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Charge carrier transfer in amorphous $(GeS)_{1-x}Bi_x$ films

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The influence of Bi additions on the electrical and photoelectrical properties of amorphous $(GeS)_{1-x}Bi_x$ films ($0 \le x \le 0.15$) has been investigated. Adding Bi to amorphous GeS condensates leads to changes in the mechanism of conductivity and inversion of the conductivity type. Bi-additives reduce the activation energy of photoconductivity and photosensitivity of the GeS films. The changes of the physical properties of the films are explained considering a heterogeneous structure of the condensates and defect states in the mobility gap.

Amorphous films / Chalcogenide semiconductors / Defect states / GeS-Bi

Introduction

Perturbation of amorphous chalcogenide systems by external factors may cause reversible or irreversible changes in their structure and physical properties. This has become the basis for the development of threshold switches, memory cells and photovoltaic convertors [1,2]. Such phenomena are mainly associated with high-flexibility amorphous networks that have a low level of coordination and large internal free volumes [3].

Bi-additions to amorphous materials based on GeS are an effective tool for changing the electrical properties, because they can produce changes in the optical properties [4] and inversion of the type of conductivity [5,6]. The physical properties of amorphous chalcogenide films are sensitive to high-energy radiation [7,8]. Preliminary results on the impact of Bi on the structure and physical properties of amorphous *a*-GeS films were presented in [9]. The aim of this work was to study the influence of Bi-additions on photovoltaic properties of amorphous $(GeS)_{1-x}Bi_x$ ($0 \le x \le 0.15$) films.

Experimental

Bulk samples $(GeS)_{1-x}Bi_x$ ($x = 0$, 0.03, 0.07, 0.11, 0.15) were obtained in ampoules by melting stoichiometric GeS with the addition of appropriate amounts of Bi. The ampoules were subjected to vibration and hardening in cold water. Thin films for the investigation (thickness of 0.3-1.2 μm) were obtained by discrete evaporation of a finely dispersed mixture in vacuum (10^{-4} Pa) onto the surface of substrates of quartz and ceramics at 293 K, followed by annealing in vacuum at $T = 350$ K. The presputtering method was applied to the substrate contact with copper. Comparison of the results of electron probe analyses, obtained on a "Camebax" device, for the $(GeS)_{1-x}Bi_x$ bulk samples and thin films ($x = 0$, 0.03, 0.07, 0.11, 0.15) showed a good correlation. The thickness of the films was measured with an optical interferometer.

The photovoltaic properties of the samples were studied by methods using unmodulated or modulated lighting, depending on the temperature and the spectral composition of the exciting light. The photocurrent was registered with an electrometric voltmeter V7E-42. We calculated the photoconductivity by the formula [10]:

$$\sigma_{ph} = v(R + r_0)^2 / r_0^2 VR - v r_0 R(R + r_0) l / S \,,$$

where v – a signal on the reference resistance of R, r_0 – resistance of the sample, V – bias voltage applied to the sample, l and S – length and cross-sectional area of the sample. The temperature dependences of the static conductivity and photoconductivity of the films were investigated in the temperature range 150-350 K.

Results

The mechanism of conductivity can be determined from the temperature dependence of the electrical conductivity and the charge carrier mobility. The electrical conductivity of the amorphous GeS films (Fig. 1a) is described by the Arrhenius equation [11]:

$$\sigma = \sigma_0 \exp(-\Delta E_\sigma / kT)$$

where σ_0 – a constant, ΔE_σ – activation energy of conductivity. This indicates the existence of an activation mechanism of conductivity.

