

PHOTOCONDUCTIVITY OF CHALCOGENIDE THIN FILM HETEROSTRUCTURES

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Abstract. The experimental results reviewed in this paper cover the following topics: optical absorption and steady-state photoconductivity of amorphous single layer structures Al-As_{0.40}S_{0.30}Se_{0.30}-Al, Al-Ge_{0.09}As_{0.09}Se_{0.82}-Al, Al-Ge_{0.30}As_{0.04}S_{0.66}-Al and heterostructures (HS) Al-As_{0.40}S_{0.30}Se_{0.30} / Ge_{0.09}As_{0.09}Se_{0.82} / Ge_{0.30}As_{0.04}S_{0.66}-Al as well. The thickness of each layer of the HS is around 1, 0.5 and 0.2 μm, respectively. It was found that the voltage dependence on the photocurrent can be varied with both the polarity of the top illuminated electrode and different excitation wavelengths. Some photocurrent spectra show rich structure which originate due to different value of the optical band gap of the amorphous interlayers (about 2.0 eV for the As_{0.40}S_{0.30}Se_{0.30} and Ge_{0.09}As_{0.09}Se_{0.82}, and about 3.0 eV for the Ge_{0.30}As_{0.04}S_{0.66}). The obtained experimental results are discussed taking into account the absorption depth of the incident light, the contact phenomena between the layer interfaces of the different compositions as well as the interfaces metal-amorphous semiconductor layer.

Key words: amorphous heterostructures, transmission spectra, photocurrent.

1. INTRODUCTION

Chalcogenide As-S-Se, Ge-As-Se, and Ge-As-S thin films attract considerable interest in IR optics, non-linear optics, photonics, optoelectronics, as registration media for holography and e-beam lithography [1, 2] due to their optical, photoelectrical and other properties. Physical properties of such glasses which are covalently bonded materials, are determined by the mean coordination number Z (average number of covalent bonds per atom) [3]. It is well known that the functionality of many photonic and optoelectronic devices is based on the intrinsic photoelectric effect. The photocurrent spectra and photocurrent kinetics can give the information regarding the mechanism of generation, recombination and drift processes of non-equilibrium charge carriers in amorphous glasses. From this point of view, investigations of stationary and transient characteristics of photoconductivity of the ternary amorphous thin films represent special interest. For the thermally deposited amorphous films, whose structure exhibits a higher level of disordered than the bulk glasses, the incorporation of impurity atoms is more easily accomplished, and in many cases the metal additives can even become electrically active under certain conditions. An effect of Sn impurities on the stationary and transient photoconductivity was demonstrated in [4] for amorphous As₂Se₃Sn _{x} thin films. It was shown that introducing of Sn into the host amorphous material increases the drift mobility and the photosensitivity of that material. According to the study of As₂Se₃:Sn _{x} glasses [5] using ¹¹⁹Sn Mössbauer spectroscopy, and As _{x} Ge _{x} Se_{1-2 x} glasses [3] using X-ray photoelectron spectroscopy (XPS), the addition of Sn or Ge elements in As-Se based-materials can form the new tetrahedral Sn(Se_{1/2})₄, GeSe₄, and quasi-octahedral SnSe structural units, respectively. Recently the experimental results of steady-state and transient photoconductivity of amorphous Ge _{x} As _{x} Se_{1-2 x} and (As₄S₃Se₃)_{1- x} Sn _{x} thin films have been presented [6]. This study has shown that the dependence of the steady-state photocurrent on light intensity is non-linear for all investigated amorphous thin films, and is described by the following relation: $I_{ph} \sim F^\alpha$, where F is light intensity, I_{ph} is photocurrent, and the parameter α can takes the value $1.0 \leq \alpha \leq 0.5$. The manifestation of nonlinearity in these materials is because the predominant mechanisms of recombination of the photo-excited carriers in amorphous materials are mono- and bimolecular, and the carrier transport is involved in a multiple-trapping-release process with exponential energy distribution of the localized states within the band gap (traps).

In the present paper we pay attention to the experimental results on optical and photoelectric characteristics of new multilayer amorphous heterostructure GeAsS/GeAsSe/AsSSe, the components of which have different values of the band gap which varies in the range of 3.0–2.0 eV. Such “tandem” of heterostructure allows to more efficiently utilize the incident light, to extend the spectral sensitivity, and to govern the spectral region of photosensitivity by changing the polarity and the value of the applied voltage.

