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Photo-induced changes in the optical properties of amorphous As–Ge–S thin films

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Changes in the transmission, absorption edge and refractive coefficient in the UV–VIS and the transmission in the IR spectrum of thin As–Ge–S films after irradiation with an argon laser with $\lambda = 488$ nm were studied. X-ray microanalysis showed that the composition of the films (with small variations) corresponded to that of the initial substances. Films with a defined concentration of the elements could also be deposited by evaporation of As_2S_3 and GeS_2 from two sources. The optical properties of thin films prepared by thermal evaporation, flash evaporation and coevaporation from two crucibles have been compared. It was found that depending on the component content, both photodarkening and photobleaching coatings in a wide region of λ can be obtained in thin As–Ge–S films. The results have been explained from the viewpoint of the photostructural changes in chalcogenide layers.

1. Introduction

The development of contemporary semiconductor techniques, integral optics, and opto- and microelectronics requires the creation of materials with defined parameters. Recently, new promising applications in the electron industry have been observed as a result of investigations of the properties of thin films of some chalcogenide glasses [1–6]. The changes occurring in thin films of the system As–Ge–S as a result of light exposure have also been the object of numerous studies [7–12]. The data have shown that the optical properties depend on the ratio between the components [7–10], and the solubility is strongly influenced by the addition of some metals such as gallium, tellurium and indium [11, 12]. A change in the preparation conditions of thin-film coatings can lead to the formation of films characterized by different structural states and physico-chemical properties. Therefore, a study of the laws governing structural formation and crystallization transitions of the films, depending on their composition, is a reliable way for developing a scientifically grounded technology for thin films.

It was the aim of this work to follow the influence of the deposition method of thin films of the system As–Ge–S on the composition and structure of the films obtained and the associated changes in their optical properties.

2. Experimental procedure

The investigations were made using vitreous semiconductors of the system As–Ge–S containing different contents of the components over a wide range of concentrations. The initial substances were prepared at the Physico-Technical Institute "A. F. Yoffe", St. Petersburg, and the University of Chemical Technology, Pardubice, by melting exactly known quantities of arsenic, germanium and sulphur with purity better than 99.999%, in a quarz ampoule welded in a vacuum of 10^{-3} Pa. The specific conditions of synthesis (maximal temperature, duration of thermal treatment and cooling rate), were chosen depending on the specific composition of the synthesized substance.

The evaporation was carried out from a molybdenum crucible at a vacuum of 6×10^{-4}–8×10^{-4} Pa, and the substrates were at room temperature, mounted on a rotating calotte. The evaporation rate was controlled by changing the intrinsic frequency of oscillation of a piezocrystal during deposition of the evaporation substance.

Three evaporation methods were used.

1. Evaporation of a pre-synthesized bulk sample from one crucible at a rate of 0.5–0.6 nm s^{-1}.
2. Flash evaporation of doses of a pre-synthesized composition from a molybdenum crucible heated to 700–800 °C.
3. Simultaneous evaporation of As_2S_3 and GeS_2 from two crucibles. Different compositions of the ternary system As–Ge–S were obtained by varying the ratio of the evaporation rates of each substance.

Thin films of As–Ge–S with eight different ratios of the components forming two crossing series were studied:

1. a series with constant arsenic content: $As_{10}Ge_xS_{0-x}$, where $x = 25$, 30 and 35,
2. a series with constant sulphur content: $As_yGe_{40-y}S_{60}$, where $y = 5$, 10, 20, 30 and 40.

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The thickness of the films was 0.4 – 1.0 µm and was measured with a profilometer Talystep. The composition of the thin films obtained by different deposition methods and coated on graphite and soda – lime glass was determined in a scanning electron microscope with an X-ray microanalyser Jeol Superprobe 733 (Japan). The experiments were performed at an electron accelerating voltage of 25 keV and a current of 1 – 3 nA at dead time of detector electronics 16% – 20% and a scanning time for each spectrum of 100 – 150 s. The accuracy was of the order of 0.5 – 1.5 at %. The optical transmission of thin films about 1.0 µm thick was measured using a UV–VIS spectrophotometer (Hewlett Packard, USA) and a Perkin – Elmer 684 spectrophotometer in the IR region. To study the changes occurring in the optical properties, the films were exposed to light with an argon laser with an intensity of 80 mW cm^{-2} at a wavelength of 488 nm.

