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PHOTOCONDUCTIVITY RELAXATION IN AMORPHOUS As-Se THIN FILMS DOPED WITH Sn, Mn, Sm AND Dy

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Steady-state and transient characteristics of photoconductivity in amorphous thermally deposited AsSe and As_2Se_3 amorphous films doped with 0.5 at.% Sn, Mn, Sm and Dy were studied. The spectral characteristics depend on composition in pseudo-binary As-Se glass system, as well as on the doping with impurities. Tin increase the decay rate in As_2Se_3, while dysprosium was found to delay the rise and decay of photocurrent, which is attributed to an increase in trapping in deep localized states produced by doping of rare-earth ions. The photocurrent rise and decay was found to be consistent with the model of trap-controlled non-stationary capture and recombination in the localized states, exponentially distributed in energy.

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1. Introduction

Arsenic selenides glasses are well known as high photosensitive materials with a wide range of application in optoelectronics and information storage systems [1]. Besides that the physical and practical interest of the impurity effect in amorphous materials arises from its structure, which has a higher degree of disorder than that of bulk glasses. Recently, the effect of copper on electroconductivity, optical band gap and photoconductivity of bulk glasses and thin films of As_2Se_3 was investigated [2,3]. The influence of impurities on transient photocurrents in amorphous As_2Se_3 films was reported in [4]. It was found that the impurities influence the dispersion parameter α, which describes the exponential density of localized states in amorphous material.

Some stationary and non-stationary electrical and photoelectrical characteristics of pure As_2Se_3 and AsSe amorphous thin films, as well doped with tin impurity also was investigated [5,6]. It was shown that tin impurity in chalcogenide glasses influences non-stationary rather than stationary physical characteristics. In thermally deposited As_2Se_3:Sn_x (x=0.5÷3.5 at.%) and AsSe:Sn_y (y=1÷10 at.%) thin films, the photosensitivity was shown to be much higher than that of bulk glass. Tin impurity, as well as Mn, Sm and Dy in amorphous As_2Se_3 thin films stabilizes the parameters of the recording media due to more rigid network of the doped glasses [7], and thus opens the way for important applications in optoelectronics. Measurements of the time-of-flight in As_2Se_3:Sn films have recently established [8,9] that adding tin to As_2Se_3 substantially increases the drift mobility and slows down the recombination. In the present paper the experimental results on stationary and long-term photoconductivity relaxation in a-AsSe thin films and a-As_2Se_3 doped with 0.5 at.% Sn, Mn, Sm and Dy are presented. The obtained data are analyzed on the base of trap-controlled recombination model in amorphous materials. The dispersion parameter α of localized state energy distribution for a-AsSe and a-As_2Se_3 doped with different metal impurities are derived from the experimental results.

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2. Experimental results and discussion

Tin impurity and Mn, Sm and Dy (0.5 at.%) was introduced into As_2Se_3 glasses during thermal synthesis of the initial material for thermal evaporation. As_2Se_3:$Me_{0.5}$ (Me-Sn, Mn, Sm and Dy) films with thickness 1.0÷11.0 μm were obtained by "flash" thermal evaporation in vacuum on glass substrates held at temperature T_{substr}=100 ^oC. The thin film samples had a sandwich configuration with two sputtered electrodes (gold and aluminum), of which the top (Al) electrode was half-transmitting.

For photoconductivity transient experiments a He-Ne laser light (λ = 0.63 μm) was used to generate a photocurrent. A photo shutter with a 10^{-3} s triggering time was used to switch the light on/off. The relaxation curves were recorded with a time constant not exceeding 0.3 s on an ENDIM 622.02 X-Y plotter using an U5-11 electrometric amplifier. The computer was used for calculations and data processing.

2.1. 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 sub linear and may be approximated by a power law $\sigma_{ph} = B \cdot F^{\gamma}$, where B is the constant weakly dependent on temperature, and γ is the power index. For amorphous As-Se films 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).

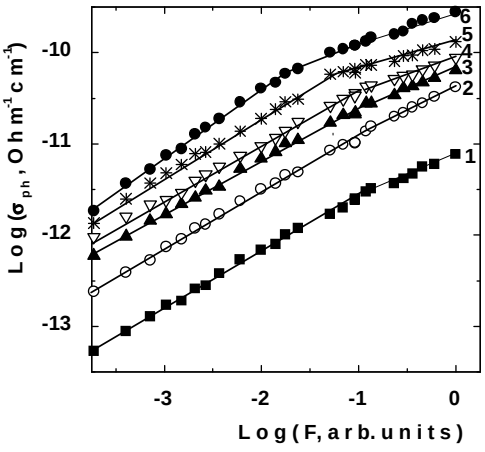

Fig. 1a. Steady-state photoconductivity σ_{ph} dependence on light intensity F of the AsSe films. Temperature T, K: 1-289; 2-321; 3-341; 4-351; 5-365; 6-388. Light intensity F_0 == 6.5×10^{14} photons·cm^{-2}·s^{-1}.

