielectric constant $\varepsilon_\infty(= n^2(\omega \to 0))$. Furthermore, we did find changes in the thickness of the films in the course of the exposure: the irradiation of the $\mathrm{GeS_2}$ glass films, deposited at an angle of incidence of ≈ 70°, showed a decrease of thickness and also a physical densification (we did not find photo-induced evaporation of the film

Table 1
Values of the single-oscillator energy or Wemple–DiDomenico gap (E_0), dispersion energy (E_d), refractive index at $\hbar\omega = 0$ ($n(0)$), optical frequency dielectric constant (ε_∞), Tauc optical gap ($E_\mathrm{g}^\mathrm{opt}$), gap ratio ($E_0/E_\mathrm{g}^\mathrm{opt}$), Tauc slope ($B^{1/2}$) and an alternative option for the optical gap (E_{04})

Film	E_0 (eV)	E_d (eV)	$n(0)$	ε_∞	$E_\mathrm{g}^\mathrm{opt}$ (eV)	$E_0/E_\mathrm{g}^\mathrm{opt}$	$B^{1/2}$ ($\mathrm{cm^{-1/2}\,eV^{-1/2}}$)	E_{04} (eV)
Virgin	4.73 ± 0.10	18.63 ± 0.03	2.222 ± 0.002	4.937 ± 0.009	2.39 ± 0.01	1.98 ± 0.05	438 ± 1	2.73 ± 0.01
Exposed	6.35 ± 0.10	20.86 ± 0.04	2.070 ± 0.001	4.285 ± 0.004	3.14 ± 0.01	2.02 ± 0.04	530 ± 1	3.48 ± 0.01

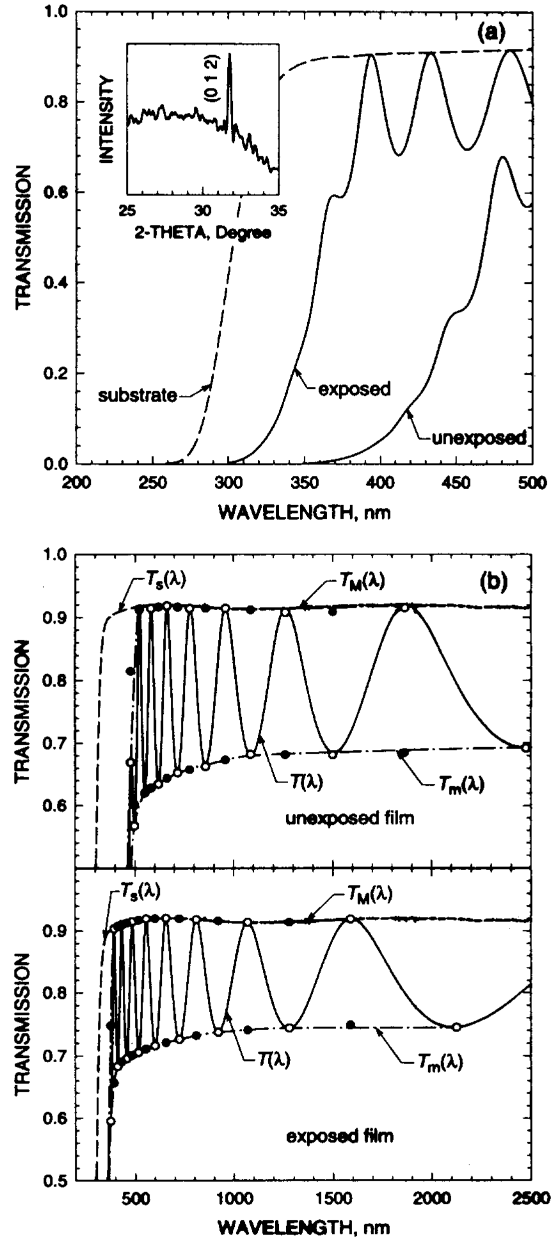

Fig. 1. (a) Typical optical transmission spectra of GeS_2 films in the region of short-wavelength edge (also, in the inset, part of the X-ray diffraction pattern (Cu Kα radiation) corresponding to the exposed sample); (b) interference fringes and the corresponding envelope curves (also the experimental (○) and the calculated (●) transmission values at the interference extrema).

material) of ≈ 8%. In the representative case under analysis, the film thickness decreased from 835 ± 7 nm down to 765 ± 7 nm (the sensitivity of the envelope method used is around 1%). In addition, the film thicknesses determined by mechanical measurements, using a surface-profiling stylus (Sloan, Dektak 3030), were 820 ± 16 nm and 752 ± 15 nm, respectively, in excellent agreement with the thickness calculated by the optical method. The difference is less than 2%.

