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Photo- and thermo-induced changes in the properties of thin amorphous As–S films

K. PETKOV
Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria
M. VLCHEK, M. FRUMAR
University of Chemical Technology, 53210 Pardubice, Czechoslovakia

Changes in transmittance, refractive index, transmissivity in the infrared spectral region, and activation energy of the dissolution process were studied for thin films of the system As_xS_{100-x} ($28.6 \leqslant x \leqslant 45$) as they result from illumination and annealing at temperatures of $\sim T_g$. It is assumed that the irreversible changes occurring in the layers after treatment are accompanied by an increase in the concentration of As–S bonds. This leads to an increase in dissolution rate, a decrease in the activation energy of the process, and considerable changes in the absorption peaks at 370 and 310 cm^{-1} obtained by infrared spectroscopy. It is shown that the photo- and thermoinduced changes in as-deposited chalcogenide films follow identical courses. The results obtained are explained from the viewpoint of the structural changes occurring in chalcogenide films.

1. Introduction

Thin films of the system As–S are an object of systematic investigations because of the changes in physical and chemical properties which occur in samples after illumination and annealing [1–4]. These photo- and thermostimulated effects can be either irreversible or reversible. The photostructural changes are interpreted as resulting from a change in the local configurations of binding induced by light [5, 6]. If sufficiently large numbers of bonds are changed, it is possible to expect commensurate changes in the infrared spectra of the exposed samples. The literature reveals a difference between the spectra of as-deposited $As_{40}S_{60}$ films and the spectra of samples subjected to annealing or illumination [7–10].

A number of papers [11–16] have shown that the changes in the dissolution rates of the layers after exposure allow the development of inorganic photoresists. The variation in activation energy of the process of dissolution of thin $As_{40}S_{60}$ films, in an alkaline solution and in the presence of surfactants, has been studied and an attempt has been made to explain the observed considerable decrease in the dissolution rate of unexposed layers.

Regardless of the numerous results reflecting the changes in the optical and physico-chemical properties of thin As–S films, it is difficult to obtain a simple explanation because all the properties of the layers (absorption edge, infrared spectra, dissolution rate, selectivity of dissolution) are dependent on the conditions and method of layer preparation.

It is the purpose of this paper to study the changes in activation energy of the dissolution process of thin As_xS_{100-x} films ($28.6 \leqslant x \leqslant 45$) after illumination or annealing at a temperature around T_g, and to connect these variations with the changes in the optical properties of the layers.

2. Experimental procedure

Bulk samples were prepared by melting high-purity (5 N) elements in evacuated quartz ampoules for 6–12 h at a temperature of 700–900 °C without oxygen introduction. X-ray diffraction (XRD) showed that the ingots were amorphous, with partial presence of a crystal phase only for the composition $As_{45}S_{55}$. Thin amorphous films were prepared by thermal evaporation of bulk samples of As_xS_{100-x} from Mo crucible ($p = 6.10^{-4}$ Pa, deposition rate 3–5 Å s^{-1}) on soda-lime glass substrates, BK-7 or quartz and polyethylene (to record the transmission in the infrared region (Sahatchieva and Petkov, personal communication). According to the chemical analysis of the layers, their composition is almost the same as that of the corresponding bulk material [16]. Optical transmittance measurements were carried out using a UV–VIS spectrophotometer (Specord M-40, Carl Zeiss Jena, Germany) in the short-wavelength edge region, and a Perkin Elmer 684 spectrophotometer connected online with a data station 3600 in the infrared region. The process of dissolution was studied with 0.3-μm-thick layers, and the other experiments were performed with 1.0-μm-thick samples. Exposure was in air with a halogen lamp without an infrared filter. The energy of the falling light was 20 mW cm^{-2}.

0022–2461

The kinetics of dissolution were studied by a method based on the change in the intensity of weakly absorbing light from a He–Ne laser ($\lambda = 630$ nm) during film dissolution [17]. A solution containing 100 g l^{-1} of K_2CO_3, pH 10.5–12.5, temperature 17–42 °C, was used. The pH values were obtained by adding o-H_3PO_4 and were measured with a glass electrode G-14 with a pH meter GTE (Seibold, Austria).

