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NATIVE CENTERS OF ELECTRON AND HOLE TRAPS IN THIN AMORPHOUS FILMS OF As_2S_3 AND As_2Se_3

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The measurements of the absorption and temperature dependence of conductivity carry out on thin amorphous films have not revealed the existence of the localized states inside a mobility band. The injection of a non-equilibrium charge through contacts and its subsequent relaxation has detected quasicontinuous distribution of trap centers (N(E)) in whole forbidden band with maxima at 0.62, 0.87 and 1.05 eV for As_2Se_3 and 0.74, 0.92, 0.99, 1.21 eV for As_2S_3. The density of such centers reaches 10^{18} cm^{-3} depending on the amount of the injected charges in the volume of the amorphous film. From admittance measurements at different temperatures the increasing of N(E) of As_2Se_3 in energy range 0.90 - 1.05 eV was obtained. Photosensitive donor- and acceptor-like centers at energies of 1.05 eV and 0.76 eV from valence band for As_2Se_3 are revealed from photoconductivity. These energies are constant and independent of light intensity in the range 1.5×10^9 - 1.5×10^{15} photons/($cm^2\cdot s$) and of light energy greater than 1.60 eV. The density of these states depends on the generation level. The results are analyzed on the base of model of two-charged centers with negative correlation energy. The localized metastable one-charged states are generated by injection of electric charges in volume of an amorphous material or by exposure to light photons with energy more than 1.6 eV for As_2Se_3 and 2.0 eV for As_2S_3. In the conditions of generation of 2 photosensitive deep levels in As_2S_3 and As_2Se_3 the properties related to recording of optical information have been investigated. The structures allow the write the positive and negative charges in regimes of both accumulation of small signals and real time.

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Keywords: Amorphous films, As_2S_3, As_2Se_3, Trap centers, Photoconductivity

1. Introduction

Amorphous and glassy chalcogenide semiconductors attract the attention of the investigators because of their exotic properties related to the interaction with light. They are widely applied in different areas of technique as media for writing and reading the optical information with the greatest possibility of resolution of phase and amplitude writing, for control of the optical information, multiplexing and demultiplexing of optical canals, amplification of optical signals, sending through waveguides. They are transparent in infrared (in area in which there are transmission of the optical information) and can be used in sensors for detecting the humidity and different gas media and as photoresist [1-4]. Recently, new applications of amorphous and glass chalcogenide semiconductors as writing of the optical information with the help of other methods of generation such as electron beam, X-ray, injection of non-equilibrium carriers through contact etc. have been opened [5].

The detection and control of the centers responsible for writing of the optical information is a promising field for further development of chalcogenide glasses applications. In the present work the localized states of free carriers in amorphous As_2Se_3 and As_2S_3 have been studied with the help of optical and electrical excitation.

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2. Experimental results

2.1. Sample preparation

As_2Se_3 and As_2S_3 amorphous films of thickness about 1 μm were obtained in vacuum (~ 10^{-3} Pa) by thermal deposition method. The bulk glass source of As_2Se_3 and As_2S_3 for evaporation was prepared by synthesis of elemental As and Se or As and S with impurity content less than 10^{-5}. Au and Al contacts were applied by thermal deposition in vacuum resulting in the planar and sandwich structures of types Au-As_2S_3(or As_2Se_3)-Al (Au)). The heterostructures SnO_2-As_2Se_3-Al, Al-Al_2O_3-As_2Se_3(As_2S_3)-Au and Si-SiO_2-As_2Se_3(As_2S_3)-Au were also obtained. SnO_2 and Au were used in As_2Se_3 and As_2S_3 as ohmic and Al as barrier contact. The metal-chalcogenide-dielectric-semiconductor (MChDS) structure Si-SiO_2-As_2Se_3(As_2S_3)-Au was prepared by vacuum thermal evaporation of As_2S_3 or As_2Se_3 and Al layers on perviously oxidized surface of silicon plate. Aluminum was used as semitransparent top contact. The resulting samples were annealed in vacuum at T= 150 °C for 1 h.

2.2. Electrophotographic spectroscopy

The electrophotographic deep-level spectroscopy was carried out in an electrode regime [6]. Deep localized states are filled in this method through the periodic connection of an upper contact on the sample to a power supply (dark charging) and then to an electrometer. During the measurement of the potential by the electrometer, an intense absorbed light pulse is applied to the test sample. This light pulse causes a sharp decrease in the potential to a so-called residual potential V_R (photoinduced discharging surface potential). A cycling diagram is shown in Fig. 1a,b. Switching of the sample was carried out with the help of a high-resistance switch based on a Gerkon relay in a glass housing. The cycling was carried out until V_R reached saturation (V_S). Several hundred cycles were usually carried out. After achieving the saturation of V_R its relaxation in time has been measured (Fig. 2).

The measurements were carried out in a vacuum cryostat, which held the sample temperature constant within 0.2 K. The light source was a halogen lamp with an interference filter with $\lambda = 0.34$ µm or an LGI-21 pulsed laser with $\lambda = 0.334$ µm.

By varying such parameters as the temperature, the cycling period T, the electrical charging potential (V_q) and of the light dose we have optimized the conditions for filling the traps in the sample. To calculate the concentration of filled traps from the residual saturation potential V_s, we need to know the spatial distribution of the accumulated charge in the film of glassy chalcogenide semiconductor. To find a qualitative picture of the spatial distribution of the charge we used a method involving the thickness dependence of the residual saturation potential. Measurements of V_R as a function of the thickness of the layer of amorphous chalcogenide semiconductors revealed that the relation $V_S \sim d$ holds. We can thus conclude that the spatial distribution of the charge trapped at trapping centers is uniformly distributed if the saturation state is reached.

