ELECTROPHYSICAL PROPERTIES OF GaSe SINGLE CRYSTALS DOPED BY Re TRANSITION ELEMENT

B.G. Tagiev, O.B. Tagiev, S.A. Abushov, G.Y. Eyyubov

Electrophysics and Electrical Materials
Oktay58@ mail.ru, phone (99412) 4396795, fax: (99412)4396795
Institute of Physics, Azerbaijan National Academy of Sciences.
Baku 370143, Azerbaijan
E-mail: Oktay@physics.ab.az

ABSTRACT

There has been investigated the influence of doping by Re transition element on the electrophysical properties of GaSe single crystals by study of static volt-ampere characteristics (VAC), temperature dependence of electroconductivity $\sigma(T)$, thermostimulated conductivity (TSC) and thermostimulated depolarization (TSD) at temperature 77-350 K. As a result of investigation sets mechanisms of electroconductivity $\sigma(T)$, TSC, TSD, activation energy, concentration and capture cross-section of deep levels have been determined.

Keywords: transition, element, temperature, mechanisms, depolarization.

I. INTRODUCTION

Recently there have been widely investigated single crystals of semiconductive compounds doped by transition elements. Impurities of transition elements give rise to sensitizing and luminescent centres in band gap of wide-band semiconductors. There have been same works on study of transition element influence on physical properties of $A^{III}B^{VI}$ laminated single crystals [1-4], where GaSe is one of the most investigated.

It is of great interest the investigation of Re transition element influence on the electric and photoelectric properties of GaSe single crystals as because of valence state changeability its atoms can have an influence on the acceptor compensation degree and create as electron as hole centres in p-GaSe band gap.

II. METOD OF EXPERIMENT

It is known that GaSe –Re system applies to simple eutectic systems. In the system small region homogeneity on GaSe based compound has been found. It is established that GaSe dissolves Re up to 0,65 at.% at room temperature [5].

Investigation samples are synthesized in evacuated up to 10^{-4} mm Hg and sealed quartz ampoules at temperatures 900÷1100 ^{o}C with the use of vibrating mixing. Initial materials for GaSe: Re thesis are: Ga of B-3 model; Se of B-4 model especially pure and Re-electrolytic, purified. Preliminarily Re is pounded with an agate pestle and is rebuilt in hydrogen flow at 1100 ^{o}C. GaSe single crystals: Re is grown by modified Bridgemen method. Re contend in single crystals is equal to 0,01÷0,03 at. %.

GaSe samples: for investigation Re is prepared by spalling big single crystals along cleavage plane (0001) into plates in thickness from 50 mkm up to 3mm. "Sandwich" and "planar" contacts to the samples are produced either by sealing in or by thermal evaporation In in vacuum.

III. VOLT-AMPERE CHARACTERISTICS (VAC)

In Fig.1 volt-ampere characteristics (VAC) for GaSe: (0,03; 0,1 and 0,3 at.%) Re at 140 and 293 K is given. For all investigated In-GaSe: Re-In sandwich structures at 293 K (1-3) the following section are resealed: I-linear, II-"trapped" quadratic; III-region of current sharp rise. With the decrease of temperature down to 140 K the behaviour of VAC changes highly. For sandwich structures In – GaSe; 0,03 at.% Re – In (curve 4) and In – GaSe: 0,1 at.% Re–In (curve 5) VAC includes 3 section: I-linear; II-"trapped" quadratic; III-cubic. For structures In-GaSe: 0,3 at. % Re-In with the rise of voltage the following sections have been revealed: I-linear; II-"trapped" quadratic; III-power (three-halves-power law $J \sim V^{3/2}$); IV-cubic; V-region of current sharp rise ($J \sim V^n$, where $n \succ 3$). The presence of quadratic section ($J \sim V^2$) after linear one (Fig.1 curves 3-5) and the fulfillment of the condition $\theta \prec\prec 1$ (where θ-capture factor) show that current is restricted by monopolar injection. At certain injection levels carrier transfer is not restricted by monopolar injection but it is due to double injection ($J \sim V^{3/2}$ law). To account for investigation results we use one of the model of Lampert ant Mark double injection theory [6] suggesting that at low voltage

