

## Transient Photoconductivity in Amorphous $As_xSe_{1-x}$ layers

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### Abstract

Experimental results of transient photoconductivity study induced by ruby laser radiation in amorphous  $As_xSe_{1-x}$  are considered. It is observed for a first time the effect of thermal annealing and laser irradiation on photoconductivity relaxation in  $As_xSe_{1-x}$  amorphous films. Irradiation with band-gap light and annealing are accompanied by recombination lifetime changes for non-equilibrium charge carriers. Based on the experimental results it is assumed that in as-evaporated amorphous layers exists an effective channel of recombination, in addition to the main channel. The latter is due to carrier transition between charged defects inherent to amorphous semiconductors. This feature appears in annealed films only. The mentioned additional recombination channel may be caused by the presence of defect states induced by homo-bonds in the mobility gap of Se-based binary alloys.

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## 1. INTRODUCTION

Binary non-crystalline semiconductors of As-Se system are of continued scientific and practical interest because of real opportunity of their technological applications (e.g. as functional elements of multi-layer photoreceptors in xerography). In the As-Se system the stoichiometric composition,  $As_2Se_3$ , and compositions from the range 30 to 50 at % As undoubtedly are the most studied compositions [2-4]. As for a most of stable binary glasses in As-Se system, which are the discussion subject of the present paper, atomic ratios can be varied in a wide range. It is necessary to accentuate that the As-Se amorphous alloy system display the main extrema of various properties at the composition where the valence requirements appear to be satisfied that is at the stoichiometric composition. It seems to be reasonable to connect the mentioned non-monotonic behavior by changes in local structure.

Another prominent feature of non-crystalline materials called chalcogenide glasses is that they exhibit various photo-induced phenomena (the reader may refer to Ke.Tanaka's review [1]). Among these are photo-structural transformations and photo-crystallization phenomena: the modification of optical, electrical and other physical properties are observed. It is well-known that the phase transformation of selenium and its alloys can also be induced relatively simply by laser illumination [2, 5-7]. This unique property makes them attractive for optical data storage and holographic recording. Many experimental results using  $As_xSe_{1-x}$  have been reported [3], but few cases dealing with some fundamental properties such as photoconductivity remain unclear.

In recent years there has been enhanced interest in structural studies of chalcogenide glasses owing to their present and potential use in electrical and optical devices. As-containing chalcogenides, especially Se-rich alloys, usually have been studied in thin film, bulk and fiber forms. Since change in the structure can affect photo-generation, charge carriers transport, trapping and other important fundamental properties, knowledge of the molecular structure of such materials is needed for further improvement of their characteristics.

Excitation of amorphous chalcogenides with band-gap light may cause simultaneously a variety of phenomena. Some of these, such as steady-state photoconductivity and charge carrier transport were studied extensively, while other are poorly studied. As an example of the latter it may be considered transient photoconductivity accompanied with unique phenomena, so-called photo-induced changes.

The experimental results on transient photoconductivity obtained for the most stable binary glasses in As-Se system where the atomic ratios can be varied in a wide range are the subject of the present paper.

## 2. EXPERIMENTAL

### 2.1. Samples

The samples used in these studies were amorphous films, about 10  $\mu\text{m}$  thick, prepared by vacuum thermal evaporation of the powdered  $As_xSe_{1-x}$  melt-quenched material at the rate of 1  $\mu\text{m}/\text{min}$  onto quartz substrates held at room temperature. The measurements were performed on sandwich cells equipped with gold electrodes. The  $As_xSe_{1-x}$  bulk glasses were prepared according to the conventional melt-quenching method. Annealing of the films was carried out in air at ambient pressure and at temperatures below the glass-transition temperature. Film samples were kept in complete darkness until measured to minimize exposure to light sources, which could lead to changes in the structure and properties of the films. It is important accentuate that after annealing procedure atomic structure as it was shown by our Raman spectroscopic data become stabilized and corresponds to the structure of melt-quenched glassy samples.

### 2.2. Measurement technique

The details of the conventional transient photoconductivity have been described in the extensive articles by Enck at al. [9] and Orenstein at al. [10]). In the present study a ruby laser was used to excite the charge carriers. The ruby laser produces pulses of visible light at a wavelength 694.3 nm. Typical laser pulses lengths are on the order of  $5 \times 10^{-8}$  s. Only non-destructive laser power density was exploited. For uniform excitation, the ruby laser beam was defocused.

