THE CURRENTS, LIMITED BY THE SPACE CHARGES IN CHALCOGENIDE VITREOUS SEMICONDUCTORS OF $Se_{95}As_5$ SYSTEM, CONTAINING THE SAMARIUM IMPURITIES

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It is established, that transition of charge (holes) carriers transfer in Al-$Se_{95}As_5$-Te structure is carried out by the current mechanism of monopolar injection, limited by the space charges at the participation of two groups of shallow traps (shallow E_{t1}), corresponding to charged intrinsic defects C_1, caused by selenium broken bonds and deep (E_{t2}), corresponding also to charged intrinsic defects P_2^-, created by arsenic atoms with the broken coordination. It is shown that samarium impurities strongly influence on the mechanism of current-going and on the parameters of shallow traps (energy state and concentration); in which connection mainly influence on the deep traps.

Such peculiarities of chalcogenide vitreous semiconductors (CVS), as structure change and electric properties under the light action, in particular, the change of index of light refraction, optical absorption edge, and also the appearance of unpaired spins, which are registered by the electron spin resonance, photoluminescence with Stokes shift, fatigue and etc. make the given materials perspective for the use in the different electric switches, storage devices, infrared technique, and also in the different acousto-optic devices [1-3]. CVS of $Se_{95}As_5$ system differs by the crystallization stability [4] and has the improved parameters of the electric charge transition at the introduction of halogen impurity (Cl, Br), and also high photosensitivity [5-6], that makes given CVS more attractive material.

The states, caused by the 4f states of rare earth element ions, form at the use of rare earth elements (REE) in the capacity of the impurities in the forbidden band CVS and in this case the optic width of the forbidden band CVS will be covered on the energy at most possible transition number, allowed for REE ion (Sm), that leads to the essential change of its optic, photoelectric and electric properties [7-10]. For the understanding of electron process mechanisms, which are responsible for above mentioned peculiarities it is necessary to define the energy spectrums of localized states in the forbidden band, for which the current investigation, limited by space charges (CLSC) is the one from the certain methods, to which the given work is dedicated.

The experiment and sampling techniques

The CVS synthesis of $Se_{95}As_5$ with samarium impurity is carried out by the melting of the corresponding quantities of chemical elements of high purity in evacuated quartz ampoules up to 10^{-6} millimeter of mercury at temperatures, higher 900°C into rotating stove with the further cooling in the mode of out stove. The impurity introduces in the synthesis process, its concentration is in the limits 0,001÷1at%.

The volt-ampere characteristics (VAC) are measured in the stationary mode on the standard technique. The samples present themselves structure "sandwich" with aluminic and telluric electrodes. The samples for the measurements are produced by the method of thermal vacuum evaporation ~10^{-6} millimeter of mercury. The film width is measured by interferometer method and varied in the range 0,2÷8mcm.

VAC of Al-$Se_{95}As_5$-Te structure with samarium impurity are investigated at the applying of electric field of both polarities. CLSC mode is observed at the application of positive potential to Te, and at the reversal polarity VAC of N-type is observed.

The results and their discussion

VAC of Al-$Se_{95}As_5$-Te structure with samarium impurity at the application of the positive (fig.1a) and negative (fig.1b) potentials to Te at room temperature is shown on the fig.1. VAC of VAC of Al-amorphous selenium-Te structure is also presented on the fig.1a. It is seen, that VAC of the given structures at the application of positive potential to Te consists in several regions.