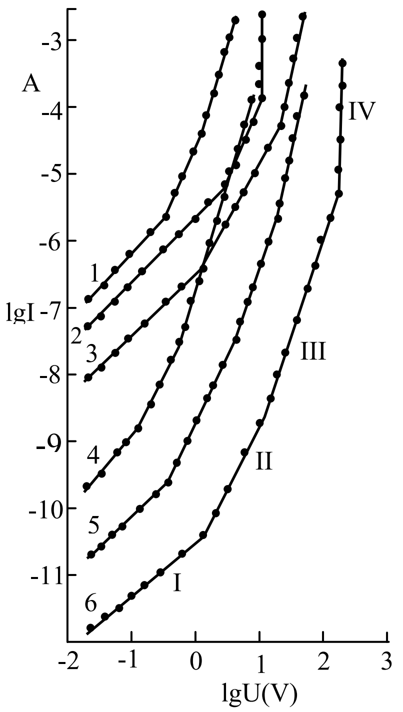

Fig.1. I-U characteristics of CaSe: 0,03 at. % Re single crystals at 140 (curve 4, 5, 6) and 293 K (curve 1, 2, 3).

carriers of one sign are happed and carriers of opposite one (being free) move. This process is determined by monopolar injection and expressed by the following formula [6]:

$$j=\frac{9}{8}\varepsilon\mu\frac{V^2}{L^3} \qquad (1)$$

where ε-dielectric constant, μ-carrier mobility, V-applied voltage, L-crystal thickness. With the rise of injection trapped carriers of one sign operate as recombination centres for the carriers of another sign. This new process is the new restriction for the current and is described by the following formula [6]:

$$j=\frac{125}{18}\varepsilon\theta_n\mu_n\tau\frac{V^2}{L^5} \qquad (2)$$

In this case monopolar injection is the hole one and current density in quadratic region is expressed by the following formula:

$$j=\frac{9}{8}\varepsilon\mu_n\theta_n\frac{V^2}{L^3} \qquad (3)$$

Thus the presence of cubic section and the section of threehalves ($J \sim V^{3/2}$) [6] shows that at low temperatures carrier transfer in the region of strong electric fields is due to the double injection.

From GaSe: Re doped single crystal VAC calculation according to Lampert theory of injection current there have been determined parameters of local levels at temperatures 140 and 193 K, which values are given in Table 1.

IV. TERMOSTIMULATED CURRENTS AND TEMPERATURE DEPENDENCE OF ELECTROCONDUCTIVITY

To obtain complete information about distribution of deep levels in band gap of GaSe: 0,1 at.% Re single crystals TSC, TSD and temperature dependence of electroconductivity have been investigated.

For trap filling GaSe: 0,1 at.% Re samples are exposed by white light for 5 min. at 77 K, then they are heated with the rate 0,34 K/s in the darkness. On TSC curve (fig. 2a) at temperatures 77÷90 K one narrow peal with the temperature maximum 82 K is revealed, and at temperatures 90÷260 K three overlapping peaks are revealed at 221, 231 and 239 K. To separate these peaks thermal "clearing" has been made. As a result three discrete peaks, temperature maxima which are in good agreement with revealed peaks on TSC without thermal clearing have been obtained.

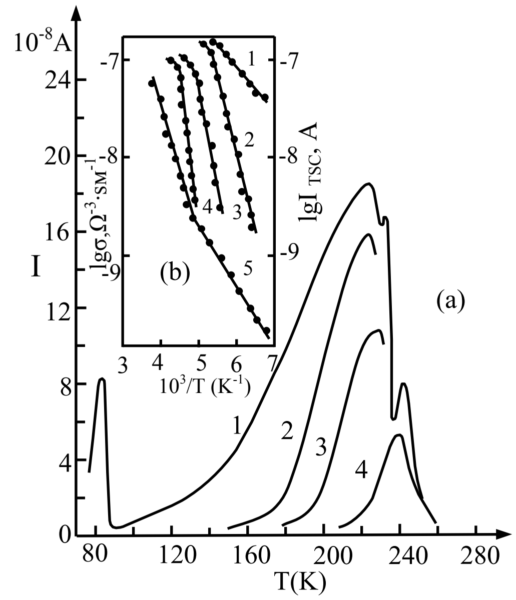

Fig. 2. Thermostimulated current and temperature dependence of current of GaSe:Re single crystals.

