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PERSISTENT PHOTOCONDUCTIVITY IN AMORPHOUS As_2Se_3 FILMS WITH Sn IMPURITY

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Persistent photoconductivity has been studied in amorphous As_2Se_3 films doped with Sn impurity by combination of transient photocurrent technique, steady-state photocurrent and photocapacitance measurements. From the both photocurrent and photocapacitance spectra the broad distributions of defect states in the band gap of As_2Se_3: Sn_x (x>0.5 at.% Sn) samples was evaluated. It was shown that these states contribute significantly to the persistent photoconductivity.

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1. Introduction

Chalcogenide glasses (ChG) are promising materials for many applications in micro- and optoelectronics, such as recording media, fiber optics amplifiers, sensors, etc. [1-4]. Recently special interests have gained the amorphous films of ChG in connection with the established possibility of "modification" of their properties at doping with metals impurities (Ni, Fe, Bi, Sn). In thermally evaporated amorphous films of ChG these impurities are electrically active and allow to obtain new materials with the improved properties. The changes in physical properties of amorphous films is caused by the modification of their structural and chemical disordering due to presence of high concentration of defects [5]. Trapping and recombination processes, which depend on the distribution and concentration of these defects, strongly influence the photoelectrical characteristics of the amorphous materials [6]. A number of recent studies have demonstrated the existence of persistent photoconductivity (PPC) in $Tl_2Se{\cdot}As_2Te_3$ due to trapping [7] and in As_2Se_3:Sn amorphous films as a result of retardation of the recombination [8]. Therefore, detailed characterization of PPC effects can provide information about deep defect states in these amorphous materials.

In this paper the study of steady-state and transient photocurrents as well as the photocapacitance spectra in As_2Se_3 amorphous films doped with different amount of tin are presented. As a result a significant PPC effects with very long decay times (τ~25 s) was observed in As_2Se_3+4.0 at.% Sn films at room temperature. The broad envelope centered at $h\nu$=1.4 eV and which was derived from the photocurrent and photocapacitance spectra has been assigned to deep defect states induced by Sn ions incorporated in amorphous chalcogenide films. Correlations between the presence of these states and the PPC effect have been established.

2. Experimental

Tin was introduced in amounts of 0.5-5.0 at.% into As_2Se_3 during standard thermal synthesis of the materials prior to sputtering. Thin films (~2 μm) samples of sandwich configuration were

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obtained by “flash” evaporation in vacuum onto glass substrates held at 100 °C. Two Al electrodes were sputtered of which the top electrode was semi-transparent. The spectrometer SPM-2 for spectral distribution measurements with the registration module was used. Photocurrent measurements were performed with a positive constant voltage bias (~2 V) applied to the top electrode that was illuminated from a tungsten lamp. The photoresponse was normalized to intensity of incident photon flux. For photoconductivity relaxation measurements a shutter was used to switch the light on/off with time constant of about 10^{-2} s. The photocapacitance was measured by a quasistatic technique at the infra-law frequency (10^{-2} Hz). All measurements were made at room temperature.

3. Results and discussion

Fig. 1 shows the relaxation of photocurrent in amorphous As_2Se_3: Sn_x films under monochromatic illumination (hν = 1.82 eV). The decay of the photocurrent appears to be non-exponential. We can observe at least two distinct regions in the $I_{ph}(t)$ curves: a fast process occurring immediately after switching off the illumination and a following long-term relaxation. A persistent photoconductivity effect is clearly observed at x = 1.0 at.% Sn and the amplitude of the PPC increase for the samples with x = 2.0÷5.0 at.% Sn (Fig. 2). The decay of the photocurrent after switching off the illumination may be approximated by a stretched-exponential function $I_{ph}(t) = I_{ph}(0) \exp[-(t/\tau)^{\beta}]+\text{const}$, where β is decay exponent, 0<β<1, which is related to the dispersion parameter α (α= 1-β), *t* is the time, τ is the characteristic time constant of the process, $I_{ph}(0)$ is the photocurrent buildup level at the moment that light excitation is removed. Least-squares fit to the experimental data yields a time constant τ~2.2-25.3 s and a decay exponent β~0.25-0.34 for the samples with x > 0.5 at.% Sn, which is comparable to previously reported values for As_2Se_3+1 at.% Sn amorphous films, (τ~10-15 s, α = 0.67) [9,10].