We measured all the $N(E)$ distributions by the method of electrophotographic deep-level spectroscopy only for values of the charging voltage in the region of the $V_S(V_q)$ plot on which V_S is essentially independent of V_q, for a cycling period greater than *2* s. We assumed that in the selected intervals of the charging voltage and the cycling period the effect of the contacts and the leakage currents due to the injection from the lower contact was minimal. We also assumed that the radiation dose of light provides an adequate reservoir of injected charge carriers (Q) to neutralize the dark charging potential ($Q > C\ V_q$, where C, is the capacitance of the film of the glassy chalcogenide semiconductor). In a study of the temperature dependence of V_s in the method of electrophotographic deep-level spectroscopy, we observed a continuous increase in Vs with decreasing temperature for the films of arsenic selenide and su1fide studied. The concentration of filled deep traps after the reaching the saturation state during the charging was calculated from the residual potential V_S for As_2Se_3 and As_2S_3 for various temperatures. It is assumed here that when the charging reaches saturation, there is a complete filling of localized states below the Fermi level to a group of traps with a constant release time, equal to the half-period of the cycling. The saturation potential forms as a result of the balance established between the release and trapping processes. This assumption seems to be valid for the deep traps under consideration here, since the time constant for the release of holes is much greater than the period of cycles.

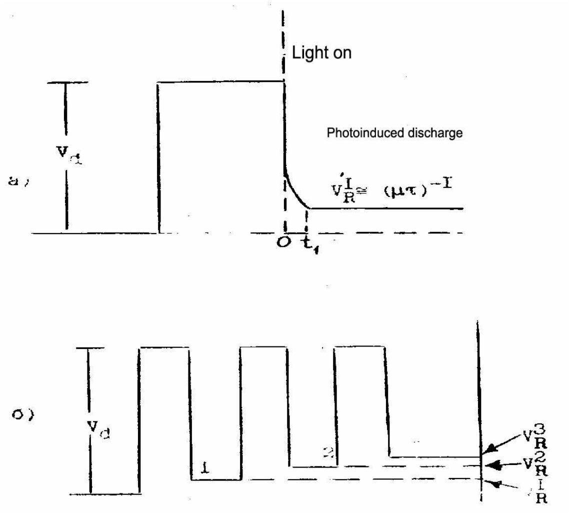

Fig. 1. The changing of residual potential signal in time. Charging-discharging cycles.

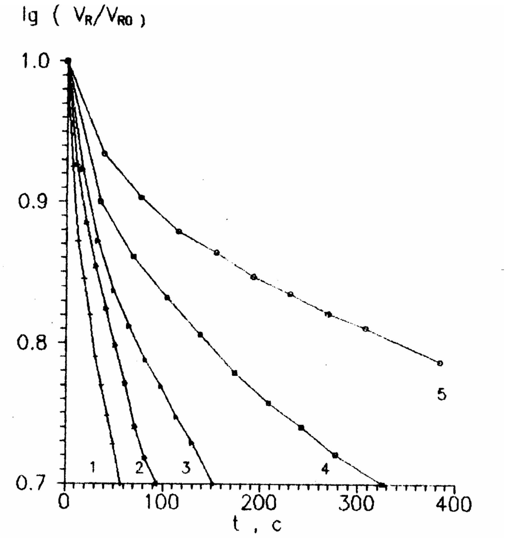

Fig. 2. The kinetic of relaxation of residual potential of As_2Se_3 films for various temperatures. T, K: 1 - 300.5 - 297.5, 3 – 292.4 – 288, 5 - 282.2.

The energy distribution of trap centers *N(E)* was calculated on the basis of an analysis of curves of the isothermal dark decay of the residual potential after the attainment of the saturation state. *N(E)* determined for the traps being filled reproduces the actual energy distribution of the glassy chalcogenide semiconductors under condition that the transit time is shorter than the time scale for relaxation of the accumulated charge, the effect of repeated trapping is negligible, all the holes emitted in time from the traps, and the trapping cross section is independent of the energy over the energy interval measured.

In the approximation of a quasicontinuous and otherwise arbitrary distribution, the density of states is calculated from [7]

$$N(E) = \varepsilon_{ChGS}\cdot t/(e\, d_{ChGS}\cdot k\cdot T)\cdot dV_R/dt \tag{1}$$

where $E= k\cdot T\cdot \ln(v\cdot t)$ is a demarcation energy (or Fermi quasilevel), k is the Boltzmann constant, T is the measurement temperature, v is the phonon relaxation frequency, and t is the relaxation time.

The physical meaning of (1) is that: at any time t, the relaxation of the residual potential occurs through the release of carriers from traps in a narrow energy interval dE at a level with an energy E. The traps at energies below E are already empty, while the traps at energy levels above E are still filled at the given time. Knowing the time dependence of the potential decay rate, we can thus determine the values of *N(E)*. The time scale is transformed into an energy scale on the basis of the formula for the demarcation energy. The values of v for arsenic selenide and sulfide are assumed to be the same, ~10^{12} Hz. The distributions *N(E)* which are found are characterized by broad asymmetric maxima (Fig. 3, 4). After even charging of volume of amorphous films ChGS positive or negative charge the nonexponential relaxation of charges takes place. From evaluations, a density of the localized states of the quasicontinuous distribution in all area of a forbidden region with maxima at 0.62, 0.87 and 1.05 eV for As_2Se_3 and 0.74, 0.92, 0.99, 1.21 eV for As_2S_3 is watched.

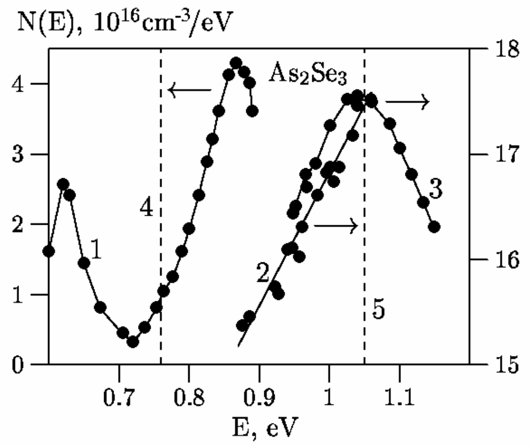

Fig. 3. Energy distribution of trap centers density in a- As_2Se_3. Data 1–3 measured by ESDL technique, 4–5–from PhC, and 2 from LFCS.

