

Mechanism of photoinduced optical effects in amorphous As_2S_3

Part 1: Irreversible changes of optical properties

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1. Introduction

Amorphous chalcogenide semiconductors (AChS) invented by B.T. Kolomiets and N.A. Goryunova nearly 40 years ago are unique solid state materials characterised by an effect of photoinduced changes of their physical properties: optical absorption in fundamental edge region [1,2], refractive index [3], microhardness [4], acid and alkali solubility [5], softening temperature [6], thickness [7], ultrasonic velocities and elastic constants [8], spectral dependence of photoconductivity [9], Raman scattering spectrum [10], ESR signals of dope ions and its own structural fragments [11,12], Mössbauer absorption of Sn^{119} radioisotope [13] and so on. These changes (first of all, changes of optical properties) are widely used in optical systems of information recording based on AChS.

It is established that photoinduced optical effects in AChS are irreversible if observed at the photoexposure of fresh-evaporated thin films by absorbed light, and reversible if observed in the second and all subsequent cycles of photoexposure and thermal annealing at the temperature near glass transition point [1,2,14–16]. The microstructural mechanism of irreversible photostructural transformations (PhST) is connected with switching of "wrong" homopolar chemical bonds created at the extremal conditions of thermal deposition of AChS into heteropolar ones, which have the highest energy of dissociation [17]. Thus, in fresh-evaporated amorphous $a-As_2S_3$ over 20% of homopolar chemical bonds can exist [15]. While some models describing irreversible PhST have been discussed yet, the models based on charged diamagnetic defects formation in AChS [14,18] are studied insufficiently. However, it was confirmed in our previous papers [19–23] that this approach is quite suitable for interpretation of wide range of induced effects.

2. Experimental

Thin layers of $a-As_2S_3$ were deposited by vacuum evaporation ($10^{-5} \div 10^{-4}$ Torr) on plates of radiation-modified polyethylene having softening temperature over $160 \div 170^\circ C$. Powder of bulk As_2S_3 glass of 99,999% purity was used as raw material for deposition. Thin films of thickness $2.0 \div 2.5$ nm were prepared at $10 \div 15$ nm/s evaporation rate.

Photoexposure of $a-As_2S_3$ layers was carried out by unfocused absorbed laser beam (442 nm wavelength) at power density 25 mW/cm² during 120 min. This first cycle of photodarkening was generally irreversible, because consecutive thermoannealing of films at temperature $T=150 \pm 2^\circ C$ during 30 min restored their initial optical transmission only partially (no more than $10 \div 20\%$).

The method of differential IR Fourier-spectroscopy (using IFS-113V Bruker spectrometer) was used for mechanism study of photo- and thermally-induced structural transformations in $a-As_2S_3$. The measurements covered the previously intensified absorption spectra in $400 \div 100$ cm⁻¹ region before and after exposure or annealing treatment. One could characterise the occurring processes using changes of optical density D in $a-As_2S_3$ main vibrational bands. Positive values of ΔD corresponded to structural complexes appearing under treatment, and negative values of ΔD corresponded to complexes disappearing under treatment.

The $a-As_2S_3$ is concerned as a model taking into account the detection and investigation of induced structural changes. It is characterised by a possibility of a good distinction of different vibrational bands corresponding to main structural fragments, in particular the pyramidal AsS_3 units ($335 \div 285$ cm⁻¹) and molecular products with "wrong" homopolar As-As (379, 340, 231, 210, 168) and S-S bonds (243 and 188 cm⁻¹) [24–26]. Factor group analysis shows that crystalline $c-As_2S_3$ are characterized by four different IR vibrational modes in $335 \div 285$ cm⁻¹ region (323.1, 307.3, 301.3 and 288.9 cm⁻¹) [27].

3. Results

Spectral distribution of additional optical density ΔD induced in fresh-evaporated $a-As_2S_3$ amorphous films by laser photoexposure (irreversible cycle) is presented in Fig. 1. It is evident that absorbed light treatment leads to decrease of 379, 340, 243, 231, 210, 188 and 168 cm⁻¹ vibrational bands and to increase of bands corresponding to pyramidal AsS_3 units ($335 \div 285$ cm⁻¹). On the general background of $335 \div 285$ cm⁻¹ band one can point out a weak overlapping bands at 324, 301 and 288 cm⁻¹ and sharp peaks at 308 and 316 cm⁻¹. In our opinion, the latter (316 cm⁻¹) is caused by superposition of equally intensive IR modes at 324 and 308 cm⁻¹. This interpretation properly correlates with results of factor group analysis in $c-As_2S_3$ [27].

