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Transient photocurrent in α-As_2Se_3 thin films with optical bias

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ABSTRACT

Relaxation of pulsed photocurrents under optical bias is studied in amorphous films of glassy alloys As_2Se_3:Sn_x (x=0 to 3.5 at.%) by the time-of-flight technique and steepness band-to-band light illumination. In frame of multiple-trapping model it is shown that by adding tin to the glass former As_2Se_3, the hole drift mobility is strongly increased and hamper the recombination.

The kinetics of the long-term photocurrent decay can be described by stretched exponential function. The dispersion parameter α, which can be deduced from the time dependence of the photocurrent $I_{ph}(t) \infty \exp[-(\tau/\tau)^{\alpha}]$ and, is about 0.47 for undoped samples, and 0.35 for tin-containing samples. The obtained results indicate the variation in occupation of deep localized centers. For the investigated samples, the width of distribution of the deep traps is approximately kT/α~50-70 meV.

I. INTRODUCTION

Arsenic serenades glasses are well known as high photosensitive materials with a wide range of application in optoelectronics and information storage systems. Besides that, the physical and practical interest of the impurity effect in amorphous materials arises from its structure, which has a higher degree of disordered than that of bulk glasses. The influence of impurities on transient photocurrents in amorphous As_2Se_3 films was reported[1]. It was found that the impurities influence the dispersion parameter α, which describe the exponential density of localized states in amorphous material.

One of the methods for determination the energy distribution of localized states in amorphous semiconductors is so-called transient photoconductivity technique[2-4]. The experimental results on α-As_2Se_3 films usually were interpreted in frame of multiple-trapping model when the photoconductivity relaxation is determined by trap-controlled recombination. Moreover, it was shown that the Sn and other metal impurities influence the relaxation of photocurrent due to appearance of new localized centers as result of doping of the amorphous material[3,5].

The time-of flight experiments also can be used to investigate photoinduced changes in electronic properties of the amorphous materials[6-9]. It was shown that bias light induces an increases in the trap density in α-As_2Se_3 and modifications of the electric field in α-Se[7]. Our first experiments on time-of-flight measurements of the hole drift in α-As_2S_3 show that under additional illumination distributed uniformly over the sample volume, the drift mobility increase, especially at lower temperatures[6]. This increase of the drift mobility and decreasing of the activation energy was attributed to the filling of deep traps under high levels of additional illumination.

Because Sn create new localized centers in the forbidden gap of the amorphous material, the goal of this paper is to investigate the distribution of localized states in α-Aa_2Se_3 doped with different concentrations of tin. For this purpose the time-of-flight technique and long-term relaxation of photocurrent were applied.

II. EXPERIMENTAL

The amorphous films of glassy alloys As_2Se_3:Sn_x (x=0 to 3.5 at.%) with thickness from 1 to 10 μm were prepared in sandwich configuration with two aluminum electrodes by "flash" thermal deposition in vacuum of the starting bulk material onto glass substrates kept at T_s=120 °C. In time-of-flight experiments, short pulses of strongly absorbed light from a nitrogen laser excited the photocurrent, and was monitored by a digital oscilloscope of type RM 3320A of Philips production. By means by time-of-flight technique we studied the relaxation of transient photocurrents in the

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films of α-As_2Se_3:Sn_x (x=0 to 3.5 at.% Sn) also under additional illumination ("optical bias"), i.e. under conditions suited to the operating regime of films in information recording devices.

For long-term relaxation of photoconductivity, the photocurrents was excited by a pulse of monochromatic light (λ=0.49 μm), through the top transparent electrode. The light intensity in pulse was 10^{12}-10^{14} cm^{-2} s^{-1}, and it duration about 25 s. The photocurrent feed to the electrometric amplifier and was registered by the two coordinate recorder. The constant voltage bias of about 4.0 V was applied to the top illuminated electrode.

