CURRENTS LIMITED BY SPACE GHARGES IN GLASS-LIKE CHALCOGENIDE SEMICONDUCTORS OF THE $Se_{95}As_5$ SYSTEM CONTAINING Sm IMPURITY

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We have established that the transfer of charge carriers (holes) in the Al– $Se_{95}As_5$–Te structure is carried out by the mechanism of a monopolar injection current limited by space charges in the presence of two groups of traps [shallow traps (E_{t_1}) corresponding to charged intrinsic defects C_1^- due to the broken bonds of Se and deep traps (E_{t_2}) corresponding to charged intrinsic defects P_2^- due to As atoms with broken coordination]. It is shown that the Sm impurity influences strongly both the mechanism of formation of the current flow path and the trap parameters (energy position and concentration); especially, it influences the parameters of deep traps.

Such pecularities of chalcogenide glass-like semiconductors (CGSs) as changes in the structure and electron properties under the effect of light, in particular a change of the refractive index, a shift of the optical absorption edge, the occurence of unpaired spins registered by electron spin resonance, photoluminesence Stokes shift, fatigue, etc. make these materials perspective for applications in various electric switches, memories, IR technique, and acoustooptic instruments [1–3]. CGSs of the $Se_{95}As_5$ system are distinguished by their crystallization resistance [4] and by the introduction of halogen impurities (Cl, Br) providing the improved parameters of electric charge transfer and a high photo-sensitivity [5, 6], which makes them more attractive. The use of rare earth elements (REE) as the impurities creates states in the band gap of CGSs due to $4f$ states of REE ions. In this case, the optics of CGSs includes most of the possible transitions resolved for a REE ion (Sm) that brings about a significant change of their optical, photoelectric, and electric properties [7–10]. To understand the electron process mechanism responsible for the above-mentioned pecularities, it is necessary to determine the energy spectra of localized states in the band gap; for this purpose, the present paper deals with the investigation of currents limited by space charges (CLSC), being one of the reliable methods.

1. Experimental Method and Sample Production

The synthesis of the $Se_{95}As_5$ composition with Sm impurity was carried out by melting the appropriate amounts of chemical elements of a special purity in quartz ampoules in vacuum up to 10^{-6} mm Hg at T above 900 °C in a rotating furnace with the subsequent cooling in the off-furnace regime. The impurity was introduced during the synthesis, its concentration being within $0.01\div1$ at.%.

Volt–ampere characteristics (VAC) have been measured in the stationary regime by the standard method. The samples were fabricated by the thermal evaporation method in vacuum $\sim 10^{-6}$ mm Hg as the “sandwich” structures with Al and Te electrodes. The film thickness has been measured by the interferometric method and varied in the range $0.2 - 8$ μm. The VAC of Al–$Se_{95}As_5$–Te structure with Sm impurity has been investigated by applying the electric fields of both polarities. The CLSC regime has been observed by applying the positive potential to the Te electrode, and the N-type VAC has been observed at the opposite polarity.

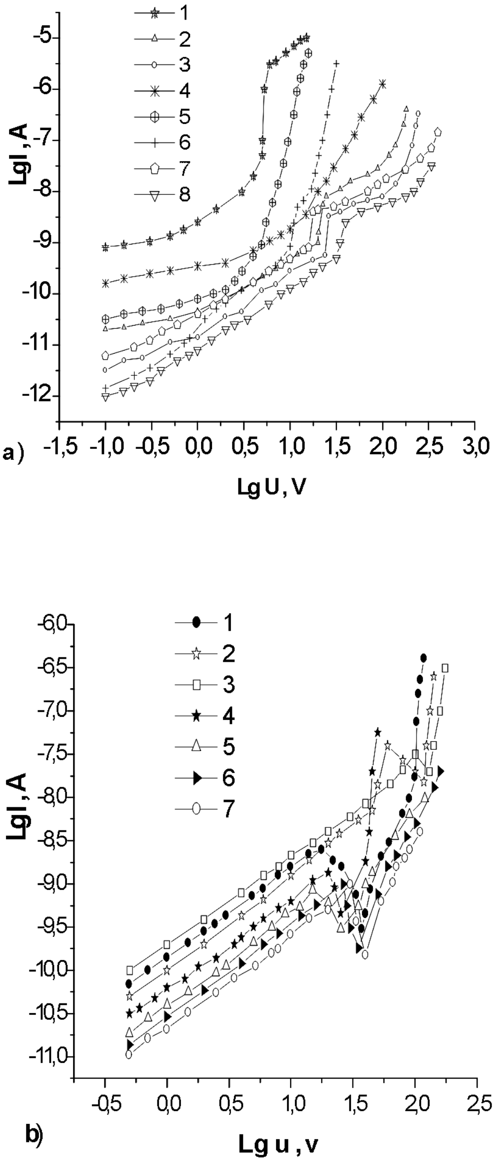
2. Results and Their Discussion

In Figure, we present the VAC of the Al–$Se_{95}As_5$–Te structure with Sm impurity in the cases where the positive (Figure, *a*) and negative (Figure, *b*) potentials are applied to the Te electrode at room temperature. In Figure, *a*, the VAC of the Al-amorphous selenium-Te structure is shown. It is seen that the VAC consists of several sections.