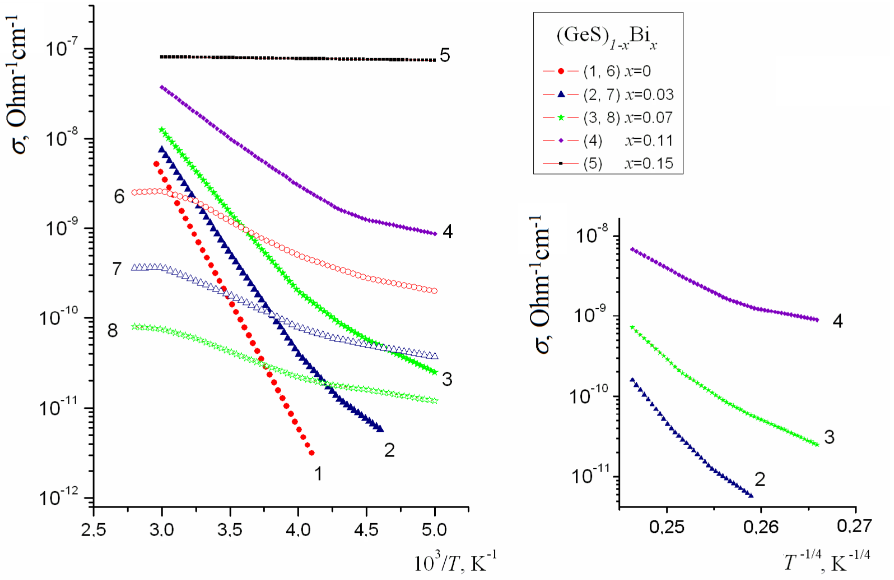
The activation energy of conductivity of the $(GeS)_{1-x}Bi_x$ ($x = 0.03$, 0.07, 0.11) condensates depends on the temperature. At temperatures below 240 K a dependence $\sigma(T) = \sigma_{01}(-T_0/T)^{1/4}$ is observed (Fig. 1b). This points on a conductivity hopping mechanism in localized states near the Fermi level with a variable hopping length. The density of states at the Fermi level $N(E_F)$ was calculated from the expression [11]:

$$T_0 = 18a^3 / kN(E_F),$$

where T_0 – a constant (determined from the slope of $\sigma(T)$), a – a parameter characterizing the attenuation of the wave function ($a^{-1} = 0.8$ nm), k – the Boltzmann constant.

With increasing Bi content, $N(E_F)$ increases and the activation energy of conductivity decreases (Table 1). The $(GeS)_{0.85}Bi_{0.15}$ sample showed weak temperature dependence of the conductivity in the investigated temperature range.

Difficulties in measuring small voltages on high-resistivity films did not allow us to obtain the temperature dependence of the thermopower and to study the Hall effect. But the sign of the thermopower indicates that the major carriers in the $(GeS)_{1-x}Bi_x$ samples containing up to 11 at.% Bi are holes, whereas in the $(GeS)_{0.85}Bi_{0.15}$ film they are electrons. This means that there is an inversion of the conductivity type of the amorphous GeS films, due to the addition of bismuth. Similar phenomena were observed for Ge-S glasses containing 20-40% Ge when Bi was added [5,6,12].



(a) (b)

Fig. 1 Temperature dependence of dark conductivity (curves 1-5) and photoconductivity (6-8) for $(GeS)_{1-x}Bi_x$ amorphous films (a), and temperature dependence of dark conductivity (curves 2-4) of the type $\sigma(T) \sim T^{-1/4}$ for $(GeS)_{1-x}Bi_x$ films (b).

Table 1 Electrical conductivity σ_{300K} at $T = 300$ K, conductivity activation energy ΔE_σ, density of states at the Fermi level $N(E_F)$, sign of thermopower, and optical gap E_o of amorphous $(GeS)_{1-x}Bi_x$ films.

Composition	$\sigma_{300\,K}$, $\Omega^{-1}cm^{-1}$	ΔE_σ, eV ($T > 240$ K)	$N(E_F)$, $cm^{-3}eV^{-1}$	Sign of thermopower	E_o, eV [9]
GeS	1.09×10^{-9}	0.72	–	+	1.55
$(GeS)_{0.97}Bi_{0.03}$	3.23×10^{-9}	0.68	1.2×10^{18}	+	1.48
$(GeS)_{0.93}Bi_{0.07}$	7.26×10^{-9}	0.54	2.9×10^{18}	+	1.40
$(GeS)_{0.89}Bi_{0.11}$	8.52×10^{-8}	0.42	7.6×10^{18}	+	1.37
$(GeS)_{0.85}Bi_{0.15}$	1.55×10^{-7}	0.15	–	–	1.32

On the curves of spectral dependence of the photoconductivity (Fig. 2), descending branches in the energy region smaller than the width of the energy gap are stretched, which may indicate a blur of the density of states near the band edges. Bi-additives of 7 at.% to GeS reduce the photosensitivity by approximately one order of magnitude. Extrapolating the linear plots $(I_{ph}h\nu)^{1/2}$ to the energy axis gives the width of the energy gap (E_g). This value of E_g is somewhat smaller than the optical gap E_0, which is calculated from the data on the absorption edge [9].

