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PHOTOCONDUCTIVITY AND TRANSPORT PROPERTIES OF As-Se THIN FILMS

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Steady-state and transient photoconductivity characteristics of thermally and laser-beam deposited chalcogenide amorphous films $As_{40}Se_{60}$ and $As_{50}Se_{50}$ are studied at varied light intensity and temperature. The lux-ampere characteristics are shown to change the power exponent from a value greater than 0.5 at low intensities to the value less than 0.5 at high intensities, indicating the change in recombination reaction. The transient photocurrents in step-function mode of excitation were found to be consistent with the model of trap-controlled non-stationary capture and recombination in exponentially distributed in energy hole traps. Evaluating of the trap energy distribution parameter independently from the photocurrent transients as well as from the dependence of steady-state photoconductivity measurements yields consistent results.

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1. Introduction

Amorphous films of chalcogenide glassy system As_xSe_{100-x} are currently of interest as materials for optoelectronic devices and optical information storage [1-3]. The composition $As_{50}Se_{50}$ of this system exhibits high light sensitivity in photostructural transformations due to the presence of homopolar As-As bonds [4-6]. Excess of As in $As_{50}Se_{50}$ relative to stoichiometry composition $As_{40}Se_{60}$ leads to increase of optical gap E_g (from 1.90 eV to 1.95 eV for bulk $As_{40}Se_{60}$ and $As_{50}Se_{50}$, respectively) and of other related energy intervals [7,8]. The evaporated films are shown to have large degree of structural disorder depending on the deposition procedure. In the present paper the results of systematic study of steady state and transient photoconductivity characteristics of thermally deposited amorphous films $As_{50}Se_{50}$ and $As_{40}Se_{60}$ are described. The obtained data are analysed on the base of multiple trapping model and some parameters of the localised state energy distribution are derived from the experimental results.

2. Experimental

The thin film samples were prepared in sandwich configuration with aluminium or gold electrodes. The $As_{50}Se_{50}$ and $As_{40}Se_{60}$ films with thickness from 1 to 6 μm were obtained by flash thermal deposition in vacuum of the starting bulk material onto glass substrates kept at T_s=375÷400 K. In some cases the laser ablation was used for obtaining amorphous films. He-Ne laser LGN-108 (λ=0.63 μm) was used as a light source with photon flow $F=6.5\cdot10^{14}$ $cm^{-2}s^{-1}$; the light intensity was controlled by calibrated neutral density filters. A shutter was used to switch the light on/off with time constant of about 10^{-3} s. The photoconductivity relaxation was registered with a time constant not greater than 0.1 s by a co-ordinate recorder ENDIM 622.01. The spectral distribution of steady-state photoconductivity was obtained with the aid of spectrophotometer SPM-2 with a tungsten lamp as a light source.

3. Results and discussion

3.1. Steady state photoconductivity

Lux-ampere characteristics of steady-state photoconductivity σ_{ph} for all investigated amorphous films in a wide intensity (F) interval at various temperatures (T) are sublinear and may be approximated by a power law:

$$\sigma_{ph} = B \cdot F^{\gamma}, \quad (1)$$

where B is the constant weakly dependent on temperature, and γ is the power index. For each σ_{ph} vs. F curve an inflection point is observed corresponding to the transition of the power index γ from the values γ_L= 0.60 ... 0.73 in the low-intensity interval to lower values γ_H = 0.5 ... 0.3 at higher excitation intensities (Fig. 1a). With the temperature increasing, γ_L and γ_H first remain constant up to 350 K and then γ_L increases while γ_H decreases. This kind of behaviour appears to be unusual as γ_L as a rule decreases with temperature increasing while γ_H is weakly temperature dependent. The intensity dependence of photoconductivity at all temperatures shows a kink (Fig. 1a), at which the power exponent γ is changed from γ>0.5 to γ<0.5. It is commonly accepted that this kink is due to change of excess-carrier recombination mechanism at increasing of excitation, i.e. to transition from the monomolecular (MR) reaction to the bimolecular (BR) one. Sublinear power γ_L is then associated with variation of the recombination rate during movement of the quasi-Fermi level through a region of quasicontinious exponential gap-state distribution (A.Rose [9]), that is $\gamma_L = T_0/(T_0+T)$, where T_0 is the characteristic temperature of the gap-state distribution (T_0>T) and $0.5 \le \gamma_L \le 1$.

