Spectroscopic study of amorphous As$_2$(S,Se)$_3$:Sn$_x$ thin films

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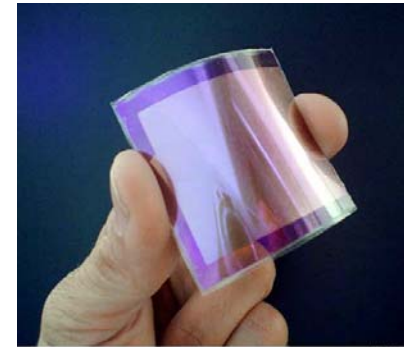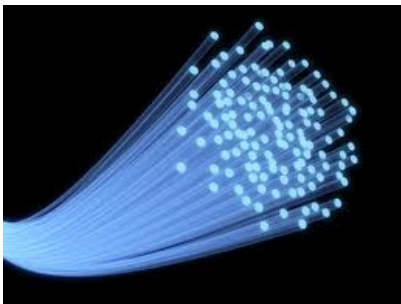Institute of Applied Physics, Academy of Sciences of Moldova
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Amorphous and glassy chalcogenides are perspective
HIGH–TECH MATERIALS
with many applications in electronics, optoelectronics, optics, medicine, chemistry and ecology

(FIBERS, MEMORIES, SENSORS, OPTICAL SIGNAL PROCESSING, …)

Large interest to amorphous chalcogenides:

- electrical and photoelectrical properties:
    photoconductivity, photovoltaics,
    switching effects (treshold and memory) – electrical memories
phase-change, ionic)
    bateries, sensors (optical and electrical)

- optics, optoelectronics:
    infrared optics, optical transmission up to IR (18µm),
    optical signal processing, memories, IR luminescence,
    sensors

- photoinduced phenomena:
    photoinduced effects, optical waveguides, optical gratings,
    microlenses, planar optical circuits and devices, memories

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- Chalcogenide glasses (As-S, As-Se, As-S-Se, As-Sb-S, Ge-As-Se) are characterized by the wide region of glass formation, high glass transition temperatures (Tg=300÷400 0C) and thermal stability.

- Chalcogenide glasses are sensitive to the external illumination and exhibit reversible and irreversible photoinduced effects. These effects are used for fabrication of different registration media, diffractive structures, waveguides, photonic structures.

- In the present work the changes of the optical constants (absorption coefficient α, optical band gap E_g, the refractive index *n, and the oscillator strength E_d*) of the investigated materials under the ionization irradiation and heat treatment are presented.

Fig.2. The transmission spectra of some amorphous $(As_2S_{1.5}Se_{1.5})_{1-x}:Sn_x$ thin films.

Figure 2 legend:
1 - $(As_2S_3)_{0,5}(As_2Se_3)_{0,5}$
2 - $(As_2S_3)_{0,5}(As_2Se_3)_{0,5}:Sn_{0,01}$
3 - $(As_2S_3)_{0,5}(As_2Se_3)_{0,5}:Sn_{0,02}$

