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Photo- and Thermally Induced Effects in an $As_2S_3 + Au$/Polymer Nanocomposite

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This paper investigates the optical properties of nanocomposites consisting of As_2S_3 nanocrystals with added Au nanoparticles embedded in a polymer matrix based on acrylic monomers. The aim of the study is to analyze photo- and thermally induced changes in the transmittance spectra in the visible and near-IR ranges and to identify the mechanisms responsible for these effects. The experimental methodology includes the synthesis of composites by mixing solutions of As_2S_3 and Au nanoparticles, followed by polymerization, transmission spectral measurements, and analysis of the Urbach absorption edge. Key results demonstrate opposite trends compared to bulk As_2S_3 films: thermal darkening and a long-wavelength shift of the absorption edge after thermal annealing (up to 150 °C), as well as a converse photoinduced shift to short wavelengths upon irradiation with a 532 nm laser (power of 20 W/cm^2). The addition of Au enhances these effects due to plasmonic interactions. The obtained results open up prospects for the application of such composites in optoelectronics, holography, and devices with controlled optical properties.

Keywords: nanocomposites, nanocrystals, polymer, controlled optical properties.

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1. Introduction

The ongoing trends in materials science and nanotechnology are aimed at finding and studying the functional materials the properties of which can be effectively regulated by external influences such as light, electric field or temperature. In this view, the chalcogenide glass-like semiconductors [1], namely, arsenic trisulfide (As_2S_3), are of specific interest because of their unique photo-induced effects [2]. These materials exhibit significant changes in optical, electrical, and structural properties under the influence of light, which makes them promising for applications in optoelectronics, photonics, holographic recording, and non-volatile memory [3].

The study of photoinduced processes in chalcogenide glasses is important not only for a fundamental understanding of the nature of the interaction of light with the electronic system of a crystal in amorphous and nanocrystalline systems, but also for the development of new functional materials with controllable properties [4,5].

As_2S_3 belongs to the class of glassy semiconductors with high sensitivity to optical radiation. The most studied photoinduced phenomena in this material are: higher optical absorption in the visible and near-infrared regions of the spectrum when irradiated with light with an energy close to the band gap and a photoinduced long-wavelength shift of the absorption edge [6]; photo-ordering — rearrangement of the local atomic structure towards a more ordered state, accompanied by a change in the refractive index [7]; photo-diffusion — migration of atoms under the influence of light, leading to a change in the chemical composition and surface morphology [8].

These effects are caused by a complex combination of electronic and structural processes [9], including: breaking and rearrangement of chemical bonds (for example, the transition from pyramidal As_2S_3 units to more layered structures); generation and redistribution of defects (vacancies, interstitial atoms, coordination deficient centers); electronic structure, including the formation of localized states in the band gap [10].

Unlike the bulk glassy As_2S_3, its nanocrystalline analogues demonstrate a number of advantages: quantum-dimensional effects lead to changes in the band gap and density of states, which affects the spectral dependence of photoinduced processes. Due to a well-developed specific surface a vast interaction with illumination and enhanced atoms diffusion are reached. Controlled morphology (size, shape, crystallinity) allows to perform a fine-tuning of the material's photo response [11].

It has been experimentally proven that reducing the size of nanocrystals As_2S_3 to 5−20 nm leads to a significantly higher rate of photoinduced changes compared with bulky samples [12]. This is due both to the increased concentration of surface defects and to changes in the relaxation mechanisms of excited states.

Of particular interest are As_2S_3 nanocomposites with metallic nanoparticles, where plasmonic effects can enhance the interaction of these nanocrystals with light [13].

In this article, the optical properties of a polymer composite with arsenic sulfide nanoparticles were investigated [14], transmission spectra of polarized light in nanocomposites from nanocrystals $As_2S_3$with the addition of Au in a polymer matrix have been studied. The polarization parameters of the light transmitted through the films of such a composite at room temperature, after annealing at temperatures up to 140°, were measured and during subsequent irradiation after annealing, as well. The effect of a change in the optical properties of arsenic trisulfide nanoparticles in the polymer matrix was observed: higher absorption and a shift of the absorption edge to the long-wavelength side after annealing, as well as a photoinduced shift of the absorption edge to the short-wavelength side and a lower absorption, which is opposite to the trends known for thick films of glassy As_2S_3.

