PHOTOCONDUCTIVITY OF AMORPHOUS Sb_2Se_3 AND Sb_2Se_3:Sn THIN FILMS

M. S. Iovu, E. P. Colomeico, I. A. Vasiliev

Center of Optoelectronics, Institute of Applied Physics, Academy of Sciences of Moldova, Str. Academiei 5, MD-2028, Chisinau, Republic of Moldova

The steady-state photocurrent spectra of Sb_2Se_3 and Sb_2Se_3: Sn films in the photon energies ranged from 1 to 2.5 eV for different values of electric field intensity and temperatures were investigated. In the photocurrent spectra the peak near 1.5 eV, caused by the defect band, was revealed. For the amorphous Sb_2Se_3 thin film samples with tin impurity the intensity of this band is higher. In the interval of relaxation times from 0.1 to 10 s the negative photocurrent under incident light pulse with wavelength from the region of fundamental absorption was detected. The comparative analyses of the experimental data, based on the model of charged defects, clear up the discovered influence of tin impurity on the photosensitivity of investigated amorphous films.

1. Introduction

The chalcogenide amorphous Sb_2Se_3 films attract attention due to switching effect, advanced photovoltaic and thermoelectric properties and their application in TV cameras, interference filters and different photonic and optoelectronic devices [1-3]. At the same time the deep localized states distributed in the mobility gap and caused by intrinsic defects with negative effective correlation energy ("U⁻" centers) essentially affect the concentration and mobility of major and minor charge carriers and restrict these applications. The reason for such influence is associated with the possibility of accumulation of the non-equilibrium charge on the deep centers due to extremely small rate of the thermal emission of electrons and holes captured on the deep levels.

In this work the experimental results on the study of the photocurrent spectra obtained for thin (thickness of about 1.0 μm) amorphous Sb_2Se_3 and Sb_2Se_3:Sn (concentration Sn of 0.01 at.%) layers with the different values of the applied electric field and temperatures are presented. From the experimental data both the width of band gap $E_g \sim 1.56$ eV and energy of the optical ionization of the defects $E_i \sim 1.2$ eV where determined. The long term photoconductivity kinetics was investigated under the conditions, when the process of charge relaxation, captured on deep centers, was predominate. The role of tin impurity in the processes of recombination of the non-equilibrium charge carriers was cleared up.

The brightest effect in these studies was the presence of the negative photocurrent, which was observed under incident light pulse with the photon energy from the region of fundamental absorption. Note, that the negative currents were formerly observed in amorphous $0.55 \cdot As_2S_3 : 0.45 \cdot Sb_2S_3$ thin films in the time-of-flight experiments [4], in amorphous As_2S_3 films modified by zinc and in Ge-Se system [5].

2. Experimental

The amorphous films with a thickness of about 1.0 μm were obtained by the thermal "flash" evaporation in the vacuum of the initial material of Sb_2Se_3: pure and with the concentration of tin impurity 0.01 at.% to the glass substrate, heated at the temperature T_{substr}= 80 ^{0}C. Samples under investigation have a "sandwich" configuration with the bottom and top aluminum electrodes, one of which was semi-transparent for the incident light.

The steady-state photocurrent, normalized to the intensity of incident light, was measured by conventional modulation technique (the frequency of the light interruption of 14 Hz) and was amplified by the electrometer B7-29. The photoconductivity was excited by incandescent lamp with the tungsten wire (power of 30 W), light from which was passed through spectrophotometer SPM-2. The intensity of photon flux ($\Phi \sim 8 \times 10^{15}$ photon/(cm^2 s) in the maximum of radiation was changed by variation in the width of spectrometer slit. The electromagnetic shutter with the time constant of about 0.2 s was used in order to form the light pulse. The curves of transient photocurrent were registered by the X-Y recorder with the integration time less than 0.1 s.

3. Results and discussion

Fig. 1 shows the photocurrent spectra for the amorphous Sb_2Se_3 films, measured at different values of applied electric field F=(0.5÷2.5) x 10^4 V/cm, and which reveal a feature near the edge of fundamental absorption in the form of spectral peak with the maximum located at 1.5 eV (the region "A" on Fig. 1). Note, that its intensity increases with the intensity of the applied field and likely related to the defect band. The absorption edge was determined from curves via the best adjustment of function $(E-E_g)^n/E$ with n=2 to the experimental data in the region of band-to-band optical transitions (the region "B" on Fig. 1). This function satisfactorily describes the optical absorption in the range of photon energy E>E_g for the most of amorphous materials [6]. In our case the experimental value of $E_g \sim 1.56$ eV is in accordance with the value of E_g= 1.46 eV, obtained for the absorption measurements in the Sb_2Se_3 films synthesized at 130 ^{0}C, as was reported in [1].

