# STEADY-STATE AND TRANSIENT PHOTOCONDUCTIVITY OF AMORPHOUS $(As_4S_3Se_3)_{1-x}Sn_x$ THIN FILMS

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*Abstract*. The experimental results on steady-state and transient photoconductivity of amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ ($x = 0 \div 0.1$) thin films are investigated. Arsenic selenide glasses are well known as high photosensitive materials with a wide range of application in optoelectronics and information storage systems. Besides, that it was found that the impurities influence the electrical, photoelectrical and optical characteristics of the amorphous material, due to the changes in the density of localized states. Introduction of the elements of IV group of periodic table in selenide and sulphide glasses, such as Sn, conduct to the appearance of tetrahedral structural units in the base glass, which change the coordination number and other parameters. These particularities lead to the non-monotonic dependence of mechanical, electrical, optical and photoelectrical properties with increasing of the concentration of four coordinated atoms. It was shown, that the spectral distribution of the stationary photoconductivity for studied glass system depends on the composition and polarity on the illuminated electrode. The dependence of the stationary photocurrent $I_{ph}$ on the light intensity $F$ for the exponential distribution of the localized states is described by a power function $I_{ph} \sim F^\alpha$, were the parameter $0.5 \le \alpha \le 1.0$. The transient photocurrent behavior in investigated amorphous materials is controlled by carrier localization and delocalization processes. The kinetics of photocurrent produced by uniform continuous bulk photogeneration of non-equilibrium carriers reveal anomalous behavior, passing through the maximum before the stationary state is reached. The relaxation curves are described by the parameters of the localized state energy distribution, and are analyzed in the framework of multiple trapping models for amorphous materials.

*Key words:* Amorphous films, coordination number, photoconductivity, localized states.

## 1. INTRODUCTION

The photoconductivity spectra can give the information regarding the processes of generation, drift and recombination of non-equilibrium charge carriers [1–3]. *Chalcogenide vitreous semiconductors* (ChVS) of the As-S-Se systems exhibit photostructural transformations with reversible and irreversible properties, and are promising materials for registration media of optical information, for fabrication of diffractive elements, integrated optics, non-linear elements, optical fibers for IR spectrum, etc. [4–7].

Majority of photonic devices based on amorphous semiconductors functioned using the photoconductivity effect. From this point of view a special interest in a sentence represents the investigation of the characteristics of stationary and non-stationary photoconductivity. It was established that the amorphous films are characterized by a large degree of structural disorder which depend on the composition, foreign impurities, and light exposure [8]. The electrical, optical and photoelectrical properties of chalcogenide glasses can be varied and controlled over quite a wide range, by modifying the composition and production technique. Recently was reported the experimental results on the influence of Sn impurity in amorphous $As_2Se_3$ and AsSe thin films on electrical, transport properties, optical and photoinduced phenomena [9–14]. It was shown that tin impurities in amorphous $As_2Se_3$ increase the drift mobility and the photosensitivity. In the last years a special attention has been devoted to the influence on the photostructural transformation in amorphous thin films doped with metal impurity. In special it was shown that the Sn impurity introduced in the $As_2Se_3$, AsSe and $Sb_2S_3$ glass network reduce the photodarkening effect. According to Mössbauer spectroscopy of $^{119}$Sn in the $As_2Se_3$:$Sn_x$ glassy system a new tetrahedral $Sn(Se_{1/2})_4$ and quasi-octahedral SnSe structural units can be formed, and which influence the photostructural transformations [15]. The reduction in optical gap of $As_2Se_3$ glass upon tin alloying, most likely, results from a broadening of the valence band, the top of which is formed from Se lone-pair electrons. It was demonstrated that the Sn impurities have a strong effect on transient rather than on steady-state photoconductivity. The enhanced deep trapping of non-equilibrium carriers in doped $As_2Se_3$ delays the recombination process and slows down the initial photocurrent relaxation. The features of transient photoconductivity are controlled by deep carrier trapping with the energy distribution and concentration of deep traps being determined by the structure and composition of doped amorphous films [16]. In this paper the experimental results of steady-state and transient photoconductivity of amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ thin films are presented. In our previous work it was shown that the spectral distribution of the stationary photoconductivity for $(As_4S_3Se_3)_{1-x}Sn_x$ thin films depends on the composition and polarity on the illuminated electrode. The spectral characteristics of photoconductivity were used for estimation of some energy parameters.