2. Experiment

The process of composites studying includes several stages. First, in complete darkness and without oxygen access, at room temperature, the chalcogenide glass As_2S_3 (0.1 g) is dissolved in a mixture of diethylamine (3 ml) with low molecular weight hydroxylamines (4 mass.%). After that, gold nanoparticles are added to the resulting solution, and the mixture is aged at 35 °C to a constant weight. Next step: liquid acrylic monomers are added to the solution. 2 phenoxyethyl acrylate and diurethane dimethacrylate containing two methacrylic groups and at least two urethane groups are used. The mixture is stirred for 5 h for homogenization. Next, the polymerization initiator — bis(cyclopentadienyl) bis2,6-difluoro3-(1-pyrryl) phenyltitane is introduced into the mixture. After adding the initiator, the mixture is stirred for one hour. After completing all these steps, the resulting composition should be stored in the dark at a temperature of 25 °C.

As a result of mixing solutions of As_2S_3 and Au, an interaction occurs between two types of nanoparticles. This interaction can be explained by the displacement of surface ligands on gold nanoparticles by arsenic ions contained in As_2S_3. Ligands such as glutathione, dithiothreitol, or cysteine can be displaced by arsenic ions [15].

When As_2S_3 is dissolved in propylamine, the sulfide atom is replaced by an alkylamino group, which is present in propylamine. In this process, the additional hydrogen in the alkylammonium group of arsenic is cleaved off, and the $R-NH^{3+}$ group is formed. This group then binds to the C−S-group located on the surface of Au. This increases the number of negatively charged S bonds on the surface of Au, which later covalently bind to Au. As a result of these chemical reactions the pyramidal clusters of As_2S_3 are formed arranged around the gold nanoparticles [16]. A mixture of monomers is a matrix in which nanoparticles are evenly distributed. The amino groups of diurethane dimethacrylate (UDMA) monomers and the phenyl ring of 2-phenoxyethyl acrylate monomer actively interact with As_2S_3nanoparticles, changing their surface. This interaction improves the compatibility of inorganic nanoparticles with the organic acrylic matrix. In addition, the presence of UDMA monomer in the solution promotes the formation of a polymer network, which, in turn, increases the durability and stability of these structures.

The method of obtaining arsenic sulfide nanoparticles by dissolving them in diethylamine together with hydroxylamine allows polymerization reactions, which, in turn, gives the nanocomposite reversible photosensitive characteristics and nonlinear optical properties. The resulting films retain their optical characteristics for a long time [17].

Two types of samples were studied: those made as described above, and those subjected to annealing at a temperature of 140 °C (Figure 1, *a,b*).

The transmission spectra of the obtained samples were measured in the energy range 1.5−3.0 eV. The light of the halogen lamp passing through the diaphragm and the linear polarizer shed on the sample. The laser spot size on the sample was about 1 mm^2. After passing through the sample, the light passed through a system of polarizers and/or a phase plate ($\lambda/4$) and focused on the slit of the spectrograph. A spectrograph with a focal length of 0.5 M equipped with a CCD detector was used to measure the spectrum. The spectral resolution of the system was about 2 A. The measurements were carried out immediately after the samples were made and after annealing at a temperature of 140 °C for 60 min. In addition, the effect of laser radiation with a wavelength of 532 nm and a power density of 20 W/cm^2 on the sample was measured.

The phenomenon of reversible optical transmission was observed in the spectra. Namely, after annealing the film at a temperature of 140 °C for one hour, the optical absorption edge shifts towards low energies and the absorption rises. A decrease in the annealing time led to a lower shear and a weaker effect on absorption. After irradiating the films with light with a quantum energy of 2.32 eV, the main edge of optical absorption shifts back to higher energies (Figure 2). It was found that the reversibility of this effect depends not on the intensity of illumination itself, but on the radiation dose. This reversibility effect was repeatedly reproducible on samples containing 0.01 % per volume of gold.

