Photoelectric Properties in Amorphous Chalcogenide Glassy Semiconductor $As_{40}Se_{30}S_{30}$ Films

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Abstract

Bipolar photoconductivity and bipolar drift of charge carriers have been established in amorphous chalcogenide glassy semiconductors $As_{40}Se_{30}S_{30}$ films, obtained by ion-plasma rf sputtering, in contrast to the films of these materials obtained by thermal evaporation. Observed results were due to the lack of deep traps for electrons in the spectrum of localized film states obtained by ion sputtering.

Introduction

Condensed semiconductor media with disordered structure is one of the most promising areas of condensed matter physics. Interest in this physics area is very big and need to understand the structure formation processes, their influence on structural-phase transformations and the nature of electronic processes occurring in the transition from media, with the translational structure symmetry to the media of long-range order in the arrangement of atoms [1-7]. Condensed matter with disordered structure is the most diverse application in practice. Crystalline analogs of electronic devices with broader functionality are based on the semiconducting properties of condensed matter with disordered structure. In addition, the now well established that the disorder in the structure of semiconductor materials causes a wide range of new specific properties and phenomena that have no analogues in the ordered (crystalline) semiconductor media. These properties such as switching and memory effects, high transparency in the infrared region, photostructural transformation lie at the basis of the optical information recording method and high-resolution lithography [1-7]. Potential application areas of non-crystalline semiconductors are the switching and holographic optical elements used in integrated optical devices, etc. Because of the unique set of properties in recent years the object of increased attention in basic and applied research is such class of materials as chalcogenide glassy semiconductors (CGS) amorphous films of with low coordinate chalcogen atoms [7]. In this paper, object of study is amorphous films of chalcogenide glassy semiconductors (CGS) on the example of a model ternary stoichiometric $As_{40}Se_{30}S_{30}$. CGS films were obtained by thermal evaporation in vacuum (TI-films) and RF ion-plasma sputtering (RF-film). Detailed experimental procedure was described in [8].

Results and discussion

Samples photoconductivity was studied at T = 300 K in fields of intensity E = 10^4 V/cm. Amorphous $As_{40}Se_{30}S_{30}$ films are characterized by a significant extension of the photoconductivity in the wavelength range from 0,45 to 0,55 μm. In the short-observed high values of photocurrent for the positive polarity of the illuminated electrode ($I_{ph+} >> I_{ph-}$), indicating the unipolar nature of the hole photoconductivity are in good agreement with published data [1, 2, 7]. Substantially different picture of the photoconductivity spectral distribution was discovered in the a-$As_{40}Se_{30}S_{30}$. In these films, the spectral dependence of the photocurrent is characterized by distinct maxima.

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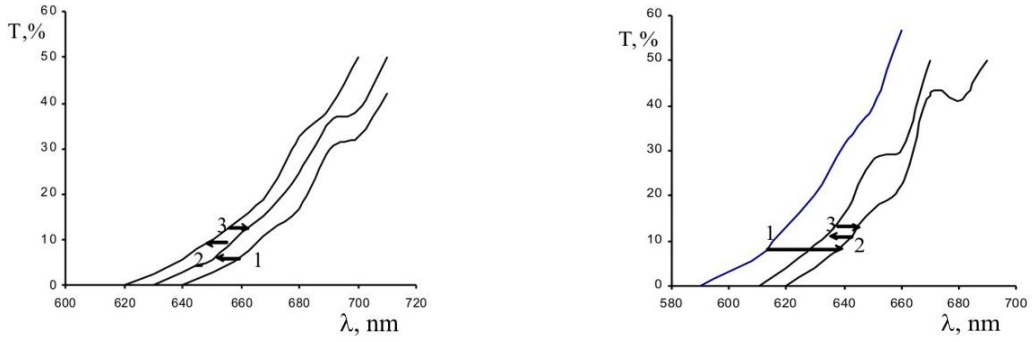
 Printed in Kazakhstan

The shape of the photocurrent spectral characteristics in the short-wavelength region is almost independent of the applied voltage polarity. This fact indicates about the bipolar photoconductivity in the a-$As_{40}Se_{30}S_{30}$ films, obtained by ion-plasma RF sputtering [8]. In many CGS compositions, and especially in the arsenic in the «light exposure – annealing» cycle occur reversible changes in physical-chemical properties, in particular, the optical band gap. In this case, the photon energy must correspond to the intrinsic absorption. This effect is called the effect of photo structure transformations.