To elucidate the mechanisms of recombination, the dependence of the photoconductivity on temperature was studied (Fig. 1a). On heating the refrigerated $(GeS)_{1-x}Bi_x$ samples, the photocurrent increases exponentially: $\sigma_{ph}(T) \sim \exp(-\Delta E_{ph}/kT)$. In the temperature range 230-290 K a steady increase of the photoconductivity is observed with increasing temperature. In the low-temperature region ($T < 230$ K) the films show lower activation energy of photoconductivity (Table 2).

The photocurrent depends nearly linearly (Fig. 3) on the light intensity (F), which corresponds to a monomolecular recombination regime in the domain of thermal quenching of photoconductivity. At higher temperatures, *i.e.* in the domains of exponential growth of the photoconductivity where a bimolecular recombination regime is implemented, the photocurrent is proportional to the square root of the light intensity ($\sigma_{ph} = \alpha F^{1/2}$).

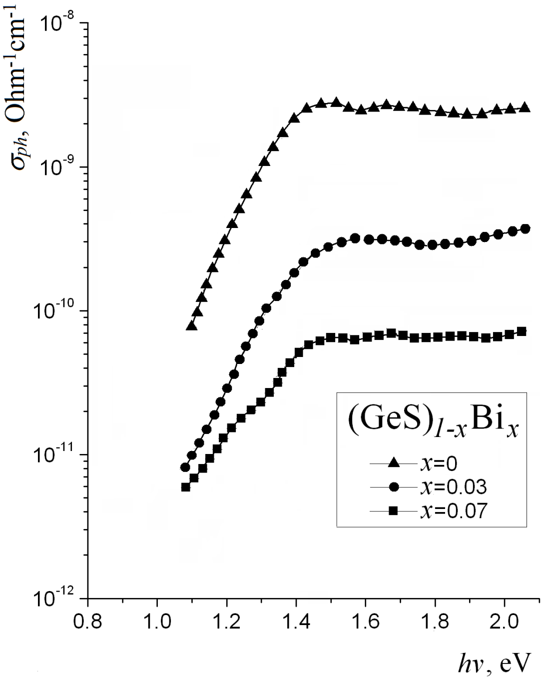


Fig. 2 Spectral dependence of the photoconductivity of $(GeS)_{1-x}Bi_x$ amorphous films.

Discussion

Bi-additives lead to changes in the mechanism of conductivity in the GeS condensates: at low temperatures a hopping conductivity mechanism through localized states near the Fermi level appears. The electrical conductivity and thermal activation energy of amorphous $(GeS)_{1-x}Bi_x$ depend nonlinearly on the Bi concentration (Table 1). For small concentrations of bismuth, ΔE_σ decreases slightly, and for impurity Bi concentrations more than 11 at.%, sharply. This indicates a certain threshold of the Bi concentration at which a change of the material properties takes place.

According to the literature [12,13], the other elements of the Bi group, except Pb, do not produce a change in the conductivity type of chalcogenide matrices, even at high concentrations. Therefore Bi atoms seem to play a special role in the processes of charge transfer when added to chalcogenide matrices.

The Bi-additives reduced the photoconductivity of the GeS films. This is consistent with the data of [6]. The activation energy of photoconductivity in the temperature range 230-290 K depends on the presence of deep traps, which control the drift mobility. In this case the photoconductivity increases as a result of the release of electrons and holes captured in the traps. With increasing Bi concentration these domains expand, which may indicate an increase of the number of impurity centers.

For unmodified GeS samples, with increasing temperature the photoconductivity passes through a maximum near 290 K. This corresponds to a temperature region where the photocurrent becomes comparable with the dark current [9]. Then the photoconductivity decreases with increasing temperature. In our opinion, the behavior of the photoconductivity in the range $T > 290$ K is related to thermal quenching of photoconductivity. The equilibrium value of the photocurrent depends on the recombination of optically excited carriers and thermally excited electrons and holes, the number of which increases with increasing temperature.

Table 2 Energy gap E_g and activation energy of photoconductivity ΔE_{ph} for $(GeS)_{1-x}Bi_x$ amorphous films.