Figure 1 legend:
As_2S_3
As_2Se_3
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,01}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,02}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,05}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,06}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,07}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,08}$
$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,09}$
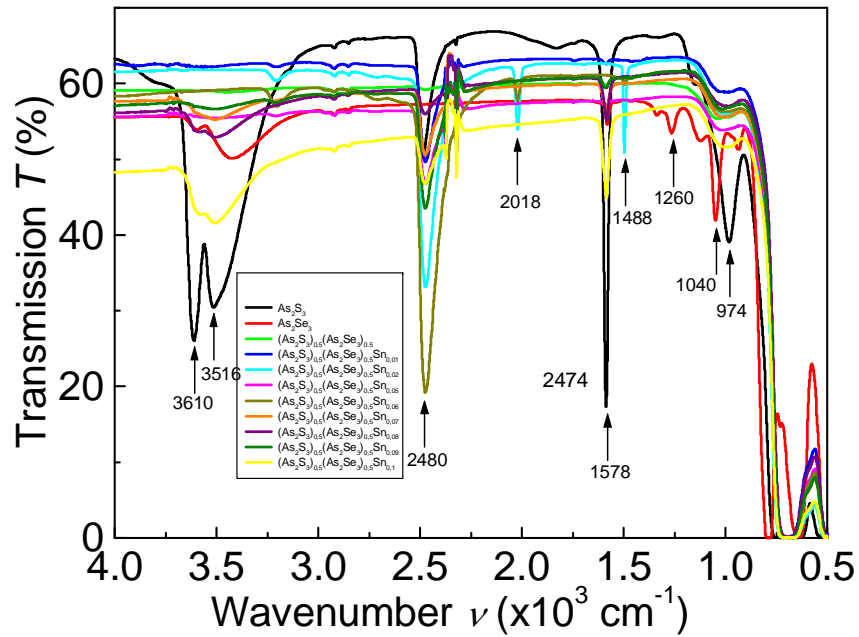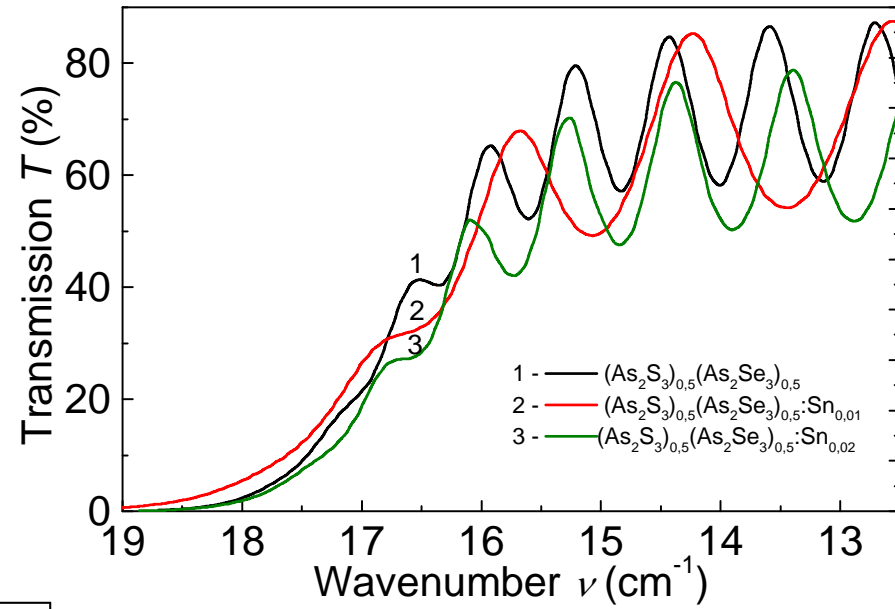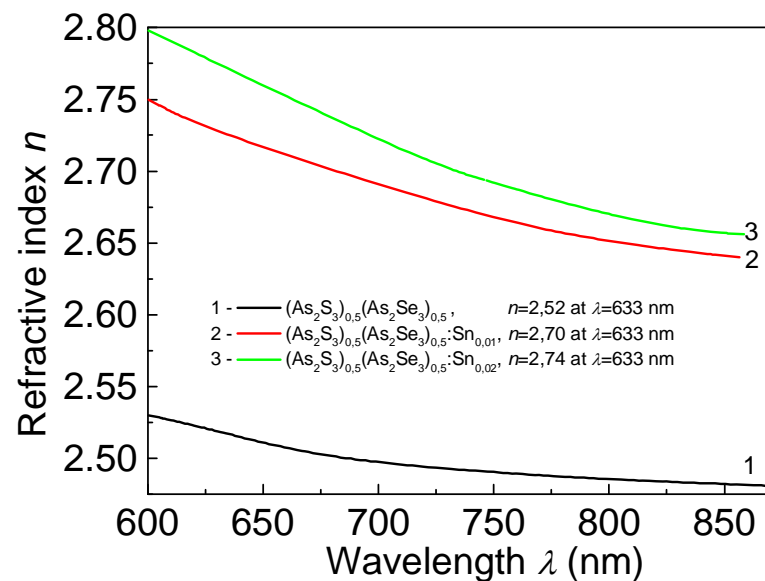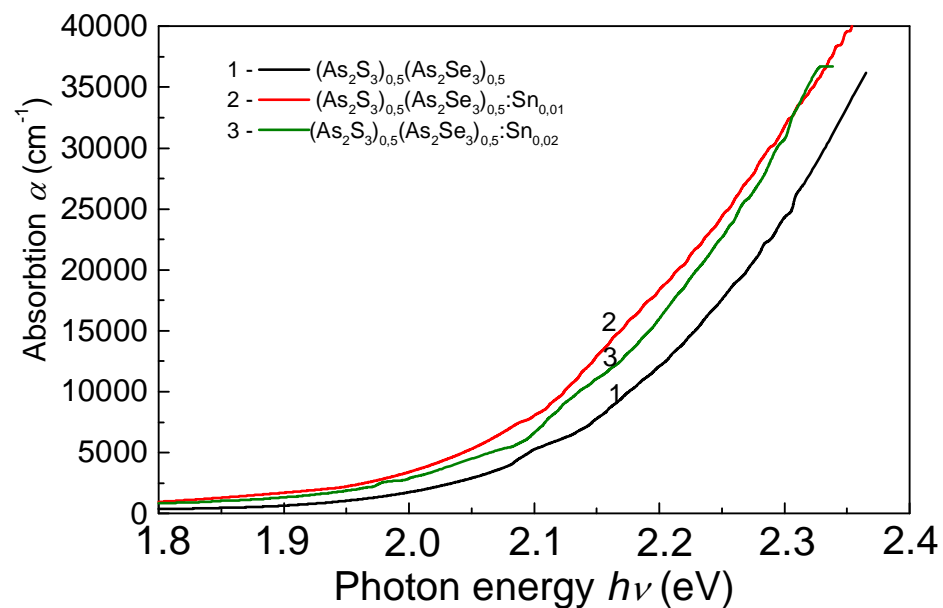$(As_2S_3)_{0,5}(As_2Se_3)_{0,5}Sn_{0,1}$