In the samples containing only arsenic trisulfide particles, but not containing gold particles, the photoinduced reversibility of shear and absorption was noticeably lower.

As can be seen from Figure 2, *a* in a sample containing no gold particles, the thermally induced shift of the absorption edge was about 400 MeV, at the initial position of the edge 2.53 eV. The reverse, photoinduced shift did not exceed 40 MeV.

In a sample containing 0.01 % by volume of gold (Figure 2, *b, c*) before all external influences, the absorption

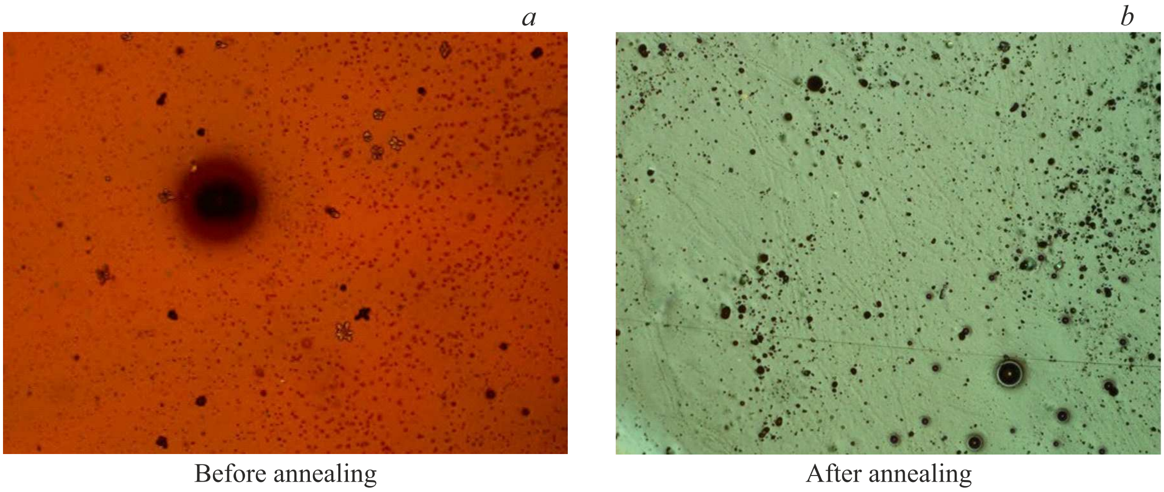

Figure 1. Image of surface of $As_2S_3 + Au$/polymer nano-composite samples. *a*) before annealing, *b*) after annealing.