Figure 1 shows the irradiation effect and subsequent annealing on the optical transmittance spectral characteristics $As_{40}Se_{30}S_{30}$ films, obtained by TE (a) and RF (b) methods. In Figure 1, curve 1 characterizes transmission of the edge position in freshly prepared films. Irradiation of these films with light at room temperature shifts the transmission edge in position 2. During subsequent annealing the transmission edge is shifted into position 3. Repeated exposure edge transmission returns to the position 2 (so-called reverse photo structural transformation) [5, 7].



a b

Fig. 1. Effect of irradiation and subsequent annealing on spectral transmission characteristics of $As_{40}Se_{30}S_{30}$ films, obtained by different methods: a - thermal evaporated film (TE) , b - ion-plasma rf sputtering (RF) film; 1 - freshly prepared, 2 - irradiated, 3 - annealed film

It is essential that the exposure of freshly prepared TE $As_{40}Se_{30}S_{30}$ films shifts the transmission edge to longer wavelengths (photo-darkening or E_g reduction). In the RF-films transmission edge during irradiation is shifted to shorter wavelengths (photo bleaching or increase E_g). During subsequent annealing of the irradiated films in the TE and RF films edge transmission shifted to shorter wavelengths (thermo – bleaching). The calculated optical band gap E_g film changes in the "irradiation – annealing" cycle are in the table.

Table

Optical band gap width (E_g) of freshly (1), irradiated (2), and annealed (3) $As_{40}Se_{30}S_{30}$ films, obtained by TE and RF methods

Films preparation method	TE			RF		
	1	2	3	1	2	3
E_g, eV	2.12	2,05	2,08	1,85	1,87	1,89

Analyzing the results of the photo induced changes in the structure, carried out earlier [8], and optical properties of TE-and RF $As_{40}Se_{30}S_{30}$ films can conclude that major changes occur in the optical band gap and in the extent regions of local ordering structure L. Moreover, reduction of irradiated L at the TE-films is accompanied by a decrease in E_g, and the increase L in the RF-films shows the increase in E_g. Thus, our studies have established that in $As_{40}Se_{30}S_{30}$ amorphous films when external factors such as temperature and light exposure there is a correlation between changes in the atomic structure of the films at the middle order and their optical band gap.

The drift mobility of charge carriers in CGS films

The importance of investigating carrier drift mobility is, firstly, that the transfer characterization is conducted in conditions close to those which usually are used in practice photovoltaic properties of CGS. Secondly, the study of the drift mobility of charge carriers can get the most complete information about the energy spectrum of localized

states, which determines the possibilities for the practical CGS use. In $As_{40}Se_{30}S_{30}$ films, obtained by thermal evaporation in a vacuum, charge carrier transport by carriers of one sign - the holes, since the drift mobility of holes (μ_p) is much greater than the electron (μ_n) drift mobility. Holes drift mobility of (μ_p) in the $As_{40}Se_{30}S_{30}$ films, received by TE-method is about 10^{-5} $cm^2/(V•s)$ at the electric field $E = 10^5$ V/cm and T = 300K. This is consistent with references [1, 2, 7]. Significant differences in the carrier transport were observed in $As_{40}Se_{30}S_{30}$ RF-films. Figure 2 shows the transient photocurrent waveforms, corresponding to the drift of electrons and holes in the $As_{40}Se_{30}S_{30}$ RF-films.

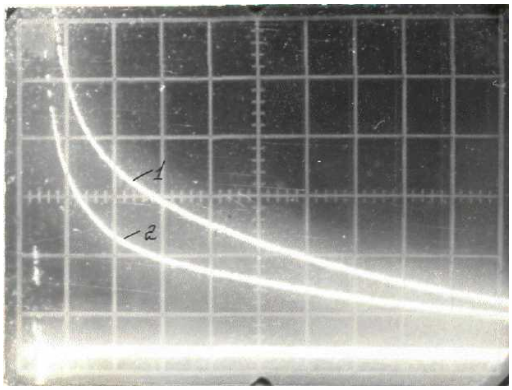


Fig. 2. Oscillograms of the transient photocurrent for electrons (1) and holes (2) in the $As_{40}Se_{30}S_{30}$ films: on the horizontal axis - 50 μms/div.; ordinate - 0,5 μmA/div., $E = 10^5$ V/cm