Fig.1. The transmission spectra of bulk samples of $(As_2S_{1.5}Se_{1.5})_{1-x}:Sn_x$ glasses

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From the transmission spectra $T=f(\lambda)$, using the expressions

$$\alpha = \frac{1}{d}\ln\frac{(1-R)^2}{T} \qquad\qquad n = \frac{\lambda_m \lambda_{m-1}}{2d(\lambda_{m-1} - \lambda_m)}$$

and the dependence $(\alpha\, h\nu)^{1/2} = A(h\nu - E_g)$, was calculated the absorption coefficient α, the refractive index n, and the value of the optical band gap E_g respectively.

Here d – is the thickness of the sample, R – the reflection, λ_m, λ_{m-1} – the minimum and maximum of the interference in the transmission spectra, A - is a constant.

The optical parameters α, E_g, and n for some amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{1-x}:Sn_x$ thin films.

Nr.	Film composition	$\alpha \cdot 10^4, cm^{-1}$ ($h\nu$=2.3 eV)	E_g, eV	n (λ=633 nm)
1	$(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}$	2.44	1.96	2.52
2	$[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{0.99}:Sn_{0.01}$	3.17	1.90	2.70
3	$[(As_2S_3)_{0.5}:(As_2Se_3)_{0.5}]_{0.98}:Sn_{0.02}$	3.07	1.94	2.74

•The arsenic selenide amorphous films usually became darkened under action of light from the region of fundamental optical absorption $h\nu \geq Eg$ and so-called photodarkening effect takes place.

• Increasing of the optical absorption is accompanied by the red shift of the absorption edge and increasing of the refractive index.

•The red shift of the absorption edge on photodarkening indicates the narrowing of the optical gap of the film due to broadening of the valence band, the top of which is formed mainly by states of lone-pare electrons of the chalcogen atom.