3. Results and discussion

3.1. Dependence of the composition of thin amorphous films on the evaporation method

To overcome the influence of the substrates, the samples were prepared in two different ways:

1. coatings with great thickness, > 2.3 – 2.8 µm, were obtained on glass substrates;
2. the amorphous films with practically usable thickness were coated on graphite substrates, preliminary treated to reduce possible contamination from other elements.

Table I shows the mean data for the element content in films 2.3 – 2.8 µm [1] and 0.3 µm [2] thick deposited by thermal evaporation of preliminary synthesized compositions on to glass and graphite substrates, respectively.

The coatings on graphite showed more accurate reproduction of the initial composition, complete homogeneity and an almost total lack of structure compared to the films with greater thickness deposited on glass substrates. It should be taken into consideration that the graphite surface is quite fragile, so polishing and consequent chemical treatment to remove the possible contaminations could affect the smoothness of the surface. In these cases, with rare exceptions, the chalcogenide coating is completely independent of the grains, and the composition remains homogeneous. As seen, deviations of the composition do not exceed ± 1.0 at %, i.e. they are within the instrumental accuracy. Greater fluctuations were seen only in the compositions $As_{10}Ge_{35}S_{55}$ and $As_{30}Ge_{10}S_{60}$.

A satisfactory result was also observed when the synthesis of the chalcogenide ternary films was carried out by evaporation of As_2S_3 and GeS_2 from two crucibles. A problem was the accurate setting and control of the evaporation rates of the two substances. The films obtained showed stability and homogeneity of the composition, though for the reasons above, the composition sought was not reproduced quite accurately. Naturally, the restrictions associated with the defined compositions of the two substances used for evaporation should be borne in mind. By maintaining the evaporation rates of $As_{40}S_{60}$ and $Ge_{33.3}S_{66.7}$ in different ratios, the expected thin film composition was $As_{11.4}Ge_{26.1}S_{62.5}$, $As_{21.0}Ge_{17.4}S_{61.6}$ and $As_{31.0}Ge_{8.5}S_{62.5}$.

Flash evaporation led to the most accurate reproduction of the composition of the bulk material in the deposited thin films. It was ± 0.2 at % for $As_{40}S_{60}$ and $Ge_{33.3}S_{66.7}$, and ± 1 at % for As–Ge–S layers.

3.2. Influence of the composition and method of deposition on the optical properties of thin As–Ge–S films

The replacement of arsenic in the thin As_2S_3 films with germanium is of interest in studying the photostructural changes after illumination as well as for obtaining inorganic photoresist with a reduced arsenic content. The photo-induced changes in the optical properties of thin As–Ge–S films were studied in the way described above, exposure was made to an argon laser at $\lambda = 488$ nm (defocused beam with an intensity of 80 mW cm^{-2}). Films about 1.0 µm thick were deposited on optical glass BK-7 for determination of the refractive index and on polyethylene for defining the IR spectra. In some cases the shift of the absorption edge was also followed on thinner films (0.25 – 0.50 µm). The exposure time to saturation (i.e. the time during which the absorption edge did not

TABLE I Average data for the element content in a bulk material and thin films with thickness (1) 2.3 – 2.8 µm and (2) 0.3 µm obtained on glass and graphite substrates, respectively

Composition	Bulk sample			Thin film (1)			Thin film (2)		
	As	Ge	S	As	Ge	S	As	Ge	S
$As_5Ge_{35}S_{60}$							5.0	34.6	60.4
$As_{10}Ge_{30}S_{60}$	9.2	35.4	55.4	10.4	34.2	54.4	10.2	30.0	59.8
$As_{20}Ge_{20}S_{60}$	20.7	19.4	59.9	23.9	22.6	53.5	20.7	19.2	60.1
$As_{30}Ge_{10}S_{60}$							31.1	10.4	58.5
$As_{10}Ge_{25}S_{65}$	10.1	26.4	63.5	14.9	40.6	40.5	10.1	25.4	64.5
$As_{10}Ge_{35}S_{55}$	11.2	36.3	52.7	10.6	36.6	50.4	9.4	34.3	56.3
$As_{40}S_{60}$	40.8		59.2	41.2		58.8			
$Ge_{33}S_{66}$		34.9	65.1		33.4	66.6		34.4	65.6

change) was experimentally established for all compositions.