3. Results

Firstly we present the results from the change of the dissolution rate of thin films of the system As–S in a solution of 100 g l^{-1} K_2CO_3 after exposure to light. Table I shows that the dissolution rate of the exposed, V_{exp}, and unexposed, V_{unexp}, areas of the films decreases with increasing the As content, and $\gamma = V_{exp}/V_{unexp}$ increases. The temperature dependence of the dissolution process was studied for various pH values, and the activation energy, E_a, during the dissolution of films with different As concentrations was determined (Table II). The activation energy of unexposed layers increases with increasing As content, and passes through a maximum for the composition $As_{42}S_{58}$ (104.5 kJ mol^{-1}). The presence of a similar maximum in the properties of the layers of the system As–S cannot be explained. This observation is not confirmed by the investigations of transmittance in the visible region and dissolution in K_2CO_3 solution. To study this phenomenon further, more precise experiments are necessary.

For the unexposed $As_{28.6}S_{71.4}$ films, rich in sulphur over stoichiometry, E_a is 51.5 kJ mol^{-1}. After exposure, E_a for all the studied samples attains equal values (about 50 kJ mol^{-1}), and the exposed and heated layers exhibit approximately equal activation energies. The existence of non-homogeneity in as-deposited As–S thin films, and the possible presence of molecules As_4S_4, leads to the necessity of higher energy for the process of dissolution. The layers rich in As have a greater quantity of such molecules, leading to an increase of E_a for unexposed layers. After exposure and annealing, E_a decreases almost twice. Exposure of the annealed films weakly influences the activation energy, which contradicts the changes registered in the absorption edge as seen below. This can be due to the fact that the calculation of E_a is made for the time of dissolution of the first 1260 A under the surface of the layers. Infrared spectra and the change of the absorption edge were taken for layers more than 1.0 µm thick.

IR transmission measurements were made between 600 and 200 cm^{-1}. A transmission spectrum of 1.0-µm-thick evaporated unexposed films of $As_{28.6}S_{71.4}$, $As_{40}S_{60}$ and $As_{42}S_{58}$ is shown in Fig. 1a. These data were obtained at 300 K; the substrate used is polyethylene. A virgin film of $As_{28.6}S_{71.4}$ clearly shows a strong peak at 312 cm^{-1} and a weak peak at 334 cm^{-1}, while the films of $As_{40}S_{60}$ and $As_{42}S_{58}$ show strong peaks at 375 and 334 cm^{-1}, and a weak peak at 310 cm^{-1}. With increasing As content in the layers, the peak at 375 cm^{-1} increases and a peak appears at 336 cm^{-1}. The existence of peaks at these wavenumbers are quite close to the peaks at 380, 340 and 314 cm^{-1} already found [7, 8, 19, 20]. Exposure of the samples leads to a considerable decrease in intensity of the peaks at 334 and 375 cm^{-1}, while the peak at 310 cm^{-1} increases and becomes dominating in the infrared transmission spectrum (Fig. 1b). These observations are consistent with the proposed optically induced change of As_4S_4 into As_4S_6 molecular units.

The optical transmissivity of thin As_xS_{100-x} layers is strongly influenced by the wavelength of illumination and the thermal history of the films (Figs 2–4). Curve 1 in Fig. 2a shows the transmissivity as a function of λ for an as-deposited, vacuum-evaporated thin film of $As_{28.6}S_{71.4}$; curve 2 is after annealing (160°C, 2 h) and curve 3 after illumination of an annealed film. In Fig. 2b, curve 1 is for an as-deposited film; curve 2 is after exposure; curve 3 after annealing the exposed sample; and curve 4 exposed once again after annealing. The optical transmission spectra in the region of the short-wavelength edge of $As_{45}S_{55}$ film are given in Fig. 3 where the curves are obtained after the same treatment as in Fig. 2.