The role of the defects induced by tin impurity was cleared up by comparison the spectra for Sb_2Se_3 and Sb_2Se_3:Sn, measured under the identical conditions (curves 2, 2'). It is seen, that in the region of spectral peak the photocurrent in the doped sample is higher, than in the undoped sample, while in the region of fundamental absorption – it is smaller. Such influence of the tin impurity we explained by the decrease in the number of recombination centers (role of which can play D^+ - centers) and by the corresponding increasing of the recombination time. On the contrary, in the region of fundamental absorption, the decrease of photocurrent for the doped sample can be associated with an increasing in the number of the trapping centers (D^- - centers) and by the significant decrease of drift mobility. Here the contribution, determined by the recombination time is small. This conclusion agrees with the common picture of a changing U^- centers concentration, caused by the charged tin impurity, and is well known for the chalcogenide films of As-Se system. In this picture the deep donor and acceptor trap levels above and below the Fermi level, correspond to the D^+ and D^- centers, respectively [7,8].
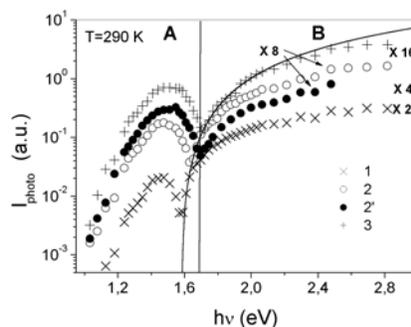
Fig. 1. The photocurrent spectra of amorphous Sb_2Se_3 films at the different values of the applied electric field F, 10^4 V/cm: 1– 1, 2, 2'– 2, 3– 2.5. The normalized factors of curves are shown in the right. Curve 2' illustrates the influence of tin impurity. Solid line presents the dependence $I_{photo} \propto (E-E_g)^{3/2}/E$ with E_g=1.56 eV.
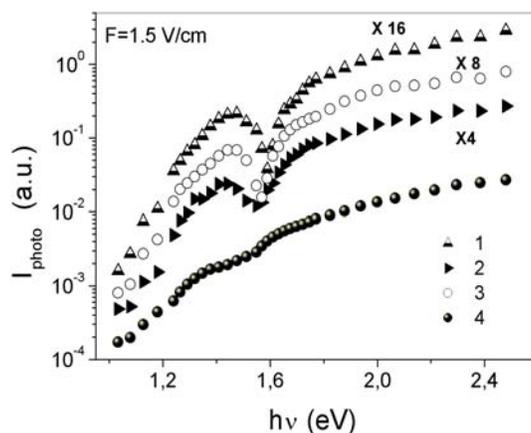

Fig. 2. The photocurrent spectra for amorphous Sb_2Se_3 measured at different temperatures T, K: 1- 290, 2- 298, 3- 304, 4- 315.5. The normalized factors of curves are shown in the right.

Fig. 2 shows the photocurrent spectra, obtained for amorphous Sb_2Se_3 films at different temperatures. It is seen, that the temperature effect is in contrast with the effect of electrical field. In the region of the spectral peak the photocurrent decrease with the growth of temperature and at T=315 K it is observed its complete degeneration. In the region of high values of photon energy $h\nu > E_g$ the photocurrent is activated with the temperature as $I_{photo} \propto exp(\Delta E_m/kT)$, were $\Delta E_m \sim 0.6$ eV, which indicates the characteristic regime of monomolecular recombination. For the model of recombination of the type "band - localized state" $\Delta E_m = E_d - E_\sigma$, were E_d is the donor energy level, lying above the Fermi level, were E_σ is the activation energy of the dark conductivity [6]. Estimations show that at $E_\sigma \sim .E_g/2 \sim 0.8$ eV the value E_d=1.4 eV, i.e., the donor level lies below the bottom of conduction band approximately on 0.2 eV.

Fig. 3 shows the kinetics of photoconductivity, measured with the light pulse illumination of samples by monochromatic light from the region of sub-bandgap absorption (Fig. 3a) and from the region of fundamental absorption (Fig.3b). It is seen that for the pure sample (Fig.3a, curve 1), after the switching on of light with a wavelength of λ=0.84 μm the photocurrent first sharply grows, and then decreases to smaller value than it was before the illumination. In the portion of the negative current is observed the minimum, after which the current increases in the absolute value, remaining negative. After the light is switching of, is observed the reverse picture: the photocurrent first sharply falls, and then increases; it penetrates the maximum and then decreases to its dark value.

Unusual picture is observed after the switching on of the light with a wavelength of λ=0.7 μm (Fig. 3b, curve 1): the photocurrent under illumination first sharply falls, becomes less than the dark current and, then, it slowly grows. In this case the spike pulse of positive photocurrent is observed only after turning off of the light.