The dependence $I{\sim}V^n$ where $n\leq1$ is observed in the most samples at small voltages. Further, the dependence $I{\sim}V^n$, where n in the different regions of VAC has the different values, evidences, that transition of charge carriers (holes) in the given structure is carried out by the current mechanism of monopolar injection, limited by space charges at the participation of shallow traps of charge carriers, is observed. The investigation shows, that the voltage, at which the nonlinear dependence of current intensity on the voltage begins, quadratically depends on the sample width that proves the CLSC mechanism embodiment once again. As it is shown from the fig.1,a, VAC of amorphous selenium at small values of applied voltages with voltage increase is obeyed to ohmic law, which transfers to quadratic law, after which the current begins to strongly increase with the increase of applied voltage, the region, called by "total trap filling" is observed [11]. Further this region is replaced by another one, in which the current quadratic dependence on voltage, $I{\sim}V^2$ is observed. Such VAC behavior corresponds to CLSC mechanism, controlled by small traps [11]. VAC of Al-$Se_{95}As_5$-Te structure differs from VAC of amorphous selenium by the fact, that region, corresponding to power law, i.e. $I{\sim}V^n$, where n exceeds 2 goes after the region, which is obeyed to ohmic law. Further, the region, where $I{\sim}V^2$ is observed. Finally, the quadratic region is changed by the other one, in which VAC slope increases again. The VAC peculiarities of Al-$Se_{95}As_5$-Te structures, investigated by us prove about the fact, that transition of electric charge in the given material is controlled by the two groups of trap centers with the depths of occurrence E_{t1} and E_{t2}, situated in the different sides of Fermi level. Simultaneously, voltage values, at which the region, corresponding to strong current increase, i.e. to the mode, corresponding to limit trap filling is observed, shifts to high voltages, that proves about the increase of the concentration of local states, being the shallow traps of the main charge carriers. The samarium impurities quite complicated influence on VAC forms and on the values of voltage transient between different regions. The concentration growth of samarium atoms up to 0,005 at% leads to gradually reconstruction of VAC form, corresponding to CLSC in the amorphous selenium. Further the concentration growth of samarium atoms, lead to the fact, that VAC becomes the same, as in CVS of $Se_{95}As_5$ system. Analogically, the halogen impurities influence on the drift mobility of charge carriers that is successfully explained in the limits of the model of charged intrinsic defects [5-6].

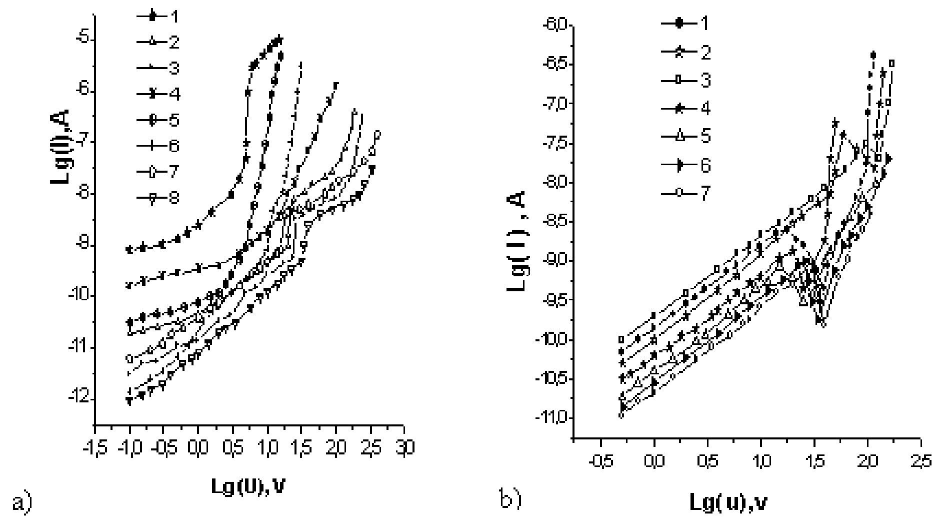

Fig.1. Volt-ampere characteristics (VAC) of Al-$Se_{95}As_5$-Te structure with samarium impurity at applied positive (fig.1,a) and negative (fig.1,b) potentials to Te at room temperature.