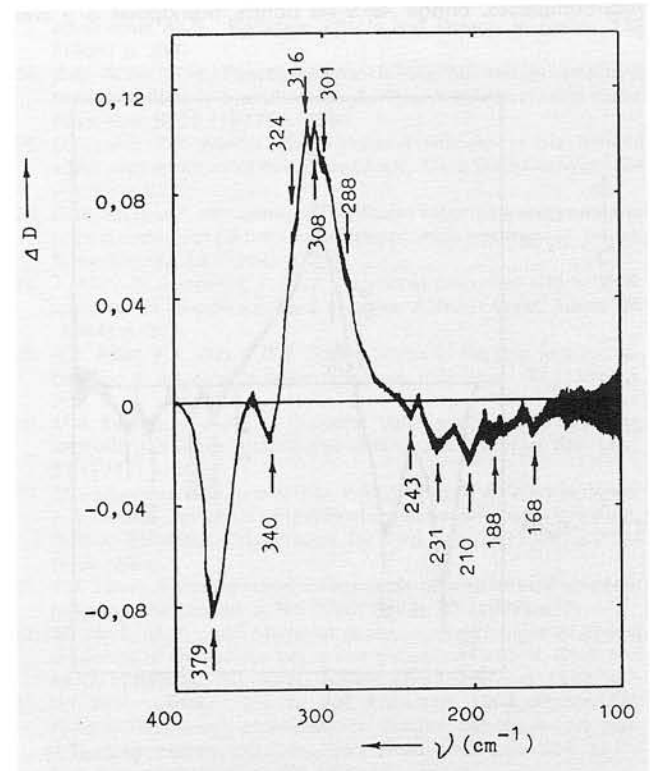
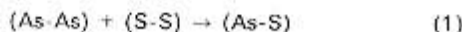


Fig. 1. Photoinduced additional optical density in fresh-evaporated $a-As_2S_3$ thin film

Usually, the observed irreversible PhST in amorphous As_2S_3 may be represented by the following destruction-polymerization reaction:



where expressions in brackets denote chemical bonds destroyed or formed in result of the photoexposure. Otherwise, irreversible photostructural changes in $a-As_2S_3$ are accompanied by transformations of products containing homopolar S-S and As-As bonds into structures based on the heteropolar As-S bonds.

Subsequent thermoannealing of photodarkened $a-As_2S_3$ films produces the same changes (see Fig. 2) described by reaction (1). However, intensities of main vibrational modes are more than two-fold smaller.

4. Discussion

4.1. Mechanism of irreversible PhST

It is well known that electron-hole pairs (exciton) autolocalization in AChS is accompanied by formation of special structural defects, i.e., over- and under-coordinated arsenic (As) and chalcogen (S) atoms [18,28,29]. Effect of external influences on AChS properties may be considered as a result of induced coordination defect formation (CDF) on the base of destruction and polymerization transformations. However, the real initial mechanism of CDF in amorphous solids (electron-hole pairs excitation, excitation of single electron and hole pairs autolocalized at certain structural fragments called soft atomic configurations, chemical bond breaking due to s-electrons excitation and so on) has not been established yet.

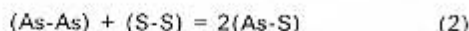
Results of photoinduced ESR investigation [12] demonstrating possibilities of bond-breaking transformations in AChS matrix may be assumed as a explanation of mechanism. Defect concentration is equal to $10^{20}-10^{21} \text{ cm}^{-3}$ [10] that corresponds to photodarkening centers concentration estimated from the magnitude of physical properties changes [30]. Topological schemes of CDF will be presented taking into account main types of structural units in fresh-evaporated $a-As_2S_3$: pyramidal AsS_3 complexes, bridge As-S-As bonds, homopolar S-S and

As-As chemical bonds in various fully or partially polymerized molecular fragments [24-27].

Photoinduced decrease of homopolar bonds concentration in the irreversible stage (see Fig. 1) indicates that they are initial components of PhST. There are eight topological schemes of CDF in this case (shown in Fig. 3) in the reason of AChS final state depends not only on destruction bonds, but also on their nearest neighbours [22,31]. Schemes N 5-8 can be excluded from further analysis since they do not change bonds types (one bond destroys, but the same bond forms instead). Schemes N 1-4 (Fig. 3) really correspond to obtained Fourier spectroscopy results and are described by destruction-polymerization reaction (1).