All experiments were single shot measurements in which the sample is pulsed from the laser and the corresponding photocurrent transient was captured on a single event storage oscilloscope. The oscilloscope (single event bandwidth 0.5  $\mu\text{s}$  pulse duration, S8-14 Model) captured the whole photocurrent signal. Additionally, the spread in the photocurrent tail can be precisely measured.

The electric field applied was within the range of several  $\text{V}/\mu\text{m}$ . One assumes a nearly uniform carrier generation in the whole volume of the sample because  $\alpha \leq 10^{-3} \text{ cm}^{-1}$  at the ruby laser wavelength.

## 2. RESULTS

Ruby laser pulse induces in the  $As_xSe_{1-x}$  sample transient photocurrent, which is demonstrated for compositions shown in the Fig. 1. Note that we have measured transient photocurrent for several laser intensities. As is clearly seen, independently of composition of the layers and ruby laser intensity, relatively slow and rapid regions in the photocurrent decay do appear. Between both parts of photocurrent relaxation a discernable transition of short duration may be resolved in the  $\log I - \log t$  plot. The initial, as well as the final part obey a power law dependence  $I \sim t^{-(1-\alpha)}$  and  $I \sim t^{-(1+\alpha)}$ , respectively, where  $0 < \alpha < 1$ . Evidently, when the photocurrent changes its decay rate from  $I \sim t^{-(1-\alpha)}$  to  $I \sim t^{-(1+\alpha)}$ , characteristic time may be determined at these two asymptotic curves intercept and identified as monomolecular lifetime  $\tau_{\text{MR}}$ . Note that  $\tau_{\text{MR}}$  value remained constant with respect to excitation intensity in the range of two orders of magnitude. The curves shown (see Fig.1) represent both mono- and bimolecular recombination kinetics. The insensitivity of  $\tau_{\text{MR}}$  to variation of the concentration of photo-injected carriers, and the universal shape of photocurrent relaxation curves are strong arguments in favor of the dominating monomolecular recombination at  $t > \tau_{\text{MR}}$ . At the same time, at  $t < \tau_{\text{MR}}$ , the photocurrent decay rate decreases with the decrease of initial concentration of charge carriers; this behavior is typical for bimolecular recombination. Some uncertainties in  $\tau_{\text{MR}}$  determination arise in the case of transition region broadening (Figs. 1a and 1b). Thus, it seems more correct to determine  $\tau_{\text{MR}}$ , instead of the method of two straight lines intercept, by the initial moment of photocurrent more rapid decrease, that is at  $t^{-(1+\alpha)}$ .