Most samples at small voltages are characterized by the dependence $I \sim V^n$ where $n \leq 1$. Later on, the function $I \sim V^n$ has been observed, where n has various values in different ranges. This indicates that the charge carrier transfer (holes) in the given structure is carried out according to the mechanism of monopolar injection with currents limited by space charges in the presence of carrier capture traps. The investigation shows that the voltage, at which the superlinear VAC starts, depends quadratically on the sample thickness that is well-proved (CLSC) mechanism. As seen from Figure, *a*, the VAC of amorphous selenium at small values of the applied voltage obeys the Ohm's law which goes into the square law. Then the current begins to increase highly with increase in the applied voltage, where the so-called section of "full filling of traps" is observed [11].

Then this section is replaced by the section, where the quadratic dependence $I \sim V^2$ is revealed. Such a behavior of the VAC corresponds to the CLSC mechanism governed by shallow traps [11]. The VAC of the Al–$Se_{95}As_5$–Te structure is different from that of amorphous selenium: after the section obeying the Ohm's law, the section corresponding to the exponential law follows, i.e. $I \sim V^2$ where n exceeds 2. Then the section, where $I \sim V^2$, is observed. Finally, the quadratic section is replaced by the section, where the slope of the VAC increases again. The pecularities of the Al–$Se_{95}As_5$–Te structures under the investigation suggest the electric charge transfer that in this material is controlled by 2 groups of trapping centers with depths E_{t_1} and E_{t_2} arranged deeper than the Fermi level.

The Sm impurity influences rather strongly the VAC form and values of the transient voltage between different sections. The growth of the Sm atom concentration up to 0.005 at% leads to the gradual reduction of the VAC forms corresponding to the CLSC regime in amorphous selenium. The further growth of the Sm atom concentration leads to that PT becomes the same as in CGSs of the $Se_{95}As_5$ system. In a similar way, halogen impurities influence the drift mobility of charge carriers that is explained within the model of charged intrinsic defects [5, 6].



Volt-ampere characteristics of the Al–$Se_{95}As_5$–Te structure with Sm impurity by applying positive (*a*) and negative (*b*) potentials to Te. *a*) *1* – Se; *2* – $Se_{95}As_5$; *3* – $Se_{95}As_5Sm_{0.001}$; *4* – $Se_{95}As_5Sm_{0.005}$; *5* – $Se_{95}As_5Sm_{0.01}$; *6* – $Se_{95}As_5Sm_{0.1}$; *7* – $Se_{95}As_5Sm_{0.6}$; *8* – $Se_{95}As_5Sm_1$. *b*) *1* – $Se_{95}As_5$; *2* – $Se_{95}As_5Sm_{0.001}$; *3* – $Se_{95}As_5Sm_{0.005}$; *4* – $Se_{95}As_5Sm_{0.01}$; *5* – $Se_{95}As_5Sm_{0.1}$; *6* – $Se_{95}As_5Sm_{0.6}$; *7* – $Se_{95}As_5$ Sm_1

The influence of a chemical composition and Sm impurities on the VAC behavior allows some considerations of the nature of local states and their energy arrangement in the band gap against a equilibrium position of the Fermi level determining the current flow path in the materials under investigation to be made. In amorphous selenium, the capture traps for majority charge carriers are shallow (E_{t_1}), i.e. they are lower than the equilibrium value of the Fermi level. It is expected that the local states determining the VAC in amorphous selenium are related to charged intrinsic defects C_1^- due to broken bonds of Se. It is expected that, in CGSs of the $Se_{95}As_5$ system with the C_1^--type defects, the charged intrinsic defects created by As atoms with broken coordination are present. In work [12], the possibilities for such defects in CGSs including Sm to exist were also reported. According to the VAC form, the energy position of local states corresponding to the mentioned defects must be above the Fermi level, i.e. they are deep ones.

At low voltages, the holes injected to CGSs of the $Se_{95}As_5$ system from the Te contact are captured by deep traps (E_{t_2}), but the conductance remains ohmic due to the presence of equilibrium holes. With increase in the voltage, the filling of E_{t_2} centers occurs, and the free hole concentration increases simultaneously. As the concentration of injected free holes exceeds the concentration of equilibrium holes, the current increases with the voltage, i.e. the so-called "limited filling of traps" happens. Then the current is controlled by traps E_{t_1}. In this case, the Fermi quasilevel remains above the level of E_{t_2}, and the square law is observed. The increase of the VAC slope in the last section appears to be related to the thermo-field emission of holes from the trap level. It is indicated that, at the opposite polarity of the applied field, the sharp growth of the current takes place, which is related to the field-induced releasing of traps (Figure, *b*). The influence of REE impurities on the VAC can be explained with the use of arguments given in the model of charged intrinsic defects [12].