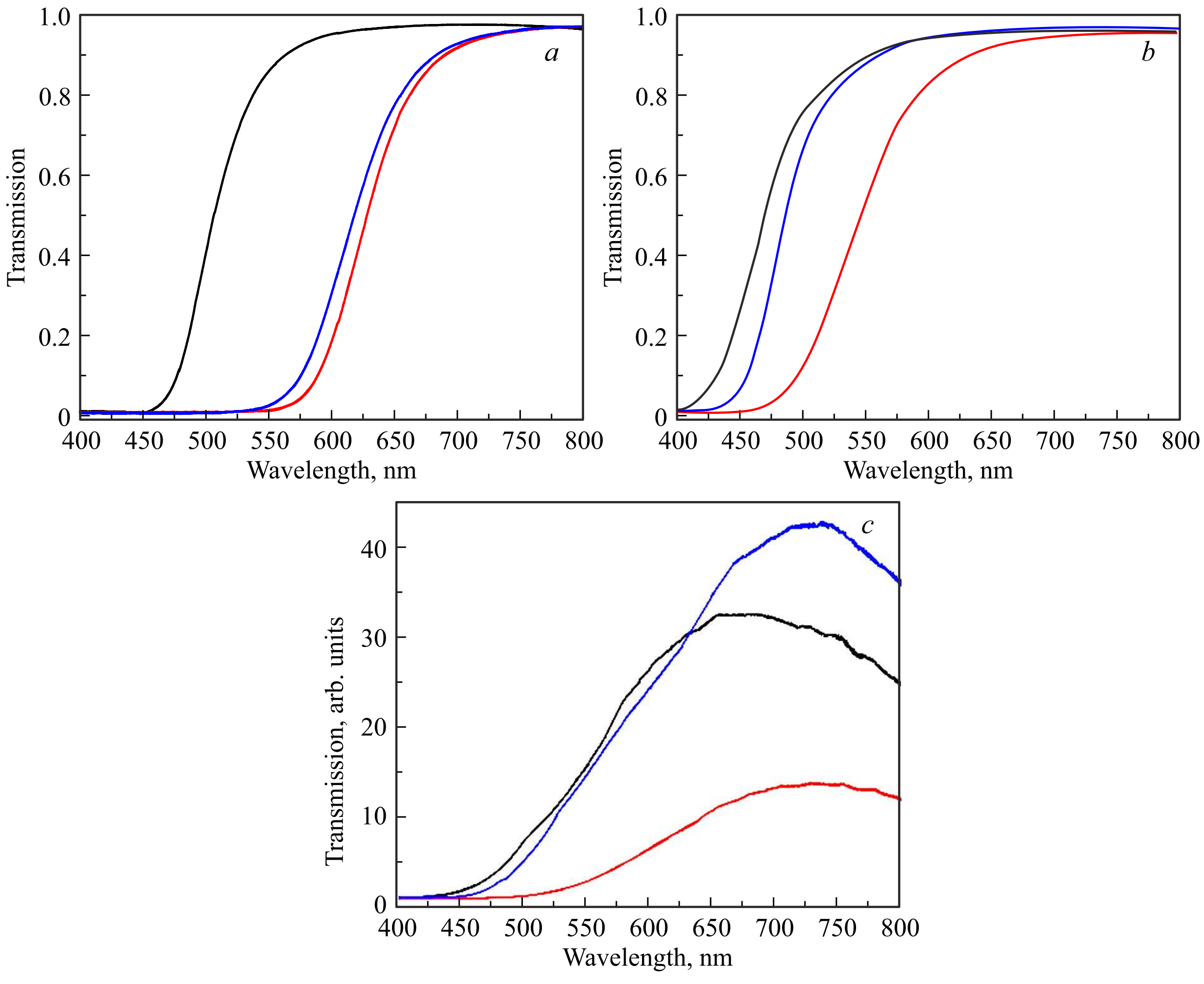

Figure 2. Transmittance spectra of samples *a*) As_2S_3 without Au particles normalized to the maximum transmittance; *b*) As_2S_3+Au normalized to the maximum transmittance; *c*) As_2S_3+Au in absolute units. Black curves — before all interactions; red curves after annealing for an hour at a temperature of 140 °C; blue curves after irradiation with the quantum energy of 2.32 eV and power density of 20 W/cm^2.