III. EXPERIMENTAL RESULTS AND DISCUSSION

a) Transient photocurrents under optical "bias" in time-of-flight experiments

The typical forms of the transient photocurrent decay are shown in Fig.1. in double-logarithmic representation in the dark and under optical bias. The photocurrent was excited by pulses of strongly absorbed light (λ=0.34 μm). The transport of photo-excited holes in amorphous As_2Se_3 films is strongly dispersive, and the observed behaviour of the transient photocurrent decay in the absence of an optical bias is typical for disordered materials. The transition consists of two power-like portions, the initial one, which is usually described as $j(t)\sim t^{-(1-\alpha)}$, characterizes the drift in the sample of the packet of photo-excited carriers. The final, faster portion of the decay $j(t)\sim t^{-(1+\alpha)}$, appears as a result of decreasing amount of carriers in transport due to their leaving the sample or due to recombination. The dispersive parameter usually take the values $0.5\leq\alpha\leq1.0$. The exit of the carriers packet out of the sample leads to a sharp current drop, which allows to determine the transit time t_T and to find the drift mobility

$$\mu_d = \frac{L}{Et_T},$$

were L is the thickness of the sample, E is the applied field.

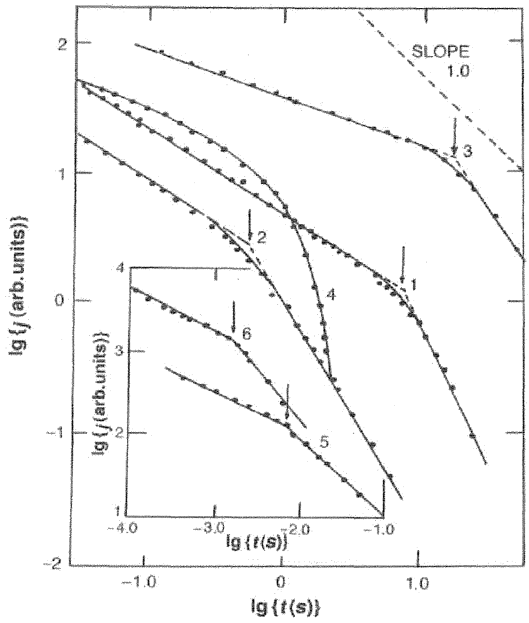

Fig.1. The transient photocurrent curves in As_2Se_3 (curves 1,2) and As_2Se_3:$Sn_{1.0}$ (curves 3,4) thin films (L=10 μm) in the dark (curves 1,3) and under bias illumination (curves 2,4). The applied field E (V/cm): (1,2)-$4\cdot10^4$; (3,4)- $8\cdot10^4$.

Insert. The transient photocurrent curves in As_2Se_3 films (L=1.5 μm) in the dark at the applied fields $1.3\cdot10^4$ V/cm (5) and $3.3\cdot10^4$ V/cm (6).

The final portion of the decay for the sample of composition in As_2Se_3:$Sn_{1.0}$ shows an exponential behaviour. For As_2Se_3 and As_2Se_3:$Sn_{1.0}$ amorphous films, under the action of an optical bias the transient decreases, its form became rounded and acquires exponential endings with time constants of about 2 s (Fig.1). The characteristic times of kinks in the transient curves, though smeared out under optical bias, decrease from about 10 s in the dark to 3 s under optical bias. For the As_2Se_3:$Sn_{2.0}$ and As_2Se_3:$Sn_{3.5}$ amorphous films, on the contrary, the optical bias leads to an increase of the transient current at almost the same form, having two power portions of decay, the characteristic times of which are

much shorter (in the region from 0.01 to 0.001 s). The characteristic times of the kinks in these samples are strongly dependent on the applied voltage, decreasing with the increase of electric field, and allow to determine the drift mobility, which increase with the increasing of tin impurity (Fig. 2).