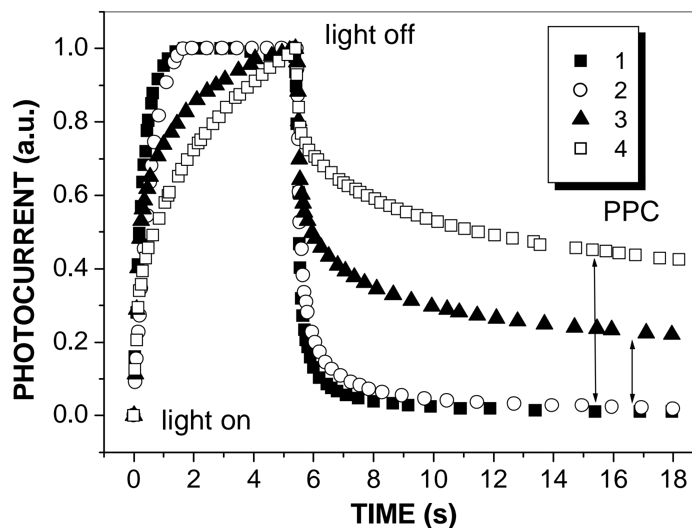

Fig. 1. Photoconductivity relaxation in the As_2Se_3: Sn_x films. Tin contents, x, at.% Sn: 1-0.0, 2- 0.5, 3-1.0, 4-3.0, T=290 K.

In order to estimate the energy distribution of deep states the photocurrent spectra were measured in the excitation energies range from 0.8 to 2.0 eV. Fig. 3 shows the photocurrent spectra for As_2Se_3: Sn_x amorphous films. The peak located at 1.8 eV corresponds to the band gap edge of As_2Se_3. Besides, we can observe a high sensitivity in the long-wavelength region of the spectrum. Near the valence band edge the photocurrent exponentially decreases with characteristic Urbach energy E_0.

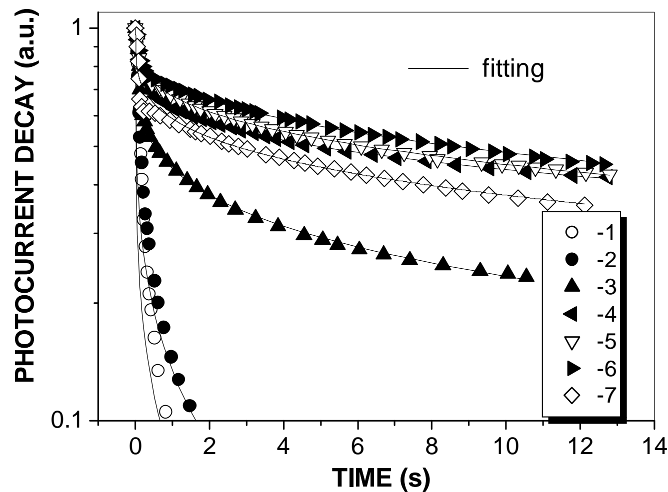

Fig. 2. The normalized photocurrent decay curves in As_2Se_3: Sn_x films. Tin contents, x, at.% Sn: 1-0, 2-0.5, 3-1.0, 4-2.0, 5-3.0, 6-4.0, 7-5.0. The solid curves are the least-squares fitting of photocurrent decay data by the stretched-exponential function.

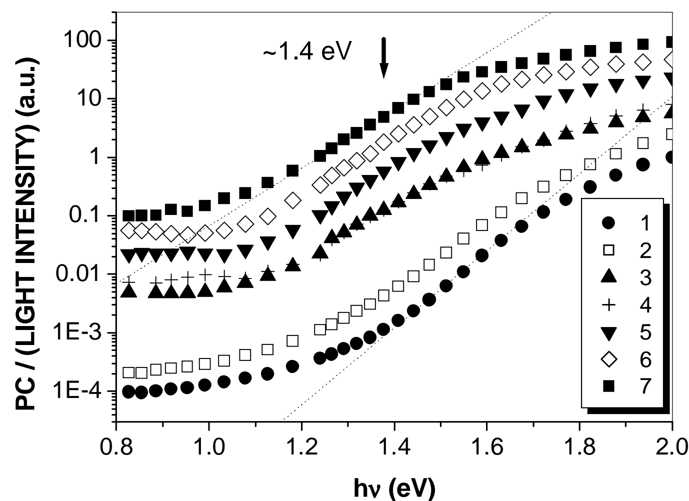

Fig. 3. Photocurrent spectra of As_2Se_3: Sn_x films measured at T = 310 K for various tin content x, at. % Sn: 1-0.0, 2-0.5, 3-1.0, 4-2.0, 5-3.0, 6-4.0, 7-5.0. The spectra are shifted along Y-axis for comparison.