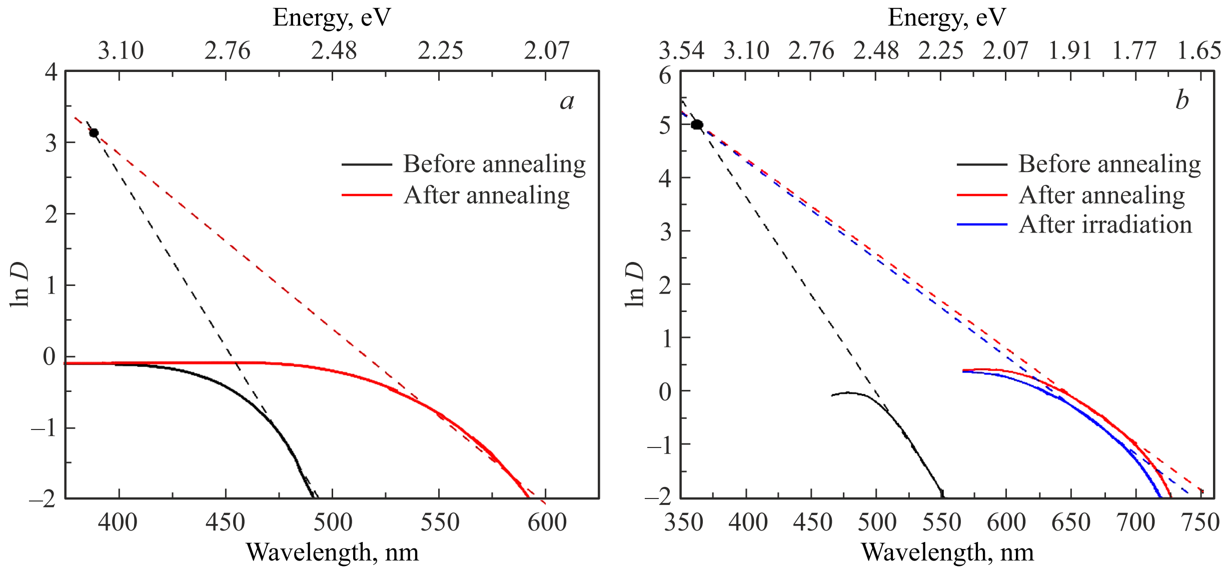

Figure 3. Absorption coefficient logarithm versus wavelength *a*) Composite with golden nanoparticles, *b*) composite without golden nanoparticles.

edge was observed at a wavelength of 450 nm (2.75 eV), which is 200MeV greater than the band gap of crystalline As_2S_3 at room temperature. After annealing for an hour at a temperature of 140° the absorption edge shifted to a wavelength of 500 nm (2.48 eV). After additional laser irradiation with a quantum energy of 2.32 eV with a power density of 20 W/cm^2, the absorption edge returned almost to its original position within an hour.

From Figure 2, *c* it can be seen that in addition to changing the band gap width, there is a change in light transmission in the area of „transparency" of the sample, while the slope of the transmission curve also changes. Similar effects were observed in different chalcogenide glasses and are known as „photo-darking" [18,19]. However, unlike the previously described phenomena in bulk materials, for arsenic sulfide nanoparticles in a polymer matrix, a short-wavelength photoinduced shift was observed, and as a result of sample annealing, the absorption edge shifted to the long-wavelength side. Since the polymer matrix itself did not show such changes, which was experimentally verified, they should be associated with changes in the properties of chalcogenide inclusions.

The samples demonstrate stable preservation of the altered optical characteristics over a long period of time (several days). This property makes them promising for practical use in various optical systems.

3. Discussion of results

Chalcogenide glasses As_2S_3 are a partially ordered semiconductor. The band gap width of the bulky As_2S_3 in its crystalline state makes 2.56 eV. In the glassy phase, it varies from 2.1 to 2.5 eV depending on the method of sample preparation. In our arsenic trisulfide samples in a polymer matrix, glassy As_2S_3 nanoparticles were used, in which the absorption edge was shifted to the short-wavelength side due to dimensional quantization. According to the estimate, thickness of nanocrystals (with effective electron mass $0.3-0.5m_0$) [20] was one — two monolayers. Nanoparticle samples have a strong variation in size and crystal structure. As a result, the absorption edge of the composite is strongly blurred. The blurring of the absorption edge reflects the presence of an exponential tail of the localized states density associated with the dispersion of nanoparticles in size, spatial orientation, and properties.

To determine the width of the tail of disordered states in our samples, we used Uhrbach rule [21], according to which the absorption coefficient near the absorption edge of a partially ordered substance is described by the formula:

$$\alpha(\omega) = a_0 \exp(E_0 - \hbar\omega/E_U)$$

where $\alpha(\omega)$ — optical absorption coefficient, E_U — amount of blurring of the absorption edge, E_0 — energy of absorption edge.

This dependence is shown in Figure 3. For the blurred absorption edge of a sample containing gold nanoparticles (As_2S_3+Au), we obtain an absorption edge blurring value of 0.612 eV before annealing and 0.810 eV after annealing. For blurring the absorption edge of the composition without gold (pure As_2S_3) — 0.674 eV before annealing and 0.727 eV after annealing. Thus, annealing causes an increase in the disorder (the tail width increases), and subsequent illumination leads to its diminishing.