Transient photocurrent of electrons and holes are almost identical in amplitude and duration, as evident from the oscillograms. This suggests the presence of mobile charge carriers of both signs in the films. Pulse shape of the transient photocurrent I (t) corresponds to the dispersive transport [9]. In this case, to determine the carrier drift mobility curve of the transient photocurrent was tuned in double logarithmic scale lg I ~ lg t (Figure 3). In such coordinates, the dependence I (t) takes place two plots of photocurrent decay: the slow and faster. Time corresponding to the transition from one section of the recession I (t) to another is interpreted as the transit time (t_{tr}). Defined in this way the t_{tr} value, corresponds to the output of the sample's center of gravity of drifting pack carriers injected light pulse [9-10]. Calculated drift mobility of holes (μ_p) and the electron (μ_n) drift mobility in the $As_{40}Se_{30}S_{30}$ films, obtained by RF-method is about $\mu_p \approx \mu_n \approx 10^{-5}$ cm^2 / (V·s) at electric field $E = 10^5$ V/cm and T = 300 K. Studies carrier drift mobility in the range of electric fields intensity from $3 \cdot 10^4$ до $3 \cdot 10^5$ V/cm showed that μ_p and μ_n increase with the electric field. In the investigated range of electric field dependence of the μ_p and μ_n versus field ($\mu(E)$) can be approximated by an exponential function μ_p, μ_n ~$\exp(E/E_o)$, where E_o=I0^5 В/см (Figure 4).

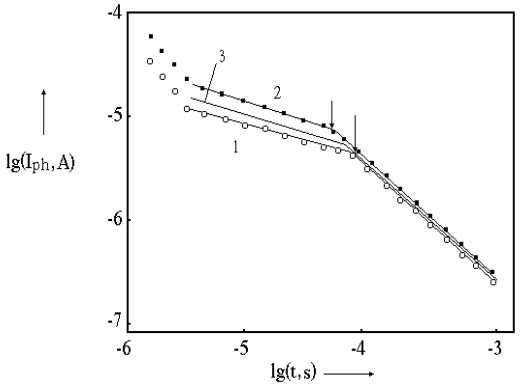


Fig. 3. Dependence of transient photocurrents for hole (1, 3) and electrons (2) versus time in the $As_{40}Se_{30}S_{30}$ films obtained by RF-sputtering (1,2) and thermal evaporation in vacuum (3). $E = 10^5$ V/cm, $T = 300$ K

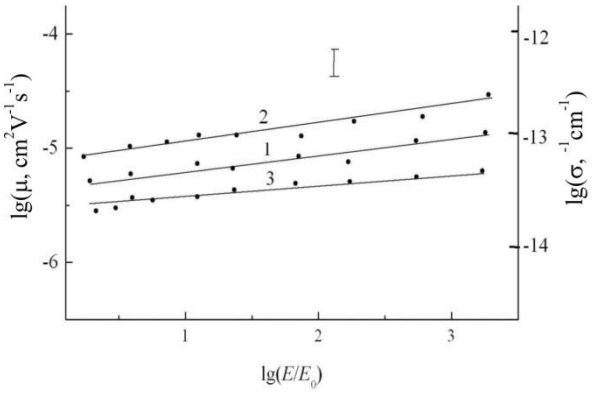


Fig. 4. Dependence of the carrier drift mobility (1, 2) and conductivity (3) versus electric field for $As_{40}Se_{30}S_{30}$ films, obtained by RF-sputtering: 1- electrons, 2- holes, T=300 K