Consequently, (As_2^-, S_3^+) and (As_4^+, S_1^-) defects formation is main process of irreversible PhST in $a-As_2S_3$ thin films. Upper index in defect signature means charge state and lower one means coordination number. Coordination defects appear in AChS matrix by pairs (negative and positive) that provide electrical neutrality of the sample.

Structural polymerization processes including transformations of As_2S_3 and S_2 molecular complexes into homogeneous $AsS_{3/2}$ network are discussed in some papers [10,32]. These processes are not accompanied by atomic coordination changes and CDF. They appear only at high concentration of initial molecules because of large structural rearrangements in thin solid films are absent at room temperature [2,31]. Instead, two chemical bonds (As-As and S-S) destroy and two ones (As-S) appear simultaneously accordingly to destruction-polymerization reaction:



All four atoms forming two homopolar bonds occupy such nodal points which assume forming of two heteropolar bonds. When (As_2^-, S_3^+) and (As_4^+, S_1^-) defect pairs appear, this strong requirement may be fulfilled only for two atoms. Hence, CDF probability in $a-As_2S_3$ increases in comparison with nondefect polymerization process. The latter is probably dominant in fresh-evaporated thin films thermoannealed in temperature close to glass transition temperature (when atomic migration increase [22,24]).

In fact, CDF are realized due to destruction-polymerization reactions (see Fig. 1):

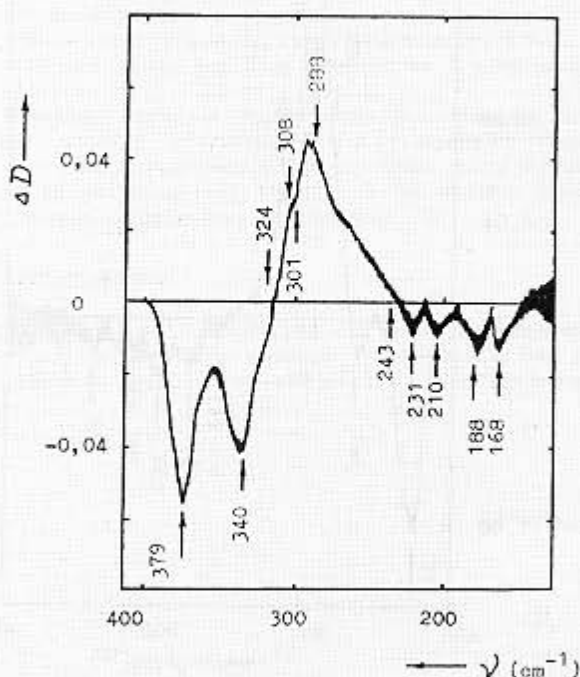


Fig. 2. Thermally-induced additional optical density in photodarkened (first cycle) $a-As_2S_3$ thin film

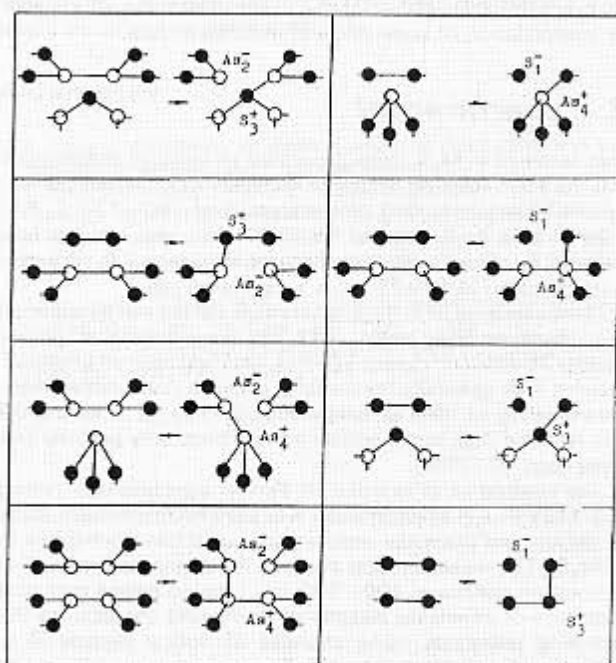


Fig. 3. Defect formation in $a-As_2S_3$ accompanied by homopolar bond-breaking transformations



which are summarised into reaction (1). Each of them is characterized by certain value of energetic activation barrier and statistical weight. Therefore, the total Fourier spectroscopy signal is complex. Its components corresponding to homo- and heteropolar chemical bonds are sufficiently varied, whereas in the case of non-defect polymerization they match up constantly. That is why non-defect polymerization is not used for microstructural explanation of experimentally obtained Fourier-spectra with variable component ratio [33].