The influence of chemical composition and samarium impurities on the VAC behaviors allows us to say the some thoughts about the nature of local states and their energy position in the forbidden band relatively to equilibrium position of Fermi level, controlling current going in the investigated materials. The shallow traps of the charge main carriers (holes) in amorphous selenium are small (E_{t1}), i.e. are situated below, than value of equilibrium Fermi level. It is supposed, that local states, which control VAC in amorphous selenium are connected with charged intrinsic defects C_1^- , caused by broken selenium bonds. It is supposed, that the charged intrinsic defects P^-_2, created by arsenic atoms with violated coordination exist parallel with defects of C_1^- type in CVS of $Se_{95}As_5$ system. The existence possibility of such defects in CVS, containing arsenic is also informed in the ref [12]. According to forms of VAC, the energy state of local states, corresponding to given defects should be higher Fermi level, i.e. are deep ones.

At low voltages the holes, injected in $Se_{95}As_5$ system from tellurium contact are captured by deep traps (E_{t2}), but the conductivity stays ohmic one because of the presence of equilibrium holes. The filling of E_{t2} centers takes place with voltage increase and simultaneously the concentration of free hole concentration increases and the moment when concentration of injected free holes exceeds the concentration of equilibrium holes, the current strongly increases with voltage increase, i.e. the so-called region of “limit trap filling” is observed. After it the current is controlled by the E_{t1} traps, moreover the trap square-law is observed still Fermi quazi-level stays higher, than E_{t1} level. The slope increase of VAC on the last region probably is connected with thermo-field hole emission from trap levels. In the proof of the last said the fact evidences, that strong current increase takes place at the same values resistance of applied field at the inverse polarity of applied field, when CLSC mode isn’t observed, that also is connected with field trap emptying (fig.1,b). The influence of rare earth element impurities on VAC can be explained, if the submissions, developed in the model limits of charged intrinsic defects [12] could be involved.

According to this model, the transition of charge carriers in CVS is controlled by U^--centers, presenting themselves the charged defects D^+ and D^-, which form from initial neutral defects D^0 on the reaction:

$$2D^0 \rightarrow D^+ + D^- , \qquad (1)$$

Where D^+ and D^- -centers are traps for electrons and holes. It is supposed, that role of C^-_1 and P^-_2 centers, connected by broken centers of selenium and arsenic atoms with violated coordination play in our case the role of D^- -centers, correspondingly.

The electric neutrality law should be carried out at the introduction of positive charged impurity A^+ into CVS (it is supposed, that samarium mainly reveals in the form of positive charged ion Sm^{+3}):

$$[A^+] + [D^+] = [D^-] \quad . \qquad (2)$$

According to the law of mass action, the quantitative relation between concentrations of charged centers is expressed by the expression:

$$[D^+]\,[D^-] = [D^0]^2 = const \quad . \qquad (3)$$

According (2) and (3), at the introduction of positive charged A^+ impurity the concentration of D^+-centers should decrease, and concentrations of D^--centers should increase, that should influence on the current-going mechanisms. If we take into consideration that hole transition in CVS of $Se_{95}As_5$ system is controlled by the local states, connected by D^--centers, then it is possible to explain the changes, taking place in VAC at the concentration change of samarium atoms. Indeed, the voltages, at which the region, corresponding to limit trap filling is observed, shifts to high value of applied voltage, that evidences about growth of trap concentration of hole shallow at relatively big concentrations (0,6 1at%). The influence of samarium impurities on VAC at small concentrations doesn't take place in the limits of the model of intrinsic charged defects, i.e. the region, corresponding to the filling of deep centers disappears; in the result of participation of samarium impurity in VAC, i.e. the concentration of deep states decreases. The halogen impurities take an effect the same influence on D^+ and D^--centers, i.e. halogen impurities in the small concentrations decrease the concentrations of intrinsic defects of both signs [5-6]. The analogous influence is observed in the present paper and probably, is caused by chemical activity of REE atoms, which are able to form the chemical compounds with selenium and arsenic, in the result of which the concentration of initial intrinsic defects decreases, too.