According to this model, the charge carrier transfer in CGSs is controlled by U^--centers representing charged defects D^+ and D^- developed from initial neutral defects D^0 by the reaction

$$2D^0 \rightarrow D^+ + D^- \tag{1}$$

where D^+ where D^+ and D^- centers are the traps for electrons and holes. It is expected that the role of D^--centers is played by C_1^- and P_2^- connected by broken bonds of Se and As atoms with broken coordination, respectively.

Under the introduction of a positively charged impurity A^+ into CGS (mainly revealed as a positively charged Sm^{+3} ion), the law of electronentrality is as follows:

$$[A^+] + [D^+] = [D^-]. \tag{2}$$

According to the mass action law, the qualitative relation between charged center concentrations looks as

$$[D^+][D^-] = [D^0]^2 = \text{const}. \tag{3}$$

According to (2) and (3), the concentration of D^+-centers must decrease on the introduction of positively charged A^+ impurity, whereas the concentration of D^--centers must increase that influence the mechanism of current flow. By assuming that the hole transfer in CGSs of $Se_{95}As_5$ is controlled by local states related to D^--centers, we can explain the changes taking place in the VAC under change of the Sm content. At relatively big concentrations of Sm (0.6–1 at.%), the shift of the section corresponding to the limited filling of traps to high values of the applied voltage indicates the growth of the concentration of hole capture traps. No influence of the Sm impurity on the VAC happens at small concentrations within the model of charged intrinsic defects. That is, as a result of the Sm impurity presence, the section of the VAC corresponding to the filling of deep centers disappears, and the concentration of deep states decreases. Halogen impurities influence D^+ and D^--centers. For example, halogen impurities at small concentrations decrease the concentration of intrinsic defects of both signs [5, 6]. A similar influence is observed in the present paper and appears to be due to the chemical activity of REE atoms capable to form chemical compounds with Se and As. As a result, the concentrations of initial intrinsic defects decreases.

Using the available theories of CLSC [11], we determine some parameters characterizing the electric charge transfer in CGSs of the $Se_{95}As_5$ system and the parameters of hole capture traps. From the ohmic section of the VAC, we calculated the specific resistance of films and, using these values, estimated the concentration of equilibrium free holes (Table) by the formula $p=(ep_0\mu)^{-1}$, where e is the elementary charge, and the mobility of free charge carriers in the allowed band $\mu=10\ \text{cm}^2/(\text{B}\cdot\text{C})$ [12]. Using these data and the formula

$$P_0 = N_V \exp\left(-\frac{F_0 - E_V}{kT}\right) \tag{4}$$

we determined the position of the Fermi level in the band gap ($F_0 - E_V$) (Table), where N_V is the effective density of states in the valence band, and kT is the thermal energy. In calculations, N_V is assumed to be equal to $10^{19}\ \text{cm}^{-3}$ [12].

The concentration (p_{t02}) of traps initially free of holes with energy E_{t_2} is calculated from the formula

$$V_{\mathrm{FCT}} = \frac{eP_{t02}L^2}{\varepsilon} \tag{5}$$

and given in the Table, where V_{FCT} is the voltage when the section with the full filling of holes, E_{t_2}, begins. As is seen from the Table, $p_{t02} \gg p_0$. As was already mentioned, the deep levels in materials under the investigation are related to $\mathrm{D}^-(P_2^-)$. Taking the concentration P_2^- of centers (N_{t2}) to be of the order of 10^{16} cm^{-3} [18] and using the formula

$$P_{t02} = \frac{N_{t2}}{1 + g_A \exp\left(\frac{E_{t2} - F_0}{kT}\right)} \approx \frac{N_{t2}}{g_A} \exp\left(\frac{F_0 - E_{t2}}{kT}\right) \tag{6}$$

we calculated the energy position of the level, E_{t_2} (Table). In formula (6), g_A is the coefficient of spin degeneracy of the level E_{t_2}. It is assumed that g_A is equal to 2. We believe that, for the section with the trap-induced square law (TSL), the Fermi quasilevel for holes (F) coincides with E_{t_1} with accuracy up to kT. By the formula

$$E_{t1} - F_0 \approx F - E_V = kT \ln \frac{N_V}{P_{\mathrm{FCT}}} \tag{7}$$

we estimated the energy position of the level E_{t_1}, where $P_{\mathrm{FCT}}$is the concentration of free holes injected to the sample at the voltage corresponding to the origin of the TSL (V_{FCT}). The values of P_{FCT} were calculated from the formula

$$V_{\mathrm{FCT}} = \frac{eP_{\mathrm{FCT}}L^2}{\varepsilon}. \tag{8}$$

The results of estimations of E_{t_1} are also presented in the Table.