## 2. EXPERIMENTAL

The bulk chalcogenide glasses $(As_4S_3Se_3)_{1-x}Sn_x$ ($x = 0 \div 0.10$) were prepared from the elements of *6N* purity (As, S, Se, Sn) by conventional melt quenching method. The thin film samples of thickness $L \approx 2$ μm were prepared by flash thermal evaporation in vacuum ($P = 10^{-5}$ Torr) of the synthesized initial glasses onto glass substrates held at $T_{substr} = 100$ °C. For photoelectric measurements were

using the thin film samples with a sandwich configuration with two Al-electrodes, the one of which (top electrode) is semitransparent for incident light ($\lambda$ = 400–1300 nm). The dark conductivity $\sigma_d$, Lux-Ampere characteristic $I_{ph} = f(F)$, spectral distribution of stationary photo current $I_{ph} = f(\lambda)$, and transient photocurrent $I_{ph} = f(t)$ were measured in the constant current conditions using the spectrophotometer SPM-2 and the electrometrical amplifier U5-11, with an error of less than $\pm$ 1.0 %. The Lux-Ampere characteristics were investigated at the wavelength of the uniform absorption light in the sample, the light intensity was varied by the calibrated neutral filters. The voltage applied to the all samples was 5 V, which corresponds to the linear portion of the I-V characteristic. All experiments were performed at room temperature. For data acquisition of the experimental data to the PC the digital card Arduino Uno was used.

## 3. RESULTS AND DISCUSSION

Figure 1 represents the spectral distribution of photocurrent curves for Al-$(As_4S_3Se_3)_{0.93}Sn_{0.07}$-Al thin film structure at positive (+) and negative (–) polarity of applied field at the top illuminated electrode. It was established that the value of the photocurrent is higher for the positive polarity on the illuminated Al-top electrode, and the maximum of the photocurrent is shifted toward higher region of the photon energies, compared to negative polarity. This can be explaining on the basis of contact phenomena at the interface of the metallic electrode with the amorphous film, as well as with the surface recombination processes. The spectral dependence of the photocurrent for all Al-$(As_4S_3Se_3)_{1-x}Sn_x$-Al thin film structures depend on the polarity of the applied voltage on the illuminated electrode and has the similar shape. Using the obtained spectra of the photocurrent and the Moss rule were estimated the band gap values $E_g^{ph}$, according which the band gap corresponds to the value of the wavelength ($\lambda_0$) $E_g^{ph} = \dfrac{1.24}{\lambda_0}$ at which the photocurrent fall down to a half value of it maximum, as is shown in Fig. 1. The magnification of the photocurrent ($k_{ph}$) represents the light sensibility, and for all investigated compositions is about $k_{ph} \sim 10^2$.

Figure 2 represents the dependence of the position of the photocurrent maximum on the photon energy $I_{ph}(\text{max}) = f(h\nu)$ (curve 1) and of the band gap energy $E_g^{ph}$, determined according Moss rule (curve 2), on the Sn concentration in $(As_4S_3Se_3)_{1-x}Sn_x$ thin films. These two dependences have a similar tendency and represent a curve with minimum. With increasing of the tin concentration in the $(As_4S_3Se_3)_{1-x}Sn_x$ thin films, the position of the photocurrent maximum is shifted in the region of lower photon energies up to $x$ = 0.06, and then it is displaced again in

the region of higher photon energy. The same behaviour on the tin concentration has the dependence $E_g^{ph}$ on the Sn concentration.
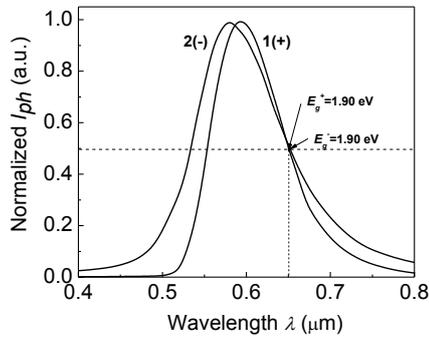


