PHOTO AND THERMOINDUCED STRUCTURAL TRANSFORMATIONS IN THIN LAYERS OF ARSENIC CHALCOGENIDES

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In this paper are presented the results of a systemized study of the factors which influence the structure and relaxation of metastable phases in As-S(Se) systems in their bulk or thin film forms. A very useful method for the investigation of local structure is the method of spectroscopy of combinatory dispersion of light (CDL). Excitation of the spectrum generated by the combinatory dispersion of light was carried out using a He-Ne laser.

The results of the spectral analysis leads us to conclude that in the unbalanced glassy melt or film, $As_nS(Se)_m$ side by side with fragments of polymeric layered structures $As_nS(Se)_m$, there could also be present molecular products of dissociation which are fixed within the matrix by the quick hardening of the melt.

1. Introduction

Chalcogens of the type AsS or AsSe are known to form metastable states during the formation of glasses or amorphous films. Such metastable states may represent energy minima that are dependent upon the temperature of formation. A multiphase metastable system may form under conditions of rapid film deposition. Upon annealing, such a system may relax, and in time, form a more stable system. The final structure is dependent upon the temperature of formation as well as the concentration of chalcogen. The relaxation process can be increased by increasing the temperature and by laser irradiation. The phenomenon of thermo- and photoinduced changes in films of As-S(Se) systems is the basis for information registering.

The thermo- and photoinduced transformations which occur in amorphous chalcogenides have been studied over a number of years [1-3]. However, much concerning the elementary mechanism of the phenomenon is still not clearly understood. These materials are vitrious semiconductors (ChVS) having short range order but long range disorder. As metastable substances they are thermodynamically unstable relative to the
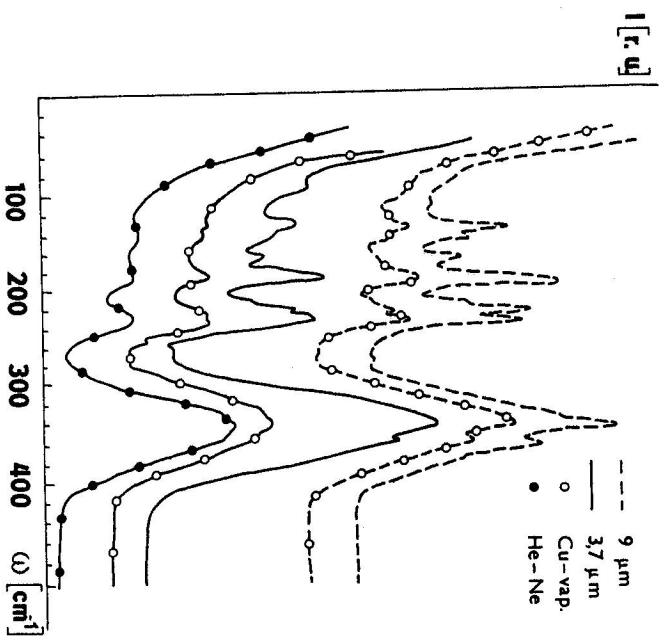
Fig. 1. CDL spectra of fresh-produced As$_2$S$_3$ films with trickness 9 and 3.7 m before (dashed line and full line) and after irradiation with Cu - vapor (- o -) and He-Ne (- • -) laser.

Legend: --- 9 μm · —— 3.7 μm · o Cu-vap. · • He-Ne

structure obtained under ideal conditions of annealing temperature and time. For this reason the characteristic parameters of ChVS materials depend a great deal upon the conditions of their production. Important production parameters are the temperature of the molten homogeneous phase, the rate of cooling (during which deposition takes place), the temperature of evaporation (T_{ev}), temperature of the substrate (T_s) and the rate of condensation (V_c) of the amorphous layers.

Below, are presented the results of our investigation into the factors which influence the structure and relaxation of the metastable phases in As-S(Se) systems in the form of bulk matter and as films.