As from the Table, the energy position of the level E_{t_1} corresponds to the activation energy for drift mobility in amorphous Se, which testifies to the relation of the mentioned states to charged intrinsic defects C_1^- due to broken bonds of Se. This consideration allows us to take 10^{19} cm^{-3} [12] as the concentration of energy centers $E_{t_1}(N_{t1})$ which corresponds to the density of localized states deetrmining the drift mobility of holes.

System	$F_0 - E_V$, eV	Pt_{02}, cm^{-3}	E_{t2}, eV	E_{t1},eV
Se	0.7	–	–	0.26
$Se_{95}As_5$	0.79	4.2×10^{14}	0.85	0.23
$Se_{95}As_5Sm_{0.001}$	0.8	5.9×10^{14}	0.84	0.23
$Se_{95}As_5Sm_{0.005}$	0.75	–	0.87	–
$Se_{95}As_5Sm_{0.01}$	0.78	–	0.88	–
$Se_{95}As_5Sm_{0.1}$	0.79	1.2×10^{14}	0.89	–
$Se_{95}As_5Sm_{0.6}$	0.8	3.3×10^{14}	0.86	0.24
$Se_{95}As_5\ Sm_1$	0.8	4.3×10^{14}	0.86	0.21

The N-like VAC observed in the investigated structure at a negative potential of the Te contact (Fig. 1,*b*) appears to be due to the increase in the hole recombination intensity through D^- centers at high values of the applied electric field. At such intensities, the hole injection through the Al electrode, though in small quantities, takes place. As a result, the centers are filled gradually by injected holes, and the number of holes in the valence band increases simultaneously.

At a certain intensity of the applied electric field, the release of holes from D^0-centers occurs. In this case, the intensity of the recombination of holes with electrons of D^--centers increases simultaneously due to the concentration of holes in the valence band, and the current intensity decreases. For the positive potential of the Te electrode, the number of injected holes is high; therefore, recombination processes cannot decrease significantly the hole concentration in the valence band and the current intensity, i.e. N-like PT is not observed.

3. Conclusion

We have established that the transfer of charge carriers (holes) in the Al–$Se_{95}As_5$–Te system is carried out by the monopolar injection current mechanism limited by space charges with two groups of capture traps [shallow traps (E_{t_1}) corresponding to charged intrinsic defects C_1^- due to the broken bonds of Se and deep ones (E_{t_2}) corresponding to charged intrinsic defects P_2^- due to As atoms with broken coordination]. It is shown that the Sm impurity influences strongly the current flow path and the parameters of capture traps (energy position and concentration); in this case, they influence the deep traps related to charged intrinsic defects P_2^- created by As atoms with broken coordination. Low contents of the Sm impurity (up to 0.01 at.%) decrease the deep level concentration and increase their energy depth. But big concentrations of the mentioned impurity (more than 0.1 at.%) increase the concentration of these traps and decrease their energy depth. The Sm impurity behavior at its low concentrations is due to the REE chemical activity capable to form the chemical compounds with Se and As. As a result, the concentration of initial intrinsic defects decreases. We have observed that the Sm impurity behavior at big concentrations is described by the model of charged intrinsic defects [12]. That is, if we assume that the Sm impurity mainly manifests itself in the form of positively charged ions, their presence leads to changes in the concentration of U$^-$-centers so that the concentration of D$^+$-centers must decrease, but the concentration of D$^-$-centers must increase.

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СТРУМИ, ОБМЕЖЕНІ ОБ'ЄМНИМИ ЗАРЯДАМИ, У ХАЛЬКОГЕНІДНИХ СКЛОПОДІБНИХ НАПІВПРОВІДНИКАХ СИСТЕМИ $Se_{95}As_5$ З ДОМІШКОЮ Sm

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Резюме

Встановлено, що транспорт носіїв заряду (дірок) в структурі Al – $Se_{95}As_5$ –Te відбувається за механізмом монополярної інжекції струму, що залежить від об'ємних зарядів, за наявності пасток двох типів: мілких пасток (E_{t_1}), що відповідають зарядженим об'ємним дефектам $C^-{}_1$, зумовленим розірваними зв'язками Se, та глибоких пасток (E_{t_2}), що відповідають зарядженим об'ємним дефектам $P^-{}_2$, зумовленим порушеною координацією атомів As. Показано, що домішка сильно впливає як на механізм транспорту зарядів, так і на параметри пасток (енергетичне положення і концентрацію), особливо глибоких.