Fig. 1 – Spectral dependence of the stationary photocurrent for Al-$(As_4S_3Se_3)_{0.93}Sn_{0.07}$-Al thin film structure at positive 1 (+) and negative 2 (−) polarity of applied field at the top illuminated electrode. The film thickness $L = 2.0$ μm.
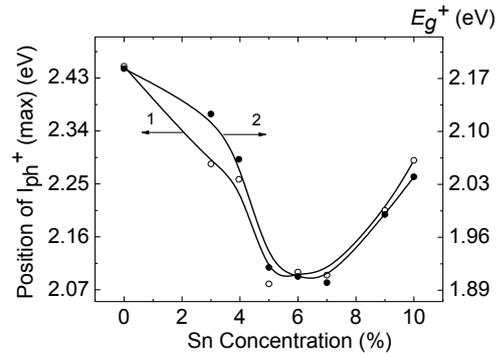
Fig. 2 – Dependence of the position of the photocurrent maximum on the photon energy $I_{ph}(max) = f(h\nu)$ and of the band gap energy $E_g^{ph}$, determined according Moss rule, on the Sn concentration in $(As_4S_3Se_3)_{1-x}Sn_x$ thin films.

Figures 3 and 4 represent the relaxation curves of photocurrent in Al-$As_4S_3Se_3$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different wavelength excitation and different light intensities, respectively.

The character of the photocurrent relaxation in Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different wavelength excitation without filters is shown in Fig. 5. For all investigated $(As_4S_3Se_3)_{1-x}Sn_x$ thin film compositions the shape of the relaxation curves of the photocurrent is the same. Usually the photocurrent on the increasing section passes through a maximum before reaching a stationary state (so-called "spike"). The height of the "spike" is more pronounced for the wavelength of the maximum in the spectral distribution of the photocurrent (for the $(As_4S_3Se_3)_{0.91}Sn_{0.09}$ composition $\lambda_{max} = 560$ nm).

Figure 6 represents the photocurrent relaxation in Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different light intensities at the wavelength excitation from the maximum sensitivity. At high levels of excitation (curves nf–0 ÷ nf–3), the photocurrent on the increasing section passes through a maximum before reaching a stationary state. At low levels of excitation (curve nf–13), the photocurrent increase monotonously and reach the stationary state very slowly. The observed "spike" in the rise portion of the curve that after a generated free-carriers was captured into the traps, an intensive bimolecular recombination (BR) take place, and the photocurrent follows down up to its stationary value. The intensive capture

process in $(As_4S_3Se_3)_{1-x}Sn_x$ thin film may be associated with deep level traps, which appear in this case. These traps are situated very deeply and significantly retardates the recombination. The same situation was observed in the case of amorphous $As_2Se_3$ and AsSe and doped with tin [10, 11, 17]. It was established that the tin impurity introducing during thermal synthesis of AsSe and $As_2Se_3$ glasses has greater effect on transient than on steady-state characteristics of photoconductivity. This was confirmed also experimentally for optical and stationary characteristic of photoconductivity of amorphous $Ge_xAs_xSe_{1-2x}$ and $(As_4S_3Se_3)_{1-x}Sn_x$ thin films [18]. The experimental results on relaxation of photoconductivity are explained in framework of multiple trapping model, according to which the non-equilibrium carriers are multiple captured in the deep traps, exponentially or quasi-continuously distributed in energy in the mobility band gap in amorphous semiconductors [19, 20]. Analysis of dispersion transport and photoinduced absorption leads to an exponential energy distribution of the density of localized states $g(E) = (N_t / kT^*)\exp(-E / kT^*)$, where $N_t$ is the total density of localized states, and $T^*$ is the distribution parameter. For $As_2Se_3$, in the energy interval E = 0.2 – 0.6 eV above the edge of the conducting states $kT^* = 0.05$ eV, and $N_t \leq 1.4 \times 10^{18}$ cm$^{-3}$ [10].
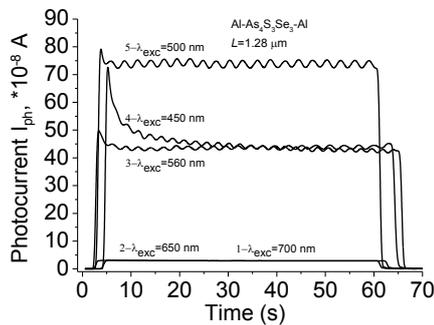