Composition	E_g, eV	ΔE_{ph1}, eV ($T > 290$ K)	ΔE_{ph2}, eV ($T = 230$-290 K)	ΔE_{ph3}, eV ($T < 230$ K)
GeS	1.44	-0.15	0.35	0.16
$GeS_{0.97}Bi_{0.03}$	1.39	-0.13	0.30	0.14
$GeS_{0.93}Bi_{0.07}$	1.30	–	0.28	0.13

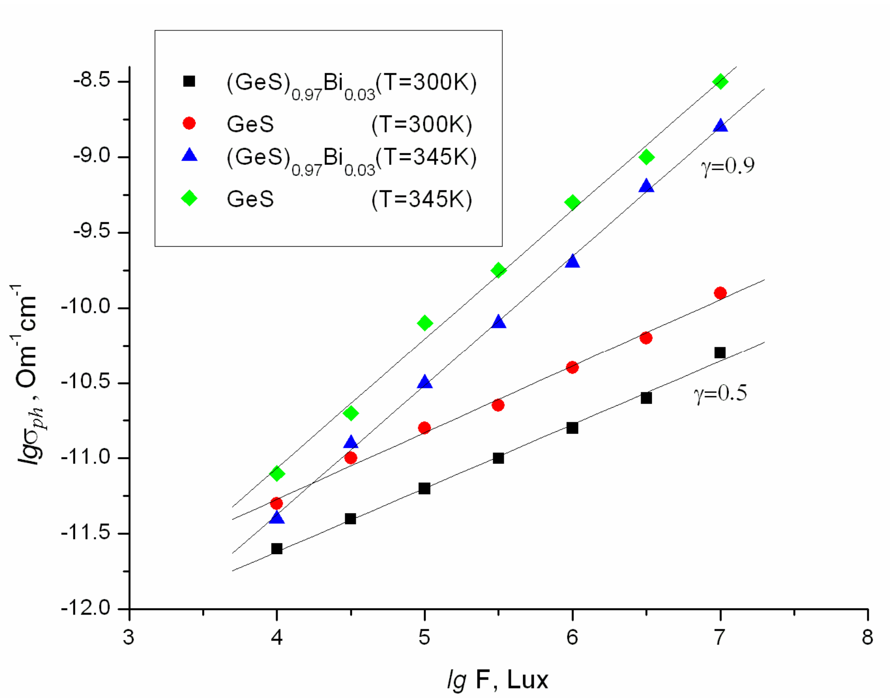


Fig. 3 Intensity dependence of the photoconductivity of $(GeS)_{1-x}Bi_x$ amorphous films at 300 K and 345 K.

An inflection at energies of about 1.3 eV is observed on the $\sigma_{ph}(h\nu)$ plots for the $(GeS)_{1-x}Bi_x$ films (Fig. 2). This energy corresponds to the band gap of crystalline Bi_2S_3. In our opinion, the inflection is due to the presence of a quasicrystalline Bi_2S_3 phase in the samples [9]. The inversion of the conductivity type observed for films with a Bi content of more than 11 at.% can be accounted for by considering Bi_2S_3 clusters, because the sulfur atoms in some Ge-S-Bi phases tend to form Bi-S bonds [12]. Since the Bi_2S_3 compound has more specific conductivity than GeS and is an *n*-type semiconductor [13], at the “threshold” Bi concentration, channels of charge transport are formed through Bi_2S_3 clusters in the studied films. This was confirmed by our study of the structure of $(GeS)_{1-x}Bi_x$ films [9] and is consistent with the data in [14].

Therefore, the spectral dependence of the photoconductivity and the change of the conductivity of the $(GeS)_{1-x}Bi_x$ films from *p*- to *n*-type in the concentration range $0.11 < x < 0.15$ is well explained assuming a heterogeneous structure of the condensates. In the model of charged defect centers [11], inversion of the conductivity type could be explained by a shift of the Fermi level to the bottom of the conduction band, leading to a situation where localized states at the Fermi level overlap with states on the edge of the conduction band. But in the absence of experimental data on photoconductivity for samples containing more than 11 at.% Bi, this cannot be confirmed.

