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NONSTEADY PHOTOCONDUCTIVITY OF LAYERS OF GLASS OF THE As-Se SYSTEM

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This article examines experimental results from a study of impulsive photoconductivity in layers of glasses of As_xSe_{100-x} ($30 < x \leq 60$). It was found that thermal and laser treatment (thermo- and photostructural changes) affect the character of relaxation processes in photoconduction in freshly prepared layers. It was also established that both annealing at temperatures near the softening point of the glass and laser irradiation with quantum energies exceeding the width of the forbidden band are accompanied by a change in the recombination lifetime of nonequilibrium carriers. It is concluded on the basis of empirical data that an efficient recombination channel complementary to the main channel (tunnel transition of the type $2D^0 \rightarrow D^+ + D^-$) is present in freshly prepared layers. The latter is present in annealed layers. The additional recombination channel is related to the existence of homopolar bonds in binary arsenic selenides and is proven to exist by data on the effect of composition on photo-current relaxation.

A whole range of physical phenomena can be observed in photoexcitation in glassy chalcogenide semiconductors (GCS): photoconductivity and drift of charge carriers, photostructural changes [1-3], etc. There has been a fairly large amount of study of steady-state photoconduction and its long-term relaxation [2, 4], as well as of charge transfer [1]. There has been almost no study of the short-term kinetics of photoconduction, especially during photostructural changes. In connection with this, here we report results of studies of nonsteady photoconduction in light-sensitive (i.e., exhibiting photoinduced changes) layers of chalcogenide glasses of the As-Se system.

Specimens of these glasses were studied by the usual method of vacuum thermal vaporization of a GCS of a specified composition on a substrate of oxide glass. As the electrodes we used SnO_2 and gold sputtered onto the substrate and a layer of the GCS to form a sandwich structure. Measurements of nonsteady photoconductivity were made in the current signal regime, i.e., the time constant of the measurement circuit $\tau_{RC} = RC < 10^{-4}$ sec (R is the load resistance from which the photoresponse signal was recorded; C is the capacitance of the specimen) was considerably less than the duration of the test signals. The specimens were excited by refocused (to ensure uniform illumination of the specimen surface) radiation from a pulsed ruby laser. The duration of the light pulse $t_p \sim 4 \cdot 10^{-8}$ sec (modulated q-factor regime). Photostructural changes in the GCS layers were caused by radiation from an He-Ne laser ($\lambda = 0.63 \mu m$). The voltage applied to the specimen was chosen within the ohmic range of the volt-ampere characteristic and was 1-3 V/ μm . It can be assumed that nonequilibrium