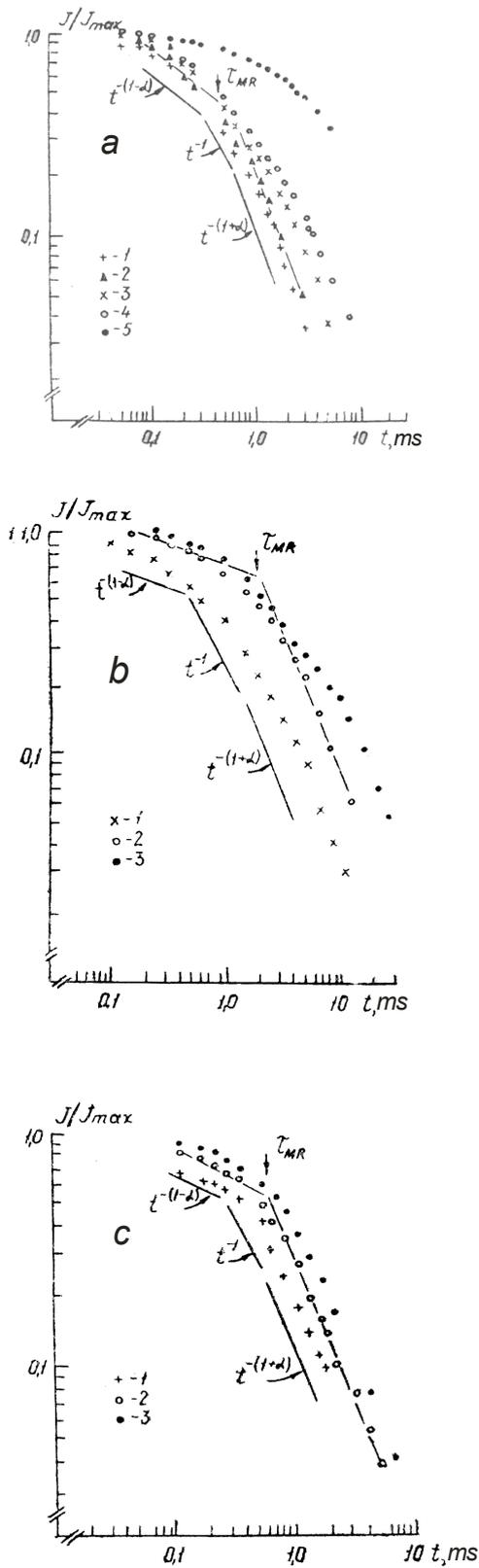


Fig. 1. Transient photocurrent in amorphous  $As_xSe_{1-x}$  layers. Pulsed excitation at  $\lambda = 690$  nm.

- a)  $x = 0.40$ ; 1 -  $I_0$ , 2 -  $0.75 I_0$ , 3 -  $0.55 I_0$ , 4 -  $0.28 I_0$ , 5 -  $0.08 I_0$ . ( $\alpha \approx 0.6$ ,  $\tau_{MR} \approx 0.5$  ms).  
 b)  $I_0 \approx 10^{16}$  photons/cm<sup>2</sup>; b)  $x = 0.32$ ; 1 -  $I_0$ , 2 -  $0.55 I_0$ , 3 -  $0.28 I_0$  ( $\alpha \approx 0.7$ ,  $\tau_{MR} \approx 0.6$  ms);  
 c)  $x = 0.50$ ; 1 -  $I_0$ , 2 -  $0.55 I_0$ , 3 -  $0.28 I_0$  ( $\alpha \approx 0.7$ ,  $\tau_{MR} \approx 1.2$  ms).

It is possible to achieve an excitation level when its further increasing does not induce a noticeably change in the transient photocurrent shape. The curve 5 in Fig. 1 exemplifies this case. As can be clearly seen, the transition to the region of final, more rapid, decay delayed: one can observe only a slight deviation from  $t^{-(1-\alpha)}$  in relaxation kinetics in the range measured. This, in turn, causes some difficulties in  $\tau_{MR}$  estimation. The charge carrier concentration in such a case (for  $t < \tau_{MR}$ ) is constant, and consequently,  $I_{ph} \sim \langle \mu \rangle$  where  $\langle \mu \rangle$  is the effective drift mobility. The photocurrent transient curve becomes smoother with temperature rising. The photocurrent decay rate and, respectively, the steepness gradually decrease. In accordance with predicted by the multiple trapping model (see, for example [8,9]) the dispersion parameter  $\alpha$  shows linear dependence on temperature.

### 3. DISCUSSION

It is necessary to note that the transient current shape is similar to that observed in time-of-flight experiments. For the latter,  $I \sim t^{-(1-\alpha)}$  and  $I \sim t^{-(1+\alpha)}$  dependencies in the pre- and post-transit time intervals, respectively, are inherent. The success achieved in understanding the physical origin of carrier transport may be explained by the appropriate application of the multiple trapping model. It was proposed that the signal shape in time-of-flight measurements is due to thermalization of charge carrier from states exponentially decaying in energy close to the mobility edge. Assuming the capture cross-section constant with respect to energy uniform occupation of states in the tail of mobility edge may be assumed. In the following, the release of charge carriers occurs preferentially from the shallow traps while the capture processes remain stochastic. Thermalized carrier distribution follows the average occupation and state density product. This approach is valid for hole transport when the influence of recombination is negligible. The situation is realized for generation of charge carriers via strongly absorbed light by the sample surface. On the contrary, in the present transient photoconductivity measurements when carrier generation occurs in the whole volume of the sample under study and the electron-hole pairs do not mutually separates, we should take into account the recombination in the presence of multiple trapping.

Transient photocurrent is related to the density of mobile charge (at the condition of quasi-neutrality) as

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

where  $e$  is the elemental charge,  $\mu$  – mobility,  $\Delta P$  – density of mobile charge carriers,  $E$  – electrical field applied.