From the slope of the exponential part of the photocurrent spectrum this parameter can be found. For undoped amorphous As_2Se_3 films E_0 take a value 0.066 eV. For Sn-doped As_2Se_3 amorphous films with x = 1.0 and 3.0 at.% Sn the parameter E_0, which describes the exponential distribution of localized states, increases and takes the values of 0.1 and 0.082 eV, respectively.

Fig. 4 shows the photocurrent spectra for the Sn-doped As_2Se_3 films as in Fig. 3, normalized to the spectra of the undoped sample. This procedure allows for distinguishing the additional absorption of the band gap states induced by doping. Only the photons which can be absorbed in As_2Se_3: Sn_x and can produce an excess of free carriers due to the localized defect states induced by tin impurity will cause an increase in photocurrent. As it seen from the Fig. 4, illumination with the sub-band gap light causes the features below the band edge around the 1.4 eV. The magnitude of the observed peak changes in dependence of tin amount in the ChG composition. We suggests that the

intensity of the absorbed light in this region is associated with the density of defect states in As_2Se_3 induced by the tin impurities.

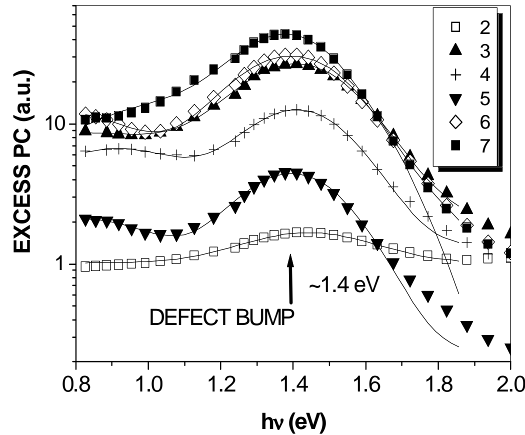

Fig. 4. Excess of the photocurrent spectra derived from the spectra as in Fig. 3 (see text for details). Solid lines represent fitting by the Gauss form distribution. The broad sub-band defect bump centered at 1.4 eV can be attributed to A^+ level of D^+ center.

The similar defect sub-band states distributions have also been observed in Al/a-As_2Se_3 Schottky diodes from the photocapacitance spectroscopy [11,12]. In our experiment the initial slope of photocapacitance transient [13,14] was used to study the weak optical absorption in mobility gap of a-As_2Se_3 films. During the "filling pulse" deep states captured the holes from valence band (because of **p**-type a-As_2Se_3) and, after restore of reverse voltage bias, - slow relaxes thanks to processes of optical holes excitation. As result a photocapacitance spectrum allows to display distribution of allowed optical transitions for deep states populated by holes and situated in overhead half of band gap. Fig. 5 shows the experimental data, obtained for the spectra of optical absorption coefficient both in non-doped film (curve 1), and in films with tin concentration 0.5 and 1.0 at.% (curves 2, 3, accordingly).

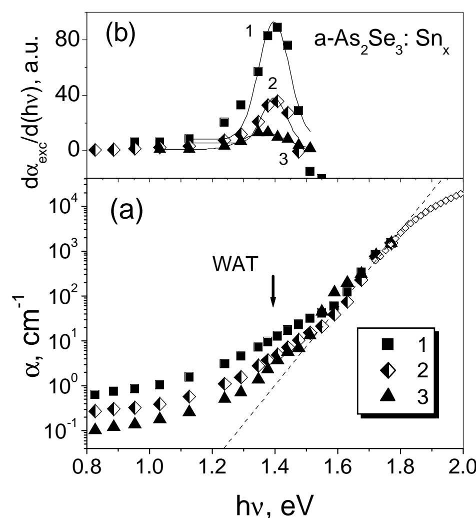

Fig. 5. (a) Optical absorption spectra deduced from the photocapacitance measurements in amorphous As_2Se_3 films: non-doped (1) and with Sn impurity, at. %: 0.5 (2), 1.0 (3); (b) excess absorption evaluated for this spectra. Fits with sub-band of optical transitions are shown by the solid lines drawn through the data points, for each curve.