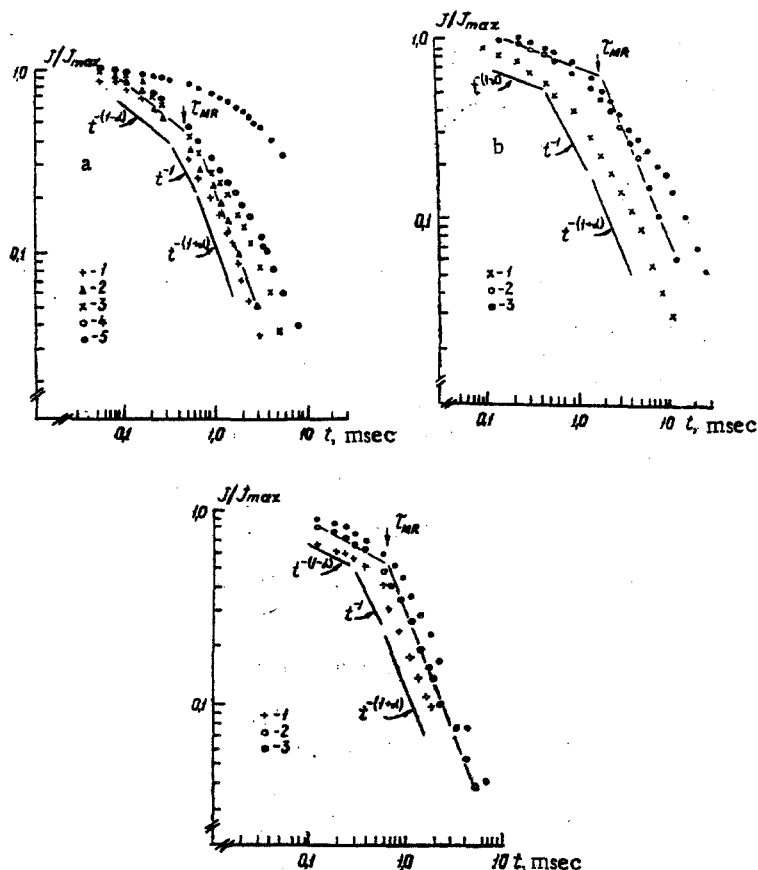


Fig. 1. Relaxation of photocurrent in layers of $\text{As}_x\text{Se}_{100-x}$ after excitation by a pulse from a ruby laser: a) $x = 40$, 1) J_0 , 2) $0.74 J_0$, 3) $0.56 J_0$, 4) $0.25 J_0$, 5) $0.008 J_0$ ($\alpha \approx 0.6$, $\tau_{MR} \approx 0.5$ msec); b) $x = 32$, 1) J_0 , 2) $0.56 J_0$, 3) $0.28 J_0$ ($\alpha \approx 0.7$, $\tau_{MR} = 0.6$ msec); c) $x = 50$, 1) J_0 , 2) $0.56 J_0$, 3) $0.28 J_0$ ($\alpha \approx 0.7$, $\tau_{MR} \approx 1.2$ msec). $J_0 = 10^{16}$ quanta/cm² [the pulses were normalized with respect to the maximum current J_{max} at the moment $t = 0$; the recombination lifetime τ_{MR} is indicated, and the figure shows straight lines with the slope $-(1 - \alpha)$, 1 and $-(1 + \alpha)$].

carriers were generated over the entire volume of the specimen, since $\alpha \approx 10^3 \text{ cm}^{-1}$ over the wavelength ($\lambda = 0.68 \mu\text{m}$) of the ruby laser radiation.

Figure 1 shows curves of the drop in photocurrent after termination of the exciting pulse for As-Se films of three compositions. The values were obtained for several amplitudes of the light pulse. It can be seen that an initial, more shallow section and a final, steeper drop are readily distinguishable on all of the relaxation curves (regardless of the composition of the GCS film or the intensity of excitation by the light pulse). There is also a short transitional section between these two sections on some of the $\log J - \log t$ curves. Both the initial and the final sections are described well by power relations of the types $J \sim t^{-(1-\alpha)}$ and $J \sim t^{-(1+\alpha)}$ ($0 < \alpha < 1$), respectively. The moment of the pronounced change in the rate of decrease in the photocurrent in the transition from the time relation $J \sim t^{-(1-\alpha)}$ to $J \sim t^{-(1+\alpha)}$ was determined from the intersection of the two asymptotes and was identified as the characteristic lifetime τ_{MR} of delocalized carriers relative to monomolecular recombination. It should be noted (see Fig. 1a, for example) that the values of τ_{MR} remain nearly constant with variation of excitation intensity over roughly two orders of magnitude. During the time interval $0 < t < \tau_{MR}$, photocurrent decreases by the power law $J_{ph} \sim t^{-(1-\alpha)}$. The curves in Fig. 1 illustrate both mono- and bimolecular recombination kinetics. The constancy of the time τ_{MR} with variation of the initial concentration of photoinjected carriers and the universal form of the curves are unambiguous evidence of the predominance of molecular recombination at $t > \tau_{MR}$. Together with this, the slowing of the kinetics of photo-

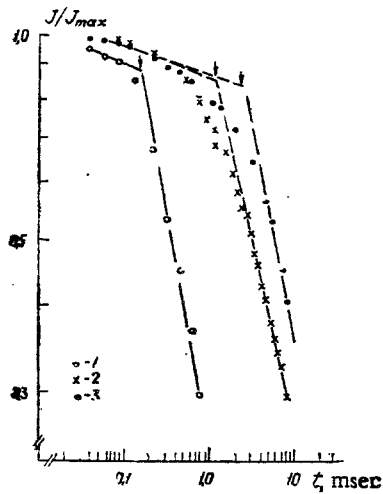


Fig. 2

Fig. 2. Effect of annealing (2) and exposure on the shape of a nonsteady current pulse in freshly prepared (1) layers of $\text{As}_{32}\text{Se}_{68}$.

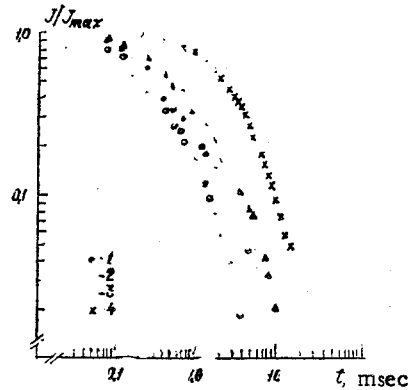


Fig. 3

Fig. 3. Photocurrent relaxation in layers of $\text{As}_x\text{Se}_{100-x}$:
1) $x = 40$, 2) $x = 50$, 3) $x = 32$, 4) $x = 60$.