4.2. Thermal bleaching of irreversible PhST

The absorbed light exposure of fresh-evaporated *a*-As₂S₃ thin films leads to heteropolar bonds forming and homopolar ones destruction. Four coordination defect pairs (see schemes N 1-4 in Fig. 4) appear during this PhST. However, in the nearest neighbour of (As₂⁻;S₃⁺) and (As₄⁺;S₁⁻) defects formed according to (1) and (2) schemes, only the highly energetic heteropolar bonds are placed (dissociation energy is equal to 2.48 eV [34]). Such defects are thermally stable at subsequent treatment. However, two other defect pairs (schemes N 3 and N 4 in Fig. 4) having homopolar bonds in the nearest neighbour annihilate at high temperatures in full agreement with experimentally obtained spectrum shown in Fig. 2 and destruction-polymerization reaction (1).

This analysis explains decrease of thermally induced vibrational modes intensities by factor two in comparison with photoinduced ones (Fig. 1). AsS₃ and As-S-As complexes of *a*-As₂S₃ take part in reversible photostructural transformations, as was stated above.

The fresh-evaporated thin film of amorphous As₂S₃ treated by absorbed light photoexposure and thermally annealed is ready for reversible optical effects observation at the subsequent cycles of treatment.

5. Conclusions

It results from far IR Fourier-spectroscopy that the irreversible PhST observed in fresh-evaporated *a*-As₂S₃ thin films are accompanied by switching of homopolar As-As and S-S bonds into heteropolar As-S ones. Four topological schemes of (As₂⁻;S₃⁺) and (As₄⁺;S₁⁻) defects formation correspond to this process. Two defect pairs are thermally stable, and two another – annihilate during subsequent annealing near glass transition temperature. Structural polymerization including transformations of As₄S₄ and S₂ molecular complexes into homogeneous AsS_{3/2} network are considered as alternative way of irreversible PhST.

References

1. J.P. De Neufville, S.C. Moss, S.R. Ovshinsky: Photostructural transformations in amorphous As₂Se₃ and As₂S₃ films. *J. Non-Cryst. Solids*, **13** (1974) p. 191.
2. K. Tanaka: Evidence for reversible photostructural change in local order of amorphous As₂S₃ film. *Solid State Commun.*, **15** (1974) p. 1521.
3. K. Tanaka, Y. Ohtsuka: Composition dependence of photo-induced refractive index changes in amorphous As-S films. *Thin Solid Films*, **57** (1979) p. 59.
4. J. Asahara, T. Izumitani: An effect of irradiation on As₆Se₄. *J. Non-Cryst. Solids*, **15** (1974) p. 343.
5. B.T. Kolomiets, V.M. Lyubin, V.P. Shilo: Photostimulated changes of solubility of chalcogenide glasses. *Phis. i Khim. Stekla*, **4** (1978) p. 351 (in Russian).
6. B.T. Kolomiets, S.S. Lantratova, V.M. Lyubin, V.P. Shilo: On connection between softening and bleaching temperature of optical recording in chalcogenide vitreous semiconductors. *Phiz. tverd. tela*, **21** (1979) p. 1020 (in Russian).