2. EXPERIMENTAL

The bulk chalcogenide glasses, $\text{As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}$, $\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}$, and $\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}$ were synthesized from the elements Ge, As, S, and Se with 6N purity by the conventional melt quenching technique. Starting materials are weighed, batched into quartz ampoule and sealed under vacuum ($P=10^{-5}$ Torr). The ampoules were then heated for 48 hours at the temperature $T=1\,000^\circ\text{C}$. The melt-containing ampoules were air-quenched to room temperature. Some glass samples were then cut, inspected visually and polished for optical measurements, other bulk glasses were prepared for subsequent film deposition.

Monolayer films of different thickness range (1 μm for $\text{As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}$, 0.5 μm for $\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}$, and 0.2 μm for $\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}$) were prepared through different individual evaporation sessions onto glass substrates for further optical and photoelectric measurements.

The heterostructures (HS) $\text{Al As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}/\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}/\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}\text{-Al}$ were prepared in the same technological cycle. Eventually, HS samples have a sandwich configuration with two Al-electrodes, one of which (top electrode) is semi-transparent for the incident light. The dark conductivity σ_d , $I_{ph} = f(F)$ (F is the light intensity), and the spectral distribution of stationary photocurrent, $I_{ph} = f(\lambda)$, were registered at the constant current conditions using the spectrophotometer SPM-2 as well as the electrometrical amplifier U1-7, with an error less than $\pm 1.0\%$. The dependence of the photocurrent on light intensity was investigated at the wavelength of maximum sensitivity of each sample ($F \sim 10^{16}$ photons/cm² s at $\lambda_{max}=560$ nm). Light intensity was varied using calibrated neutral density filters. All experiments were performed at room temperature ($T \approx 20^\circ\text{C}$).

3. RESULTS AND DISCUSSIONS

Figure 1 represents the transmission spectra $T=f(\lambda)$ of amorphous thin films $\text{As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}$ (1), $\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}$ (2), $\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}$ (3), and HS $\text{As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}/\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}/\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}$ (4), as well.

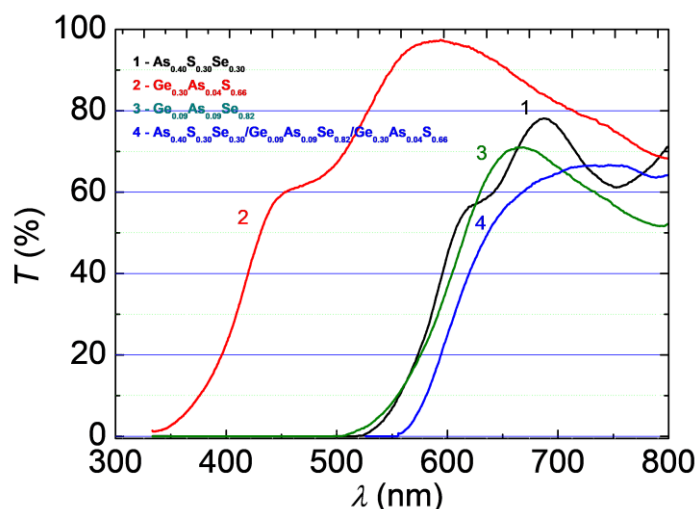


Fig. 1 – Transmission spectra $T=f(\lambda)$ of amorphous thin films and HS.

Thin film layer $\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}$, with the largest forbidden energy band $E_g \approx 3.0$ eV, was placed on the top of the multilayer structure having a thickness of about $d \approx 0.2$ μm and was transparent for the incident light so that it reaches other layers with the forbidden energy band about $E_g \approx 2.0$ eV with the thickness of about $d \approx 0.5$ μm for $\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}$ and about $d \approx 1$ μm for $\text{As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}$, respectively. It was observed that the absorption edge of the multilayer structure is shifted in the red region of the spectra (Fig. 1, curve 4).

Figure 2 shows the dependence of the currents in the dark and under illumination with the wavelength of peak sensitivity of the photocurrent for amorphous HS $\text{Al-As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}/\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}/\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}\text{-Al}$ for the case when the positive voltage is applied to the top aluminum electrode. The steady-state photocurrent spectra for all amorphous thin film structures were registered in a uniform electrical field $E = 5 \cdot 10^4$ V/cm, within the acceptable range of linearity in the dependence of the currents upon applied voltage.

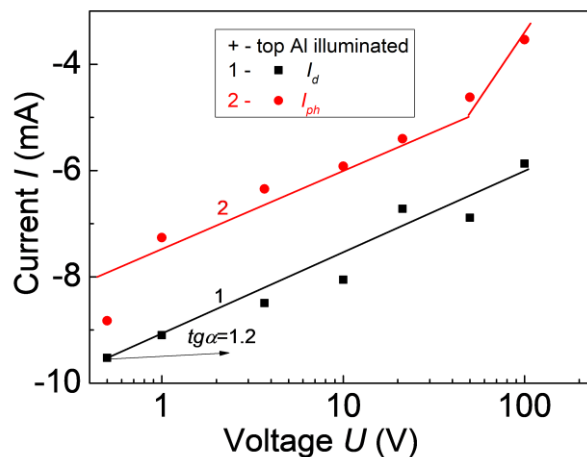


Fig. 2 – The dependence of the currents in the dark (1) and under illumination (2) for amorphous HS for a positive applied voltage to the top Al-electrode.