After exposure to saturation (the time of irradiation after which no more changes in the optical properties and solubility of the films occur) and after annealing at T_g, the adsorption edge is displaced to greater wavelengths, λ, i.e. photodarkening is observed (Figs 2 and 3, curves 1–3). This effect is expressed more strongly in films with higher As content (Fig. 3). Photodarkening is more clearly observed after exposure than after annealing of the samples (Fig. 3, curves 1 and 2). This comparison is made in Fig. 4 for the composition $As_{45}S_{55}$ where curves 1 and 2 are for unexposed samples; curve 1′ for exposed film, and curve 2′ for film

TABLE I Experimental values of V_{unexp}, V_{exp} and γ for As_xS_{100-x} thin films dissolved in 100 g l^{-1} K_2CO_3 and dimethylamine.

	20 g l^{-1} dimethylamine			100 g l^{-1} K_2CO_3		
Contents	V_{exp} (nm s^{-1})	V_{unexp} (nm s^{-1})	γ	V_{exp} (nm s^{-1})	V_{unexp} (nm s^{-1})	γ
$As_{33}S_{67}$	125	40	3.1	20	10	2.0
$As_{38}S_{62}$	40	10	4.0	13.5	6	2.3
$As_{40}S_{60}$	35	5.3	6.6	10	2	5.0
$As_{42}S_{58}$	25	2.5	10.0	10.5	0.7	15.0
$As_{45}S_{55}$	5.5	0.45	12.2	6.0	0.3	20.0

$r = V_{exp}/V_{unexp}$ (arb. units)

TABLE II Activation energies of the dissolution process of thin As_xS_{100-x} films in 100 g l^{-1} K_2CO_3 solution.

	E_a(J mol^{-1})			
Contents	Unexposed	Exposed	Heated	Heated and exposed
$As_{28.6}S_{71.4}$	51.5	41.8	37.5	32.4
$As_{40}S_{60}$	84.1	46.6	40.4	48.0
$As_{42}S_{58}$	104.5	57.2	55.3	52.5
$As_{45}S_{55}$	88.7	58.7	–	–