Obviously, annealing and illumination cannot affect the size spread of nanoparticles and only affects their properties. The thermally induced shift of the absorption edge to the long-wavelength side, accompanied by thermal darkening, and the photoinduced, reverse shift to the short-wavelength side are associated with electronic transitions in arsenic trisulfide nanoparticles and subsequent structural rearrangement.

It has been reliably established that As_2S_3 has an amorphous structure consisting of layers (or chains) of As and S atoms bonded covalently. This structure is distinguished by multiple defects: dangling bonds „unpaired“ electrons (e. g., on atoms S).

During photo-excitation with photon energy above the band gap, electron-hole pairs are generated. These pairs do not recombine immediately, but are captured on defects. Electron capture on defects leads to local structural rearrangements: changes in bond types (for example, from S−S to As−S or vice versa), the formation of new defects (for example, pairs with alternating valence As^3/As and S^2/S). This effect is metastable, so the amorphous structure of „freezes“ in a new state. In nanomaterials, this effect is enhanced due to mechanical stresses and dimensional quantization.

The state of the glassy substance, its energy structure and the degree of glass transition depend on the method of its preparation. With very slow cooling of the melt, a crystalline substance is obtained, if the cooling rate is high, a metastable glassy state will result upon cooling. Depending on the cooking conditions, a glassy substance with varying degrees of disorder and different steady state energy in configuration coordinates will be obtained.

In our case nanocrystals As_2S_3 were formed of a solved glassy As_2S_3. When the glass is dissolved, the least stable clusters with low binding energy dissolved first. Clusters with higher binding energy remained undissolved. After solidification in the polymer matrix, it turned out that the obtained nanocrystals are not in a state with minimal energy, but rather in metastable stable states [22].

Thermal annealing causes nanoclusters As_2S_3, which are in metastable states with higher energy, to relax into other metastable states with lower energy. At the same time, if the initial state corresponds to a sufficiently high energy, the spread of nanocluster states by energy rises. Along with that, the effective band gap width is reduced.

The addition of gold nanoparticles during its chemical interaction with As_2S_3 can lead to an increase in the diversity of metastable configurations in nanoclusters $As_2S_3 + Au$, and in the absence of chemical interactions can promote photo-induced transitions involving nano-plasmons.

In bulky chalcogenide glass samples, similar photo- and thermo-induced phenomena have been studied for more than 40 years, but a single model describing all the observed features has not been created so far. The study of nanoobjects (thin films and nanoparticles) has only recently started, and the effect of opposite trends in optical properties has not yet been studied in detail. The mechanisms of how the gold nanoparticles impact the photo- and thermal effects are also unclear.

4. Conclusion

In this paper, the light transmission spectra in nanocomposites based on As_2S_3 nanocrystals with the addition of 0.01 %Au in a polymer matrix are studied. Composite films were studied: (a) after preparation without external impact, (b) after thermal annealing for an hour at temperatures up to 140 °C and (c) after subsequent intense irradiation with a quantum energy of 2.32 eV and a power density of 20 W/cm^2 for an hour.

The key findings demonstrate changes in the optical properties under the influence of annealing and irradiation: thermally induced shift of the absorption edge to the long-wavelength region with the rise of absorption (thermo-darkening), as well as a photoinduced shift in the opposite direction with a declining absorption (photo transparency). These effects are the opposite of those observed in thick films of arsenic trisulfide. The introduction of gold nanoparticles into a composite with As_2S_3nanoparticles significantly enhances both types of changes in optical properties.

All observed phenomena are explained by the structural instability of the chalcogenide glass lattice As_2S_3, which highlights the potential of nanocomposites for applications in optical memory and sensors. These findings contribute to a better understanding of metastable transitions in chalcogenides and require further research to improve the properties of such materials. The results obtained will contribute to the development of optical switching devices, optical memory elements, and sensors, where reversible changes in absorption under the influence of light and heat can be used to store data or detect external impact [23].

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Conflict of interest

The authors declare that they have no conflict of interest.

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