The spectral distribution of steady-state photoconductivity of amorphous thin films and HS $\text{Al-As}_{0.40}\text{S}_{0.30}\text{Se}_{0.30}/\text{Ge}_{0.09}\text{As}_{0.09}\text{Se}_{0.82}/\text{Ge}_{0.30}\text{As}_{0.04}\text{S}_{0.66}\text{-Al}$ at positive and negative applied voltage to the top Al-illuminated electrode is represented in Figs. 3 and 4. The steady-state photocurrent spectra show that the position of the maximum of photosensitivity of the component layers of multilayer HS has in a good correlation with the absorption spectra. The spectral distribution of photocurrent for the HS is situated in the intermediate region between the separate layers, and depends on the polarity of illuminated electrode.

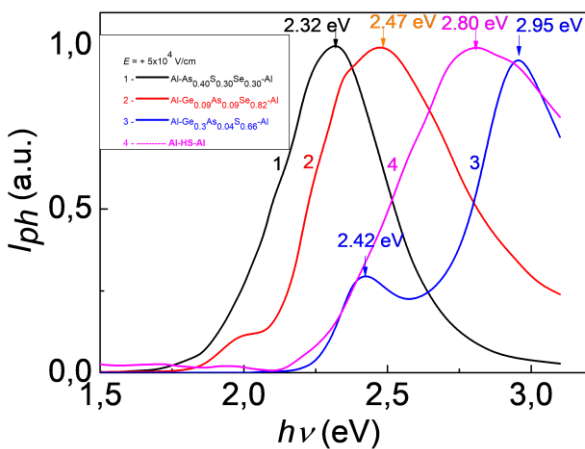


Fig. 3 – Photocurrent spectra of separate amorphous thin films and multilayer HS at positive applied voltage to the top Al-illuminated electrode.

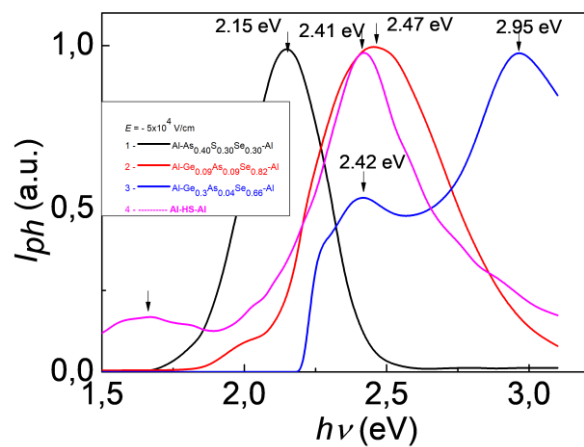


Fig. 4 – Photocurrent spectra of separate amorphous thin films and HS at negative applied voltage to the top Al-illuminated electrode.

The more stable composition in respect of the polarity of applied voltage is the thin film structures Al-Ge_{0.09}As_{0.09}Se_{0.82}-Al with the maximum of photocurrent situated at $h\nu = 2.47$ eV and Al-Ge_{0.30}As_{0.04}S_{0.66}-Al with the maximums situated at $h\nu = 2.95$ eV and $h\nu = 2.42$ eV, and the position of these maxima do not depends on the polarity of applied voltage. The presence of two maximums in the photoconductivity spectra indicate on the probability of existence of phase separation in this composition, which contain trigonal (AsS_{3/2}) and tetrahedral (GeS₄) structural units. At the same time, Figures 3 and 4 show that for the thin film structure Al-As_{0.40}S_{0.40}Se_{0.30}-Al and for multilayer HS the position of the maximum of the photocurrent depends on the polarity of applied voltage, at the positive applied voltage to the Al-illuminated electrode the maximum is shifted in the region of higher energies of the spectrum.

As was mentioned in [6], this behavior can be associated with the contact phenomena at the interfaces of the metallic electrode, as well as with the drift and surface recombination of the non-equilibrium carriers [7]. Figure 5 represents the normalized photocurrent spectra of multilayer thin film HS at different values (0.1–200 V) of negative applied voltage to the top Al-illuminated electrode. It is evident that increasing of the applied voltage leads to an essential shift of the maximum of the photocurrent to lower energies. This shift can be attributed to different resistance of the component layers of the HS, to the different dependencies of the current vs applied voltage (current-voltage characteristic). In this case the distribution of the applied voltage between each layer depends on it values and the contribution of each layer in the summary photocurrent also is different.