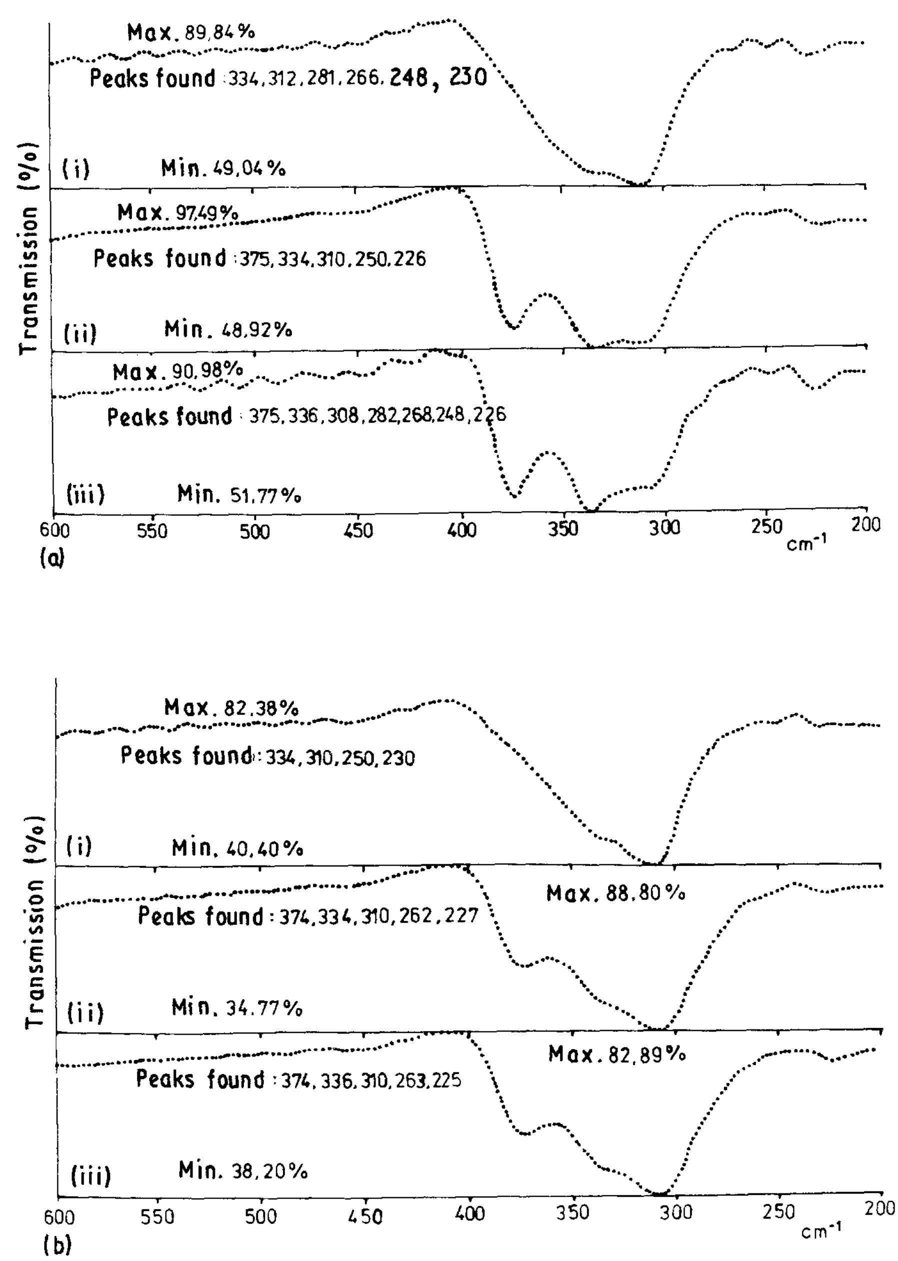

Figure 1 Infrared spectra of (a) unexposed and (b) exposed $As_{28}S_{72}$, $As_{40}S_{60}$, $As_{42}S_{58}$ films. (i) As_2S_5, (ii) As_2S_3, (iii) $As_{42}S_{58}$.

exposed after annealing. It is seen that regardless of prehistory, after exposure to saturation the optical properties of the layers do not change further. Fig. 3b shows the limits of reversivity of the processes of exposure and annealing of the samples. Layers with a composition $As_{45}S_{55}$ have reduced sensitivity which requires longer illumination times in order to obtain the changes in the absorption edge and dissolution of the films.

The spectral dependence of the transmissivity of the thin films of the system As–S in the interval 500–900 nm was followed. Using layers about 1 μm thick, it became possible to record a series of minima and maxima (curves $T = f(\lambda)$; Fig. 5) and by the method of Swanepoel [18] the refractive index and thickness were calculated. It is shown that the spectral dependence of the refraction coefficient of the layers studied is expressed by the linear dependence of the function $(n^2 - 1)^{-1} = f[(nV)]^2$.

The increase in As content in the layers leads to an increase of n both for exposed and unexposed samples (Fig. 6). This result differs from that obtained by Tanaka [6], showing the existence of an extreme in the optical properties for the composition $As_{40}S_{60}$. This is due to the influence of the conditions of layer preparation on properties. An increase in refractive index is also observed in our experiments when the films are annealed at temperatures around T_g.

The films studied show an increase in dissolution rate after exposure and annealing at T_g. This result differs from some data in the literature [21]. However, the changes observed in the transmissivity for the visible and IR spectra are in good accordance with numerous investigations. Greater photoinduced changes are observed in films with a higher As content. Photoinduced changes in the infrared vibration spectra of evaporated As_2S_3 have been reported by Strom and Martin [7] and the experimental results were interpreted in terms of the photopolymerization of As_4S_4 molecular units and sulphur chains into