The some parameters, characterizing the transition of electric charge in CVS of $Se_{95}As_5$ system, and also parameters of hole shallow traps are defined, using the known CLSC theory [11].

The film specific resistance is calculated from the ohmic region of VAC and using these values, the concentration of equilibrium free holes (table) from the formula $\rho=(e\rho_0\mu)^{-1}$, where e is elementary charge and μ is mobility of free carriers in the allowed band μ=10cm^2/ (V.s.) is estimated. Using this formula

$$\rho_0 = N_v \, exp\left(-\frac{F_0 - E_v}{kT}\right) \quad (4)$$

Fermi level in the forbidden band (F_0-E_v) (table №1), where N_v is effective state density in the valency band, kT is thermal energy, is defined. At calculations N_v was equal to 10^{19}cm^{-3} [12].

The concentration (p_{t02}) of traps, initially disengaged by the holes with E_{t2} energy is calculated from the equation:

$$V_{FCT} = \frac{ep_{t02}L^2}{\varepsilon} \quad (5)$$

and is presented in the table №1, where V_{FCT} is voltage, at which the region of total filling of E_{t2} traps begins. As it is seen from the table p_{t02}>>p_0. As it was mentioned above, the deep levels in the investigated materials are connected with $D^-(P^-_2)$. Taking into consideration the concentration of P^-_2-centers (N_{t2}) in 10^{16} cm^{-3} order [18], on the formula

$$p_{t02} = \frac{N_{t2}}{1 + g_A \, exp(\frac{E_{t2} - F_0}{kT})} \approx \frac{N_{t2}}{g_A} exp(\frac{F_0 - E_{t2}}{kT}) . \quad (6)$$

The energy position of E_{t2} level (table №1) is calculated. G_A is the coefficient of spin degeneration of E_{t2} level in the formula (6). It is considered, that $g_A=2$.

Taking into consideration, that Fermi quazi-level for the holes (F) coincides with E_{t1} with accuracy up to kT on the region, where trap quadratic law (TQL) begins, the energy position of E_{t1} level, where P_{FCT} is concentration of free holes, injected into the sample at the voltage, corresponding to beginning of TQL (V_{FCT}) regions, is estimated.

$$E_{t1} - F_0 \approx F - E_V = kT \ln \frac{N_V}{p_{FCT}} \quad (7)$$

The ρ_{FCT} values are calculated from the formula:

$$V_{FCT} = \frac{ep_{FCT}L^2}{\varepsilon} . \quad (8)$$

The estimation results of E_{t1} also are presented in the table №1.

Table №1

	F_0-E_V,eV	Pt_{02}, Sm^{-3}	E_{t2},eV	E_{t1},eV
Se	0,7	-	-	0,26
$Se_{95}As_5$	0,79	4,256×10^{14}	0,856	0,23
$Se_{95}As_5Sm_{0.001}$	0,8	5,9×10^{14}	0,847	0,23
$Se_{95}As_5Sm_{0.005}$	0,75	-	0,875	
$Se_{95}As_5Sm_{0.01}$	0,78	-	0,887	
$Se_{95}As_5Sm_{0.1}$	0,79	1,22×10^{14}	0,89	
$Se_{95}As_5Sm_{0.6}$	0,8	3,33×10^{14}	0,859	0,24
$Se_{95}As_5$ Sm_1	0,8	4,34×10^{14}	0,86	0,21

As it is seen from the table the energy state of E_{t1} level corresponds to the activation energy of the hole drift mobility in the amorphous selenium, that also evidences about the connection of the given states with the charged intrinsic defects C_1^-, caused by the broken selenium bonds. This fact allows to accept the value 10^{19} cm^{-3} [12], which corresponds to the density of localized states, controlling the hole drift mobility for center concentrations with energy $E_{t1}(N_{t1})$.