In Fig. 2b there has been presented temperature dependence of dark conduction from ohmic region of VAC (straight line 5). It is seen that the dependence consists of 2 sections where along their slopes energy activation 0,12 and 0,27 eV are determined. Trap deposit depths are defined from TSC initial current rise (Fig.2b, straight lines 1-4), constructed on the base of the curves 1-4 (Fig. 2a). Levels with energy activation 0,06; 0,27; 0,34; 0,43 eV are resealted. Being calculated from the initial rise of TSC curve trap deposit depth according to the formulae [7, 8]

$$J \approx const\exp\left(-\frac{E_t}{kT}\right) \qquad (1)$$

at temperatures 144÷220 K is equal to 0,06 eV (curve 1).

Table 1

Crystals	GaSe: 0,03at.%Re		GaSe: 0,1at.%Re		GaSe: 0,3at.%Re	
	293 K	140K	293 K	140 K	293 K	140 K
Deposit depth, eV $E = kT\ln\frac{N_V}{gN_t}$	0,48	0,24	0,46	0,19	0,35	0,32
$\lg\sigma \sim \frac{10^3}{T}$	$2\cdot10^{11}$	10^{11}		0,12 0,27	0,11 0,30	
Trap concentration, cm^{-3} $N_t = 1{,}1\cdot10^{-6}\frac{V_{LTF}}{L^2}$ [6]			$1{,}2\cdot10^{12}$	$2{,}6\cdot10^{12}$	$2\cdot10^{13}$	$2\cdot10^{13}$
Capture factor $\theta = \frac{8}{9}\frac{jL^3}{\varepsilon\varepsilon_0\mu V^2}$ [6]	0,83	0,2	8,4·10	$5\cdot10^{-5}$	0,35	$3\cdot10^{-5}$

Table 2

Trap parameters	E_1	E_2	E_3	E_4
Deposit depth, eV $E_t = kT_m\ln\frac{N_v}{n_m}$ [12]		0,27	0,36	0,42
$J_{TSC} \sim \exp\left(-\frac{E_t}{kT}\right)$ [13]		0,27	0,36	0,43
$E_t = \frac{2kT_m^2}{T_2 - T_1}$ [8]	0,08			
Concentration of originally filled traps, cm^{-3} $n_{t_0} = \frac{\alpha kT_m^2}{e\mu\tau FE_t\beta}\exp\left(-\frac{E_t}{kT_m}\right)$ [13]	$5\cdot10^{13}$	$1{,}1\cdot10^{14}$	$7{,}3\cdot10^{12}$	$7{,}1\cdot10^{13}$
Trap concentration, см$^{-3}$ $N_t = \frac{N_v kT_m^2}{E_t\beta}\exp\left(-\frac{E_t}{kT_m}\right)$ [13]	$1{,}5\cdot10^{14}$	$1{,}8\cdot10^{18}$	$1{,}2\cdot10^{16}$	$1{,}5\cdot10^{15}$
Capture cross-section, см^2 $S_t = \frac{1}{\vartheta_{th}}\left\{N_t\tau\left[\exp\frac{2kT_m}{E_t} - 1\right]\right\}^{-1}$ [13] $S_t = \frac{3}{2}\frac{0{,}7\beta\frac{0{,}7kT_m}{T_2 - T_1}}{N_V v_{th}(T_2 - T_1)}$ [8]	$8\cdot10^{-22}$	$1{,}1\cdot10^{-21}$	$2\cdot10^{-13}$	$2{,}2\cdot10^{-19}$

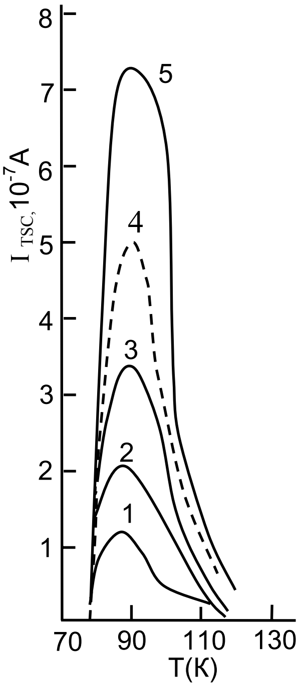

Fig. 3. Thermostimulated conductivity of undoped GaSe single crystals at applied voltage, V. 1– 66,6; 2 –100; 3 – 133; 4 – 166; 5 – 200