Exponential dependence of μ(E) took place in the $As_{40}Se_{30}S_{30}$ TE-CGS films. Conductivity and drift mobility of charge carriers increasing with the field according to [9, 11] has been due to the delocalization of the shallow localized state in the energy interval $\Delta\varepsilon = er_oE$, below the bottom mobility, where r_o – states size, delocalized by electric field. To explain the exponential dependence of $\mu_p(E)$ and $\mu_n(E)$ for $As_{40}Se_{30}S_{30}$ RF-films we can draw a model developed in [9, 11] for TE-films and bulk As_2Se_3, obtained by different

methods as observed similar values of the exponent n in the dependence of $\mu \sim E^n$. Consequently, the electric field influence leads to a lowering of the energy level corresponding to the mobility threshold on the value of $\Delta\varepsilon$. Shown curves in Figure 3 of the transient photocurrent in a double logarithmic scale lg I – lg t usually extrapolated by straight lines with slopes $-(1 - \alpha_i)$ for the initial slower site and $-(1 + \alpha_f)$ for a more rapid final section. In this case, the dispersion parameters α_i and α_f vary within $0 < \alpha_i, \alpha_f \leq 1$. As noted above, transition from one slope to another takes place at the time, which is taken as the transit time t_{tr}. It should be noted that the activation energy of drift mobility of electrons and holes depend on the electric field and sample thickness. As the thickness of the samples, $\varepsilon_{\mu n}$ and $\varepsilon_{\mu p}$ increase (Figure 5). Such behavior $\varepsilon_{\mu n}$ and $\varepsilon_{\mu p}$ with increasing electric field intensity correlates with the hypothesis that delocalization of the shallow localized states at high electric fields.

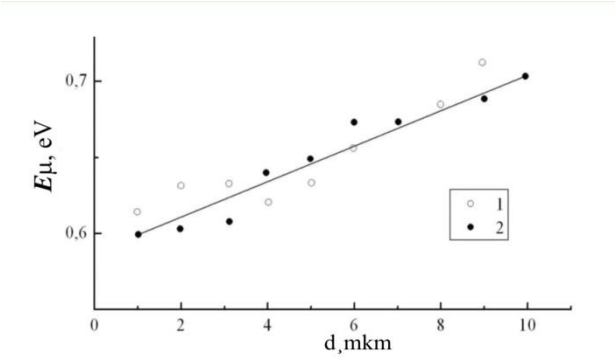


Fig. 5. Dependence of the activation energy of hole drift mobility (1) and electrons (2) versus thickness of the RF-films $As_{40}Se_{30}S_{30}$: E = I0^4·V/cm, d = 1,5 μm

Low values μ_p, μ_n and the values of their activation energies $\varepsilon_{\mu n}$ and $\varepsilon_{\mu p}$ are characteristic for the hopping mechanism of charge transport [1-2, 9]. Estimated Mott [1] the highest value of the hopping mobility $\mu_{пр}$ equal to the preexponential factor in expression $\mu_{пр} = (eR^2\nu/kT) \exp(-\varepsilon_\mu/kT)$, and does not exceed 10^{-2}cm^2/(Vs). In the $As_{40}Se_{30}S_{30}$ RF-films preexponential factor reaches~10^5cm^2/(Vs) which significantly exceeds the10^{-2}cm^2/(Vs). Such high values of the preexponential factor, apparently, can be understood by assuming the band transport mechanism, which is controlled by trapping at localized states (the so-called "relay" mechanism) [9]. In this case, the charge carriers for some time to move from the high mobility μ_o of the allowed energy band, then trapped in localized states, where there are some time τ_t and then released and moved back to the allowed band with mobility μ_o

$$\mu = \mu_o \frac{\tau_o}{\tau_o + \tau_t} = \mu_o \frac{n_o}{n_o + n_t}$$

where – μ_o the band mobility, n_o, and n_t – the concentration of carriers in the respective allowed band and localized states, respectively.

Localized states can be either monoenergetic or distributed in energy in a certain range. Thus, the transport of charge carriers in the $As_{40}Se_{30}S_{30}$ RF-films represents carriers motion that are in delocalized states, which repeatedly interrupted by acts of capture.