Conclusion

In the result of the carried investigations it is established, that transition of charge carriers (holes) in Al-$Se_{95}As_5$-Te structure is carried out by the mechanism of currents of monopolar injection, limited by space charges at the participation of two group of shallow traps (small E_{t1}), corresponding to charged eigen defects C_1^-, caused by the broken selenium bonds and deep (E_{t2}), corresponding to charged eigen defects P_2^-, formed by arsenic atoms with violated coordination. It is shown that samarium impurities strongly influence on the mechanism of current going and on the parameters of shallow traps (energy state and concentration); moreover, mainly influence on deep traps, connected by charged intrinsic defects P_2^-, formed by arsenic atoms with violated coordination. The small content of Sm impurity (till 0,01 at%) increases their energy deep, decreasing the concentration of deep traps, and big concentrations of the given impurities (more than 0,01 at%) decrease their energy deep, increasing the concentrations of these traps. The behavior of Sm impurity in small concentrations is explained by chemical activity of REE, which are able to form the chemical compounds with selenium and arsenic, in the result of which the concentration of initial intrinsic defects decreases. The behavior of samarium impurity in big concentrations takes place according to the model of charged intrinsic defects [12], i.e. if it is taken into consideration, that samarium impurities mainly reveal in the form of positively charged ions, then in the result of their presence the concentration of U^--centers should change: concentration of D^+-centers decreases, and D^--centers increases, that indeed is observed in experiments.

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TƏRKİBİNDƏ SAMARİUM AŞQARI OLAN $Se_{95}As_5$- ŞÜŞƏVARİ HALKOGENİD YARIMKEÇİRİCİ SİSTEMLƏRİNDƏ FƏZA YÜKLƏRİ İLƏ MƏHDUDLANMIŞ CƏRƏYANLAR

Müəyyən olunmuşdur ki, Al-$Se_{95}As_5$-Te strukturunda yükdaşınması iki qrup zəptetmə tələsinin iştirakı olduqda (qırılmış selen rabitələri ilə bağlı olan C_1^- məxsusi yüklü defektlərə uyğun gələn dayaz (E_{t1}) və arsen atomları tərəfindən yaradılan -P_2^- məxsusi yüklü defektlərə uyğun gələn dərin (E_{t2})) fəza yükləri ilə məhdudlanmış monopolyar injeksiya cərəyanları ilə baş verir. Göstərilmişdir ki, samarium aşqarları cərəyanın keçmə mexanizminə və zəptetmə tələsinin parametrlərinə (energetik vəziyyəti və konsentrasiyası) nəzərə çarpan səviyyədə təsir göstərir. Lakin qeyd olunmuşdur ki, samarium aşqarları əsasən arsen atomları ilə yaradılan -P_2^- məxsusi yüklü defektlərlə bağlı olan dərin zəptetmə tələlərinə təsir edir.

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ТОКИ, ОГРАНИЧЕННЫЕ ПРОСТРАНСТВЕННЫМИ ЗАРЯДАМИ В ХАЛЬКОГЕНИДНЫХ СТЕКЛООБРАЗНЫХ ПОЛУПРОВОДНИКАХ СИСТЕМЫ $Se_{95}As_5$, СОДЕРЖАЩИЕ ПРИМЕСИ САМАРИЯ

Установлено, что перенос носителей заряда (дырок) в структуре Al-$Se_{95}As_5$–Te осуществляется по механизму токов монополярной инжекции, ограниченных пространственными зарядами, при участии двух групп ловушек захвата (мелкие E_{t1}, соответствующие заряженным собственным дефектам C_1^-, обусловленные оборванными связями селена и глубокие E_{t2}, соответствующие также заряженным собственным дефектам P_2^-, создаваемыми атомами мышьяка с нарушенной координацией). Показано, что примеси самария сильно влияют на механизм токопрохождения и на параметры ловушек захвата (энергетическое положение и концентрация); в основном, на глубокие ловушки.

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