The analysis of the transient photocurrents obtained in the time-of-flight experiments with optical bias in the presence of dispersive transport presents a rather complicated problem. Optical bias induces changes in the electric field distribution[7], influences the value of the drift mobility[10,11] and recombination rate[9,12,13], leads to changes in the occupation function and in the concentration of localized states[7]. For interpretation of our experimental results we use the model of multiple trapping in disordered materials[14,15], which successful have been explained some transport, photoelectrical and photoinduced optical absorption phenomena in α-As_2Se_3. Some results of the multiple trapping model with optical bias were reported by Pandya and Schiff in 1985[16].

The transient photocurrents in the multiple-trapping model with optical bias were examined, taking into account the regimes of mono- and bimolecular recombination.

a) b)

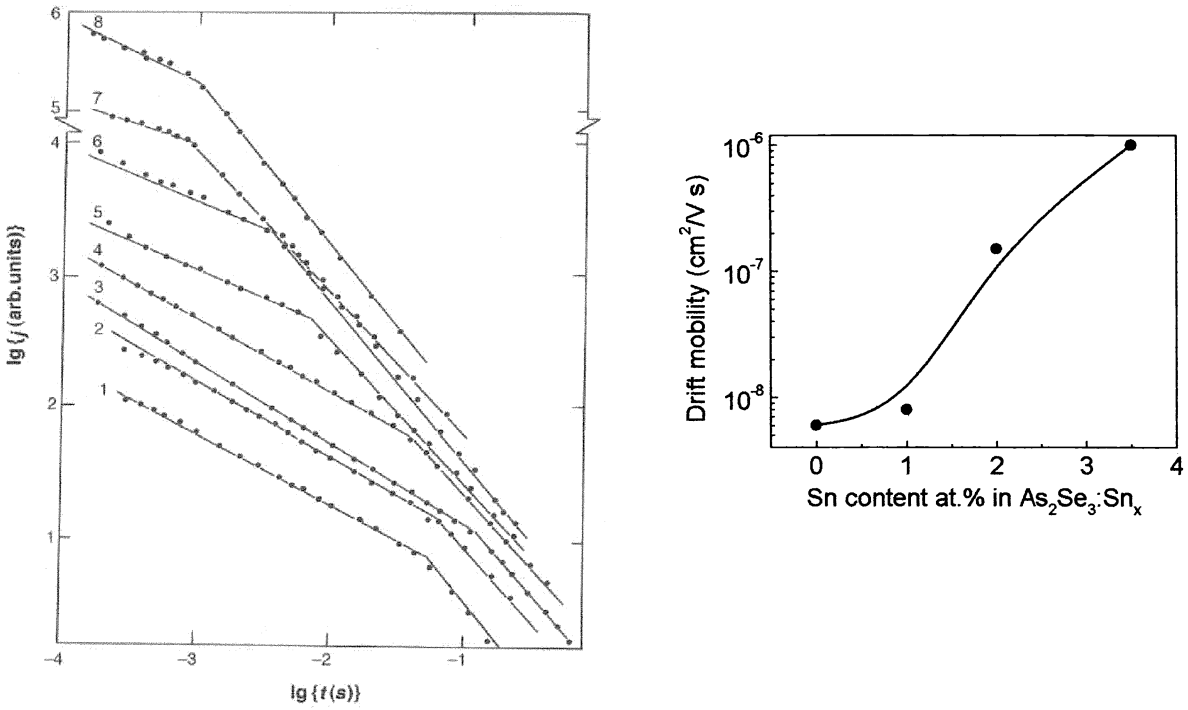

Fig.2. The transient photocurrent curves (a) in α-As_2Se_3:$Sn_{2.0}$ (curves 1,2) and As_2Se_3:$Sn_{3.5}$ (curves 3 to 8) thin films (L=10 μm) in the dark (curves 1,3,5,7) and under bias illumination (curves 2,4,6,8). The applied field E (V/cm): (3,4)-$2\cdot10^4$, (5,6)-$5\cdot10^4$, (1,2,7,8)-$1\cdot10^5$. The dependence of the drift mobility μ_d versus tin concentration for α-As_2Se_3:Sn_x tin films (b).