The results of the X-ray analysis performed showed that the bulk samples as well as the evaporated As–Ge–S layers are amorphous. The surface morphology of thin films deposited by thermal evaporation of pre-synthesized compositions is characterized by a very low grain contrast. The latter is considerably increased in samples prepared by co-evaporation of $As_{40}S_{60}$ and $Ge_{33.3}S_{66.7}$ from two crucibles.

Fig. 1 shows the change in transmission of thin films of the system $As_xGe_{40-x}S_{60}$ $(5 \leqslant x \leqslant 40)$ in the region 350–650 nm before and after exposure to light with $\lambda = 488$ nm. It is seen that for all films with constant sulphur content (60 at %) and with the presence of germanium in the coating, a shift of the absorption edge to the short wavelength of the spectrum is observed. The shift increases with increasing arsenic content, reaches a maximum for films with composition $As_{20}Ge_{20}S_{60}$, then decreases and then again reaches high values, but is already directed to long wavelengths for films of $As_{40}S_{60}$ (Fig. 2).

The transmission change in another system studied ($As_{10}Ge_yS_{90-y}$, $25 \leqslant y \leqslant 35$) is given in Fig. 3. With increasing sulphur content at constant arsenic concentration (10 at %), one observes a decrease of photobleaching. This effect is analogous to the system As–S where light exposure provokes considerably smaller photostructural changes in films with composition $As_{40}S_{60}$. It seems that the excess sulphur hinders the transformation of the film bonds. Quite interesting results were obtained for the change in transmission in thin films prepared by evaporation of As_2S_3 and GeS_2 from two crucibles (Fig. 4). Here, as already mentioned, the sulphur concentration remains almost constant (61.5–63.0 at %). With increasing arsenic content, the effect of photobleaching decreases, and for $As_{31}Ge_{8.5}S_{60.5}$, obtained by evaporation at a ratio of As_2S_3 to GeS_2 of 3:1, photodarkening is already observed. There is a difference in the behaviour of thin films obtained from two crucibles and films with similar composition coated by thermal evaporation of a pre-synthesized substance. Obviously, the transformation of the bonds As–As and S–S into As–S is of decisive importance for photostructural changes to proceed in such films.

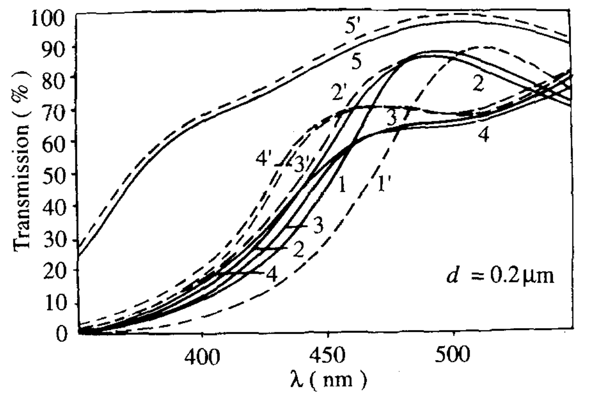

Figure 1 Transmission spectra of (1–5) unexposed and (1'–5') exposed thin films of the system $As_xGe_{40-x}S_{60}$; (1, 1') $As_{40}S_{60}$, (2, 2') $As_{30}Ge_{10}S_{60}$, (3, 3') $As_{20}Ge_{20}S_{60}$, (4, 4') $As_{10}Ge_{30}S_{60}$ and (5, 5') $Ge_{33.3}S_{66.7}$.

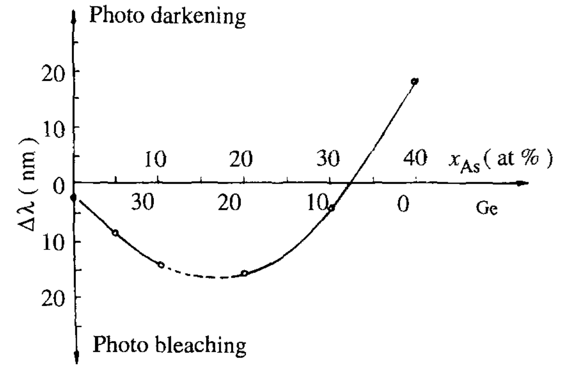

Figure 2 Dependence of the absorption edge shift on the As (Ge) content in the $As_xGe_{40-x}S_{60}$ films.