The mobility of holes is significantly greater than that of electrons (the latter is of order  $10^{-9} \text{ cm}^2/(\text{Vs})$ ). Thus the electron component in the average of current is negligible and for the density of mobile carriers we obtain

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

Here  $\Delta P, \Delta P_t$  – is the concentration of photoinjected and captured carriers,  $b_r$  – recombination coefficient. For bimolecular and monomolecular recombination at high and low level of excitation, respectively, we have

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

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

In the latter case  $b_t$  is the capture coefficient,  $P_0$  initial density of photoexcited carriers,  $K$  – coefficient which depends on  $P_0$ . Equation (3) and (4) at  $t < \tau_{MR}$  then simplified to  $\Delta P \sim e^{-(1-\alpha)}$ . This is valid for high as well as for low initial density of charge carriers and analogical to carrier transport in the absence of recombination.

Fig. 1 exemplified this case. The photocurrent decay at the initial region ( $t < \tau_{MR}$ ) obeys power-law dependence  $I_{ph} \sim t^{-(1-\alpha)}$ . Then, after some delay (trapping time of order  $10^{-12}$  s), carriers “condensed” on states localized with distribution according to the distribution of the states in the band gap. Recombination during this time is negligible and photocurrent decays due to carrier trapping by gap states. The decrease of photocurrent decay rate with temperature rising seems to be a strong argument in favor of the latter conclusion. It should be noted here that  $\alpha$  changes from 0.65 to 0.80 in the temperature range 290 – 380 K. The rate of photocurrent decay at  $t \approx \tau_{MR}$  significantly increased and the transition from  $I_{ph} \sim t^{-(1-\alpha)}$  to  $t^{-(1+\alpha)}$  take place. The transition indicate the influence of recombination processes.

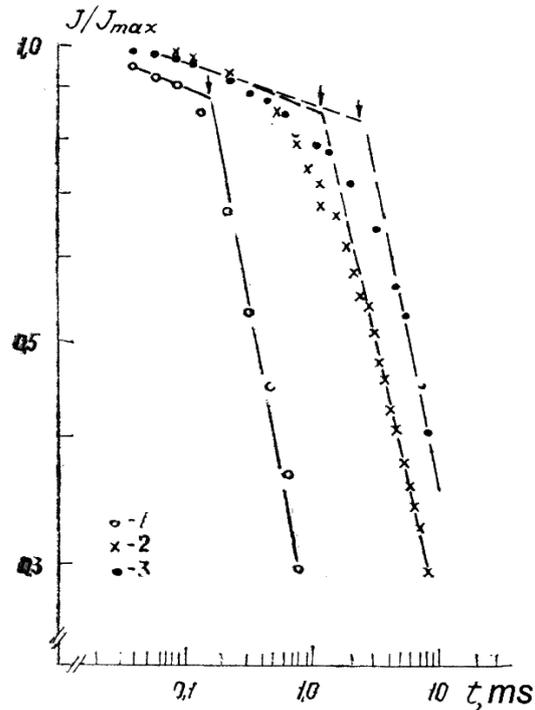


Fig. 2. Effect of annealing (2) and irradiation (3) on the shape of transient photocurrent for as-evaporated (1)  $As_{0.32}Se_{0.68}$ .

Undoubtedly, the character of recombination processes depends on the pre-history (previous treatment) of the as-evaporated sample. Fig. 2 shows the transient photocurrents for as-evaporated, annealed and irradiated  $As_{0.32}Se_{0.68}$  layer (curves 1 – 3, respectively). One can see that photocurrent decay rate decreases with irradiation and annealing; and the  $\tau_{MR}$  value increased from 0.15 ms to 2.30 ms for as-evaporated and irradiated film, respectively. Probably, more rapid photocurrent decay in as-evaporated films may be explained by the existence of additional (to the main  $2D^0 \rightarrow D^+ + D^-$ ) recombination channel. Annealing and the following illumination caused increasing of hole lifetime through carrier transport accompanied by multiple trapping by localized states near valence band edge.

#### 4. CONCLUSIONS

Transient photoconductivity in amorphous  $As_xSe_{1-x}$  irradiated with 639 nm is considered. It is observed for the first time the effect of thermal annealing and laser irradiation on photoconductivity relaxation in as-evaporated amorphous films. The irradiation with band-gap light and annealing was accompanied by recombination lifetime change for non-equilibrium charge carriers. Based on experimental results it is assumed that in as-evaporated amorphous layers exists an effective channel of recombination, in addition to the main channel. The latter is due to tunneling (transition between charged defects) inherent to amorphous

semiconductors and takes place in annealed films only. The additional channel mentioned may be caused by the existence of homo-bonds in Se-based binary alloys.

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