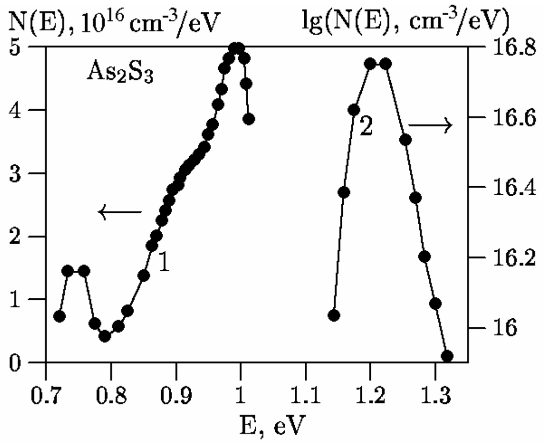

Fig. 4. Energy distribution of trap center density in a- As_2S_3. Data 1,2 got by ESDL technique.

2.3. Admittance spectroscopy

In the admittance spectroscopy method, *N(E)* was found by measuring the capacitance of depletion-layer on boundary Al-As_2Se_3 in equilibrium conditions in the frequency range 10^{-4}-10^{1} Hz and temperatures of 277-366 K ([8]) (Fig. 5,6,7).

The inflection points of the *C(f)* curves are related to the emission time constant τ_e of defects according to

$$2\pi\nu = 2/\tau_e = 2\sigma\, v_{th}\, N_{eff} \exp(E_\omega/kT) \tag{2}$$

where σ is the capture cross section of the defect, v_{th} – the thermal velocity of free electrons, N_{eff} – the effective density of states in the band and E_ω is the binding energy of trapped carriers (Fig. 5). We consider the parabolic potential approximation in space charge region and calculate the N_{eff} from the relationship [8]

$$N_{eff}(E\omega) = 2\ Ud1/2\ /\ (w\ sqrt(q(E\omega\ E_F(\infty))))\omega/(kT)dC/d\omega \tag{3}$$

where U_d is the diffusion potential, w – the space charge width, and $E_F(\infty)$ denotes the position of the Fermi-level at the edge of the space charge region. The capacitance data supply estimates for these parameters.

2.4. Photoconductivity

We investigated the properties of stationary photoconductivity (PhC) in the planar geometrical configuration of electrodes, because it characterizes more adequately the sample, and introduces less errors in calculation of PhC, do not depend of non-uniformity of volume illumination, contact effects, etc. [9]. Monochrome He-Ne laser light (λ= 0.63 μm) was used for PhC excitation with maximal intensity $F_0 = 1.5 \times 10^{15}$ photons/(cm^2 s), which was loosened more than to 6 orders by neutral filters. The spectral dependence of PhC was measured at different temperatures using MDR-4 monochromator at illumination by a halogen lamp.

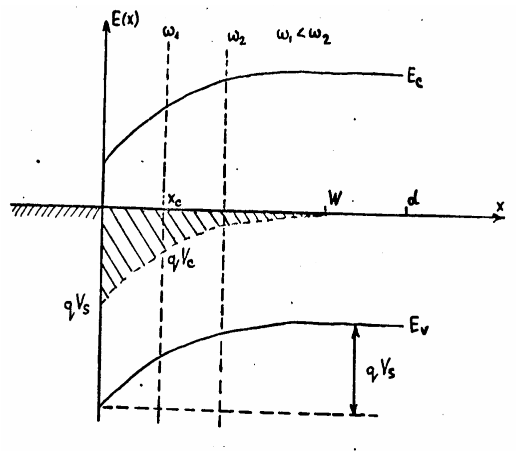

Fig. 5. The energetically diagram of barrier As Se –Al.

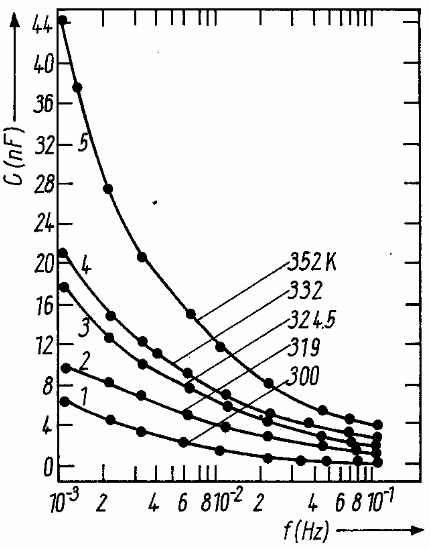

Fig. 6. Dependence of the capacity on frequency for a SnO_2 -As Se -Al structure.

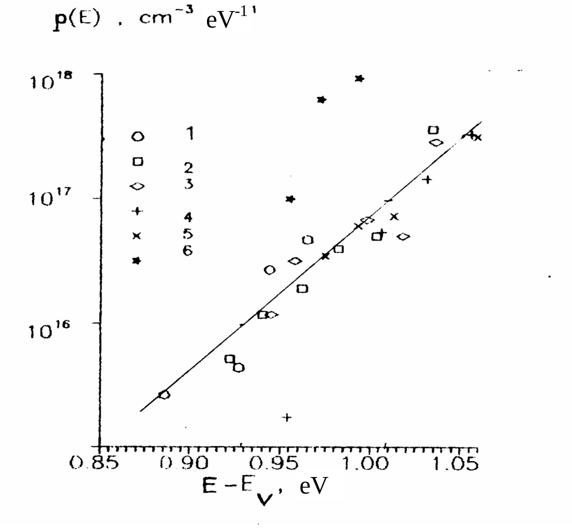

Fig. 7. The density of states p(E) of As_2Se_3 derived from C(ω) measurements (explanation in the text). T, K: 1 – 282, 2 – 288, 3 – 292.5, 4 – 297.5, 5 – 300.5.

