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To cite this version:

HAL Id: jpa-00220840
https://hal.archives-ouvertes.fr/jpa-00220840
Submitted on 1 Jan 1981

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EFFECT OF COMPOSITION AND STRUCTURE ON TRANSPORT PROPERTIES OF CHALCOGENIDE GLASSES


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Abstract. - The effect of preparation regime and molecular composition on dispersive transport properties of amorphous chalcogenide films of As-Se, As$_2$S$_3$-Sb$_2$S$_3$ and As$_2$S$_3$:Sn has been investigated by time-of-flight method. Hole transit time (corresponding to drift mobility) in the system As-Se was found to be dependent on preparation regime, this dependence being mostly exhibited in non-stoichiometric films. In As$_2$S$_3$-Sb$_2$S$_3$ system the transit time and its activation energy are gradually decreased with increasing of Sb$_2$S$_3$ content. The transit time of As$_2$S$_3$ films doped with Sn up to 0.3 at.% is decreased by as much as 3 to 4 orders of magnitude at room temperature and in the interval from 295 to 360 K increases with temperature. The results are discussed in frames of a model for anomalous charge carrier drift controlled by capture in a system of energy distributed traps.

It was established by recent investigations that properties of chalcogenide amorphous films are strongly dependent on composition and preparation regime, as these factors determine the spatial and electronic structure of the films. In this report the results of experimental study of non-equilibrium hole drift in amorphous chalcogenide films of As-Se, As$_2$S$_3$-Sb$_2$S$_3$ and As$_2$S$_3$:Sn. This species are considered as the variation of its composition causes different modification in the structure.

In the system As$_x$Se$_{1-x}$ (x=0.2-0.5) the deviation from stoichiometry is followed by formation of additional bonds between the components; the character of these bonds is strongly dependent on the film preparation regime. In the system (As$_2$S$_3$)$_y$(Sb$_2$S$_3$)$_{1-y}$ (y=1.0-0.45) the basic type of a structural unit is retained under variation of composition. Finally, one may expect four-fold coordination units to appear when adding Sn to As$_2$S$_3$. The films were prepared on glass substrates by stationary or discrete thermal deposition technique as well as by laser pulse evaporation of a chalcogenide glass target (1). The structure of the condensate was controlled by long-wave infrared spectroscopy.

The transport investigations were made by measurements of transit time $t_T$ of a light pulse excited charge packet travelling through a sandwich specimen of thickness L in the electric field $E=V/L$ ($V$ is the voltage applied to electrodes). As in most cases so called dispersive transport was observed (2), the current signal $i(t)$ was of featureless form and the transit time was determined at the point of intersection of the two straight lines, presenting the power-law type
The dependence of drift mobility in As-Se films on E/L ratio. 1- As$_2$Se$_3$ (2) (thermal evaporation), 2- As$_2$Se$_5$, 3- As$_2$Se$_2$, 4- As$_2$Se$_3$, 5- As$_2$Se$_8$ (pulse evaporation).

In Fig. 1 the dependencies of $\mu_d$ on E/L are shown for As-Se films obtained by pulse evaporation on the substrate held at room temperature. The field dependence of the drift mobility of As$_2$Se$_3$ films thermally evaporated on a hot substrate at 170°C (2) is also schematically indicated (dashed line). It is seen that the pulse evaporated films have the mobility values 2 to 4 orders of magnitude lower than that of the stabilized stoichiometric film. The films of As$_2$Se$_3$ composition obtained by both methods as well as the film of As$_2$Se$_5$ or As$_2$Se$_8$ have compatible field dependences of the mobility. For the AsSe film the field dependence is much stronger and, after repetition of measurements shows instability, is apparently due to photostructural changes of the film under excitation.

According to the theory of the dispersion transport controlled by energy distributed traps (3), the exponent of the mobility field dependence is determined by the trap distribution function, while the mobility value is reverse proportional to its concentration. In the case of exponential trap distribution $n(\xi) = n_0 \exp(-\xi/\xi_0)$ the drift mobility

$$\mu_d \sim (1/n_0)(E/L)(\xi_0/kT)^{-1}$$

(1)

In frames of this model the similarity of slopes of the lines 1, 2, 4 and 5 (Fig. 1) may be considered as the reflection of the similarity of the energy distribution of defects in As$_2$Se$_3$, As$_2$Se$_5$ and As$_2$Se$_8$, while the difference in mobility corresponds to the difference in concentration of them. From the other hand, the different exponent
Infrared absorption spectra of As$_x$Se$_{1-x}$ films obtained by pulse evaporation for lower (solid lines) and higher (dashed lines) degree of polymerization. Vertical marks show the absorption peak position for the corresponding glasses. 