The decay of photocurrent in amorphous As_2Se_3 and As_2Se_3:$Sn_{1.0}$ films can be characterized as:

(i) the transient has a characteristic kink, after which the decay rate is larger;
(ii) optical bias shortens the time, after which the decay become faster, and turn the decay to a rounded form;
(iii) the final portions of transients of As_2Se_3:$Sn_{1.0}$ have an exponential form.

The absence of long plateau indicates that the time constants of thermalization and recombination are close to each other. The kink observed on the transient curves corresponds to the recombination time t_R after thermalization, that is after t_R the decay has an exponential form (Fig.3). The recombination time t_R in the experiments with optical bias is less (~2 s) than in the dark (~10 s). The fact that that the observed kink occurs at times much greater than the transit time t_T

is supported by the experiments on thin (L=1.5 μm) samples (Fig.1), for which the transition from the before-transit portion $j(t)\sim t^{-(1-\alpha)}$ to the after-transit one $j(t)\sim t^{-(1+\alpha)}$ is clear defined ($t_T\sim10^{-2}\div10^{-3}$ s). The corresponding values of drift mobility are $\mu_d\sim10^{-6}$ cm^2/V s.

For the samples with high content of tin (As_2Se_3:$Sn_{2.0}$ and As_2Se_3:$Sn_{3.5}$) the behaviour of the photocurrent transients corresponds most likely to the common experimental time-of-flight conditions and the kink is a measure of the transit time t_T. The experimental results indicate a significant increase (about 200 times) of the drift mobility in the films with high content of tin in As_2Se_3. The optical bias leads to an increase of drift mobility and an enhancement of the photocurrent in the initial portions of relaxation. The drift mobility depends on the bias intensity following a power law. The optical bias significantly lowers the temperature dependence of the dispersion of photocurrent transients, leading to the decrease of the dispersion parameter. This fact indicates that the observed variations of the drift behaviour are due to changes in the occupation of deep localized states under the action of the optical bias.

The t_R values appear to be anomalously high, which is characteristic of the multiple trapping model, describing the recombination process in amorphous materials (Table 1). The recombination time is weakly dependent on the applied voltage and decreases by several times under the action of the optical bias. Adding Sn impurities gives an about fivefold increase of the recombination time.

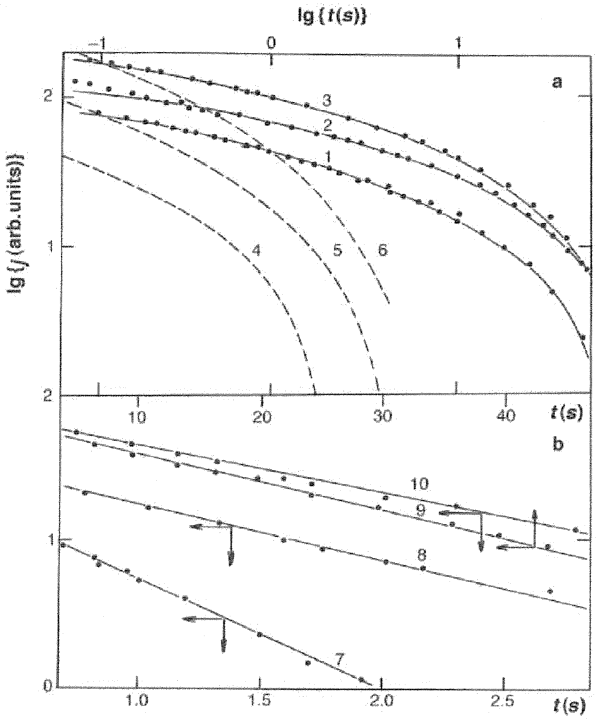

Fig.2. The transient photocurrent curves in As_2Se_3:$Sn_{1.0}$ thin films (L=10 μm) in (a) double-logarithmic and b) semi-logarithmic coordinates in the dark (curves 1,2,3,9) and under bias illumination (curves 4,5,6,7,8,10). The applied field E (V/cm): (1,4,7)-8·10^4; (2,5,8)-1.3·10^5; (3,6,9,10)-1.9·10^5