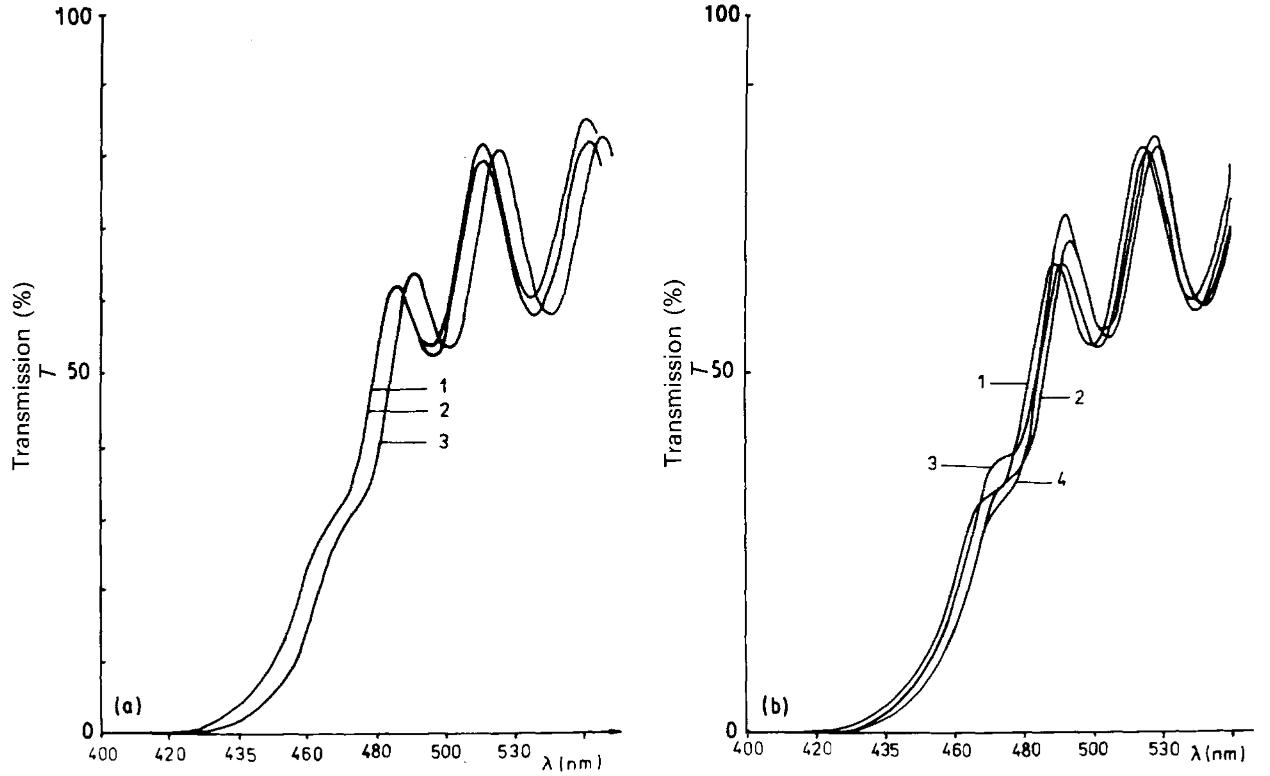

Figure 2 Optical transmission spectra in the region of the short-wavelength edge of $As_{28.6}S_{71.4}$ films. (a) 1, Unexposed; 2, annealed for 1 h at 160 °C; 3, exposed after annealing. (b) 1, Unexposed; 2, exposed; 3, annealed for 1 h at 160 °C after exposure; 4, exposed once again. Layer thickness ~ 1.0 μm.