On the other hand, we assume that the photobleaching of amorphous chalcogenide films is due to an increase of the optical gap, E_g^{opt}. The E_g^{opt}s

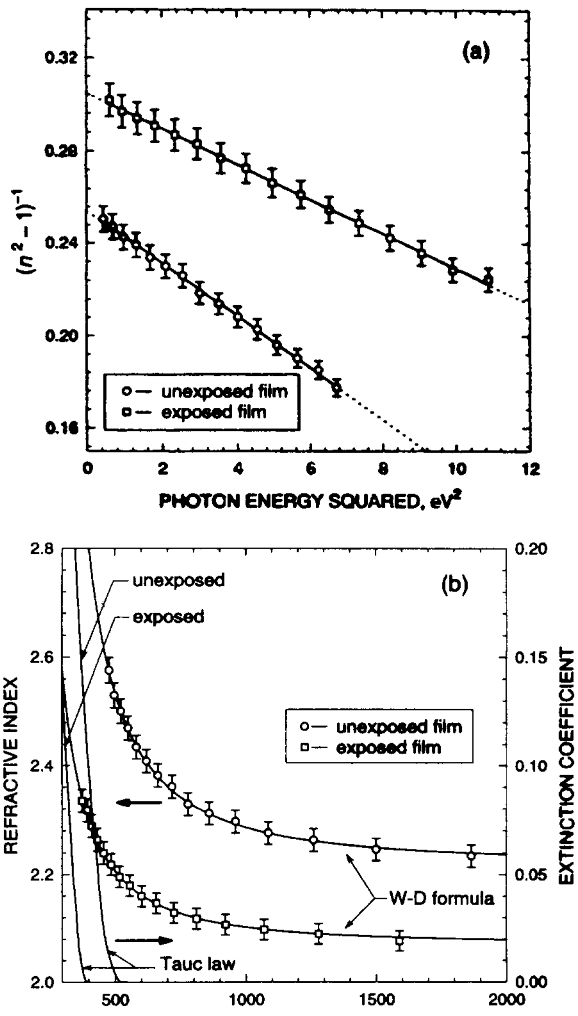

Fig. 2. (a) Refractive-index dispersion of GeS_2 amorphous films in $(n^2-1)^{-1}$ against $(\hbar\omega)^2$ coordinates; (b) refractive index, n, and extinction coefficient, k, vs. wavelength.

can be derived from the intercept of a plot of $(\alpha\hbar\omega)^{1/2}$ vs. $\hbar\omega$, for $(\alpha\hbar\omega)^{1/2} = 0$, within the standard parabolic approximation for valence and conduction bands (the well-known Tauc law) [17]. The photo-induced blue shift of the optical-absorption edge and the corresponding Tauc's extrapolations are shown in Fig. 3; moreover, the photo-induced change of k is displayed in Fig. 2. The Tauc gaps and slopes, along with an alternative option for the optical gap, E_{04}s (the energy at which the absorption coefficient is 10^4 cm^{-1}) are summarised in Table 1. It is evident that the blue shift of the optical gaps induced by illumination of virgin films is similar to those reported in the literature [18,19]. However, it should be noted that in contrast to these last results found in the literature, Rajagopalan et al. [6] have reported a shift in the absorption edge towards longer wavelengths (increased absorption) in obliquely-deposited thin films of GeS_2. Moreover, we emphasize that the present photo-bleaching phenomenon is irreversible, in the sense that annealing does not restore the gap to the initial gap for virgin films.