Using the formula from[17] relating the recombination time t_R to the dencity of recombination centres N_{rec} with the constant b_tN_t/b_R=2.3x10^{20}cm^{-3}determined for As_2Se_3, we have estimate the density of recombination centres in thermal equilibrium for the investigated samples:

$$\tau_R = (1/\nu)[(b_t/b_R)(N_0/N_{rec})]^{1/\alpha},$$

where α is the dispersion parameter (α=0.5 for As_2Se_3). Therefore,

$$N_{rec} = (b_tN_0/b_R)(\nu\tau_R)^{-\alpha}.$$

For $\nu = 10^{12}s^{-1}$, estimation yields

$$N_{rec} = 10^{14}cm^{-3}$$

for the As_2Se_3 films and

$$N_{rec} = 7x10^{13} cm^{-3}$$

for the As_2Se_3:$Sn_{1.0}$ films.

This estimation of the recombination centre density is about two orders of magnitude larger than that predicted in[17] by extrapolation of the data obtained for bulk samples. Introduction of tin lowers the density of recombination centres in As_2Se_3 films causing the lifetime of non-equilibrium holes to increase. For the As_2Se_3:$Sn_{2.0}$ and As_2Se_3:$Sn_{3.5}$ samples the behaviour of the transient photocurrents correspond most lakely to the experimental time-of-flight conditions and the kink is a measure of the transit time t_T. For these samples the optical bias leads to an increase of the drift mobility.

Table 1. The experimental values of the recombination time t_R for As_2Se_3 and As_2Se_3:$Sn_{1.0}$ thin films.

	Sample composition	Applied field *E*, (x10^4 V/cm)	t_R (s) (without optical bias)	t_R (s) (with optical bias)
1.	As_2Se_3	4	6.0	1.7
2.	As_2Se_3	8	2.3	-
3.	As_2Se_3:$Sn_{1.0}$	8	11.8	1.8
4.	As_2Se_3:$Sn_{1.0}$	13	10.0	1.4
5.	As_2Se_3:$Sn_{1.0}$	19	5.7	0.9

b) Long-term relaxation of the photocurrent

Results of the long-term relaxation of the photocurrent in As_2Se_3 and As_2Se_3:Sn_x, thin film samples without optical bias (curve 1) and for successively larger three levels of optical bias (curves 2-4) are presented on Fig.3 and 4, respectively. It seems that influence of additional illumination upon the shape of the photocurrent transient for both samples essentially differs.

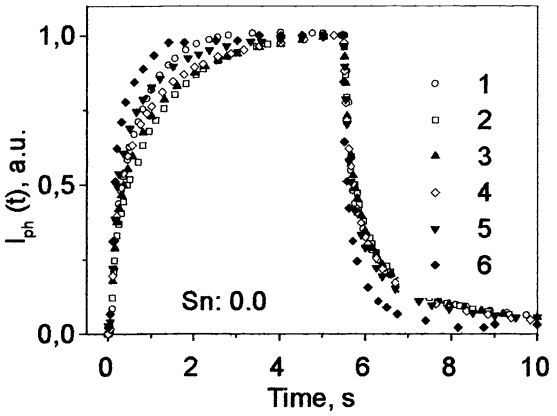

Fig.3. Normalized photocurrent transient for α-As_2Se_3 samples without bias illumination (curve 1), and under bias illumination (curves 2,3,4,5,6).
Excitation light intensity F=10^{13} photon/(cm^2 s).