Assuming that recombination occurs between carriers that are captured at one of the levels of localized states and free carriers in the bands, we can roughly estimate the energy of localized states in the mobility gap [15-17] (Fig. 4), knowing the activation energies of dark conductivity and photoconductivity. We cannot determine the value of ΔE_{ph1} precisely, since only a limited number of data points are available in the higher temperature range. The energy of recombination centers above the Fermi level (E_1), calculated from the edge of the valence band, is given by the relation [17]:

$$E_1 = \Delta E_\sigma + |\Delta E_{ph1}|,$$

where ΔE_{ph1} is the activation energy of photoconductivity at $T > 290$ K. The energy of recombination centers below the Fermi level (E_2, E_3) is determined by the relations [17]:

$$E_2 = 2\Delta E_{ph2} \text{ and } E_3 = 2\Delta E_{ph3},$$

where ΔE_{ph2} and ΔE_{ph3} are the activation energies of photoconductivity in the domains of exponential increase of the photoconductivity at $T = 230$-290 K and $T < 230$ K, respectively.

The above models do not always clearly explain the change of the conductivity type. According to [18], addition of 3 at.% Bi to selenium causes an inversion of the conductivity from *p*- to *n*-type, which is difficult to explain within the framework of heterogeneous structures of condensates. However, Sb additions (Sb is an element of the Bi group) do not change the conductivity type of GeS matrices (*p*-type for any content of Sb) [12,13].

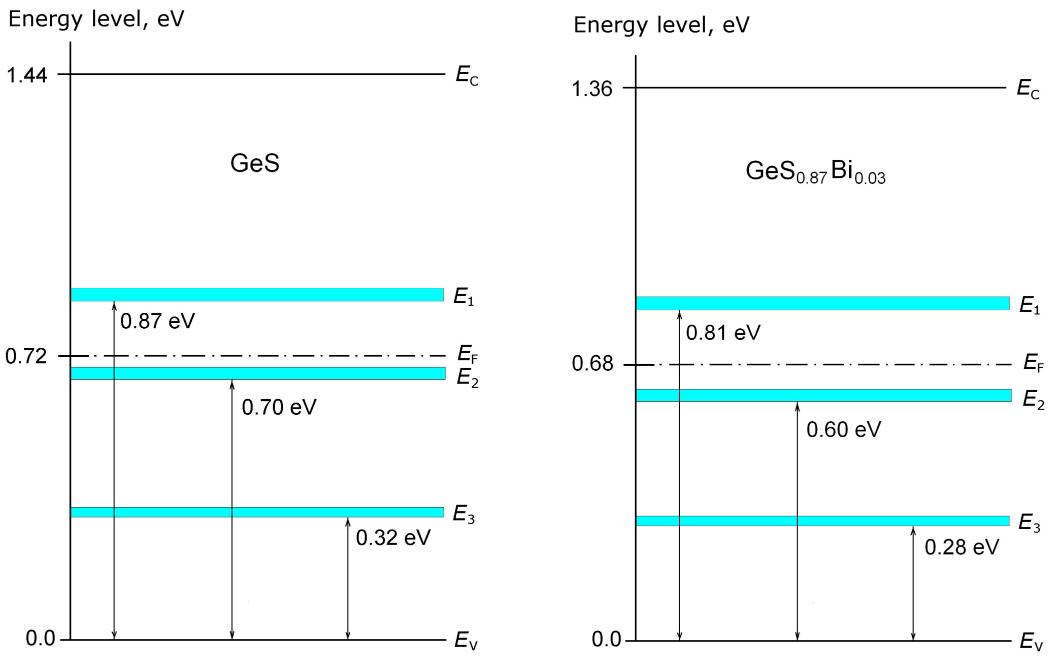


Fig. 4 Energy level diagram for defects states in the mobility gap of $(GeS)_{1-x}Bi_x$ amorphous films.

Conclusion

It was found that amorphous GeS films exhibit an activation mechanism of the conductivity in the temperature range $T = 150$-350 K. Bi-additives to the GeS condensates cause an increase of the conductivity and the appearance of hopping conductivity through localized states near the Fermi level with variable hopping length. Increase of the Bi concentration reduces the photoconductivity and the spectral region of photosensitivity of the films. In the concentration range $(GeS)_{1-x}Bi_x$, $0.11 < x < 0.15$, inversion of the conductivity from *p*- to *n*-type takes place.

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