Before PhC measurements, films were subject to heat treatment in vacuum during 1 hour at 160 ^{0}C, to guarantee the attainment of the equilibrium of material properties. Due to the strong dependence of electrical properties of amorphous As_2Se_3 films on humidity [10], and in order to eliminate the effect of air humidity, all measurements were carried out in vacuum (10^{-5} bar). The maximum of applied electrical field for a sample was 600 V/cm. The sizes of contacts were about 1.5×0.3 cm^2, and distance between them was about 0.5 cm. The large attention was paid to contacts. At measurement of dark- (σ_d) and photoconduction there was monitored that the current-voltage characteristics of samples were linear, and the Ohm's law was always satisfied. Hence we got, uninfluenced by contacts, the conductivity and PhC in a-As_2Se_3 layers.

The temperature dependence of dark conductivity $\sigma_d(10^3/T)$ of a-As_2Se_3 is presented in Fig. 8. In all range of measured temperatures the curve $log(\sigma_d) - (10^3/T)$ reveals the same slope. The activation energy obtained from this dependence is approximately equal to half of forbidden band and, apparently, corresponds to fixing the Fermi level in the middle of the gap. For a-As_2Se_3 the activation energy is 0.85 ± 0.03 eV.

The measured stationary PhC in the temperature interval 286 - 413.4 K and at sample illumination intensity in range F_0 - 10^{-6} F_0 are shown in Fig. 8. PhC dependence of (10^3/T) has a mixed character, i.e., in the dependence of temperature exist positive and negative slopes, to which donor- and acceptor-like levels correspond. It was found that with increase of light intensity $\sigma_{ph}(10^3/T)$ is shifted without slope change. Even as light intensity is varied on 6 orders, the slopes remain constant $\Delta E_m = 0.20 \pm 0.04$ eV for donors and $\Delta E_b = 0.38 \pm 0.02$ eV for acceptors. The maximum of $\sigma_{ph}(10^3/T)$ moves to higher temperatures when the light intensity increases. Close results have been obtained on bulk samples in [11].

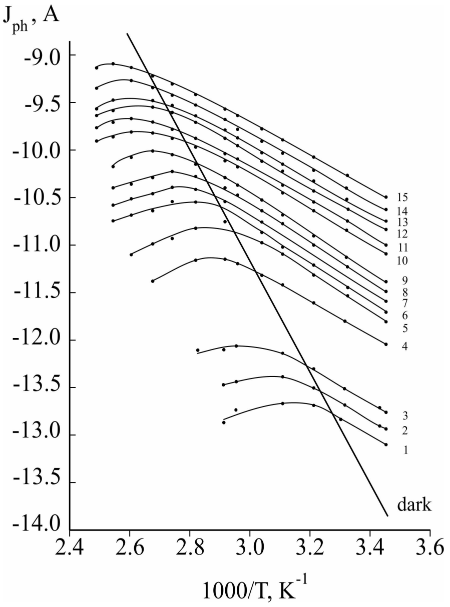

Fig. 8. The dependences of photoconductivity on temperature of As_2Se_3 films at different light intensities (λ = 0.63 μm). Lines 1 – 15 correspond to intensities from 1.5×10^{10} to 1.5×10^{15} photons/cm^2.

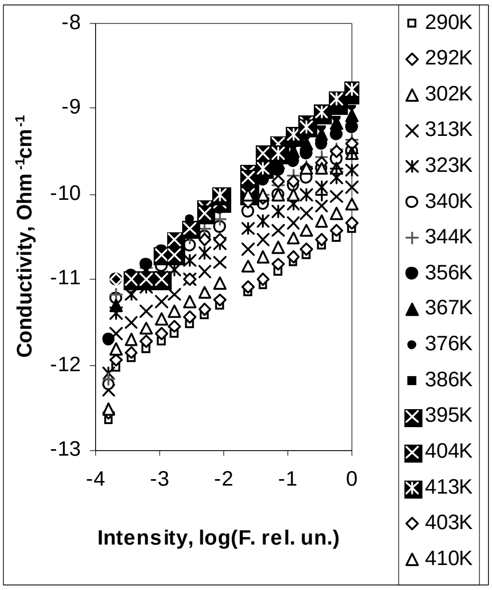

Fig. 9. The dependences of photoconductivity on intensity of As_2Se_3 films at different temperatures (Lux - Ampere characteristic; λ = 0.63 μm).

Lux-Ampere characteristics ($\sigma_{ph}(F)$) of a-As_2Se_3 thin films are shown in Fig. 9. At temperatures higher than 404 K the dependence is linear in coordinates $log\sigma_{ph}$ - $logF$, i.e., is of the type $\sigma_{ph} = \sigma_0 F^{\gamma}$, where σ_0 is a constant and γ is a constant slope at given temperature. At temperatures higher than 404 K, the dependence $log\sigma_{ph}$ - $logF$ has a second slope with $\gamma > 0.5$. It is necessary to note the sharp transition from $\gamma = 1$ to $\gamma = 0.5$. These slopes correspond to monomolecular and bimolecular recombination of photoexcited carriers [9]. The γ dependence of temperature in coordinates $1/\gamma$ - T is non-linear (Fig. 10). At low temperatures it is almost constant and changes from 0.5 till 0.65 for all temperatures. The average straight line slope corresponds to the characteristic temperature $T_0 = 590$ K.

We can conclude from experimental data that at least two types of centers (donors and acceptors) participate at PhC. The photoconductivity stipulated by acceptors predominates at lower temperatures and at large intensities of light. The increase of light intensity yields PhC increase and shift of its maximum to higher temperatures. It is necessary to note that energies of activation levels are constant and do not depend on intensity and energy of exciting light photons.