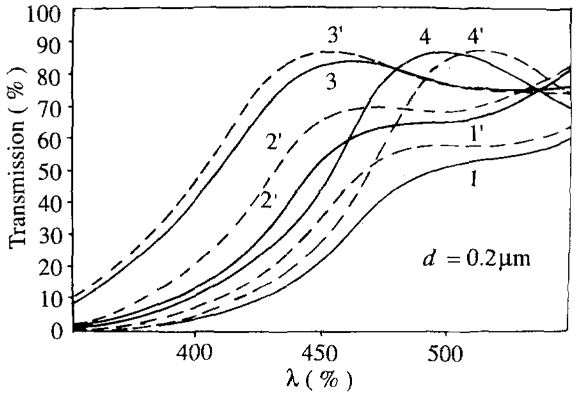

Figure 3 Transmission spectra of (1–4) unexposed and (1'–4') exposed thin films of the system $As_{10}Ge_yS_{90-y}$ $(25 \leqslant y \leqslant 35)$; (1, 1') $As_{10}Ge_{35}S_{55}$, (2, 2') $As_{10}Ge_{30}S_{60}$, (3, 3') $As_{10}Ge_{25}S_{65}$ and (4, 4') $As_{40}S_{60}$.

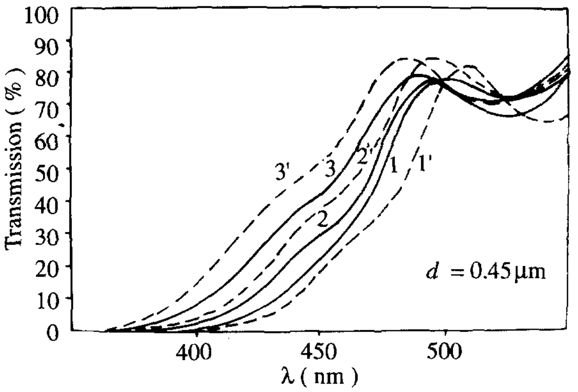

Figure 4 Transmission spectra of (1–3) unexposed and (1'–3') exposed thin films of the system As–Ge–S obtained by evaporation of As_2S_3 and GeS_2 from two crucibles; (1, 1') $As_{31}Ge_{8.5}S_{60.5}$, (2, 2') $As_{21}Ge_{17.4}S_{61.6}$ and (3, 3') $As_{11.4}Ge_{26.1}S_{62.5}$.

The refractive index, *n*, and the film thickness were calculated using the method of Swonepoel [13] and a special computer program developed by Konstantinov [14]. The method allows the calculation of *n* for the substance if the position of the interference extremes are known in the interference picture obtained by building the transmittance spectrum in the ultraviolet and visible spectrum. Fig. 5 shows the

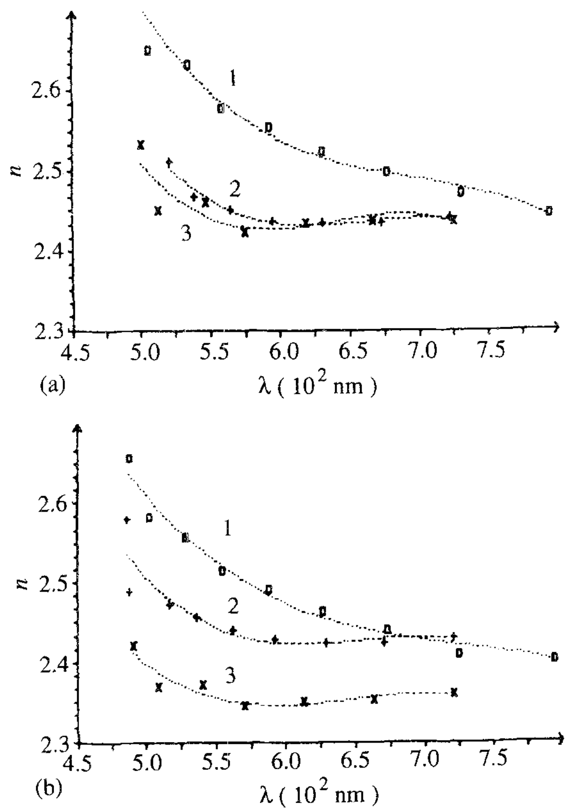

Figure 5 Refractive index dispersion of $As_xGe_{40-x}S_{60}$ amorphous films in n against λ coordinates: (a) unexposed; (b) exposed. (1) $As_{20}Ge_{20}S_{60}$, (2) $As_{30}Ge_{10}S_{60}$ and (3) $As_{10}Ge_{30}S_{60}$.