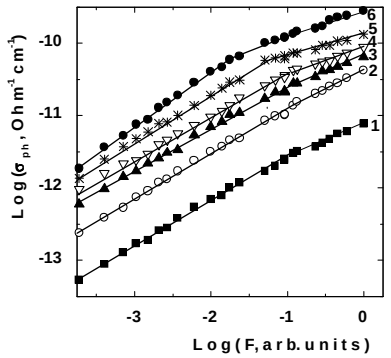

Fig. 1a. The steady state photoconductivity σ_{ph} dependence on. light intensity F of the $As_{50}Se_{60}$ films. Temperature T, K: 1-289; 2-321; 3-341; 4-351; 5-365; 6-388. F_0==$6.5 \cdot 10^{14}$ $cm^{-2} \cdot s^{-1}$.

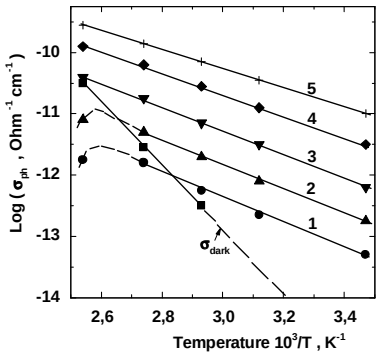

Fig. 1b. The steady state photoconductivity σ_{ph} dependence on temperature T of the $As_{40}Se_{60}$ films. Light intensity F, $cm^{-2} \cdot s^{-1}$: 1- $6.5 \cdot 10^{10}$; 2-$6.5 \cdot 10^{11}$; 3-$6.5 \cdot 10^{12}$; 4-$6.5 \cdot 10^{13}$; 5-$6.5 \cdot 10^{14}$. The temperature dependence of dark conductivity σ_{dark} is also shown.

The obtained value of γ_L=0.6 leads to T_0=450K, which is lower than T_0=550K obtained for the characteristic temperature of the state distribution in the valence-band tail of the stoichiometry composition $As_{40}Se_{60}$ [10]. The observed independence of γ_L up to 350K and its further rise at increasing of the temperature could be understood in the frames of the mentioned model if we suppose that T_0 is also increased with the temperature, i.e. the hole quasi-Fermi level crosses the region of quasicontinious distribution of localised states with varying steepness. At high temperatures and intensities of light the power exponent γ_H deviate from the standard value γ_H=0.5 characteristic for bimolecular recombination and takes lower values, which indicate the participation of another recombination path. Low γ_H values (γ_H<0.5) are expected for tail-to-tail or tail-to-defect tunnelling recombination (a-Si:H [11,12]) or in the case of light absorption in the metal-semiconductor contact region for sandwich-cell samples (a-$As_{40}Se_{60}$ [13]).

The temperature dependence of steady-state photoconductivity (Fig. 1b) is activated with an activation energy E_b= 0.33 eV, which becomes somewhat lower (0.30 eV) at highest light intensity. In the high-temperature region a tendency to change of the recombination mechanism is observed. The estimation of the transition temperature T_m from the expression [14]:

$$T_m = (\sigma_{ph}/\sigma_{dark})E_a/2k \quad (2)$$

yields the temperature about 400K, which is out of the interval of measurements.

According to the model of quasidiscrete gap states of charged defects the activation energy of photoconductivity in low-temperature region ($T<T_m$, $\sigma_{ph}>\sigma_d$) accounts for the position of the acceptor-like level E_2-E_v = $2E_b$ [8,12,15]. For the $As_{50}Se_{50}$ films E_2-E_v = 2x0.33 eV = 0.66 eV, in agreement with the similar results for the films of stoichiometric composition $As_{40}Se_{60}$ [8]. This value is also

close to the results of time-of-flight drift mobility measurements [16], in which there was found that the drift mobility activation energy in $As_{50}Se_{50}$ films equals to 0.69 eV and sharply increases with further growth of As content (0.97 eV for $As_{55}Se_{45}$).