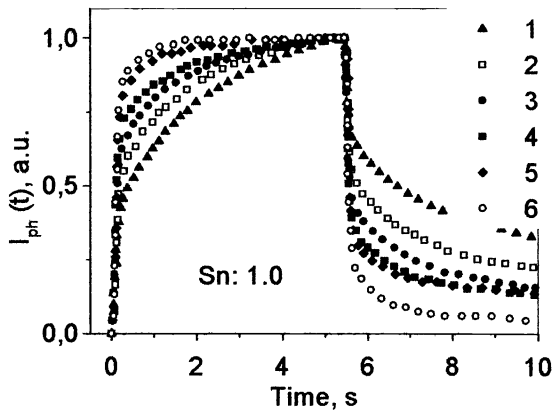

Fig.4. Normalized photocurrent transient for α-As_2Se_3:$Sn_{1.0}$ samples without bias illumination (curve 1), and under bias illumination (curves 2,3,4,5,6).
Excitation light intensity F=2 10^{13} photon/(cm^2 s).

For undoped samples, the additional illumination leads to some decreases of the transient photocurrent. The steepness of rise and decay portions of a photocurrent pulse also is little increased. For the samples with tin impurity, the shape of the photocurrent two portions of a pulse specifies the overextended character of relaxation. Both portions of curves significantly change under influence of optical bias and this change testifies to sharp increase relaxation rate. Influence of optical bias on the persistent photoconductivity is especially appreciable: the photocurrent on this slow domain of the

relaxation sharply decreases under illumination even at small levels of optical bias (I_{OB}~1.5 x 10^{-9} A). Simultaneously to reduction of the photocurrent, there is the decrease of the decay time constant τ (from 20 up to 1.5 s).

Table 2. Some parameters of the deep traps estimated from the experimental photocurrent curves.

Sample composition at.%	Number of the curve	Optical bias	N_t, cm^{-3}	N_d, cm^{-3}	E_d, eV
As_2Se_3	1	Without optical bias	$5\ 10^{19}$	$6\ 10^{15}$	0.639
	2	With optical bias	$5\ 10^{19}$	$5\ 10^{15}$	0.636
	3	With optical bias	10^{20}	10^{16}	0.648
	4	With optical bias	$1.5\ 10^{19}$	$1.5\ 10^{15}$	0.632
	5	With optical bias	$2\ 10^{20}$	10^{16}	0.623
As_2Se_3:$Sn_{1.0}$	1	Without optical bias	$4\ 10^{19}$	$1.2\ 10^{18}$	0.875
	2	With optical bias	$4\ 10^{19}$	$1.2\ 10^{18}$	0.924
	3	With optical bias	$3.5\ 10^{19}$	$1.2\ 10^{18}$	0.954
	4	With optical bias	$5\ 10^{19}$	$1.2\ 10^{18}$	0.968
	5	With optical bias	10^{19}	10^{17}	1.06

The dispersive parameter α which can be deduced from time dependence of photocurrent I_{ph} (t) ∞ exp $[-(t/\tau)^{\alpha}]$ is about 0.47 for the undoped sample, and 0.35 for the sample with tin impurity, that is in the good agreement with[1] in which the photocurrent relaxation in amorphous As_2Se_3 and As_2Se_3:Sn films was fitted to the power law. The width of distribution of the deep traps is approximately κT/α~50–70 meV for the investigated samples.