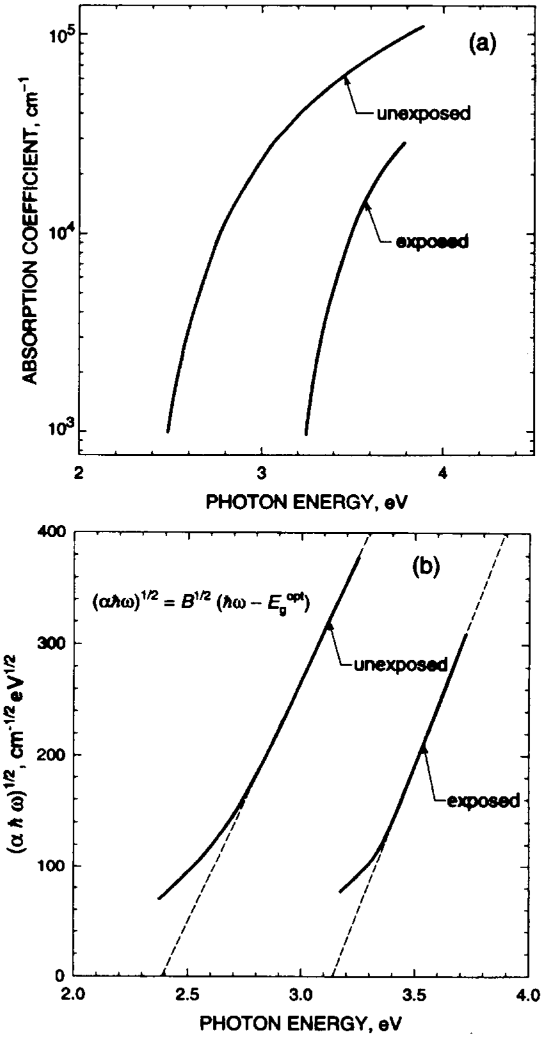

Fig. 3. (a) Optical-absorption edge for the as-deposited and exposed films; (b) photo-induced change in the Tauc gap and slope, E_g^{opt} and $B^{1/2}$, respectively.

3.2. Medium to far infrared spectroscopy

To know whether the photo-bleaching process is connected with the incorporation of oxygen into the Ge–S matrix of amorphous films, the IR spectra of unexposed and exposed films deposited on silicon wafers were measured. The results are shown in Fig. 4. The strongest features in the spectral region 1000–700 cm^{-1} are the vibrational bands at ≈ 870 cm^{-1}, at ≈ 820 cm^{-1}, at ≈ 795 cm^{-1} and at ≈ 740 cm^{-1}. In the spectral range 700–300 cm^{-1}, two absorption bands appear, one at ≈ 670 cm^{-1} and another at ≈ 370 cm^{-1}. Also, to complete the IR study, differential infrared (DIR) spectroscopy has been performed, in such a way that individual spectra were transformed into absorbance–frequency coordinates, then the spectra were subtracted and the results were, finally, transformed back into transmission-frequency coordinates. The DIR spectrum (see Fig. 4) indicates observable changes of IR activity in the spectral region around 370 cm^{-1}, and also in the regions around 670 cm^{-1} and 825 cm^{-1}.

4. Discussion

From Table 1 it follows that due to exposure of the 70°-GeS_2 film E_0 and E_d increase, while $n(0)$ decreases. We shall discuss quantitatively all these changes. In the As_xS_{100-x} amorphous system, it was found that there exists a correspondence between $E_0(x)$ and $E_g^{opt}(x)$, which can be expressed as $E_0 \approx 2E_g^{opt}$ [20]. Hence, the increase of E_0 is due to an increase of the optical gap, i.e. bleaching, as we have found. In chalcogenide