The spectral dependence of photoconductivity for the $As_{50}Se_{50}$ and $As_{40}Se_{60}$ films represents a curve with a broad peak (Fig. 2). The films demonstrate high photosensitivity in the visible region of the light spectrum (from 0.50 μm to 0.8 μm at the half-peak level) with light-to-dark conductivity ratio more than 10^2 at F= $5 \cdot 10^{14}$ cm^{-3} s^{-1}.

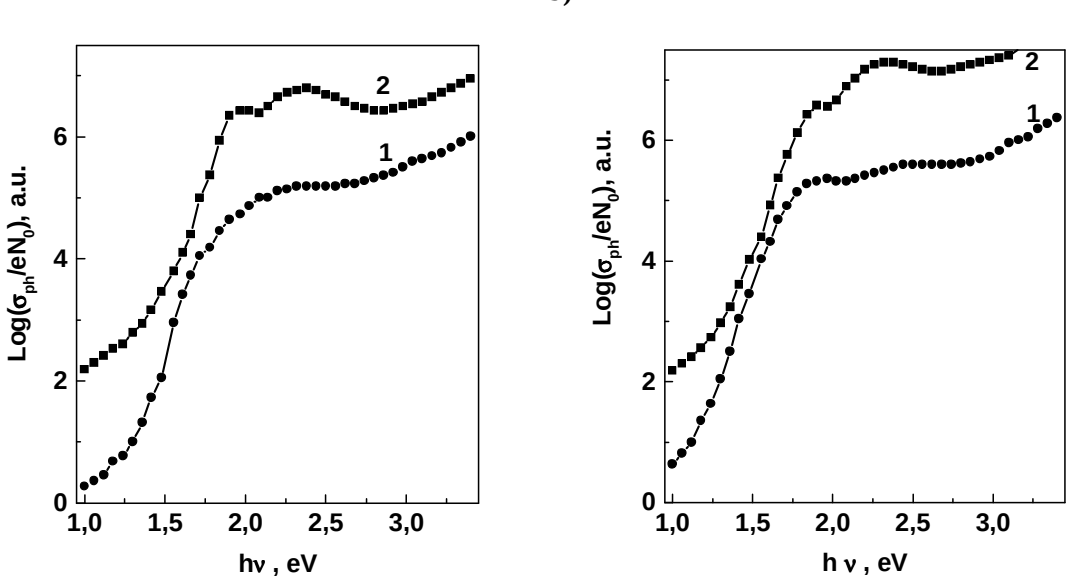

Fig. 2. The spectral dependence of the photoconductivity of laser (1) and thermal (2) deposited $As_{40}Se_{60}$ (a) and $As_{50}Se_{50}$ (b) thin films. The positive voltage is applied to the top illuminated electrode.

The position of the main peak of the photoconductivity spectrum of the amorphous arsenic selenide films at hν=1.97 eV corresponds to the optical gap E_g at the absorption coefficient $\alpha=10^4$ cm^{-1}. This value coincides with E_g=1.95 eV [7] obtained from optical measurements in bulk samples.

The photoconductivity spectra contain information about generation, transport, and recombination processes of the non-equilibrium carriers:

$$\sigma_{ph}=(1/d)e\mu_d\tau\beta N_0[1-exp(-kd)], \quad (3)$$

where N_0 is the number of the incident photons, d is the thickness of the sample, β is the generation rate, μ_d is the drift mobility, k is the absorption coefficient, and τ is the lifetime.

In the region of high absorption coefficients ($exp(-kd)<<1$), for the negligible low surface recombination, the photoconductivity weakly depends on the photon energy

$$\sigma_{ph}=(1/d)e\mu_d\tau\beta N_0, \quad (4)$$

For the weak absorption region ($exp(-kd)\approx 1-kd$) the photoconductivity spectra are described as

$$\sigma_{ph}=e\mu_d d\tau\beta N_0, \quad (5)$$

In this region the slope of the photoconductivity spectra expresses the parameter of the localised states $E_0=kT_0$, which depends on composition and on the preparation method of the amorphous thin film ($E_0\approx$0.07 eV for $As_{50}Se_{50}$, and $E_0\approx$0.06 eV for $As_{40}Se_{60}$). For the $As_{50}Se_{50}$ and $As_{40}Se_{60}$ thin films prepared by laser deposition an increase of photosensitivity in all investigated spectral domain is observed.