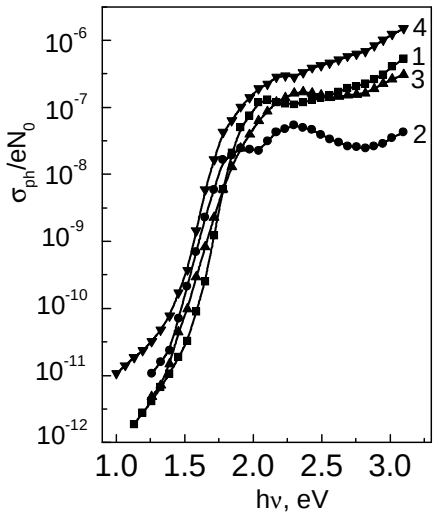

Fig. 1b. Photoconductivity spectra of amorphous films of the system As_xSe_{1-x}. x: 1-0.28; 2-0.40; 3-0.50; 4-0.60.

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.

In Fig. 1b the photoconductivity spectra are presented for thin films of the As_xSe_{1-x} chalcogenide system obtained by thermal deposition technique. Photoconductivity spectral distribution of thin films is typical for disordered materials as well. The spectra to a considerable extent depend on the parameters of the deposition technique. The slope of the photoconductivity edge is sensitive to the modification of the glass composition and to the conditions of preparation of amorphous thin films. For As-Se system it was found that when the contents of arsenic increases, the value of the slope decreases from 16.7 eV^{-1} for As_2Se_5 to 14.3 eV^{-1} for As_2Se_3 for thin films prepared by deposition from vapor phase and from 16.2 eV^{-1} to 11.8 eV^{-1} for thin films obtained by laser evaporation and may be connected with the specific structure of these layers. For the films obtained by laser deposition the energy of spectral distribution maximum corresponding to the fundamental optical absorption edge is higher for all compositions than that for thermally deposited samples. For the laser deposited films an increase of photosensitivity in all investigated spectral region is observed.

Fig. 2a shows the lux-ampere characteristics of amorphous As_2Se_3 films pure and doped with 0.5 at.% of metals at room temperature. Doping of As_2Se_3 affects the slope $\gamma = \frac{T_0}{T + T_0}$, the value of which increase from $\gamma = 0.51$ for As_2Se_3 up to $\gamma = 0.75$ for As_2Se_3+0.1 at.% Mn. This means that the parameter of the distribution of the localized states T_0 is changed.

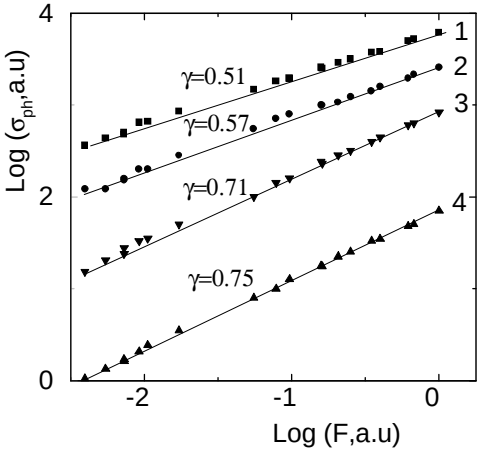

Fig. 2a. Steady-state photoconductivity σ_{ph} dependence on light intensity F for the amorphous As_2Se_3 (1), As_2Se_3+0.1 at.% Dy (2), As_2Se_3+0.1 at.% Mn (3), and As_2Se_3+0.1 at.% Sm (4) films. Temperature T, K: 1 - 289; 2 - 321; 3 - 341; 4-351; 5-365; 6-388. Light intensity F_0==6.5×10^{14} photons·cm^{-2}·s^{-1}.