Fig. 3 – The relaxation curves of photocurrent in Al-As$_4$S$_3$Se$_3$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different wavelength excitation.
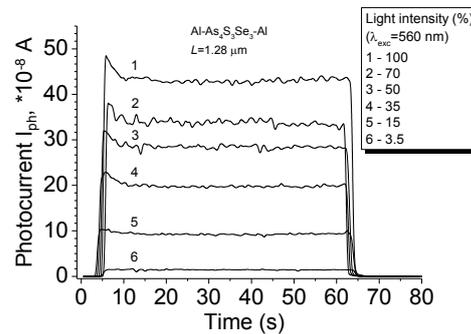
Fig. 4 – The relaxation curves of photocurrent in Al-As$_4$S$_3$Se$_3$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different light intensity.

Figure 6 shows that the behavior the initial portions of the photocurrent rise depend on the excitation intensity. At low intensities corresponding to *monomolecular recombination* (MR) the photocurrent monotonously increases and saturates at the steady-state value (curve nf–13). At higher exposure intensities a quasistationary portion is observed (curves nf–0 ÷ nf–3), which is followed by a decreasing portion of the photocurrent was the bimolecular recombination is dominant. The "spike-like" portion in the increasing section of the photocurrent

follows from a model of multiple trapping of the non-equilibrium carriers (holes) with high generation levels, when the *bimolecular recombination* (BR) became the determining mechanism. The "spike" is due to time-dependent nonstationary recombination, whose the light intensity changes the density of the captured nonequilibrium holes.
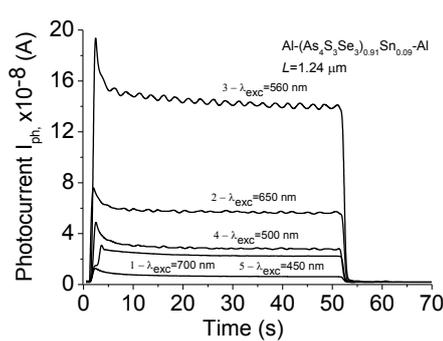


Fig. 5 – The relaxation curves of photocurrent in Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different wavelength excitation.
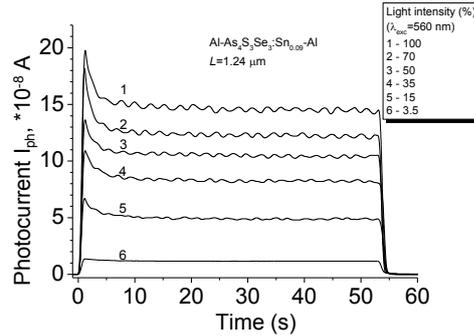


Fig. 6 – The relaxation curves of photocurrent in Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structure at positive (+) polarity of applied field at the top illuminated electrode at different light intensity.
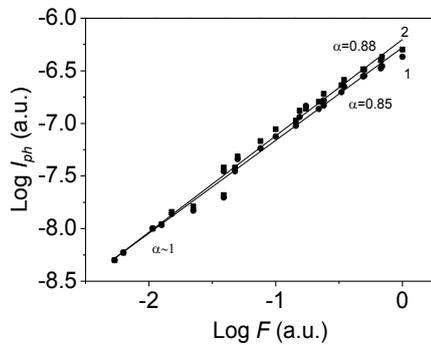