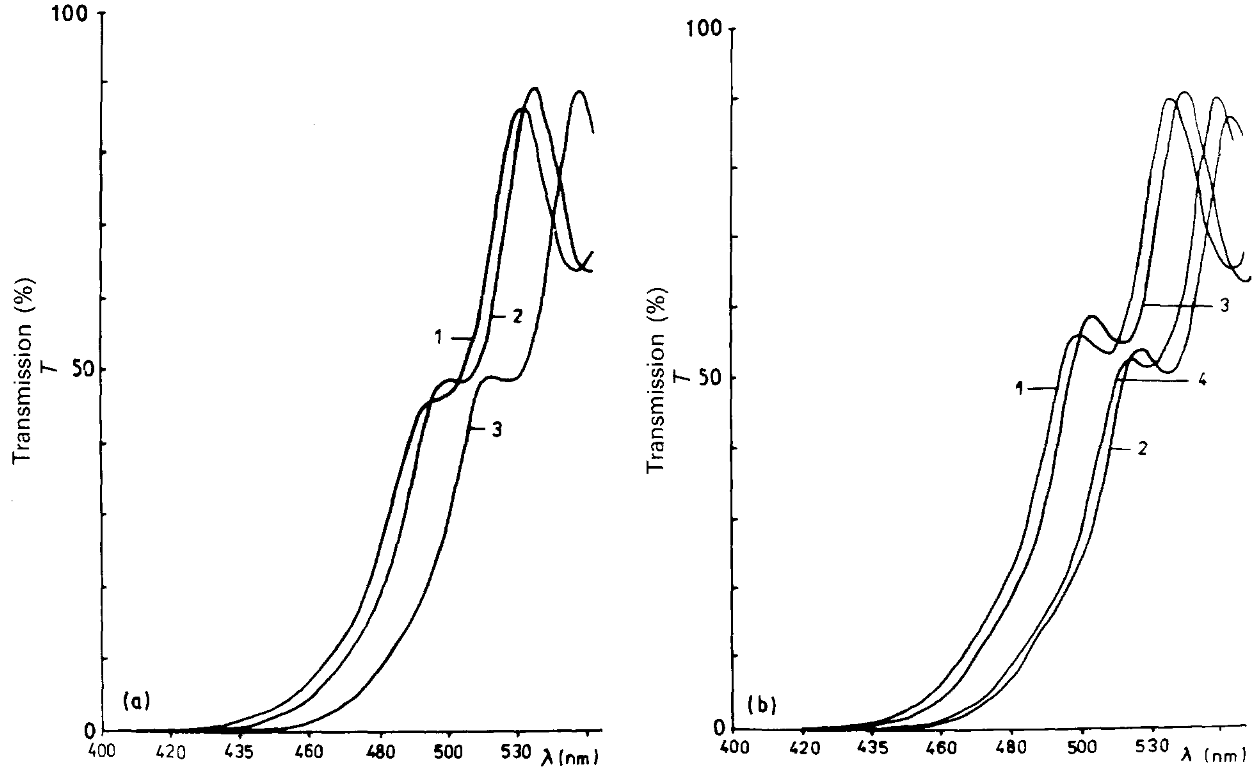

Figure 3 Optical-transmission spectra in the region of the short wavelength of $As_{45}S_{55}$ films. (a) 1, Unexposed; 2, annealed for 1 h at 170 °C; 3, exposed after annealing. (b) 1, Unexposed; 2, exposed; 3, annealed after exposure; 4, exposed once again. Layer thickness ~ 1.0 μm.

an As_2S_3 glassy network [11, 20, Doubrava and Kolobov, personal communication].

4. Conclusions

According to some authors, the as-evaporated layers of amorphous As_xS_{100-x} (for $x \geqslant 0.4$) films represent a heterogeneous mixture of structural units of the type As_2S_3, As_4S_3, As_4S_4, As_4S_8 and contain some homopolar bonds (As–As, S–S). The presence of As_4S_4 is responsible for the appearance of peaks at 375 and 336 cm^{-1} in the infrared spectra, and the AsS_3 pyramids for the peak at 310 cm^{-1}. These values are very close to those cited in the literature [7–11].

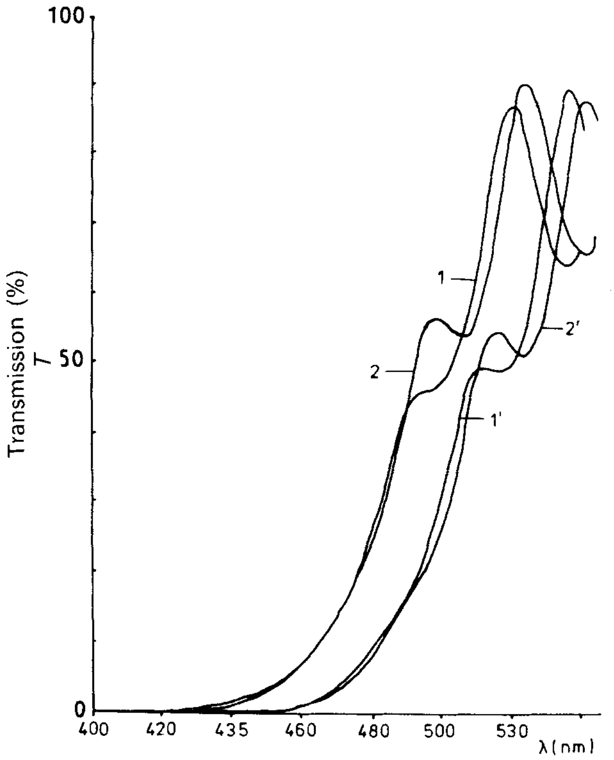

Figure 4 Comparison of absorption edge changes of $As_{45}S_{55}$ films. 1, 2, Unexposed; 1′, exposed; 2′, exposed after annealing.