dependence $n = f(\lambda)$ for (a) unexposed and (b) exposed thin films of the system $As_xGe_{40-x}S_{60}$ prepared by thermal evaporation of pre-synthesized composition. The accurate concentration of the elements in the coatings can be seen in Table I. Obviously, after exposure, the refraction coefficient decreases for all three compositions, the decrease being highest for $As_{10}Ge_{30}S_{60}$ ($\Delta n = 0.12$ for $\lambda = 488$ nm). This corresponds to the photobleaching of the samples with the compositions indicated (Fig. 1). The highest values for n are obtained for thin films with composition $As_{20}Ge_{20}S_{60}$. This confirms the result of Vateva *et al.* [8] showing that n decreases monotonically with increasing germanium concentration from 19 at % to 28 at %. The results for Δn obtained for the two boundary cases are also in good agreement.

The values of $n = f(\lambda)$ for thin films of the system As–Ge–S obtained by evaporation of As_2S_3 and GeS_2 from two crucibles (Fig. 6) are situated between those for $As_{40}S_{60}$ and $Ge_{33.3}S_{66.7}$ from which the ternary system is formed. The films containing germanium are bleached after exposure and the refractive index for the composition $As_{21}Ge_{17.4}S_{61.6}$ (curve 4) decreases considerably ($\Delta n = 0.06$). This is almost equal to the decrease in Δn for $As_{40}S_{60}$ films undergoing photodarkening. For the films with composition $As_{31}Ge_{8.5}S_{60.5}$ obtained by evaporation, subjected to photodarkening after exposure, the refractive index strongly increases at $\lambda = 488$ nm, $\Delta n = 0.1$ (curve 5). Obviously the as-deposited thin films represent an undefined mixture of different structural units (GeS_4, As_4S_4, AsS_3, As_2S_3, S, As) because no monotonic change of n as a function of λ is observed.

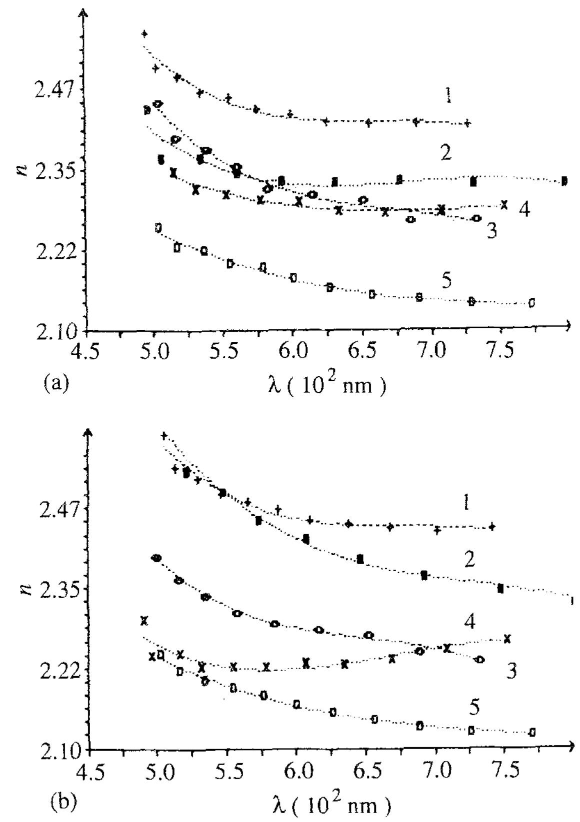

Figure 6 Refractive index dispersion of amorphous As–Ge–S thin films, deposited by co-evaporation of As_2S_3 and GeS_2; (a) unexposed and (b) exposed. (1) $As_{40}S_{60}$, (2) $As_{31}Ge_{8.5}S_{60.5}$, (3) $As_{11.4}Ge_{26.1}S_{62.5}$, (4) $As_{21}Ge_{17.4}S_{61.6}$ and (5) $Ge_{33.3}S_{66.7}$.