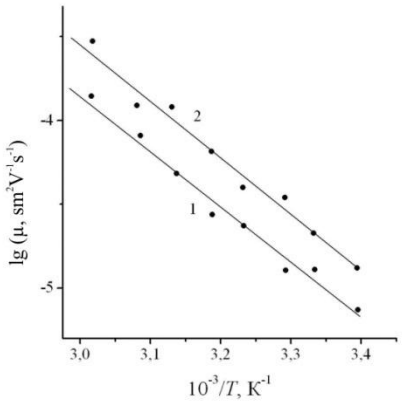


Fig. 6. Temperature dependence of hole drift mobility (1) and electrons (2) in the $As_{40}Se_{30}S_{30}$ RF-films: E = 10^4·V/cm, d = 1,5 μm

The experimentally observed transient photocurrent of electrons and holes (Figure 2) decreases monotonically with time, indicating the dispersive nature of charge transport. Dispersive nature of charge transport could be due to the presence of a broad quasi-continuous spectrum of localized states. Analysis of the dispersion parameters α_i and α_f, provides information about the degree of dispersion (nonequilibrium) transport. α_i Parameter was determined from the initial part of decay slope of the transient photocurrent in при $t < t_{fl}$, and α_f from the slope of the final site at $t > t_{fl}$ (Figure 3). Studies of the dispersion parameter α_i in the $As_{40}Se_{30}S_{30}$ RF-films showed that for both electrons and holes depends on the temperature, electric field and sample thickness. Thus, the research value α_i in the range $3\cdot10^4$ до $3\cdot10^5$ V/cm of electric fields on V/cm, established that the first slightly increases with the electric field to values α_i first slightly increases with the electric field to

values $E \leq 10^5$ V/cm and in fields $E \geq 10^5$ V/cm virtually independent of the electric field (Figure 7, curve 1).

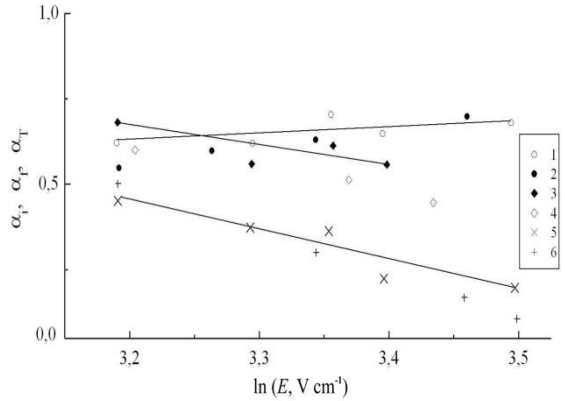


Fig. 7. Dependence of the dispersion parameters α_i (1, 2), α_T (3, 4) and α_f (5, 6) on the electric field in the $As_{40}Se_{30}S_{30}$ RF-films. 1, 3, 5 - experimental values of 2, 4, 6 - values calculated by formulas (3.7) - (3.11) for ε_o = 0,15 eV; $\mu_o\tau_o = 10^{-10}$ cm^2/V

In the same electric fields range there is a tendency to decreasing in α_f (Figure 7, curve 2. 3). With the samples thickness (d) increasing from 1 to 10 micron size α_i and α_f increase (Figure 8, curve 2. 3 respectively). Experimentally determined temperature dependence α_i and α_f suggest a weak and decreases α_i with increasing temperature α_f in amorphous films as well as $As_{40}Se_{30}S_{30}$, obtained by RF sputtering.

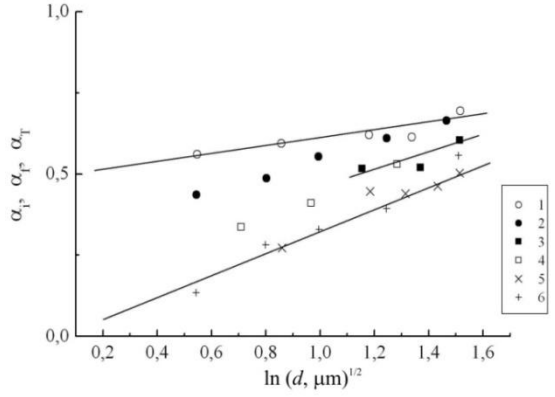


Fig. 8. Dependence of the dispersion parameters α_i (1, 2), α_T (3, 4) and α_f (5, 6) versus thickness in the $As_{40}Se_{30}S_{30}$ RF-films. 1, 3, 5 - experimental data; 2, 4, 6 - data calculated by formulas for ε_o = 0,15 eV; $\mu_o\tau_o = 10^{-10}$ cm^2/V; E = 10^5 V/cm