2. Experimental Results and Discussion

The characteristics of optical absorption near the Urbah edge show a clear dependence on the temperature at which the hardening of the specimen begins (350—950°C). With increasing hardening temperature the absorption edge shifts to lower energies. Here it should be mentioned that with annealing, the absorption edge shifts to higher energies compared to specimens which have not been annealed. The change in the steepness of the Urbah edge is hardly noticeable. Variation of the optical pseudogap,
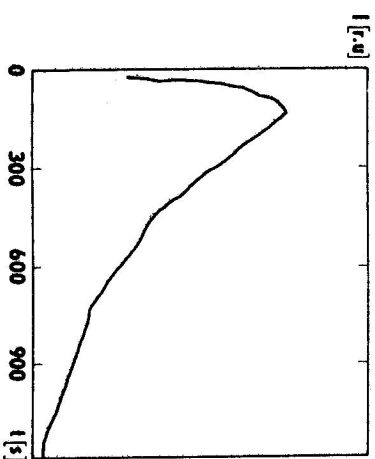
Fig. 2. I_{cat} time dependence under irradiation of fresh-produced As$_2$S$_3$ film with He-Ne laser ($\omega = 340$ cm^{-1}).
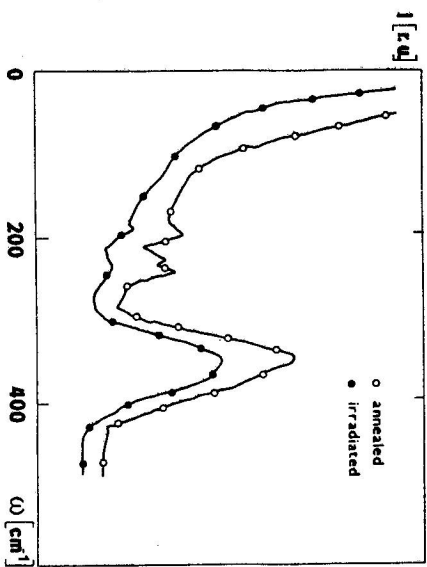

Fig. 3. Stimulated transformations of CDL spektrum of As$_2$S$_3$ films, annealed at T = 440 K during an hour (- o -) and after Ar-laser (- • -) irradiation.

Legend: o annealed · • irradiated

E_0, was defined according to the change of photon energy (with the meaning $\alpha \doteq 2.10^3$ cm^{-1}). With increasing hardening temperature, E_0 is seen to decrease for both hardened and annealed specimens As$_2$S$_3$, with considerable decrease in E_0 taking place at the T_g 800°C. The difference between energy gaps for hardened and annealed specimens is 50 meV. The same difference is noticed between E_0 of condensed films and bulky glass films. From the dependence on hardening temperature of As$_2$S$_3$ glass was found that the average value of energy gap E_0 is about 2.30 eV.

Our data indicate that specimens with $T_g > $ of 800°C are hardened from the gaseous state. This process is similar to the one in which films are produced by vacuum evaporation. The investigation shows that the pseudogap of hardened specimens increases

to 30 meV when annealing is conducted at the T_g.

It is generally recognized that the structure of freshly-produced unprocessed films differs from that of glasses of identical composition but which have been formed by cooling from the melt [2,3]. This is clearly seen from the studies utilizing As_2S_3 films.

For the investigation of local structure, the best method is the technique of spectroscopy of combinatory dispersion of light (CDL). The data for As_2S_3 are given below.

The investigated film samples were produced by thermovacuum evaporation according to the procedures described in references [4] and [5]. The thickness of the films varied from 3 to 20 μm. Annealing of the freshly-produced films was carried out at 450 K for 1-3 hours. Irradiation of the specimens was carried out using Ar ($\lambda = 0.514\mu m$), He - Cd ($\lambda = 0.440\mu m$) lasers and laser on Cu vapor ($\lambda = 0.510\mu$ m). The excitation spectrum of combinatory dispersion of light was generated using a He - Ne laser ($\lambda = 0.638\mu m$) having an irradiation density of P = 50 mW/cm². "Backward" dispersion geometry was used.