In the samples with the tin impurity (Sb$_2$Se$_3$:Sn) the kinetics of photoconductivity differs from the same for the pure sample (Sb$_2$Se$_3$), and this difference can be explained by the noted predominance of the positive photocurrent in the former. Indeed, after the switching on of light with a wavelength of λ=0.84 μm (Fig.3a, curve 2) negative photocurrent is not observed at all, but with the illumination by light with the wavelength of λ=0.7 μm (Fig.3b, curve 2), photocurrents follows the trace of curve 1 from the pure sample, displaced towards the positive values of current. This is in agreement with an increase in the intensity of spectral peak at 1.5 eV, seen from the comparison of curves 2 and 2' in the Fig. 1 and by the assumed increase in the recombination time in the samples with the tin impurity.
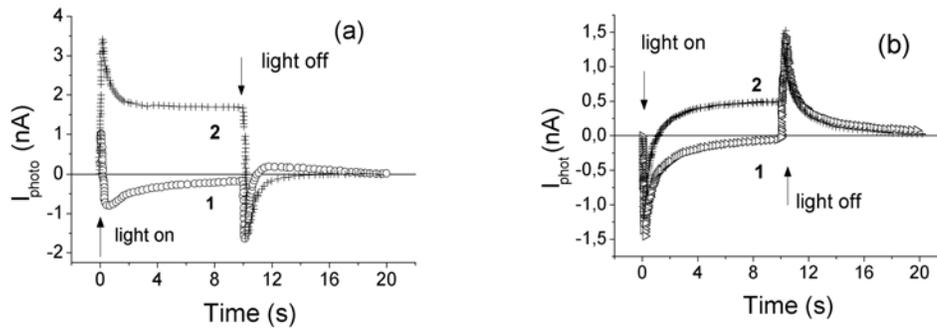

Fig.3. The kinetics of photoconductivity, measured in amorphous Sb$_2$Se$_3$ (curve 1) and Sb$_2$Se$_3$:Sn (curve 2) thin film under monochromatic light pulse illumination with a wavelength of λ=0,84 μm (a) и λ=0,7 μm (b); T=290 K, F=1.5 x 10^4 V/cm.

For the explanation of the observed transient photocurrents, such as shown in Fig. 3a (curve 1), it is possible to assume (following, for example, the authors [9]) that at first stage of relaxation the electron excitation from the filled D$^-$ centers into the conduction band (with the subsequent thermal ionization of holes into the valence band) take place. Here it is possible to expect also an increase in the emission of holes due to Pool-Frenkel effect: holes overcome the potential barrier, which is reduced in the presence of electric field [10]. At the second step the capture of non-equilibrium electron to the D$^+$ center take place. Finally, at the third step – the recombination with involvement of this center of free holes and trapped electrons occurs.

The first spike pulse of photoconductivity, immediately after the switching on of light, is associated with rapid capture of electrons to the D$^+$ - centers. If the concentration of this centers is sufficiently large, then, being the filled by electrons, they can serve as "reservoir" for the drain and the additional recombination of holes; as a result the photoconductivity rapidly decreases and it becomes less than the equilibrium one.

After the cessation of the illumination the formation of free holes break off, which leads to an even larger drop in the conductivity. Following this begins the slow ionization of holes from the D$^-$ centers into the valence band, and the photoconductivity again grows to its dark value. The explanation of the transient photocurrents in the region of photon energy hν>E$_g$ (Fig.3b) within the framework of this model is impossible, since the process of the thermal emission of holes into the band of the conducting states (part from which will give the contribution to the positive photocurrent) always precedes the process of recombination.

We assume that in this case, the effect of negative photoconductivity is associated with the direct recombination of electrons and holes situated on the centers D^0 during capture of free charge carriers in centers D$^+$ and D$^-$ in accordance with the reactions: D$^+$+e→D^0, D$^-$+h→D^0 [6]. Since the process of capture runs more rapidly than thermal ionization of D^0 centers, reduction in current can

be significant (i.e., less than it was before the illumination). Further, the process of recombination stabilizes photocurrent and negative photoconductivity slowly increases with the time constant of the order of the thermal ionization of D^0 - centers. The optical extinction of photocurrent or negative photoconductivity in single CdSe crystals were also explained on the basis of the model of recharging of recombination centers under illumination [11].

4. Conclusions

Thus, the steady-state and transient photocurrents in the chalcogenide amorphous Sb_2Se_3 and Sb_2Se_3:Sn thin films demonstrate the features (the presence of the spectral peak and negative photoconductivity), probably caused by D^+ and D^- defect centers. These features change upon the transfer from the pure sample to the sample doped with tin and indicate an increase in the photosensitivity of the amorphous material.

The proposed interpretation of the observed phenomena involves the examination the processes of deep capture and recombination on the charged defects and is in accordance with the general tendency of a change in concentration of U^- centers during the introduction into the chalcogenide film of the positively charged impurity such as tin.

References

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