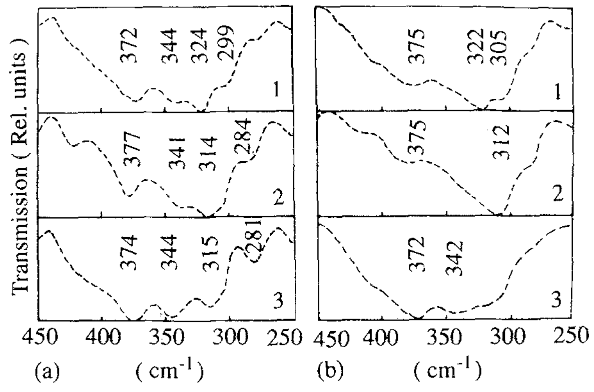

Figure 7 Infrared spectra of (a) unexposed and (b) exposed As–Ge–S thin films: (1) $As_{21}Ge_{17.4}S_{61.6}$, (2) $As_{31}Ge_{8.5}S_{60.5}$ and (3) $As_{11.4}Ge_{26.1}S_{62.5}$.

The assumption made is supported by the IR spectra in the region 600–200 cm^{-1} for some compositions of the ternary system obtained by evaporation from two crucibles (Fig. 7). The observed peaks in the spectra of the unexposed samples (a), are characterized by the following molecular structures and bonds: GeS_2 (Ge–S), 377–8 cm^{-1}; GeS_4 (Ge–S), 372 cm^{-1}; (Ge–As), 284 cm^{-1}; As_4S_4 (As–As), 380, 344 cm^{-1}; AsS_3 (As–S), 315 cm^{-1}. It is seen that after exposure to saturation (b), the peak at 284 cm^{-1} decreases for layers with composition $As_{21}Ge_{17.4}S_{61.6}$. This change is very much more clearly expressed for layers with composition $As_{31}Ge_{8.5}S_{62.5}$, the peak characteristic

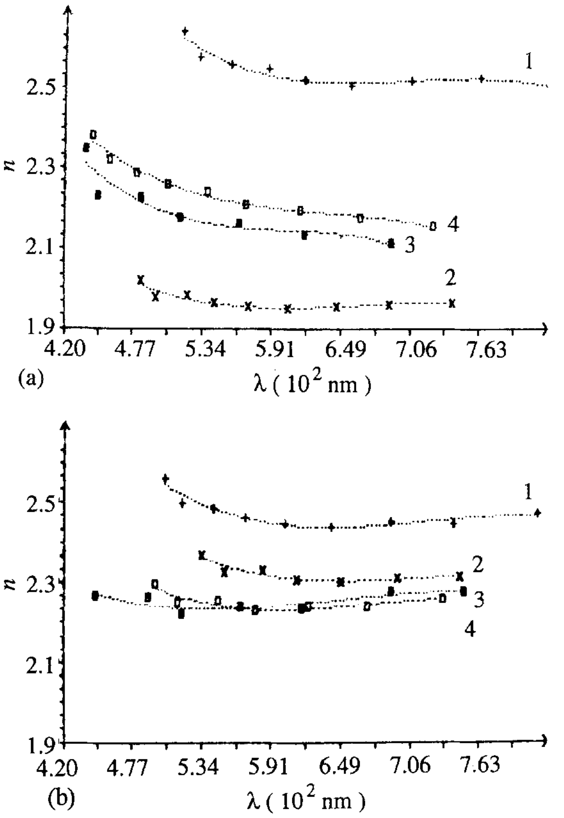

Figure 8 Refractive index dispersion of amorphous (1) $As_{40}S_{60}$, (2) $As_{20}Ge_{20}S_{60}$, (3) $Ge_{33.3}S_{66.7}$ and (4) $As_{10}Ge_{25}S_{65}$ thin films obtained by flash evaporation; (a) unexposed and (b) exposed.

for the bonds (As–S) being even more evident at 312 cm^{-1} [15]. The behaviour of layers with an evaporation rate ratio of As_2S_3/GeS_2 of 1:3 is more difficult to explain. The peak at 284 cm^{-1}, characteristic for the bonds (Ge–As) disappears, but at the same time the peak at 315 cm^{-1}, characteristic of the bonds (As–S), also disappears. The peak at 372 cm^{-1} is most clearly expressed which is due to the bonds (Ge–S) and the composition GeS_2. It seems that in this case the effect of transitions in GeS_2 is prevailing.

