Chalcogenide Letters Vol. 5, No. 1, January 2008, p. 11 - 16

SPACE CHARGE LIMITED CURRENTS LIMITED IN CHALCOGENIDE GLASS-LIKE SEMICONDUCTORS OF $Se_{95}As_5$ SYSTEM WITH Sm IMPURITY

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It was established that the transfer of charge carriers (holes) in Al-$Se_{95}As_5$-Te system made by monopolar injection current mechanism limited by space charges with two groups of capture traps (shallow (E_{t1}) corresponding to charged intrinsic defects C^-_1 due to the broken bonds of Se and the deep traps (E_{t2}) correspond to charged intrinsic defects P^-_2 due to As atoms with broken coordination. It is shown that Sm impurity highly influences the path of current flow 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 content of Sm impurity (up to 0.01 at%) decreases the deep level concentration and increases their energy depth. High concentration of mentioned impurities (>0.1 at%) increases the concentration of these traps and decreases their energy depth.

(Received December 3, 2007; accepted December 10, 2007)

Keywords: Chalcogenide glass, $Se_{95}As_5$, Sm impurity, Space-change limited currents, Al-Se_{95} As-Te structure

1. Introduction

It is established that transfer of charge carriers (holes) in Al - $Se_{95}As_5$ –Te structure is carried out by monopolar injection current mechanism limited by space charges with two groups of capture traps (shallow, Et_1) corresponding to charged intrinsic defects C^-_1 due to the broken bounds of Se and deep traps (Et_2) also corresponding to charged intrinsic defects P^-_2 due to As atoms with broken coordination. It is shown that Sm impurity influences heavily on the mechanism of path of current flow and capture trap parameters (energy position and concentration); especially they influence the deep traps related to charged intrinsic defects P^-_2 due to As atom with broken coordination.

Thepeculiarities of chalcogenide glass-like semiconductors (CGS) as e.g. structural change and electron properties under the effect of light, in particular light diffraction, index change, optical absorption edge, as well as the occurrence of unpaired spins identified by electron spin resonance, photoluminescence, Stock shift and fatigue, etc., make the above-mentioned materials as perspective materials to be used in electric switches, memories, IR technique, various acousto-optic instruments [1-3]. CGS of $Se_{95}As_5$ system is different by crystallization resistance [4], and, by introduction of halogen impurities (Cl,Br) they assume improved parameters of electric charge transfer, as well as high photo-sensitivity [5-6] that makes CGS a very attractive material. By using rare earth elements (REE) as impurities in CGS band gap are formed states due to 4 f states of REE ions and in this case CGS optical band gap overlaps the most possible number of transitions resolved for REE (Sm) ion that brings about significant change of its optical, photoelectric and electrical properties [7-10]. To understand the electron process mechanism responsible for above-mentioned peculiarities it is necessary to determine the energy spectra of localized states in the band gap. To this aim the paper deals with the investigation of currents limited by space charges (CLSC), this method being one of the most reliable methods.

2. Experimental method and sample preparation

CGS synthesis of $Se_{95}As_5$ composition with Sm impurity is carried out by melting appropriate quantities of chemical elements of special purity in vacuum quartz ampoules down to 10^{-6} Torr at T above 900 ^oC in rotating furnace with subsequent cooling in the regime off-furnace. The impurity is introduced during the synthesis, its concentration is within 0.01 ÷1 at%.

Thermal power (TP) has been measured in stationary regime by standard method. Samples were in the "sandwich" structures with Al and Te electrodes. The samples have been prepared by thermal evaporation method in vacuum at ~10^{-6} Torr. Film thickness has been measured by interferometrical method and is situated in the range 0.2÷8 micrometers. TP of Al - $Se_{95}As_5$ –Te structure with Sm impurity has been investigated by applying an electric field of negative and positive polarity. CLSC regime has been observed by applying to Te a positive potential and at reverse polarity n-type conduction has been observed.

3. Results and discussion

In Fig.1 there is shown TP of Al-$Se_{95}As_5$-Te structure with Sm impurity as the positive (Fig.1a) and negative (Fig.1b) potentials to Te are applied at the room temperature. In Fig.1a there has been presented TP of Al-amorphous selenium-Te structure. It is seen that TP of mentioned structures by applying positive potential to Te consists of several regions.

Most samples at low voltages behave as $1\sim V^n$, where $n\leq 1$. For higher n, it was observed a function $1\sim V^n$, where n has various values in different ranges of TP , that indicates that charge carrier transfer (holes) in given structure is carried out according to the mechanism of monopolar injection currents limited by space charges carriers due to capture traps. The investigation shows that the voltage when superlinear function of current intensity on the voltage depends as a square power on the sample thickness. A well known (CLSC) mechanism is responsible for this behaviour. As it is seen from Fig.1a TP of amorphous selenium at low values of applied voltage obeys the Ohm's law which passes into square law, thereafter the current begins to strongly increase with the increase of the applied voltage, where the so-called region of "full filling of traps" is observed. [11].