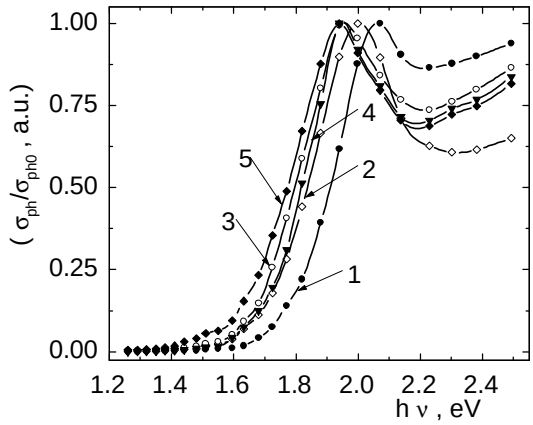

Fig. 2b. Photoconductivity spectra for the amorphous As_2Se_3 (1), As_2Se_3+0.5 at.% Sn (2), As_2Se_3+0.5 at.% Mn (3), and As_2Se_3+0.5 at.% Sm (4), and As_2Se_3+0.5 at.% Dy (5) films.

The spectral dependence of photoconductivity for As_2Se_3 films doped with metals also represents a curve with a broad peak (Fig. 2b). Doping with metals practically did not affect the slope of long wave tail and shift the maximum of photoconductivity in low energy region. This may be associated with the lowering of the band gap energy as a result of the different degree of intermolecular interactions, as in the case of As_2S_3 doped glasses [10].

2.2. Transient photoconductivity

The character of the photocurrent relaxation changes appreciably in dependence on the chalcogenide glass film composition as well as when metal impurity is introduced into the glass is

shown in Fig. 3. In all investigated samples the photocurrent on the increasing section passes through a maximum before reaching a stationary state (so-called "spike"), while in As_2Se_3+0.5 at.% Dy the photocurrent increases monotonously up to a stationary value. The presence of the "spike" in As_2Se_3:Me_x films means 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_2Se_3:0.5 at.% Dy may be associated with deep level traps, which appear in this case. These traps are situated very deeply and significantly retardates the recombination. According electrical and photoelectrical measurements on As_2Se_3 doped glasses with rare earth metals, these traps are situated in the middle of band gap (around 1.02 eV), which also quenched the photoconductivity [11].

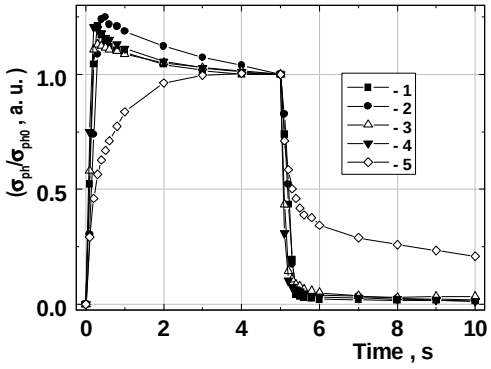

Fig. 3a. Photoconductivity relaxation curves in As_2Se_3:Me_x amorphous thin films: 1–As_2Se_3; 2-As_2Se_3:0.5 at.% Sn, 3-As_2Se_3:0.5 at.% Mn, 4-As_2Se_3:0.5 at.% Sm, and 5-As_2Se_3:0.5 at.% Dy. Light intensity F_0=1×10^{15} photons·cm^{-2}·s^{-1}. Temperature T = 289 K.

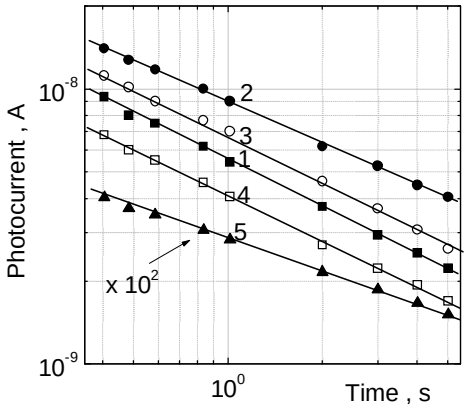

Fig. 3b. Log-log plot of the photocurrent decay curves in As_2Se_3:Me_x amorphous thin films: 1–As_2Se_3; 2-As_2Se_3:0.5 at.% Sn, 3-As_2Se_3:0.5 at.% Mn, 4-As_2Se_3:0.5 at.% Sm, and 5-As_2Se_3:0.5 at.% Dy. Light intensity F_0=1×10^{15} photons·cm^{-2}·s^{-1}. Light intensity F_0 = 1×10^{15} photons·cm^{-2}·s^{-1}. Temperature T = 289 K.