The change of the refractive index $n = f(\lambda)$ in four of the compositions studied, obtained by flash evaporation ($As_{40}S_{60}$, $Ge_{33}S_{67}$, $As_{20}Ge_{20}S_{60}$ and $As_{10}Ge_{25}S_{65}$) is shown in Fig. 8. The composition of the two ternary systems confirms the bleaching of the films observed up to this point, and the decrease, Δn, is drastic for the $As_{20}Ge_{20}S_{60}$ films (more than 0.2) and visualizes the greatest change occurring after exposure of the thin layers with the compositions studied. Although it is expected that flash evaporation would lead to the obtaining of films with smaller disorder of the structural units and more weakly expressed photostimulated changes, for $As_{40}S_{60}$ the increase of Δn is greater compared to the films obtained by thermal evaporation ($\Delta n_1 = 0.12$ for flash evaporation and $\Delta n_2 = 0.04$ for thermal evaporation). It seems that the higher deposition rate hinders the denser arrangement of the film components, and the greater internal free spaces favour the changes due to light exposure.

4. Conclusions

Our results show that the widely accepted concepts for photobleaching of the films after exposure are confirmed for all films of the ternary system studied, regardless of the method of coating. The only exception observed is for the composition $As_{31}Ge_{8.5}S_{61.5}$ synthesized by evaporation of the coating components from two separate crucibles. The assumption of Tanaka [16] that for the ternary As–Ge–S system, the photo-induced structural changes are most strongly expressed for compositions with coordination value $z = 2.6-2.7$ is confirmed. During evaporation of pre-synthesized compositions the films bleach and n decreases. The $As_{31}Ge_{8.5}S_{60.5}$ films obtained by evaporation of As_2S_3 and GeS_2 from two crucibles exhibit interesting properties: they photodarken, n increases and the change of Δn reaches a comparatively high value. The results show that due to light exposure, some of the films undergo considerable changes in their optical properties. The great changes of n obtained allows a certain composition to be used as media for irreversible recording as well as for anti-reflective protective coatings. If a developer is found to visualize these changes, i.e. to make the solubility selective, it can be expected that an inorganic photoresist with reduced arsenic content can be developed.

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References

1. J. S. BERKES, S. W. ING, W. J. HILLEGAS Jr, *J. Appl. Phys.* **42** (1971) 4908.
2. J. P. de NEUFVILLE, S. C. MOSS and S. R. OVSHINSKY, *J. Non-Cryst. Solids* **13** (1973/74) 191.
3. K. TANAKA, *Appl. Phys. Lett.* **26** (1975) 243.
4. A. YOSHIKAWA, O. OCHI, H. NAGAI and Y. MUZUSHIMA, *Appl. Phys. Lett.* **29** (1976) 667.
5. K. PETKOV, PhD thesis, Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences (1988).
6. N. TOHGE, M. KIMOTO, T. MINAMI and M. TANAKA, *Jpn J. Appl. Phys.* **19** (1980) 213.
7. L. TICHY, H. TICHA, L. BENES and J. MALEK, *J. Non-Cryst. Solids* **116** (1980) 206.
8. E. VATEVA, P. MINKOV, E. SCORDEVA, D. ARSOVA and M. NIKIFOROVA, *ibid.* **90** (1987) 481.
9. GAN FUXI, MAO XILAI, WANG HAO and YANG PEIHONG, *ibid.* **56** (1983) 303.
10. YOSHIRO OHMACHI and TAKEO IGO, *Appl. Phys. Lett.* **20** (1972) 506.
11. E. VATEVA, M. NIKIFOROVA and E. SCORDEVA, *J. Non-Cryst. Solids* **77–78** (1985) 1133.
12. C. RAPTIS and Z. G. IVANOVA, *J. Appl. Phys.* **64** (1988) 1.
13. R. SWANEPOEL, *J. Phys.* **E16** (1983) 1214.
14. I. KONSTANTINOV, private communication (1989).
15. K. PETKOV, M. VLCEK and M. FRUMAR, *J. Mater. Sci.* **27** (1982) 3281.
16. K. TANAKA, *Phys. Rev. B* **39** (1989) 1270.

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