For comparison the spectra were normalized to absolute scale of optical absorption obtained from measuring of optical transmission in the region of band-to-band optical transitions (continuous set of symbols in plot). In the region of Urbach edge the value of absorption coefficient in non-doped samples (curve 1) and in samples with tin impurity (curves 2, 3) do not differ essentially one from another. They are described by the exponential dependence $\alpha_U \propto \exp(\Gamma E)$, with the slope $\Gamma = 20$ eV^{-1} which is typical for a-As_2Se_3 (straight line on the plot). At the same time the absorption coefficient spectra in the region of weak absorption tail ($h\nu<1.6$ eV) show that dopping with Sn results in decrease of the absorption coefficient. In this range, the absorption coefficient α is associated to defects and/or impurities and its value may be found by extraction of the exponential part from the apparent absorption values [15]: $\alpha_{exc}=\alpha-\alpha_U$.

The density of states, calculated from the differentiation of the excess absorption spectra, are shown in Fig. 5b; notations correspond to curves in Fig. 5a. It has a peak, to which a defect band of Gauss-form distribution may be attributed (fits curves in figure). It is seem, that the peak position of the density of states distribution remains about 1.4 eV (curve 1, 2), close to the energy of optical ionization of D^+-centers. Estimations of the deep states concentration N_T done from the area under these curves [16] shows, that at 1.0 at.% of Sn introduced into material it decreases about 10 times (from 1.05×10^{16} down to 1.5×10^{15} cm^{-3}), in comparison with this concentration in non-doped films.

These experimental results are in a good agreement with the model of recombination in which electron traps play the major role in the photocurrent decay [8,17]. The following explanation is suggested for the description of our experimental results on long-term photoconductivity in As_2Se_3: Sn_x amorphous films. During electron-hole pair generation by band-to-band light absorption some electrons, that do not recombine with holes are captured by traps. The trapped electrons increase the number of excess hole carriers in the valence band and enhance the photocurrent intensity. The photocurrent gain, which can be determined by the ratio between the trapping time and transit time, also increases.

However, no PPC effect was observed in undoped As_2Se_3 samples. This implies that the number of holes traps is equal to that of electron traps and no excess holes exists. We believe that the native D^+ and D^- centers with negative effective correlation energy [5] are responsible for the observed PPC effect. Indeed, as discussed in [18] metal additives such as Ag (or Br), that tend to form negative ions will induce an increased concentration of D^- centers and, by the law of mass action, together with the requirement of over-all charge neutrality of the sample, cause a reduction of the D^+ concentration. Therefore, equality between electron and hole traps can be disturbed.

Our experimental results clearly indicate that photocurrent spectra and PPC effect evidence the strong correlation in properties related to deep levels. Samples, which exhibit a photocurrent peak at 1.4 eV in the photocurrent curve due to the photoionization of A^+ level have PPC, whereas samples with no photocurrent peak have no PPC. In our previous paper we have pointed out that in as-deposited films some tin atoms are present in the form of divalent tin, and the 5s electrons can play the role of deep donors [10].

4. Conclusions

The detailed studies of persistent photoconductivity, photocurrent and photocapacitance spectra in As_2Se_3 and As_2Se_3: Sn_x amorphous films were performed. The decay of persistent photoconductivity with a typical time constant of about τ=2.2-25.31 s is found to follow a stretched-exponential function. PPC effects arising from deep defect states were observed. Measurements of photocurrent and photocapacitance spectra performed using samples with different tin content allowed us to distinguish between spectral features arising from deep levels in the As_2Se_3 layer and those originating in As_2Se_3: Sn_x films. Broad distributions of defect states with excitation energies lower than the optical band gap were detected in both the As_2Se_3 and As_2Se_3: Sn_x films. A level with excitation energy of 1.4 eV was observed in the structure, with detailed analysis indicating that excitation of carriers from this level contributes primarily to the PPC. It is believed that the D^+ centers are predominantly responsible for the PPC effect in As_2Se_3: Sn_x amorphous films. The PPC effect is important for elaboration on the basis of amorphous semiconductors different photoelectrical memory devices.

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