The PhC dependence of light intensity and temperature was calculated in two-level (donors and acceptors) model inside the conduction band [12]. Two different PhC areas are analyzed:

$$J_{ph} = q\ \mu\ E\ F/(v\ \sigma_{tD}\ N_{tD})\exp((E_F-(E_D-E_v))/kT) \quad (4)$$

$$J_{ph} = q\ \mu\ E\ (F\ N_0\ /(v\ \sigma_{tA}\ N_{tA}))^{1/2}\ \exp((E_A-E_v)/(2kT)) \quad (5)$$

Activation energies $\Delta E_m = (E_D - E_V) - E_F$, $\Delta E_b = (E_A - E_V)/2$. Here q is the charge of an electron, k is Bolzmann constant, μ is mobility, E is electric field intensity, F is light intensity, v is thermal velocity of free carriers, $\sigma_{tD,tA}$ is capture cross-section of of donor and acceptor centers, E_A and E_D are, correspondingly, energies of acceptor and donor centers, which are situated at different sides of the Fermi level, E_V is the energy at the edge of the valence band.

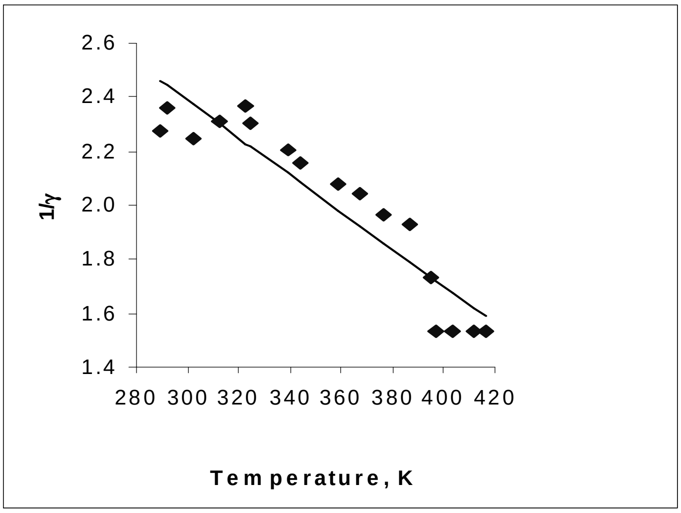

Fig. 10. Parameter γ vs temperature.

We obtained E_A = 0.76 eV, E_D =1.05 eV, and the bond energy of centers D_1^+ and D_2^- is equal $E_A - E_D$ = -0.29 eV. The concentrations N_{tA}, N_{tD} were calculated at $\sigma_{tD}=\sigma_{tA}= 10^{15}$ $cm^{-2}s^{-1}$, are equal $N_{tA}= 2.1 \times 10^{18}$ cm^{-3} and $N_{tD}=1.5 \times 10^{18}$ cm^{-3} and increase with increasing intensity. Therefore, the density of centres participating in photoconduction is not constant.

Lux-Amper characteristics exhibit the monomolecular, bimolecular and mixed recombination of charge carriers. The slope of acceptor type in the dependence $\sigma_{ph}(10^3/T)$ is $\gamma \approx$ ½. Lux-Amper characteristics described above characterizes also the model of trap centers quasicontinuously distributed within the forbidden band of the semiconductor. The dependence $\gamma(T)$ is of the type $1/\gamma = T/T_0$-1 with characteristic temperature T_0 = 590 K. It means the distribution is close to exponential within the forbidden band [13].

The constant value of the activation energy for both types of levels and its independence on the photon energy of exciting light is apparently connected to transportation of carriers with repeated trap. This transportation is dominant and responsible for a current in amorphous semiconductor and is determined by exchange of carriers between zones and traps irrespective of places where this carrier was generated. At energies equal or higher than threshold, there is apparently an excitation D_1^+ or D_2^- center, which results in the neutral charge D_1^0 or D_2^0. These ones are thermally ionized and return the charge carrier in the conduction or valence band.

2.5. Electroinduced absorption of light

The spectral dependence of the absorption *α(hν)*, is shown on Fig. 12. The dependence *α(hν)* rebuilt in coordinates $(\alpha \cdot h\nu)^{1/2}$ - *hν* is connected with direct optical transitions and energy of forbidden band obtained from extrapolation of this dependence to zero. At energy lower than the edge absorption, the good transparency to light down to wavelength of ~ 8 microns is shown.

The transparent heterostructures SnO_2-As_2Se_3-Al, Al-Al_2O_3-As_2Se_3(As_2S_3)-Au have been studied. The injection of a charge (hole) was carried out through contacts from Au or SnO_2 at application of impulses of voltage to contacts. The transmission of light and its changing through a sample was registered simultaneously in a perpendicular direction. In Fig. 11 are shown the time functions of impulse injection of a current and the induced absorption $\alpha_{ind}(t)$. The $\alpha_{ind}(t)$ impulse has some delay in comparison to the injection impulse of a current. This apparently, is connected with the fact that not all injected charge has time to be seized on defects, while the absorption mirrors an amount of charged defects.

The spectral dependence of an absorption and maximum value of an induced absorption $\alpha_{ind}(t)$ for a constant level of injection of charges is shown in Fig. 12. It is shown, that in case of injection of a charge in an absorption spectrum there is an adding absorption connected with the injected charge (or more correctly with generation of new optically active centers). The value $\alpha_{ind}(h\nu)$ depends only on level of injection of free charges. More detailed description of results on an electroinduced optical absorption is given in [14]. It is remarkable that the spectrum of an induced absorption $\alpha_{ind}(h\nu)$ have not revealed any singularities and for energies between 0.55 and 1.5 eV $\alpha_{ind}(h\nu)$ exhibits a plateau.

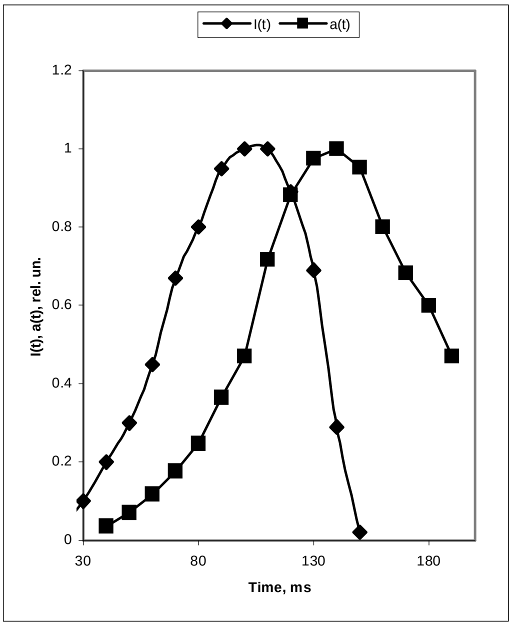

Fig. 11. Time dependence of injected current I(t) and induced absorption (α_{ind}(t)).