The CDL spectra freshly-produced As_2S_3 irradiated with laser on Cu vapor (P = 0.25 W/cm²) are shown in Figure 1. The sharp lines in the region of 100-250 cm⁻¹ are characteristic of spectra from amorphous, unprocessed films. These lines are explained as being due to the "presence of homopolar connections. As a result of irradiation, the general tendency of "smoothing" of the spectrum is clearly seen. The decrease of intensity of some lines (138, 169, 194, 225 cm⁻¹) and suppression of lines at 114, 169, 388 cm⁻¹ is seen. For the thin layer samples, the effect of smoothing of the spectrum results from the considerably stronger effectiveness of the irradiation. Similar CDL spectra are observed after irradiation of films using a strong (P = 104 W/cm²) He - Ne laser. It is obvious that during this process ($h\nu < E_{opt}$) excitones or localized pairs of carriers recombine without radiation and release energy to the atomic subsystem (i. e. the absorption edge, upon heating, shifts to the long wavelength region and the films become sensitized to the irradiation of the He-Ne laser.) [6]. Actually, after such irradiation, the CDL spectrum becomes very similar to the corresponding spectrum of a massive glass.

When intensely irradiated by He-Ne laser, the film heats up as indicated by the resonance strengthening of the intensity of the CDL (I_{cd}) (Fig. 2). The growth of the I_{cd} at the beginning of the irradiation is explained by the gradual shift of the absorption edge towards the long wavelength region at the expense of the heating maximum. This means that the I_{cd} is reached when the E_{opt} gets closer to the irradiation energy (resonance) of the He-Ne laser. The above mentioned resonance behavior of the I_{cd} is seen in the whole frequency range of the CDL spectrum of freshly-produced As_2S_3 films.

A smooth CDL spectrum is characteristic of an annealed film. For example, in Figure 3, we see the CDL spectrum of an As_2S_3 film annealed at T = 440 K for one hour. Under such conditions, we conclude that some annealing has occured as indicated by the lines at 220 cm⁻¹. It is understandable that irradiation of such films should produce some change in the spectrum. In reverse cycles (irradiation of films annealed for 3 hours at T = 450 K) changes in the CDL in the 100-500 cm⁻¹ frequency range is not observed. It must be mentioned that there exists only a small difference in the spectra of the irradiated and not-irradiated films in the region of low frequency ($\omega < 100$ cm⁻¹).

3. Conclusions

From these results we can state that in reverse cycles of irradiation-annealing of As_2S_3 films (innitially annealed at $T \doteq T_g$), a change in the As-S bond concentration does not take place because of the stability and tendency toward cluster formation. The only structural changes which take place are deformation of the bonds in the structural units. If annealing takes place at high temperature (T = 480 K), extensive structural deformation of the polymeric network is possible. These transformations are more favorable for As_4S_4 and As_4S_3 molecules. Although such changes are reversed in the following annealing steps, they are not the well-known reversible photostructural changes found in many chalcogenide glassy semiconductors. They are phase changes of a certain type which are characteristic of As-S compounds.

In films based on As-Se, structural changes are less evident. The reason for such "insensitivity" to the conditions of formation may be the lower stability of the As_4Se_4 molecules. They possibly undergo spontaneous relaxation.

From the above results we come to the conclusion that in an (unbalanced) glassy melt or film of ordered $As_nS(Se)_m$ in a matrix of polymeric-layered structure, can be found molecular products of dissociation fixed by the quick hardening of the film matrix. Therefore, the initial structure of glassy $As_nS(Se)_m$, or its thin films, is conditioned by the regime of evaporation. It is the result of the internal nature of the disordered materials. These regions of disorder may be short range or middle range and they occur as metastable states in the glassy materials. These states, under the influence of external factors (heating or irradiation) can relax from one into another.

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