Later this region is replaced by the section where quadratic voltage function of the current $1\sim V^2$ is revealed. Such behavior of TP is corresponding to CLSC mechanism that takes into account the shallow traps [11]. TP of Al-$Se_{95}As_5$-Te structure is different from TP of amorphous selenium. After the region obeying Ohm's law an other region corresponding to exponential law follows. The law is $1\sim V^2$ when n exceeds 2. Then the region characterized by the law $1\sim V^2$ has been observed. Finally the quadratic region is replaced by the region where the slope of TP increases again. The peculiarities of TP of Al-$Se_{95}As_5$-Te structures under the investigation suggest that in above-mentioned material the electric charge transfer is achieved by 2 groups of trapping centre with depth Et_1 and Et_2 arranged in depth on both sides of the Fermi level.

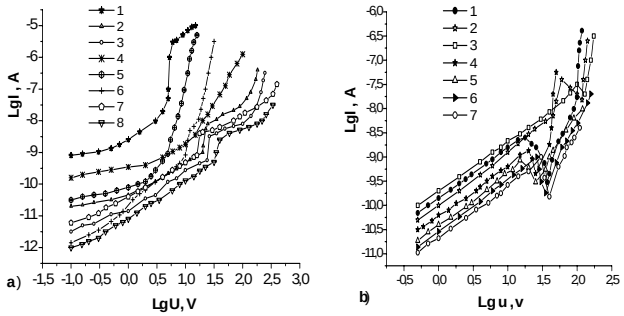

Fig. 1.Thermal power of Al-$Se_{95}As_5$-Te structure with Sm impurity by applying positive (a) and negative (b) potentials to Te. a) 1-Se; 2-$Se_{95}As_5$; 3-$Se_{95}As_5Sm_{0.001}$ 4-$Se_{95}As_5Sm_{0.005}$; 5-$Se_{95}As_5Sm_{0.01}$; 6-$Se_{95}As_5Sm_{0.1}$; 7-$Se_{95}As_5Sm_{0.6}$; 8-$Se_{95}As_5Sm_1$: 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-$Se_{95}As_5\,Sm_{0..6}$; 7-$Se_{95}As_5\,Sm_1$

Sm impurities influences rather difficult on TP forms and values of transient voltage between different sections. Growth of Sm atom concentration up to 0.005 at% leads to the gradual reduction of TP forms corresponding to CLSC regime in amorphous selenium. Further growth of Sm atom concentration brings about the fact that PT becomes the same as in CGS of $Se_{95}As_5$ system. In an analogous way halogen impurities influence the drift mobility of charge carriers that is explained within the model of charged intrinsic defects [5-6].

Influence of chemical composition and Sm impurities on TP behaviour allows for some considerations on the nature of local states and their energy arrangement in band gap against equilibrium position of Fermi level by checking the path of current flow in the materials under investigation. In amorphous selenium the traps of majority charge carriers capture are low (Et_1), i.e. they are lower than the equilibrium value of Fermi level. It is expected that in amorphous selenium the local states is related to charged intrinsic defects C^-_1 due to Se broken bonds. It is expected that in CGS from the $Se_{95}As_5$ system with the C^-_1-typed defects, the charged intrinsic defects are created by As atoms with broken coordination. In paper [12] there have been also reported the possibility of existing such defects in CGS including Sm. According to TP, the energy position of local states corresponding to mentioned defects must be above the Fermi level, i.e. they are deep states.

At low voltages holes injected in $Se_{95}As_5$ from Te contact are captured by deep traps (Et_2) but conductance remains ohmic due to the presence of equilibrium holes. With the voltage increase filling of Et_2 centers takes place and free hole concentration increases. As the concentration of injected free holes exceeds the concentration of equilibrium holes the current increases with the voltage increase, i.e. we have the so-called "limited filling of traps". Then the current is controlled by the traps Et_1. In the case quasi-level Fermi remains above level Et_1, trapped square law is observed. Increase of TP slope in the last section appears to be connected to the thermo field emission of holes with trap level. It is indicated that by reversed polarity of applied field sharp growth of current is taken place that is related with the field releasing of traps (Fig.1b). Influence of REE impurities on TP can be explained in the frame of considerations given in the model of charged intrinsic defects [12].

According to this model charge carrier transfer in CGS is checked by U^--centers representing charged defects D^+ and D^- developing from initial neutral defects D^0 according to the reaction

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

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 bonds of Se and As atoms with broken coordination, respectively.