Fig. 7 – Intensity dependence of steady-state (1) and maximum (2) photocurrent (Lux-Ampere Characteristic) in Al-$As_4S_3Se_3$-Al thin film structure. $L$ = 1.28 μm, $\lambda_{exc}$ = 560 nm.
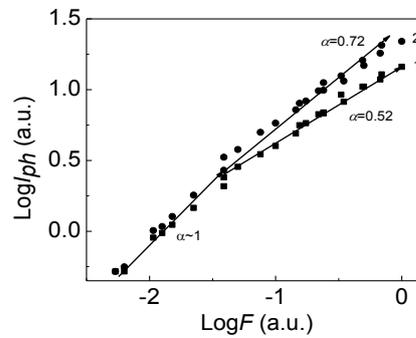


Fig. 8 – Intensity dependence of steady-state (1) and maximum (2) photocurrent (Lux-Ampere Characteristic) in Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structure. $L$ = 1.24 μm, $\lambda_{exc}$ = 560 nm.

Figures 7 and 8 represent the intensity dependence of steady-state (1) and maximum (2) photocurrent (Lux-Ampere Characteristic) in Al-$As_4S_3Se_3$-Al and Al-$(As_4S_3Se_3)_{0.91}Sn_{0.09}$-Al thin film structures, respectively. For other Al-

$(As_4S_3Se_3)_{1-x}Sn_x$-Al thin film structures the Lux-Ampere Characteristic ($I_{ph} \sim F^\alpha$) has a similar character, with the exception that the parameter $\alpha$ take a different values, in the dependence $Log I_{ph} = f(Log F)$, where $0.5 \le \alpha \le 1.0$ is the power index. For a simple model, $\alpha = 1.0$ at low excitation intensities corresponds to the mechanism of *monomolecular recombination* (MR), and $\alpha = 0.5$ to the mechanism of *bimolecular recombination* (BR). For amorphous semiconductors with exponential distribution of localized states in the band gap, for interpretation of Lux-Ampere Characteristics was successfully used the Rose model [1]. According to model Rose [21] in the assumption that the mobility is constant, the parameter $0.5 \le \alpha = \dfrac{T^*}{T + T^*} \le 1.0$, and can takes the intermediate values between 0.5 and 1.0. Parameter $T^* \ge T$ describe the distribution of localized states in the band gap of the amorphous semiconductor.

As it seen from Fig. 6, for amorphous $(As_4S_3Se_3)_{0.91}Sn_{0.09}$ thin films in the low intensity range, where the process is governed by *monomolecular recombination* (MR), the photocurrent is linearly dependent on light intensity ($\alpha = 1.0$). At high levels of light intensity where the process is governed by the *bimolecular recombination* (BR), the dependence of the steady-state and maximum photocurrent on light intensity becomes sublinear and takes the values $\alpha = 0.52$ and 0.72, respectively.

## 4. SUMMARY

The experimental results on steady-state and transient photoconductivity of amorphous $(As_4S_3Se_3)_{1-x}Sn_x$ ($x = 0 \div 0.1$) thin films are investigated. It was shown, that the spectral distribution of the stationary photoconductivity depends on the composition and polarity of voltage applied on the illuminated electrode. The dependence of the stationary photocurrent on the light intensity is described by a power function $I_{ph} \sim F^\alpha$, were $0.5 \le \alpha \le 1.0$ is the parameter which describe the distribution of the localized states in the band gap. The kinetics of photocurrent produced by uniform continuous bulk photogeneration of non-equilibrium carriers reveal anomalous behavior, passing through the maximum before the stationary state is reached. The relaxation curves are described in the framework of multiple trapping model for amorphous materials.

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