At positive polarity (0.1 ÷ 200 V) applied to the top Al-illuminated electrode the structure of the photocurrent spectra is more complicated. At low applied voltage (0.1 ÷ 0.5 V) the predominated is the negative photocurrent, and at $U = 1.0$ V take place the inverse of the sign of the photocurrent to the positive. This behavior is very important for the practical point of view, because we have a possibility to create the kind of photodetectors with different sign of photocurrent. This phenomenon of sign inverter of photocurrent guided by polarization was also observed for the photodetectors based on ZnAs₂ anisotropic crystals [8].

Figure 6 demonstrates the dependence of magnifying power K (the ratio of the photocurrent to the dark current $K = I_{ph}/I_{dark}$) for amorphous thin film HS vs. applied voltage at positive (1) and negative (2) polarity to the top Al-illuminated electrode.

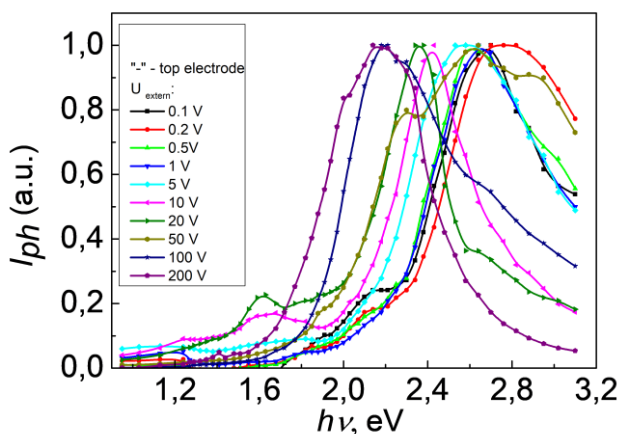


Fig. 5 – Normalized photocurrent spectra of multilayer HS at different values of negative applied voltage to the top Al-illuminated electrode.

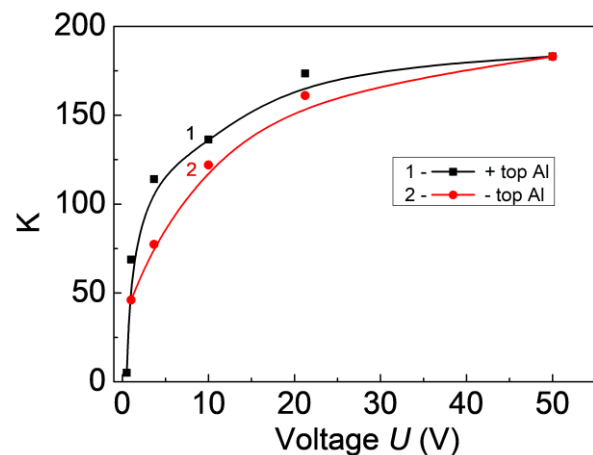


Fig. 6 – The dependence of magnifying power K of amorphous thin film HS vs. applied voltage at positive (1) and negative (2) polarity applied to the top Al-illuminated electrode.

The fact that photosensitivity of the amorphous multilayer thin film HS is higher for the positive polarity at the top illuminated Al-electrode has also been demonstrated in the case of single thin film structures [6].

4. CONCLUSIONS

The experimental results on optical absorption and steady-state photoconductivity spectra of amorphous single layer structures Al-As_{0.40}S_{0.30}Se_{0.30}-Al, Al-Ge_{0.09}As_{0.09}Se_{0.82}-Al, Al-Ge_{0.30}As_{0.04}S_{0.66}-Al and

heterostructures (HS) Al-As_{0.40}S_{0.30}Se_{0.30}/Ge_{0.09}As_{0.09}Se_{0.82}/Ge_{0.30}As_{0.04}S_{0.66}-Al at different values of the applied voltage at the illuminated top Al electrode for positive and negative polarity are investigated. It was established the energetic position of the photocurrent maximum on the thin film composition. In the case of the HS the rise of the applied voltage shifts the maxima of the photocurrent toward lower energy. It was established that rising of applied voltage increases the photosensitivity of the HS as well. We suggest that the observed peculiarities of photoelectric properties of single layered structures and HS are caused by the drift processes of non-equilibrium carriers in amorphous material, by the contact phenomena at the interfaces of the different composition of the amorphous materials and between amorphous layer and metallic electrodes.

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