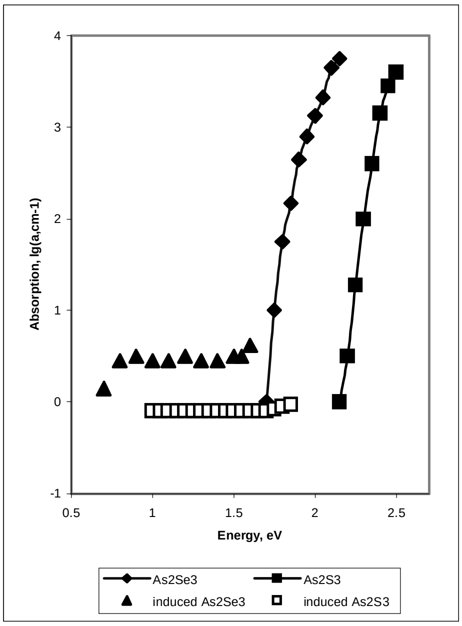

Fig. 12. Energy dependence of absorption and electroinduced absorption α(hν) in chalcogenide.

2.6. Memory properties

Reversible writing and repetitive readout of the image and other operations on images were carried out on MChDS Si-SiO_2-As_2Se_3(As_2S_3)-Au [15].

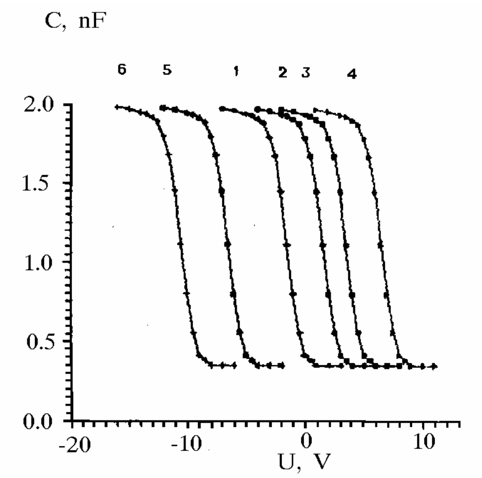

Fig. 13. C-V-Ch of MChDS structure. 1 - no charged structure, 2, 3, 4 - negative charged, 5, 6 - positive charged.

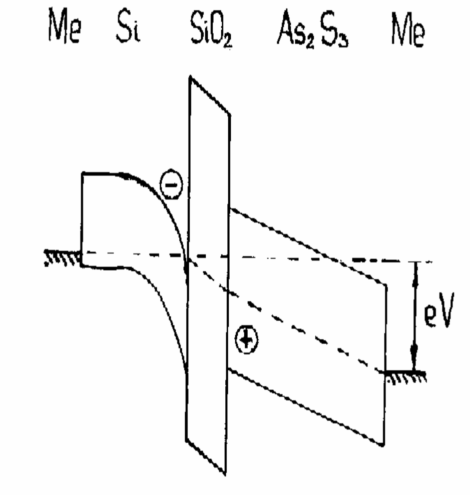

Fig. 14. The energy band diagram of MChDS structure under writing process.

The charging and discharging characteristics of the structure were studied by the method of measuring high frequency (10^5 Hz) capacitance - voltage - characteristics (C-V-Ch). At these frequencies ChGS behaves like a dielectric. Fig. 13 shows C-V-Ch of the structure, which was measured immediately after its preparation (curve 1). These dependencies are similar to the standard one of MDS structure, which is characterized by two boundary capacitances C_{max} and C_{min} and the transitive part, the width of which dependent on the thickness of the dielectric. In the multilayer case $C_{max} = \varepsilon_0 \varepsilon_x / d^*$, where $d^* = d_x + d_0 \varepsilon_x / \varepsilon_0$ and C_{min} is described by the formula $C_{min} = \varepsilon / d_x^* + (\varepsilon_x / \varepsilon_0) W_m$, where $W_m = (\varepsilon_s kT \backslash \ln(N_a / N_i))^{1/2}$, where N_a and N_i are the concentration of the impurity and of the carriers themselves in the silicon, ε_s is the silicon dielectric constant. Under irradiation of the MChDS structure by the light with energy both from the absorption range and application of the positive potential to Al, C-V-Ch are moved parallel towards the negative potential (Fig. 12, curve 6). On the contrary the application of the negative potential in the same charge conditions *C-V-Ch* are moved parallel to the positive bias part. Curve 2 corresponds to smaller lighting intensity than curve 3. The shift of the *C-V-Ch* is connected with the charging of the ChGS as dielectric under illumination.

Schematic energy-band diagram of MChDS structure during the positive writing is shown on Fig. 14. In the case of positive charging the volume of films As_2S_3 near the As_2S_3/SiO_2 interface has positive charge and induces through SiO_2 in Si the negative charge. As a result the band profile bends down until they attain the surface inversion state of conductivity, the creation of p-n-junction. The creation of the p-n-junction determines the photoemf.

During projecting the object image on the surface of the structure under simultaneous action of the voltage, the charging of ChGS by positive or negative charge exists. The maximum accumulation of the charge places at the SiO_2/ChGS interface. Its quantity depends on absorption light dose. In such way the light image is memorized by the structure in a relief charge. This relief of captured charge induces in Si substratum through dielectric SiO_2 the same charge relief of opposite sign as in ChGS or otherwise the relief of the surface potential. By connecting the top and down contacts by electric circuit and scanning the surface from top electrode side by laser beam with energy of the quants $E_{g1} < h\nu < E_{g2}$, where $E_{g1,g2}$ are the values of the forbidden bands of the Si and ChGS respectively, we obtain the electric impulses, whose amplitude depends on quantity of the charge that is accumulated in ChGS layer. In such way we obtained the invisible image that is written through charge relief. The space separation of the writing and readout processes of the visible light permits us to provide the repeated readout of one image.