$\chi$: 1- 0.2, 2- 0.286, 3- 0.4, 4- 0.5.

of the field dependence for AsSe films is apparently due to another kind of traps in this material. The mentioned peculiarities are correlated with the data of structural study.

According to infrared spectra the absorption bands of the films obtained by pulse deposition are shifted to the high-energy side of the spectrum relative to the absorption band of the corresponding glass (Fig. 2). This shift is caused by the distortion of the basic structural unit - the pyramid AsSe$_{3/2}$ due to high condensation rate (10 \mu m/s) and high vapour temperature. The greatest shift is observed for films of $\chi$=0.286. For Se contents higher than 72% the bands corresponding to Se-Se bonds (272 cm$^{-1}$) were observed in the spectra, while they were absent in freshly deposited films. On the contrary, an excess content of As (more than 40%) leads gradually to As-As bond formation and to rearrangement of the structure from the orpiment type to realgar type. Depending on the condensation regime only one type of bonding could be observed in these films (Fig. 2).

In the pseudobinary amorphous system As$_2$S$_3$-Sb$_2$S$_3$ there is quasieutectic interaction of components of similar structural units (4,5). With Sb$_2$S$_3$ loading the mobility increases (Fig. 3). The greatest variation takes place at low temperatures, where the activation energy of the mobility is significantly lowered. The study of the dispersive transport in (As$_2$S$_3$)$_{0.55}$(Sb$_2$S$_3$)$_{0.45}$ have shown (6) that the quantitative agreement of drift characteristics with exponential trap distribution model can be obtained providing the dependence of capture probability on energy is taken into account. If the capture probability $c(\xi)$ increases with energy exponentially as $c(\xi)=c_0 \exp(\xi/\xi')$, then $\mu_d$ is expressed as:

$$\mu_d = \sqrt{2}(\mu_0 N_o/n_o \delta_{eff})(\sqrt{2}/\mu_0 \tau E/L)/(1/kT)-(1/\xi')^{-1}$$

where $(1/\delta_{eff})=(1/\delta_o)-(1/\xi')$, $\mu_0$ and $\tau$ are mobility and lifetime of carriers in conductive states. The mobility activation energy $\delta_a$ is related to $\delta_{eff}$ by expression

$$\delta_a = \delta_{eff} \ln(1/\sqrt{2}/\mu_0 \tau E)$$.

The energy parameters of the model for (As$_2$S$_3$)$_{0.55}$(Sb$_2$S$_3$)$_{0.45}$ are $\delta_o=0.037$ eV and $\delta'=0.051$ eV. The experimentally observed region of the mobility activation energies is 0.46 to 0.18 eV in the interval of $E/L=(4$ to $40) \times 10^8$ V/cm$^2$. 
Temperature dependence of drift mobility in films \((\text{As}_2\text{S}_3)_y(\text{Sb}_2\text{S}_3)_{1-y}\) (1 to 4) and \(\text{As}_2\text{S}_3\text{Sn}_{0.03}\) (5).

\(y: 1, 1.0, 2, 0.99, 3, 0.9, 4, 0.55\)

A similar analysis of transport in \(\text{As}_2\text{S}_3\) showed that the drift mobility is controlled by much deeper local centres in interval from 0.86 to 0.70 eV. The parameters of the model for \(\text{As}_2\text{S}_3\) are \(\varepsilon_0 = 0.033\) eV and \(\varepsilon' = 0.068\) eV. For films of \(\text{As}_2\text{S}_3\) doped with Sn the room temperature drift is increased by about three orders of magnitude. When temperature is raised up to 360 K, the mobility drops down to the value somewhat higher than that of pure \(\text{As}_2\text{S}_3\) (Fig.4). The observed negative activation energy is caused by the negative value of \(\varepsilon_{\text{eff}}\), as for Sn doped \(\text{As}_2\text{S}_3\) \(\varepsilon' < \varepsilon_0\) (\(\varepsilon_0 = 0.032\) eV, \(\varepsilon' = 0.024\) eV).

The variation of composition slightly affects the value of \(\varepsilon_0\), indicating the energy distribution of trap density, while the capture probability characteristic \(\varepsilon'\) is several times varied. The decrease of activation energy in \(\text{As}_2\text{S}_3\)-\(\text{Sb}_2\text{S}_3\) system is also due to strong rise of \(\mu_0 \varepsilon_0\), as the corresponding values of \(\varepsilon_{\text{eff}}\) are increased. Hence the obtained results suggest that the changes of transport properties under loading of \(\text{As}_2\text{S}_3\) with impurities is caused mainly by changes in capture parameters.

The authors are indebted to A.I. Rudenko and V.I. Arkhipov for useful discussions.

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