3.2. Transient photoconductivity

Long-term relaxation of photoconductivity in the amorphous $As_{50}Se_{50}$ and $As_{40}Se_{60}$ films under light excitation in step-function mode are shown in Fig. 3 at various laser light intensities. Illumination by the He-Ne laser corresponds to the absorption coefficient near 10^4 cm^{-1} therefore the incident light is totally and nearly uniformly absorbed in the film volume. As it is seen from the Fig. 3, at low intensities the photocurrent rises in monotonous manner up to the steady-state value. At higher intensities an overshoot appears on the increasing portion of the transient, i.e. the steady state is reached after passing a peak on the rise [17,18].

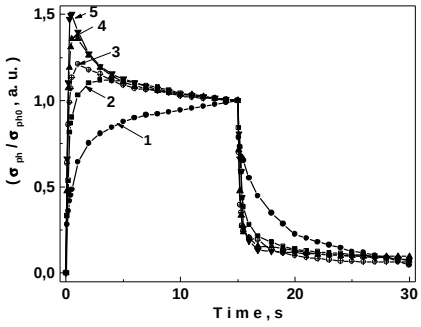

Fig. 3a. Photoconductivity relaxation curves in Au-$As_{40}Se_{60}$- Al thin films (L=9.7 μm) at T=290 K. Light intensity F, %: 1-0.008; 2-2.2; 3-13; 4-37; 5-100. $F_0=6.5\cdot10^{14}$ $cm^{-2}\cdot s^{-1}$, λ=0.63 μm.

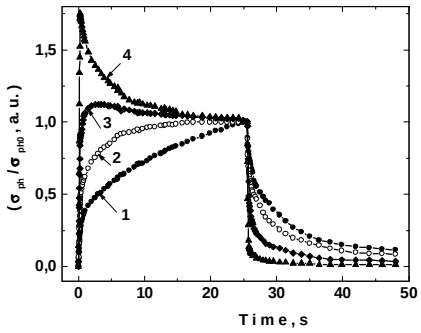

Fig. 3b. Photoconductivity relaxation curves in Au-$As_{50}Se_{50}$-Al thin films (L=5.87μm) at T=290 K. Light intensity F, %: 1 - 0.008; 2 - 0.3; 3 - 2.2; 4 - 100. $F_0=6.5\cdot10^{14}$ $cm^{-2}\cdot s^{-1}$, λ=0.63 μm.

Photoconductivity relaxation in amorphous chalcogenides has gained satisfactory interpretation in frames of the model of multiple trapping in gap states quasicontiniously distributed in the mobility gap of an amorphous semiconductor [10,18,19]. Application of this model allows understanding also some other nonequlibrium processes specific for the chalcogenide glassy semiconductors such as dispersive transport and induced optical absorption. An analysis of these processes leads to an exponential form of the energy distribution N(E) of localised state density of the form:

$$N(E) = (N_t/E_0)\exp(-E/E_0), \quad (6)$$

where N_t is the total gap-state density and $E_0=kT_0$ is the distribution parameter.

The theoretical consideration of the photocurrent relaxation in frames of the multiple-trapping model with gap states exponentially distributed in energy allows revealing several definite time domains in transient curves [18]. Each of these domains corresponds to a power dependence of photocurrent upon time and is determined by capture of free carriers in traps or by their recombination in monomolecular (MR) or bimolecular (BR) regimes. These processes govern the dependencies of relaxation both on excitation intensity and on the temperature. The detailed calculations and relaxation patterns have been presented in Ref. [19]. In Fig.4 the rise and decay curves for $As_{50}Se_{50}$ thin films are replotted in double-logarithmic scale to visualise the power-law portions of the transients discussed below.

Over the initial portion up to the moment t_1 the photocurrent rise is governed by the capture process, while recombination so far is not significant: $i_{ph}\sim G\cdot t^{\alpha}$, where G is the generation rate and $\alpha=(T/T_0=kT/E_0)$ is so called dispersion parameter. Further behaviour of the transients depends on excitation intensity. At low intensities (corresponding to MR) the photocurrent monotonously increases and reaches the steady-state value. At higher exposure intensities a quasistationary portion is observed, which at certain moment is followed by a decreasing portion of the transient, where the BR mechanism is dominant. Along this portion $i_{ph}\sim G^{1/2}\cdot t^{[(1-\alpha)/2]}$. At highest excitation level the relaxation is governed by BR and the quasistationary portion of photocurrent is absent ("an overshoot", see Fig.4a).