By introduction of positively charged impurity A^+ into CGS (mainly revealed as positively charged Sm^{+3} ion) the law of electro-neutrality must be respected:

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

According to mass action law qualitative relationship between charged center concentrations is defined by the function:

$$[D^+]\,[D^-]=[D^0]^2=\text{const} \quad (3)$$

According to (2) and (3) by introduction of positively charged A^+ impurity D^+-centers concentration must decrease, and D^--centers concentration must increase that influences on path of current flow mechanism. It is considered that hole transfer in CGS of $Se_{95}As_5$ is checked by local states related to D^--centers we can explain changes taking place in TP by changes of Sm at relatively large concentrations of Sm (0.6; 1at%). The voltage when the region corresponding to the limited filling of traps shifts to the high value of applied voltage indicates the increase of the

hole capture trap concentration. Influence of Sm impurity on TP at small concentrations does not take place within the model of charged intrinsic defects, i.e. as a result of Sm impurity presence in TP the region corresponding to the filling of deep centers disappears, i.e. the concentration of deep states decreases. Halogen impurities have an influence on D^+ and D^--centers, i.e. halogen impurities at small concentrations decrease the concentration of intrinsic defects of both signs [5-6]. Similar influence is observed in this paper and appears to be due to the chemical activity of REE atoms able to form chemical compounds with Se and As, as a result of the decrease of the concentration of initial intrinsic defects. Similar influence is observed in other papers that is due to the chemical activity of REE atoms able to form chemical compounds of Se and As as a result of the decrease of the concentration of initial intrinsic defects.

Using the well known theories of CLSC [11] we determined some parameters featuring electrical charge transfer in $Se_{95}As_5$ system CGS, and, also the parameters of hole capture traps. From ohmic region of TP the resistivity of the films was calculated and using these values there has been estimated the concentration of equilibrium free holes (Table 1) from the formula $p=(ep_0\mu)^{-1}$, where e is the elementary charge and μ-mobility of free charge carrier in allowed band μ=10 cm^2/Vs [12]. Using these data from the formula

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

there has been determined the position of Fermi level in band gap (F_0–E_V) (Table 1) where N_V is the effective density of states in valence band, and kT is the thermal energy. The calculated N_V is equal to 10^{19} cm^{-3} [12].

Concentration (p_{t02}) (of initially free traps) of holes with energy E_{t2} is calculated from the formula

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

and given in Table 1, where V_{FCT} is the voltage when the section of full filling of holes E_{t2} begins. As it is seen from Table 1 $p_{t02} >> p_0$. As it is mentioned deep levels in materials under the investigation are related to $D^-(P^-_2)$. Taking into consideration concentration P^-_2 of centers (N_{t2}) in order of $10^{16}cm^{-3}$ [18] from the formula there was

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

calculated energy position of level E_{t2} (Table 1). In formula (6) g_A is the coefficient of spin degeneracy of level E_{t2}. It is assumed that g_A is equal to 2. We believe that at the section where trapped square law (TSL) is valid, the Fermi quasi-level for holes (F) coincides with E_{t1} with accuracy up to kT from the formula

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

The energy position of level E_{t1} is estimated, where P_{FCT} is the concentration of free holes injected the sample at the voltage corresponding to the origin of TSL (V_{FCT}). P_{FCT} values have been calculated from the formula

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

Results of E_{t1} estimations are also presented in Table 1.

As it is seen from Table 1 energy position of level E_{t1} is corresponding to activation energy of drift mobility in amorphous Se that is the testimony to the connection of mentioned states with charged intrinsic defects C^-_1 due to broken bonds of Se. This fact allows the value 10^{19} cm^{-3} [12] for the concentration of energy centers $E_{t1}(N_{t1})$, which corresponds to the density of localized states when drift mobility of holes is assumed.

Table 1.

Sample	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

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

By certain intensity value of applied electric field hole release from D^o-centers takes place and in this case the intensity of hole recombination with D^--centre electrons increases simultaneously, due to hole concentration in valence band, and current intensity values decrease. In the case of positive potential of Te electrode the number of injected holes is high, therefore recombination processes, can not reduce significantly the hole concentration in the valence band and the current intensity value, i.e. n-like PT is not observed.

4. Conclusions

As a result of our investigations it was established that the transfer of charge carriers (holes) in Al-$Se_{95}As_5$-Te system made by monopolar injection current mechanism limited by space charges with two groups of capture traps (shallow (E_{t1}) corresponding to charged intrinsic defects C^-_1 due to the broken bonds of Se and the deep traps (E_{t2}) correspond to charged intrinsic defects P^-_2 due to As atoms with broken coordination. It is shown that Sm impurity highly influences the path of current flow 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 Sm impurity (up to 0.01 at%) decrease the deep level concentration and increase their energy depth. High concentration of mentioned impurities (more than 0.1 at%) increases the concentration of these traps and decreases their energy depth. Sm

impurity behaviour at low concentrations are due to REE chemical activity capable of forming chemical compounds of Se and As as a result of concentration decrease of the initial intrinsic defects. It is observed that behaviour of Sm impurity at high concentrations occurs according to the model of charged intrinsic defects [12], i.e. under the hypothesis that Sm impurity mainly manifest in the form of positively charged ions. In their presence the U^--centre concentration undergo changes, D^+-centre concentration must decrease, but D^--center concentration must increase.

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