current reduction ($t < \tau_{MR}$) with a reduction in the initial concentration of photocarriers characterizes the process of bimolecular recombination. In isolated cases, the transitional region between the two asymptotes $t^{-(1-\alpha)}$ and $t^{-(1+\alpha)}$ is not very narrow (Fig. 1a, curve 4; Fig. 1b, curve 3): It may be elongated as a result of shifting of the "final" asymptote to the region of higher t . Here, some error is possible in establishing the characteristic time τ_{MR} . This error increases with a decrease in the length of the second rectilinear section (i.e., $t^{-(1+\alpha)}$) on the curve $\log J - \log t$. Given this specific form of relaxation, it seems more convenient to determine the time τ_{MR} not from the "intersection" of the two power sections of the curve $\log J - \log t$, but from the moment of beginning of the steeper section $t^{-(1+\alpha)}$.

Such a level of excitation can be achieved when its further sequential change does not entail a change in the form of the nonsteady current pulse. Curve 5 in Fig. 1a can serve as an example. It can be seen that the transition to the final, steep section has become more "acute;" there is only a very slight deviation of relaxation from the relation $t^{-(1-\alpha)}$ throughout the measured time interval, which complicates the evaluation of τ_{MR} . For this case, the concentration of nonequilibrium carriers on the section $t < \tau_{MR}$ is constant, and, thus, $J_{ph} \sim \langle \mu d \rangle$ ($\langle \mu d \rangle$ is the effective value of drift mobility). An increase in temperature is accompanied by "smoothing" of the curve of nonsteady photocurrent, a gradual slowing of the rate of current reduction and, thus, a gradual reduction of the slope of $\log J_{ph} - \log t$ on the section $0 < t < \tau_{MR}$. The dispersion parameter α exhibits a linear dependence on temperature, which agrees well with the behavior predicted by the multiple-capture model in [5].

The nonsteady current pulses are typically similar in form to the pulses seen in experiments involving drift of charge carriers and can be described by the relations $J \sim t^{-(1-\alpha)}$ and $J \sim t^{-(1+\alpha)}$ at $t < t_{tr}$ and $t > t_{tr}$, respectively (t_{tr} is the transit time). Determination of the physical nature of dispersive transport in amorphous semiconductors is related to a large extent with the repeated successful application of the multiple-capture model to the analysis of electronic properties [5]. The authors of [6] proposed a model which well describes the drift signal in the time interval from the end of the exciting pulse to t_{tr} . The present model explains thermalization processes by examining localized states distributed exponentially below E_0 (the value of E_0 is such that mobility decreases sharply for $E < E_0$). Assuming the capture cross section to be independent of the energy, we have uniform occupation of the states below E_0 by carriers localized after the impulsive excitation. Mainly carriers with fine levels are subsequently freed, since capture processes remain random. The distribution of thermalized carriers is determined by the product of the mean population and the density of localized states. However, this model is valid only when examining unipolar

transport with the assumption that recombination processes are insignificant (pairs are separated by the field before they recombine), i.e., under the conditions realized in transit-time measurements using surface generation of charge carriers by illumination with a heavily-absorbed light. In contrast to drift, when studying nonsteady photoconduction - where the bulk regime of carrier generation prevails and electron pairs are not separated - it is also necessary to account for recombination under conditions whereby multiple capture has an effect.

In the quasineutrality approximation, the nonsteady photocurrent is related to the density of mobile carriers by the equation

$$J_{ph} = e\mu\Delta P(t) E, \quad (1)$$

where e is the electric charge; μ is mobility; ΔP is the density of mobile (delocalized) carriers; E is the strength of the electric field. Since the mobility of the holes is considerably greater than that of the electrons (according to the data in [7], $\mu_e \sim 10^{-9}$ cm²/V·sec), the contribution of the electrons to the total current can be ignored. The equation reflecting the dynamics of recombination [8, 9] has the form:

$$\frac{d\Delta P_t}{dt} = -b_r\Delta P\Delta P_t - b_rP_t\Delta P. \quad (2)$$

Here, ΔP and ΔP_t are the concentrations of photoexcited free and captured carriers; P_t is the concentration of equilibrium captured carriers; b_r is the recombination coefficient. Under conditions of high and low excitation levels, we have the following for bi- and monomolecular recombination, respectively

$$\Delta P = K \frac{P_0^2}{b_r\tau_{MR}} (t/\tau_{MR})^{-2-1} \quad (P_0 \gg P_t), \quad (3)$$

$$\Delta P = \frac{P_0^2}{b_rP_t\tau_{MR}} \frac{[1 + (t/\tau_{MR})^2] (t/\tau_{MR})^{2-1}}{[1 + (t/\tau_{MR})^2]^2} \quad (P_0 \ll P_t). \quad (4)$$

Here, b_t is the capture coefficient; P_0 is the initial density of photoexcited carriers; K is a certain coefficient dependent on P_0 . At $t < \tau_{MR}$, Eqs. (3) and (4) are simplified to the form $\Delta P \sim t^{-(1-\alpha)}$ (which is valid for both high and low initial carrier densities), analogous to nonequilibrium transport in the absence of recombination.