The readout of the relief image are measured by two photoelectric methods, namely: method of measuring the photoelectromotive force (photoemf) under illumination of the structure with light from the energy range described above; the method of the observation of the recharging photocurrents under illumination of the structure such as in case 1, the readout of the information about the optical image by photoemf method was carried out by the optical scan system depicted in Fig. 15.

The impulse signals of photoemf (U_i) generated by the carrier photoexcited in space charge range of Si were obtained with the help of point scan of the He-Ne laser ($\lambda = 6328$ Å) and were registered consequently. About charge in ChGS one can make the same conclusion from the flat bands shift but in this case one cannot carry out the local readout when we are used whole electrode on the area of the structure. If in the structure the big electric charge is memorized, which causes to depletion of the Si surfaces the U_i signal is observed without external potential. The value of the maximum signal was equal to 0.3 V. The ratio U_{imax}/U_{imin} is about 100.

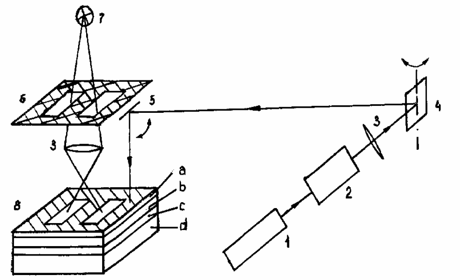

Fig. 15. The scheme of writing and readout of image in MChDS structure. 1 - He-Ne laser, 2 - modulator, 3 - condensors, 4, 5 – the galvanometer mirrors, 6 - the mask (object), 7 - source of illumination, 8 - MChDS structure. Layers: a - semitransparent Al, b - As_2S_3, c – SiO_2, d – Si .

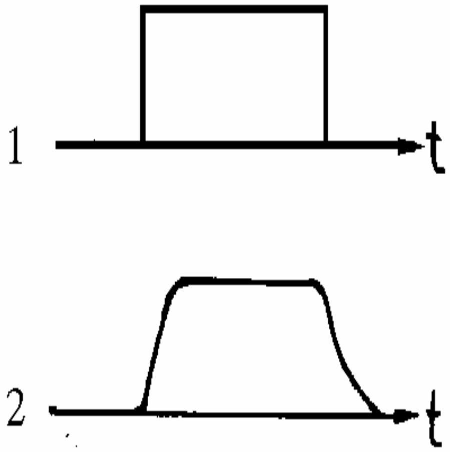

Fig. 16. The time dependence of the signal form of the input (a) and output (curves) (b).

The forms of readout impulses in the photoemf and photocurrent methods are shown in the Fig. 15. The velocity of readout in the photoemf is limited by the product of RC_{str} of the scheme (where R is the external load resistance and C_{str} is the capacitance of the structure) and there is reached the frequency 10^5 Hz. To decrease the time readout it is necessary to decrease sufficiently the parameters of the scheme (R and C_{str}).

The readout by measuring the recharging photocurrents is more promising for practical applications as compared with photoemf. The photocurrent readout consists in applying the depletion voltage impulses and illuminating by the light impulses (Fig. 16). The maximum frequency of readout in this method is limited by the time of transition of the depletion voltage to a steady state and attains some MHz. In our experiment we do not reach the space resolution, peculiar the photoconductive writing layer of ChGS. The obtained resolution is limited by the laser scan beam diameter of used scan system (in our case it was 3 μm). The usage of well focusing laser beam and more fast and precise electrooptic or acoustooptic scanning deflectors makes this possible.

For above mentioned effects of the writing and readout of the information we can propose the following applications: the writing of the low intensity signal in time of the accumulation; the processing of the images in the real time regimes of the observation under normal and high light intensities; for carrying out practical work in the wide range of the radiation spectrum as the visible, ultraviolet and the X-ray ranges; the realization of the bit regime processing of the information; for carrying out different operations under image as the making of positive or negative images, the measuring of sum and difference of the images and their areas, the recognition of the images and other operations such as the formation of the contour of the object, the obtaining of the moving object trajectories etc.

3. Discussion

In chalcogenide glasses the special centers were revealed, which cannot be investigated by standard measurements. Two types of metastable centers were detected: 1) the centers with small lifetime which disappear after an extinction of generation and 2) continuous existing centers which relax only after a heat treatment or exposure to infrared light. For explaining these and other experimental results (the absence of doping, the fixing of a Fermi level etc.) Anderson [17] postulated the existence of centers with identical two elementary charges, which are stable because of strong electron - phonon interaction. Kastner [18] used this postulate for the explanation of the existence of such centers in amorphous Se and later for heteropolar materials and now they are known as D^+ and D^- with negative correlation energy (polaron's interaction). Result of strong electron-phonon interaction is the appearance of the new classes of impurity centers - twofold charged, that are energetically more favorable, i.e. centers with negative correlation energy ($U < 0$). The density of such centers, apparently, is comparable to the amount of atoms of film. Besides there are large quantities of centers connected with dangling bonds of (DB), which compensate all types of impurity centers saturating their excess charges and also are twofold charged. They control the radiant and radiation recombination, photoinduced absorption, pinning of Fermi level etc. [20].

From experimental results on measurement of temperature dependence of the photoconduction the existence of a threshold energy necessary for PhC (> 1.6 eV for As_2Se_3), independence of an energy of a PhC from light intensity and increasing of density of photosensing centers at higher intensity of light was found. There are found donor- and acceptor-like type centers with activation energies 1.05 eV and 0.76 eV from the top of the valence band, accordingly.