This value is underrated as the trap deposit depth defined from pronounced low-temperature peak (T=80 K) by the formula $E = \frac{0,7kT_M^2}{T_2 - T_1}$ [9, 10] is 0,08 eV. In papers [11÷14] it is shown that at big degree of initial filling of happing centres expression for TSC initial curve rise has a form:

$$J = const\exp\left(-\frac{E_t}{2kT}\right) \qquad (2)$$

Trap deposit depth calculated by the formula (2) for temperatures 140÷200 K is equal to 0,12 eV. The same value E_t is found from temperature dependence of electroconductivity. So in this case condition $n_{t_0} = N_t$ is fulfilled, i.e. the condition of big degree of initial filling of trapping centres. Defined trap deposit depth for low-temperature peak (T_M=80 K) from works [7, 15, 16] is unlikely (Table 2) as from TSC theory it is known that deposit depth of low-temperature peat must be less than high-temperature one, i.e. at first there have been unfilled shallow adhesion levels, then deep ones.

By various methods TSC curves there has been calculated deposit depth, concentration and capture crass-section of traps which values are given in Table 2. In this case carrier mobility μ_p and effective density of states in valence band N_V are taken as 75 cm^2/Vs and $1,08\cdot10^{19}$s, respectively [17]. Charge carrier lifetime is measured at temperature corresponding to TSC maxima by the method given in paper [18] and varied within $10^{-4} \div 10^{-3}$ s.

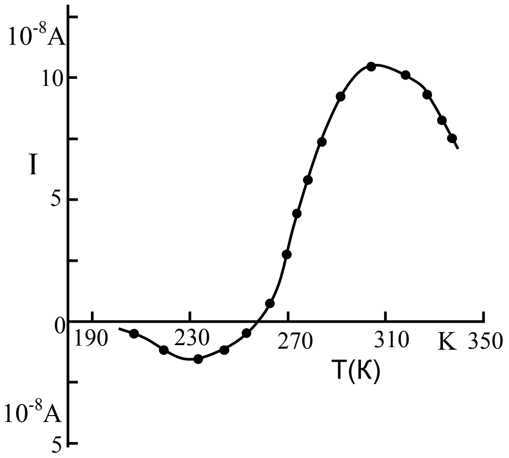

Fig. 4. Thermodepolarization current in GaSe:0,3 at.% Re single crystals.

The use of various methods for TSC mechanism determination shows that formulae referring to quick levels of adhesion and being independent of recapture are in a good agreement. In GaSe: 0,1 at.% Re single crystals levels of adhesion with energy 0,27; 0,34; 0,43 eV are arranged above the top of valence band and they are the levels of adhesion for holes.

V. CONCLUSION

For comparison with TSC doped samples there has been also studied TSC of GaSe undoped single crystals. As it is seen from Fig. 3 TSC of such samples has a maximum at temperature 92 K. With the increase of electric field the maximum temperature does not change and TSC current value in maximum rises on voltage quadratically.

In Fig. 4 there has been given TSD current curve of GaSe: 0,3 at.% Re single crystal. In this case at temperature 77 K trap filling by injected carriers is made out by applying to the crystal constant electric field from non-linear region of VAC in the darkness. After taking off external voltage the samples are heated with constant speed 0,54 K/s and short-circuit current is measured. It is seen that on TSD two peaks with maximum at 230 and 305 K have been revealed. Trap deposit depth determined by method of various heating rates in peak half-width and from initial current rise are 0,38 and 0,55 eV. Thus as a result of VAC, TSC temperature dependence of dark current and TSD in GaSe: Re single crystal it is established that GaSe single crystal doping by Re transition element leads to the compensation of shallow acceptor centres and creates new recombination and adhesion centres in band gap. Increase of Re percentage in GaSe single crystals brings about the increase of specific resistance and photosensitivity in impurity region of absorption.

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