A good example of this situation is shown by Fig. 1. During the initial stage ($t < \tau_{MR}$), photocurrent relaxation is subject to a power law $J_{ph} \sim t^{-(1-\alpha)}$, where at the elapse of the capture time ($\tau_{capt} \sim 10^{-2}$ sec) the nonequilibrium carriers "condense" to localized states distributed in accordance with the distribution of the corresponding levels in the forbidden band. Recombination is still highly improbable in this time interval, and the photocurrent decreases in connection with a reduction in the density of nonequilibrium carriers as a result of their capture at traps. Convincing evidence of this is the observed reduction in the rate of photocurrent decrease with an increase in temperature (α changes from 0.64 to 0.80 in the temperature range 290-380 K), since recombination should have the opposite effect on the relaxation curves. At $t = \tau_{MR}$, the rate of current decrease increases significantly and the transition takes place from $J_{ph} \sim t^{-(1-\alpha)}$ to $J_{ph} \sim t^{-(1+\alpha)}$ - recombination processes come into play. The fact that the moment of the change in the rate of current reduction does not depend on intensity is evidence of the monomolecular character of recombination.

It should be noted that the character of recombination processes will depend to a significant extent on the method of preliminary treatment of freshly prepared GCS film. Figure 2 shows the nonsteady photocurrent measured at $T = 300$ K for a freshly prepared, annealed, and exposed film of $As_{32}Se_{68}$ (curves 1-3, respectively). It can be seen that the drop in the photocurrent is slowed by treatment (thermal or by light); the value of τ_{MR} increases from 0.13 msec (freshly prepared film) to 2.30 msec (annealed exposed film). The data obtained suggests that the brevity of relaxation in freshly prepared films is due to the existence of an additional efficient recombination channel different from the channel [1, 4] associated with intercenter tunneling $2D^0 \rightarrow D^+ + D^-$. Annealing and subsequent exposure of the GCS leads to an increase in the lifetime of holes effecting charge transfer in the GCS in regard to recombination, due to their multiple capture by local levels near the valence band. Along with defects such as disturbed-coordination atoms D^+ , D^- in the lattice structure, there are undoubtedly a certain number of defects of other types. The latter in particular include

"irregular" bonds between similar atoms. The concentration of such atoms increases when there is a deviation from stoichiometry, which should somewhat suppress defects D^+ , D^- . In connection with this, we can evidently expect a slowing of relaxation processes in the compositions As_xSe_{100-x} ($x \neq 40$) due to a reduction in the concentration of excited D^0 -centers formed by the capture of carriers of the corresponding sign by D^+ and D^- defects. Confirmation of this can be obtained from the experimentally observed fact (see Fig. 3) that photocurrent relaxation in glasses of the As-Se system occurs most rapidly in specimens of stoichiometric composition.

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MEASUREMENT OF CHARGE-CARRIER CONCENTRATION IN INDIUM PHOSPHIDE

BY MEANS OF AN ELECTROLYTE-SEMICONDUCTOR CONTACT

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An electrolyte-semiconductor contact is used to study the conductivity of epitaxial layers and single crystals of n-type indium phosphide obtained by gas transport. Some of the specimens were alloyed with tin and sulfur. The volt-farad characteristics are used to find the potentials of planar zones, which amount to 0.8-1.3 V for different electrolytes. Values of concentration of charge carriers calculated from measured values of capacitance of the electrolyte-indium-phosphide contact showed good agreement with measurements of the Hall effect on single crystals in the range 10^{16} - 10^{18} cm^{-3} . The use of measurements of the capacitance of the electrolyte-semiconductor contact with simultaneous etching of a local region made it possible to study the electron distribution in epitaxial layers of indium phosphide.

Methods which have proven effective in studying silicon and gallium arsenide are not always effective with indium phosphide, especially in regard to measurement of charge-carrier concentration and the profile of its distribution through the specimen depth. This relates in particular to the widely used method of measuring the volt-ampere characteristics of a metal-semiconductor barrier or p-n junction. In contrast to GaAs and Si, it is difficult [1-4] to obtain a quality barrier with a high breakdown voltage and low leakage currents on InP. Another approach to solving the problem of measuring the concentration of charge carriers in indium phosphide is the use of an electrolyte-semiconductor barrier [5-7]. Here, by using electrochemical or chemical etching of a local region of the semiconductor, it is possible to measure the distribution of charge carriers through the thickness to the required depth even when there is a high level of alloying.

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