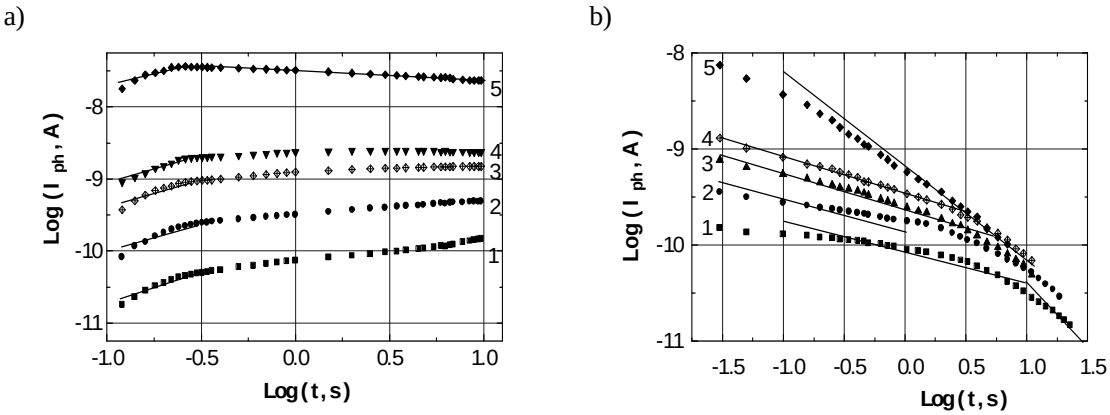

Fig.4. Double-logarithmic plot of photocurrent rise (a) and decay (b) in the $As_{50}Se_{50}$ film at various light intensities F, $cm^{-2}\cdot s^{-1}$: 1 - $5.3\cdot10^{11}$, 2 - $2.4\cdot10^{12}$, 3 - $6.6\cdot10^{12}$, 4 - $1.5\cdot10^{13}$, 5 – $6.5\cdot10^{14}$. Straight-line portions are calculated with $\alpha = 0.67$ (see text for details).

The photocurrent decay depends on the initial density of photogenerated charge carriers. If during the generation pulse the total filling of gap states is not achieved then an initial portion of the decay governed by capture process exist and the recombination is delayed. Over this portion $i_{ph} \sim i_{ph0}\cdot t^{-(1-\alpha)}$ where i_{ph0} is the photocurrent at the moment when the light is switched off. At low generation intensities (MR regime) the starting portion turns into final decay, along which $i_{ph} \sim i_{ph0}\cdot t^{e-(1+\alpha)}$. If the generation intensity provides the BR regime, then an intermediate portion exists, where $i_{ph} \sim i_{ph0}\cdot t^{-1}$. The above-described behaviour of photocurrent kinetics is in good agreement with the experimental curves of transient photocurrent for a set of generation rates presented in Fig.4. The dispersion parameter α was determined from the experimental relaxation curves as an asymptotic of the power-law portions of the rise and decay of the photocurrent plotted in double-logarithmic co-ordinates. Using the experimentally calculated values of the dispersion parameter α, the parameter of localised states distribution E_0 was estimated, which increase from E_0=0.037 eV (T_0=429 K) for $As_{50}Se_{50}$ up to E_0=0.046 eV (T_0=533 K) for $As_{40}Se_{60}$, respectively.