It was mentioned earlier that the different portions of relaxation curves of the photocurrent in the investigated chalcogenide films may be described analytically with the dispersion parameter $\alpha=kT/E_0$ [7]. In our case the dispersion parameter α was determined from the experimental relaxation curves as an asymptotic of the power-low portions of the rise and the decay of the photocurrent plotted in double-logarithmic co-ordinates (Fig.3b). For As_2Se_3 the values of α are α=0.54 and decrease for the samples doped with Sn, Mn and Sm, and increase up to α=0.66 for the sample doped with Dy (Table 1). The fact that the complex picture of the photocurrent kinetics can be described by a single parameter α justifies the use of the trap-controlled recombination model [12]. According to the model [12], the time t_1 at which the recombination starts to predominate over trapping in the photocurrent kinetics is proportional to the total density N_t of localized states $t_1 = \tau_0(N_t/N_c)(\tau_R/\tau_0)^{1/\alpha}$, where τ_0 is the hole lifetime with respect to trapping in all localized states, N_c is the density of delocalized states, and τ_R is the lifetime of non-equilibrium holes with respect to recombination. Carrier trapping strongly affects the photoconductivity in amorphous semiconductors determining the specific initial portions of relaxation. Enhancement of the carrier trapping leads to a delay of recombination and shifts t_1 to longer times. The shortest time t_1, corresponding to the onset of recombination in the investigated glasses, is found for the stoichiometry composition As_2Se_3 to be t_1=10^{-2} s while it is about 3.3 s in AsSe films (containing excess As atoms) and becomes even longer (up to 10-15 s) in As_2Se_3 films doped with 1.0at.% Sn [5]. The time delay of recombination is supported by the results of time-of-flight measurements in As_2Se_3:Sn films [8,9]. The observed strong effect of dopping on the transient process is in contrast to the well-known insensitivity of equilibrium characteristics of glassy semiconductors to doping. Enhancement of the carrier capture in a given time domain strongly affects the dependence of the transients on the light intensity and the temperature as

well as on the optical bias. For example, the "overshoot" in the rising portions of the photocurrent disappears in As_2Se_3+0.5 at.% Dy.

Table 1. The parameters α, E_0 and T_0 for amorphous As_2Se_3:Me films.

Composition	T, K	α	$E_0=kT_0$, EV	T_0, K
As_2Se_3	288	0.54	0.046	533
As_2Se_3:0.5 at.% Sn	289	0.50	0.050	580
As_2Se_3:0.5 at.% Mn	289	0.40	0.062	719
As_2Se_3:0.5 at.% Sm	289	0.43	0.058	672
As_2Se_3:0.5 at.% Dy	289	0.66	0.038	441

The kink points t_1 in the decay of photocurrent correspond to the onset time of intense recombination. These times in the tin doped As_2Se_3 samples are several times longer than in undoped samples (t_1=25 s at T=290 K) and decrease with increasing temperature. The delay of recombination may be reduced by the constant bias illumination. Bias illumination increases the decay rate, which is growing with increasing illumination intensity, by accelerating photo ionization and recombination of localized non-equilibrium charge carriers [5,8,9].

A possible nature of the states engendered by tin added to As_2Se_3 can be gleaned from an investigation of tin as an impurity in As_2Se_3 by the Mössbauer spectroscopy [13]. In the glassy As_2Se_3, tin is tetravalent (Sn^{4+}), and all four valence electrons of a tin atom participate in chemical bonds with the matrix atoms and are not manifested in the electrical properties. However, in unannealed films, some tin atoms are in the form of divalent tin (Sn^{2+}). In such atoms only the 5p electrons participate in the formation of a chemical bond, and the 5s electrons can play the role of deep donors. Another possibility is photoinduced charge exchange of tin impurity centers $Sn^{4+} \Rightarrow Sn^{2+}$ with capture of the electrons on the tin centers. The influence on the Mn with the concentration about $N_a \approx 5 \cdot 10^{17}$ cm^{-3} on electronic properties of glassy As_2Se_3 was reported [14]. It was shown that As_2Se_3 glasses with higher concentration of Manganese could also contain aggregates of MnSe molecules. The appearance of deep impurity centers in Mn and Dy doped As_2Se_3, as well as the appearance of the crystalline phase DySe also was demonstrated [10].

3. Conclusion

The steady-state and transient characteristics of photoconductivity in amorphous thermally deposited chalcogenide As_2Se_3 and AsSe films, as well as doped with different amount of metal impurities were studied at various light intensities and temperatures. The 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 band gap. 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 localized charge carriers has not been established, similar to the situation characteristic for the dispersive transport of photoinjected carriers.

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