From experiments on a relaxation of an entrapped monocharge the quasicontinuous distribution in all forbidden region chalcogenide with maximums at energies in As_2Se_3 0.62, 0.87, and 1.06 eV and 0.74, 0.92, 0.99, 1.21 eV for As_2S_3 was found. These centers are only trap and the subsequent release centers of free carriers.

Let us consider the availability of diatomic centers such as consisting from homo-or heteropair from different coordination because of reaction $2D^0 \rightarrow D^+ + D^-$. The most probable combination of such pairs there can be atoms (S, S), (Se, Se), (As, S) or (As, Se)). The availability of such pairs with alternate coordination is energetically more favorable because of the polaron interaction. However, they do not give the contribution to one-electron band states, apparently, that the minima of potentials do not coincide at same configuration coordinate. Other pairs may be introduced also.

The collapse of a metastable state takes place through an energy barrier. The energy barrier is caused by electron-phonon interaction, which takes place on a center with two electrons and causes a lattice relaxation. As a result of relaxation this may be accompanied with a modification of a symmetry and reorganization of chemical bonds.

Pairs are considered together connected with negative bond energy U^-, which originates from an exothermic reaction

$$\mathrm{D_i{}^0D_j{}^0 \rightarrow D_i{}^+ + D_j{}^- + E} \tag{6}$$

where $D_i{}^a, D_j{}^a$ - centers from the atoms of a chalcogenide glass, i, j number of coordinating, a - charge of centre (0, + or -) (for example for atoms As is $D_j{}^a \rightarrow P_i$, Se - $D_j{}^- \rightarrow (C_j{}^a)$ and E – is difference energy of pairs ($D_i{}^0, D_j{}^0$) and ($D_i{}^+, D_j{}^-$). Except for reactions such as (6) with identical atoms, there are possible similar relations with heterotype atoms

$$C_2^0 P_3^0 \rightarrow P_2^- + C_3^+ + E \tag{7}$$

The following types of reactions are offered for the mixed type with generation of electrons or holes

$$P_2{}^- C_3^0 + 2h \rightarrow P_3^0 + C_3^+ \tag{8}$$

The above reactions are of a new type where the pairs of electrons or holes are produced and appropriate centers exist by pairs. These new states will derivate metastable states which can last long enough.

The initial energy of two centers in reactions (6-8) is less than energy of the excitation state. If we shall designate a total energy of a system of two centers in mentioned states through ground (E_1+E_2) and excited ($E_1^*+E_2^*$) energy then the relation takes place

$$E_1+E_2+U^- = E_1^*+E_2^* \tag{9}$$

where U^- is negative correlation energy.

The obtained results of PhC and electrophotografical spectroscopy measurements led us to the existence of such centers inside a forbidden band in amorphous As_2Se_3 and As_2S_3 films. We give the scheme of energy levels and possible energetic configuration diagram (Fig. 17).

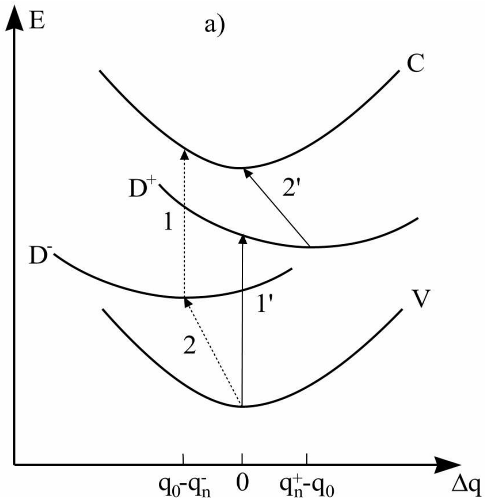

Fig. 17. The scheme of energy levels for a pair with alterative valency D^+ and D^- relative to the edges of valency zone V and conductivity zone C.

It is possible to explain the obtained results on the basis of existence in amorphous ChGS films of special centers, whose detection in one-electron mobility band is impossible. They can be related to the existence of two-charged states with negative correlation energy, which for the first time were postulated by Anderson [17]. Kolobov and Tominaga [21] evidenced the crucial role played by lone-pair electrons that give rise to dynamic interchange bonds responsible for these centres. Their density is apparently great enough and is comparable to a density of atoms of the main structure of a film. The ESR measurements in such materials has not discovered the availability in such ChGS of the one-electron localized states [19]. Such centers stand exposed only at both an exposure on films by light of energies close to a boundary absorption and injection of non-equilibrium charge carriers. The new generation states are metastable, disintegrate in time or during increasing of temperatures. Such unstable states are the basis for creation of different devices and equipment on their basis for writing and storage of information.

4. Conclusions

The measurements of the absorption and temperature dependence of dark conductivity conducted on thin amorphous films of As_2S_3 and As_2Se_3 have not revealed the proofs of existence of the localized states inside a mobility band. The localized metastable one-charged states are generated by injection of electric charges in the volume of an amorphous material or by exposure to light photons with energy more than 1.6 eV for As_2Se_3 and 2.0 eV for As_2S_3. The density of such centers more than 10^{18} cm^{-3} and depends on the amount of the injected charges in the volume of an amorphous film.

The new type of metastable centers with a negative correlation energy was established which one have a fixed energy level position and their density is possible to change with the help of light or injection of free charges (holes or electrons) generation. These centers make modifications of physical properties of amorphous films.

The induced optical absorption was found by injection homocharge. $\alpha_{ind}(h\nu)$ not reveals definite maxima. The results are considered on the basis of existence of two-charged centers with a negative effective correlation energy and subsequent generation on their basis of the metastable states, which one further relax back on initial more energetic stable states. These metastable states exhibit an induced absorption and give a photoconduction.

The density of D centers has been not determined by standard experimental methods because the density of metastable states in our experiments has no saturation with intensity or with amount of the injected charge.

Taking into consideration the existence of 2 photosensitive metastable deep levels in As_2S_3 and As_2Se_3 the properties of writing the optical information have been investigated. The devices allow the writing by positive and negative charges in regimes of both accumulation of the small signals and real time.

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