As noted above, the transit time nonlinearly depends on the ratio (E/d): $t_{fl} \sim (E/d) = (E/d)^{-1/\alpha_T}$. In [12], the exponent of this dependence, constructed in the coordinate's lg (t_{fl}) of lg (E/d), was used to determine the dispersion parameter α_T. Dependence $t_{fl} \sim (E/d)^{-n}$ characterized by n, equal to 1.86 was in our experiments. Then, the exponent depending $\mu \sim (E/d)^{n-1}$ would take the value 0.86. However, exponent, defined on the basis of experimental data lgμ from lg$E$ the addiction matter (1,1 ÷ 1,3). In turn, the value of the exponent, defined on the basis of experimental data from the dependence lgμ from lg$d$ is 0,5. Consequently, t_{fl} and, accordingly, the drift mobility are not universal function of the quantity (E/d), and depend on the electric field and the thickness of the samples.

Conclusion

Low coordinative films of condensed matter with disordered structure based on chalcogenide glassy semiconductors (CGS) of triple-stoichiometric $As_{40}Se_{30}S_{30}$ were investigated. CGS films were obtained by thermal evaporation in vacuum (TE-film) and ion-plasma high-frequency sputtering (RF-film). It was established that electronic properties of non-crystalline semiconductor media based on films of arsenic chalcogenide glassy semiconductors obtained by ion-plasma RF sputtering and thermal evaporation in a vacuum, greatly depend on how they are received. In amorphous $As_{40}Se_{30}S_{30}$ films, obtained by ion-plasma RF sputtering, in contrast to the films of these materials obtained by thermal evaporation, observed bipolar photoconductivity and bipolar drift of charge carriers. This is due to the lack of deep traps for electrons in the spectrum of localized states of the films obtained by ion sputtering. External influences on the $As_{40}Se_{30}S_{30}$ film such as light exposure (fundamental absorption region) and annealing, has been accompanied by changes in the optical band gap and the extent of a medium-range order of atomic structure. In the "light exposure – annealing" cycles these changes are reversible, i.e. such fundamental parameters as the band gap of the studied non-crystalline semiconductor films was determined not only near, but also as medium-range order of atomic structure.

Acknowledgements

This work was supported by Ministry of Education and Science of the Republic of Kazakhstan Fundamental Investigation grant (FI-13.10) and was done in the Scientific Investigation Institute of Experimental and Theoretical Physics.

References

1. Mott and E.A. Davis. *Electronic Processes in Non- Crystalline substance*, Moscow: Mir, 1982, 560 p.
2. *Amorphous Semiconductors*, Ed. Brodsky M. - Moscow: Mir, 1982, -320 p.
3. Felz A. *Amorphous and vitreous inorganic solids*, Moscow: Mir, 1987, 403 p.
4. Dembowski S.A., Chechetkina E.A. *Glass formation*, Moscow: Mir, 1990, -278 p.
5. Minaev V.S. *Glassy semiconductor alloys*, Moscow: Metallurgiya, 1991, 408 p.
6. *Disordered semiconductors*, Ed. Aivazova A. – Moscow. 1995, 352 p.
7. *Electronic phenomena in chalcogenide glassy semiconductors*, Ed. Tsendin K.D. Moscow: Science. 1996, 486 p.
8. Prikhodko O. Electronic processes in amorphous films $As_4Se_3S_3$, obtained by different methods, *Proceedings of the National Academy of Sciences of Kazakhstan. Physical and Mathematical Series*, 6:30(2007).
9. Lebedev E.A., Kazakova, L.P. *Carrier drift in chalcogenide glasses*, Ed.Tsendin K.D. Electronic phenomena in chalcogenide glassy semiconductors. - Saint-Petersburg: Nauka. – 1996, 141-192 p.
10. Rfister G., Scher H. Dispersive (non -Gausian) transport in disordered solids, *Adv. Phys.* 6:747(1978).
11. Lebedev, E.A., Rogachev N.A. Conductivity of chalcogenide glassy semiconductors in high electric fields, *Phys. Rev. B*, 15(8): 1511(1981).
12. Rfister G., Scher H. Time dependent electrical transport in disordered solids As_2Se_3, *Phys. Rev. B*, 15(4): 2062(1977).

Received 6 May 2010