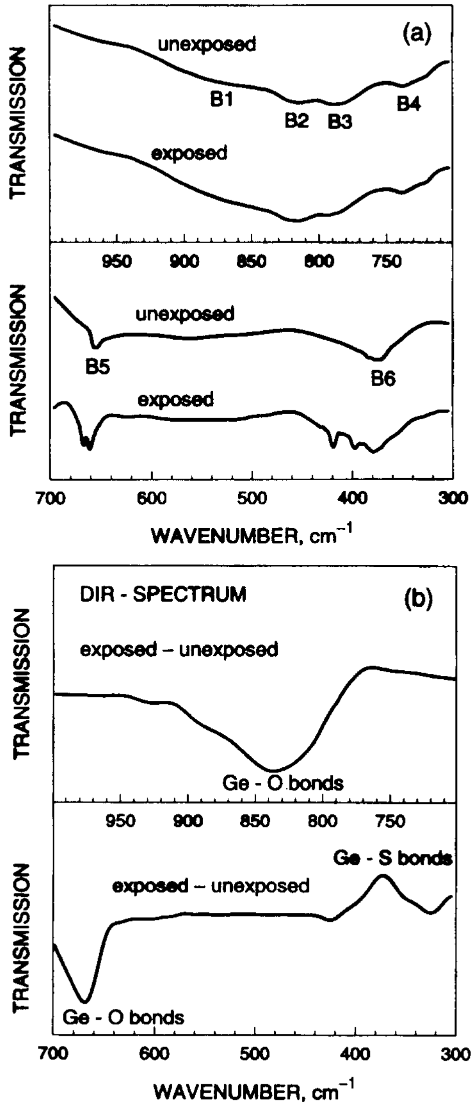

Fig. 4. (a) Typical IR-transmission spectra of the studied GeS_2 glass films (in this particular case, the unexposed film is partly oxidized); (b) typical DIR spectrum of the exposed film against the unexposed film.

glasses E_0 can be taken as a mean energy of transition between filled lone-pair p states of the valence band and empty antibonding states, while the optical gap, E_g^{opt}, could be taken as an energy of transition from the vicinity of the top of filled lone-pair p states of the valence band to the vicinity of the bottom of the antibonding states. Hence, the observed quantitative correspondence in the changes of E_0 and E_g^{opt} has a reasonable physical meaning.

The dispersion energy, E_d, obeys the empirical relation [15,16]

$$E_d = \beta N_c Z_a N_e, \tag{6}$$

where N_c is the coordination number of the cation nearest-neighbour to the anion, Z_a is the formal chemical valency of the anion, N_e is the total number of valence electrons (cores excluded) per anion and $\beta = 0.37 \pm 0.04$ eV for covalent crystalline and amorphous materials. According to Wemple [16], and before drawing any conclusion about the coordination number, we propose the following relationship

$$E_d^v/E_d^e = (\rho^v/\rho^e)(N_c^v/N_c^e), \tag{7}$$

where ρ is the mass density (we could instead use the film thickness), and v and e refer to the virgin and exposed films, respectively. Moreover, we now have to take into account the physical photodensification due to void collapse (in the case of thin evaporated films deposited at oblique angles of incidence, a 'shadowing' effect of the material on the substrate for incoming evaporant atoms leads to the formation of a columnar-growth morphology) [21], found in the present glassy composition, $\approx 8\%$. Then, if we make use of Eq. (7), we find that the difference between N_c, before and after exposure, is less than 4%. Therefore, the small change in N_c indicates insignificant change in the average coordination number in the short-range region. Additionally, E_d calculated from Eq. (6) ($N_c = 4$; $Z_a = 2$; $N_e = (4 \times 1 + 6 \times 2)/2 = 8$) was found to be 23.7 ± 2.6 eV; that is, allowing the corresponding scatter in β, E_d is close to the experimental E_d (the difference is about 1%). On the other hand, regarding the light-induced change in $n(0)$, we propose that this change, a decrease of $\approx 7\%$, mainly arises from the change in the Tauc gap E_g^{opt}, an increase of $\approx 28\%$ (as per the well-known empirical relation $n^4(0)E_g^{opt}$ = constant ≈ 58 eV, in this particular case).