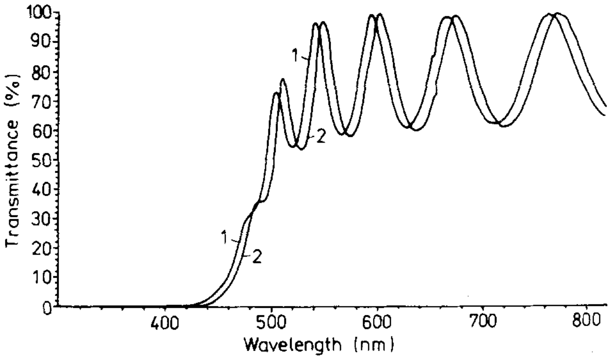

Figure 5 Typical transmission spectra of unexposed amorphous $As_{40}S_{60}$ film (1) and after exposure (2).

The dissolution of the layers containing As_4S_4 units (or As–As bonds) is therefore slow with higher activation energy, and the dissolution rate of layers without these units is higher with lower activation energy. These units are not present in samples with overstoichiometric sulphur ($x < 40$). We conclude that the dissolution of thin As_xS_{100-x} layers is controlled by the lowest process. The dissolution rates of exposed, annealed and sulphur-rich layers are therefore higher than the ones of as-evaporated or As-rich layers ($x = 40$) because of another dissolution mechanism.

The irreversible changes occurring after exposure of as-deposited films are accompanied by a density increase for the As–S bonds, i.e. a photopolymerization process of As_4S_6 molecules. This leads to an increase in refractive index and dissolution rate, a decrease in activation energy of the process, and considerable changes in the absorption peaks at 375 and 308 cm^{-1} obtained by infrared spectroscopy. The thermoinduced changes observed in the samples follow an identical course to the photoinduced changes seen in the initial treatment of the as-deposited samples.

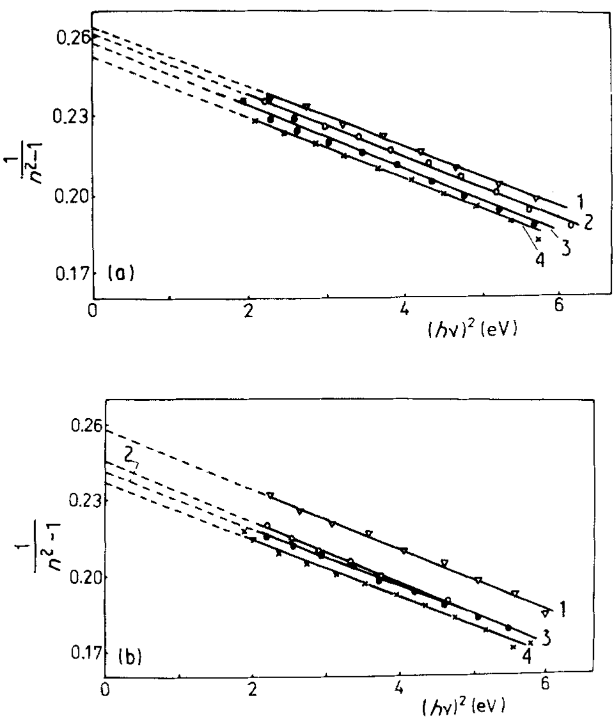

Figure 6 Refractive index dispersion of As–S amorphous films in $(n^2 - 1)^{-1}$ against $(hy)^2$ coordinates. (a) Unexposed; (b) exposed. 1. $As_{28.8}S_{71.4}$; 2. $As_{36.5}S_{63.5}$; 3. $As_{40}S_{60}$; 4. $As_{45}S_{55}$.

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