The value of the parameter T_0=533 K for amorphous $As_{40}Se_{60}$ films is in a good agreement obtained by Vaninov and co-workers [20] ($T_0 \approx 550$ K$<T_g \approx 450$ K) from the relaxation curves of the transient photocurrent in a-$As_{40}Se_{60}$ thin films. This parameter was studied in dependence of the nature of the metal dopants in a-$As_{40}Se_{60}$ (Ga, Na, Ag, Cu, Tl, In). Unfortunately the obtained results for different metallic dopants don't permit to obtain an adequate interpretation. For-example, the value of the dispersion parameter α for different dopants is different: $\alpha(As_{40}Se_{60}{:}In) > \alpha(As_{40}Se_{60}) > \alpha(As_{40}Se_{60}{:}Tl)$. The indium impurity (In) increases the value of the parameter $\alpha \approx 0.65$, while the impurity of thallium (Tl, $N_A \sim 10^{20}$ cm^{-3}) decreases it down to α=0.45 with respect to that for undoped a-$As_{40}Se_{60}$ (α=0.54). According to [20], the parameter T_0 reflects the temperature at which the impurities or the fluctuations of the potential are frozen at the cooling process of the chalcogenide glass. That means that the value of the parameter T_0 determined for different impurities reflects the temperature for which the diffusion coefficient of the impurities became negligible small [21].

The parameters α, T_0 and E_0 were estimated from the relaxation curves of the photocurrent as well as from the lux-ampere characteristics for $As_{50}Se_{50}$ and $As_{40}Se_{60}$ amorphous thin films and compared with the data from optical absorption [22] (Fig. 5). In Fig. 5 there are also presented the values of the parameter α, determined from the relaxation curves of the photoconductivity and photoinduced absorption for different values of the parameter T_0 for the exponential distribution of the localised states according to [23].

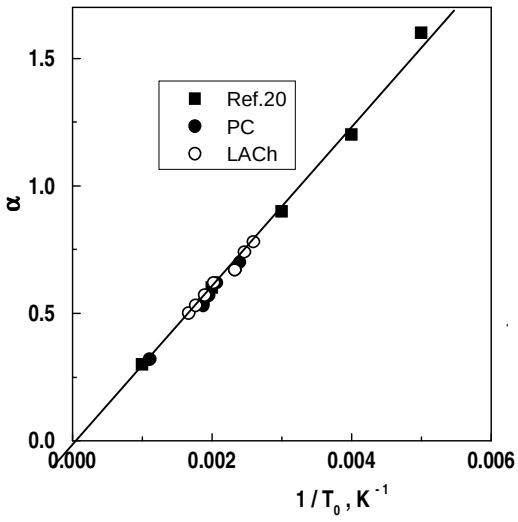

Fig. 5. The dependence of the dispersion parameter α vs. T_0 for $As_{50}Se_{60}$, and $As_{40}Se_{60}$ films determined from the transient photocurrent (•), from lux-ampere characteristics (○) , and according to Ref. [23] (■).

The fact that the complex picture of the photocurrent kinetics can be described by single parameter justifies the use of the model of multiple-trapping controlled recombination. The variation of the kinetics with temperature corresponds to the predictions of the model as well, as the transition moment t_1 is exponentially shifted to shorter times as the temperature is increased. It is worth noting the important role, which capture plays in photoconductivity of amorphous semiconductors, determining the specific initial portions of relaxation. Capture enhancement leads to the delay of recombination and to shift of the moment t_1 to longer times. The shortest time t_1, corresponding to the onset of recombination in investigated glasses, appears for the stoichiometry composition $As_{40}Se_{60}$ (t_1=10^{-2} s), it is about 3.3 s in $As_{50}Se_{50}$ films (containing excess As atoms).

4. Conclusion

The steady-state and transient characteristics of photoconductivity in amorphous thermally deposited chalcogenide $As_{50}Se_{50}$ and $As_{40}Se_{60}$ films were studied at various light intensities and temperatures. The set of photoconductivity characteristics are adequately interpreted in the frame of the multiple-trapping model, according to which transport and recombination of non-equilibrium holes are controlled by multiple capture in exponentially distributed in energy hole traps. Evaluating of the trap energy distribution parameter kT_0 independently from the photocurrent rise and decay as well as from the dependence of steady-state photocurrent on light intensity yields consistent results. The photoconductivity occurs under condition that the thermal equilibrium between fractions of delocalized and localised charge carriers has not been established, similar to the situation characteristic for the dispersive transport of photoinjected carriers. By this reason the activation energies of photoconductivity and of drift mobility have close values. Spectral distribution of steady-state photoconductivity was shown to depend from the thin-film deposition technology.

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