To describe the relaxation of the relative transmission $T(t)/T(0)$ curves we used so called stretched exponential presentation:

$$T(t)/T(o) = A_0 + A\exp[-(t-t_0)/\tau]^{1-\alpha}$$
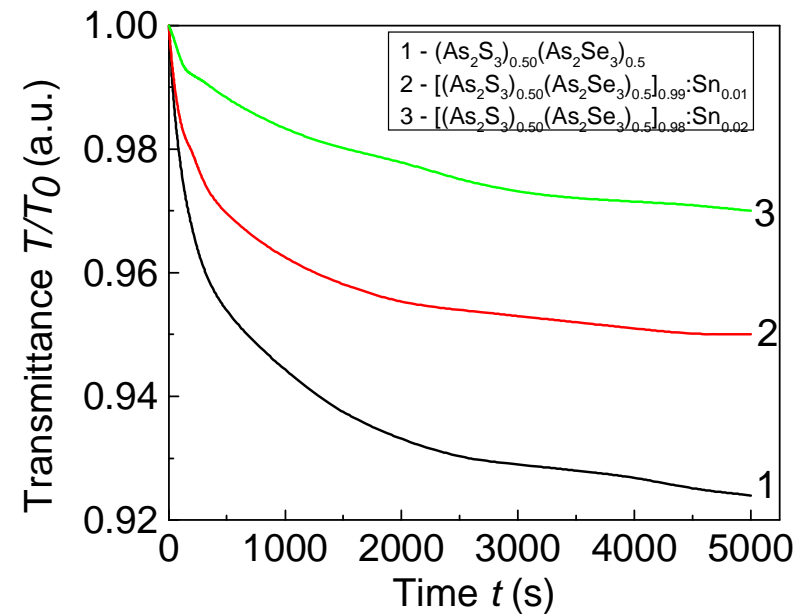
The relaxation curves of photodarkening $T/T_0 = f(t)$ for amorphous $[(As_2S_3)_{0.5}:(As_2Se_3)0.5]_{1-x}:Sn_x$ thin films.

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■MODEL: Schematic illustration of the layers in a-As$_2$Se$_3$

Recently, a novel model (*"slip-motion")* for photodarkening in a-As$_2$Se(S)$_3$ has been proposed, in which photoexcited charge carriers in extended states are considered as responsible for photodarkening.

Unlike to the previous conceptions the new model takes into account the layered cluster structure of a chalcogenide glass.

Expansion

Slip Motion

Layers

Layers

Slip Motion
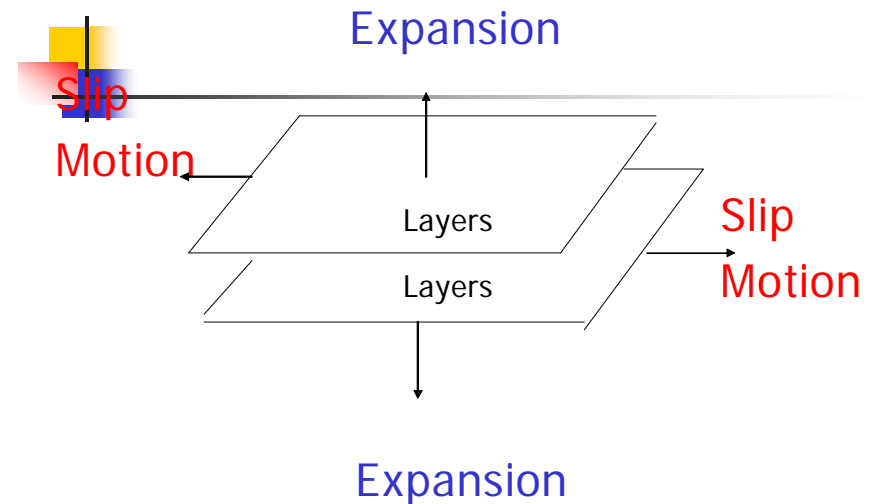
Expansion

During exposure the layer is negatively charged due to capture of photoexcited electrons, and repulsive forces are built between the layers.

These forces cause enlargement of the interlayer distance (leading to photoexpansion) and slip motion along the layers. This latter process alters the interaction of lone-pair electrons between the layers leading to the photodarkening effect.

Thank you for your attention!