We now discuss the possible nature of the vibrational bands found in GeS_2 glass films. It should be noted that the results of these IR measurements are in agreement (< 3%) with those reported by Tichý et al. [22,23] for normally-deposited $Ge_{30}S_{70}$ and $Ge_{35}S_{65}$ glass films. Concerning the 870 cm^{-1} band, in crystalline and vitreous GeO_2, the main feature in the IR spectra is the absorption band due to Ge–O–Ge stretching at about 878 cm^{-1} [24]. Hence, we assume that the vibrational band at ≈ 870 cm^{-1} is due to the GeO_2 species – a product of the photo-oxidation of the film. The origin of the vibrational bands at ≈ 820 cm^{-1} and ≈ 795 cm^{-1} can also be associated with oxygen in the films. We assume that these bands are due to Ge–O–Ge stretching in entities with a mixed coordination of germanium: it is plausible to assume that an idealized entity of a photo-oxidized layer can be represented by a nine-atom cluster $S_{3-x}O_xGe{-}O{-}GeO_xS_{3-x}$, where $x = 3$ for GeO_2 and $x = 0,1,2$ for mixed coordination of Ge atoms [19]. It seems that the assignment of the vibrational band at 795 cm^{-1} to the antisymmetric-stretch motion of oxygen in $S_{3-x}O_xGe{-}O{-}GeO_xS_{3-x}$ clusters with $x \to 0$ and that at 820 cm^{-1} to a similar motion of oxygen in clusters with $x = 1$ or $x = 2$ is reasonable. Additionally, the absorption band at ≈ 670 cm^{-1} can be explained by the existence of GeO_2 entities with symmetry close to tetragonal GeO_2 [25]. Further evidence supporting this particular proposal concerning the origin of the IR band at ≈ 670 cm^{-1}, in terms of the existence of GeO_2 species, comes from X-ray diffraction (XRD) experiments. In Fig. 1 is shown part of a typical XRD-pattern for an exposed GeS_2 film. The observed Bragg peak at $2\theta = 31.75°$ is consistent with the presence of tetragonal c-GeO_2 (the corresponding d-spacing is 0.282 nm; see ASTM card 21-902). It should be pointed out that in contrast to this last result, Tichý et al. [19] have reported for normally-evaporated $Ge_{30}S_{70}$ glass films the presence of crystalline GeO_2 corresponding to the hexagonal modification.

Thus, the appearance and position of all the Ge–O–Ge vibrational bands in the IR spectra indicate the degree of photo-oxidation of the films (or, simply, the degree of oxidation, under 'normal laboratory conditions', as in the case of the unexposed 70°-GeS_2 film under analysis). Finally, the main IR feature around 370 cm^{-1} results from the Ge–S stretching vibrations [26]; in addition, the absorption band around 740 cm^{-1} could be associated with second-order processes (transverse optical modes $\approx 2 \times 370$ cm^{-1}).

The very interesting DIR spectrum shows: (i) the increase of extrinsic absorption around 670 cm^{-1} and 825 cm^{-1} due to the photo-oxidation effect, and (ii) the simultaneous decrease of absorption around 370 cm^{-1}, indicating a decrease of the Ge–S heteropolar bonds in the course of oxidation. This result shows that in the process of photo-oxidation, the matrix of the GeS_2 film experiences structural changes.

5. Conclusions

1. The radiation-induced thickness contraction effect observed in GeS_2 glass films, obtained by oblique deposition, and having a tailored columnar structure, represents a remarkable solid-state phenomenon from the standpoint of the technological applications (especially for reprographic and lithographic applications); it should be emphasized that the photo-induced optical changes are affected by the microstructure of the starting films.
2. The dispersion of the refractive index of the unexposed and exposed films can be described using the Wemple–DiDomenico single-oscillator formula. The exposure-induced changes of the single-oscillator energy (E_0), and the refractive index at $\hbar\omega = 0$ ($n(0)$), follow the change of the Tauc optical gap (E_g^{opt}); the change of the dispersion energy (E_d) follows the change of the mass density, i.e. it is mainly related to the observed photo-densification, which is due to the collapse of the gross columnar structure. Lastly, the increase of E_g^{opt} perhaps reflects the decrease of density of localized states at the band edges and an increase of the 'mean' bond energy, since new strong Ge–O bonds are formed [19].

Acknowledgements

The authors are very grateful to Dr L. Tichý (Joint Laboratory, Pardubice, Czech Republic) for many valuable discussions.

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