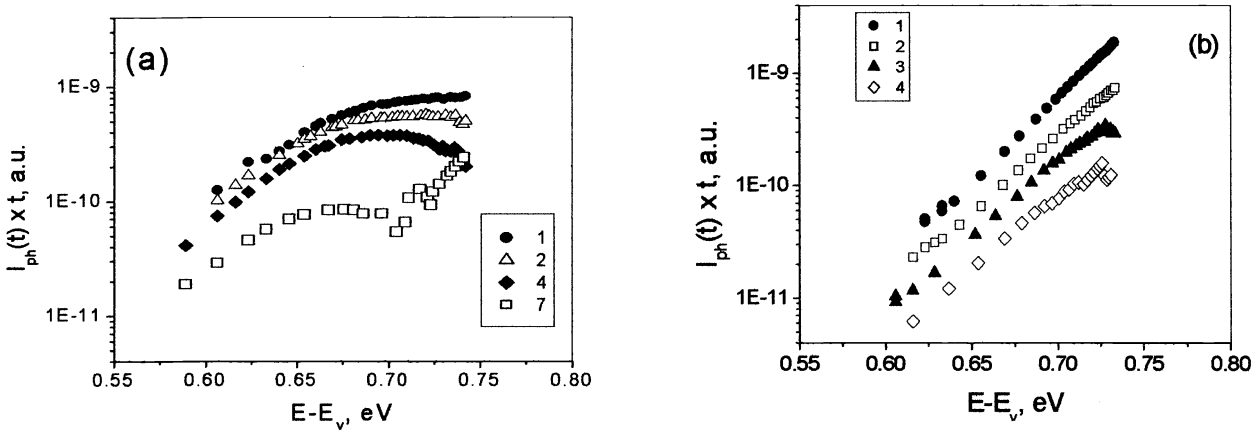

Fig.5. Product I_{ph} (t) x t for a-As_2Se_3:$Sn_{2.0}$, obtained from the relaxation curves in darkness (curve 1) and at various levels of optical bias (curves 2-4).

The dependence of product of the photocurrent on time versus energy E=kTln(ντ), $\nu=10^{12}$ s^{-1}, deduced from the curves of photocurrent relaxation are presented on Fig.5a and b. According to[18] the product I_{ph} (t) x t characterizes the energy distribution of effective density of deep traps

$$g(E) \approx ti(t)\left(\frac{N_t}{N\ e\mu\varepsilon A t_0 kT}\right),$$

where N_t is the total density of localized states,

$$N' = N_0(t_0/(t_0 + \tau_t))$$

and τ_t is the overall trapping time into the ensemble of localized states. Some estimation of the deep traps parameters are given in the Table 2.

For the undoped sample (curve 1) it has bump shaped form with a maximum about Ei~0.64 eV; the measurements of the modulated photocurrents, also result in similar peak near 0.66 eV[8]. Under influence of optical bias, the effective concentration of traps is suppressed, which coincide with our analysis of the transient photocurrent. It is assumed, that in case of the curves presented in a Fig.5b the position of deeper levels induced by tin impurity changes; these levels are in middle of the gap (near to Fermi level) and can effectively re-filled under action of optical bias. For example, significant suppression of deep capture occurs already when stationary photocurrent I_{OB} exceed about 3 times the dark current, that corresponds only the small (~0.03 eV) shift of quasi-Fermi level from its position in the dark, although another explanation also is possible[4].

IV. SUMMARY

Relaxation of transient photocurrents excited in a sandwich structure containing amorphous films of $As_2Se_3:Sn_x$ (x=0 to 3.5 at.% Sn) by a pulse of strongly absorbed light in experimental "time-of-flight" configuration with optical bias is studied. The form of transients photocurrents observed in the experiment is correlated with the results of calculations of non-equilibrium carrier relaxation made in the frame of the multiple-trapping model. Small concentrations of tin lower the density of recombination centres in As_2Se_3 significantly increasing the lifetime of non-equilibrium holes. For the tin concentrations more than 2.0 at.% Sn the drift mobility increase, a fact which indicate the compensation of active capture centres. The kinetics of the long-term photocurrent decay is non-exponential and is described by stretched exponential function. Optical bias increase the rate of photocurrent relaxation due to changes in the occupation of deep localized centres.

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