7. K. Tanaka: Reversible photoinduced change in intermolecular distance in amorphous As₂S₃ network. *Appl. Phys. Lett.*, **26** (1975) p. 243.
8. K. Tanaka, Y. Ohtsuka, K. Imai, Y. Abe: The variation of sound-wave velocity in amorphous As-S films under photostructural transformation. *Thin Solid Films*, **31** (1976) p. L15.
9. V.L. Averjanov, B.T. Kolomiets, V.M. Lyubin, M. Taguyrdzhanov: On changes in localized states energy spectrum of chalcogenide vitreous semiconductors at photostructural transformations. *Proc. Int. Conf. "Amorphous and Liquid Semiconductors"* Edinburgh, (1977) p. 802.
10. M. Frumar, A.P. Firth, A.E. Owen: A model for photo-structural changes in the amorphous As-S system. *J. Non-Cryst. Solids*, **59-60** (1983) p. 921.
11. M. Kumeda, Y. Nakagaki, M. Suzuki, T. Shimizu: The reversible photostructural change studied by ESR of Mn²⁺ in As₂Se₃ films. *Solid State Commun.*, **21** (1977) p. 717.
12. I.L. Liholit, V.M. Lyubin, V.F. Masterov, V.A. Fedorov: Investigation of photostructural transformations in As₂S₃ films by photoinduced spin resonance method. *Phiz. Tverd. Tela*, **26** (1984) p. 172 (in Russian).
13. S.S. Lantratova, V.M. Lyubin, P.P. Seryegin: Investigation of photostructural transformations in vitreous AsSe semiconductor by Mossbauer spectroscopy method on impurity atoms of stannum. *Phiz. Tverd. Tela*, **25** (1983) p. 2494 (in Russian).
14. N. Mott, E. Davis: *Electronic processes in noncrystalline materials*. Mir, Moscow 1982 (in Russian).
15. *Amorphous semiconductors*, ed. M. Brodsky. Mir, Moscow 1982.
16. *Non-silver photographic processes*, ed. A.L. Kartuzhansky. Khimiya, Leningrad 1984.
17. A. Feltz: *Amorphous and vitreous neorganic solids*. Mir, Moscow 1986.
18. R.A. Street: Recombination in amorphous semiconductors. *Phys. Rev. B*, **17** (1978) p. 3984.
19. T. Budinas, P. Mackus, I.V. Savvitsky, O.I. Shpotyuk: Spectroscopic investigations of induced processes in arsenic sulphide chalcogenide glasses. *J. Non-Cryst. Solids*, **90** (1987) p. 521.
20. O.I. Shpotyuk, A.P. Kovalsky, M.M. Vakiv, O. Ya. Mrooz: Reversible radiation effects in vitreous As₂S₃. 1. Changes of physical properties. *Phys. Stat. Sol. A.*, **144** (1994) p. 277.
21. O.I. Shpotyuk: Reversible radiation effects in vitreous As₂S₃. 2. Mechanism of structural transformations. *Phys. Stat. Sol. A.*, **145** (1994) p. 69.
22. O.I. Shpotyuk: Photostructural transformations in amorphous chalcogenide semiconductors. *Phys. Stat. Sol. B.*, **183** (1994) p. 365.
23. O.I. Shpotyuk: Mechanism of radiation-structural transformations in amorphous As₂S₃. *Radiation Effects and Defects in Solids*, **132** (1994) p. 393.
24. S.A. Solin, G.N. Papatheodorou: Irreversible thermo-structural transformations in amorphous As₂S₃ films: A light scattering study. *Phys. Rev. B*, **15** (1977) p. 2084.
25. U. Strom, T.P. Martin: Photo-induced changes in the infrared vibrational spectrum of evaporated As₂S₃. *Solid State Commun.*, **29** (1979) p. 527.
26. D.W. Scott, J.P. McCullough, F.H. Kruse: Vibrational assignment and force constants of S8 from a normalcoordinate treatment. *J. Molec. Spectroscopy*, **13** (1964) p. 313.
27. T. Mori, K. Matsuiishi, T. Arai: Vibrational properties and network topology of amorphous As-S systems. *J. Non-Cryst. Solids*, **65** (1984) p. 269.
28. N.F. Mott, E.A. Davis, R.A. Street: States in the gap and recombination in amorphous semiconductors. *Phil. Mag.*, **32** (1975) p. 961.
29. M.A. Kastner, D. Adler, H. Fritzsche: Valence-alternation model for localized gap states in alone-pair semiconductors. *Phys. Rev. Lett.*, **37** (1976) p. 1504.
30. M. Babacheva, S.D. Baranovsky, V.M. Lyubin, M.A. Taguyrdzhanov, V.A. Fedorov: Influence of photostructural transformations in As₂S₃ films on absorption Urbach edge. *Fiz. tverd. Tela*, **26** (1984) p. 2194 (in Russian).
31. S.R. Elliott: A unified model for reversible photostructural effects in chalcogenide glasses. *J. Non-Cryst. Solids*, **81** (1986) p. 71.
32. M. Vlcek, M. Frumar: Model of photoinduced changes of optical properties in amorphous layers and glasses of GeSb-S, Ge-S and As-Se systems. *J. Non-Cryst. Solids*, **97-98** (1987) p. 1223.
33. O.I. Shpotyuk, K.K. Shvarts, V.N. Kornelyuk, Yu.N. Shunin, F.V. Pirogov: Destruction-polymerization transformations in chalcogenide vitreous semiconductors. *Prepr. Acad. Nauk Latv. SSR, LAFI-163, Salaspils* (1991) p. 105 (in Russian).
34. K.J. Rao, R. Mohan: Chemical bond approach to determining conductivity gaps in amorphous chalcogenides and pnictides. *Solid State Commun.*, **39** (1981) p. 1065.