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TRANSPORT PHENOMENA IN SINGLE CRYSTALS $Tl_{1-X}In_{1-X}Ge_XSe_2$ (x=0.1, 0.2)

ZJAWISKA TRANSPORTU W MONOKRYSZTAŁACH $Tl_{1-X}In_{1-X}Ge_XSe_2$ (x=0.1, 0.2)

Temperature dependences of electroconductivity for single crystals $Tl_{1-x}In_{1-x}Ge_xSe_2$ were analyzed. It was established an occurrence of thermoactivated states within the temperature range 100-300 K. The conductivity is formed by delocalized carriers within the conductivity band and the jumping conductivity over the localized states which are situated in the narrow localized states near the Fermi level. Following the performed data the activation energy was evaluated with accuracy up to 0.02 eV. The density of the localized states as well as the distribution of the energy over the mentioned states was evaluated. Additionally the average distance between the localized states is evaluated at different temperatures.

Keywords: $Tl_{1-x}In_{1-x}Ge_xSe_2$ single crystal, chalcogenide crystals, transport features, photoinduced birefringence, electroconductivity mechanisms, Urbach rule.

Analizowano zależności temperaturowe przewodności elektrycznej dla monokryształów $Tl_{1-x}In_{1-x}Ge_xSe_2$. Ustalono pojawienie się stanów termo-aktywnych w zakresie temperatur 100-300 K. Przewodnictwo tworzone jest przez zdelokalizowane nośniki w paśmie przewodnictwa i skoki przewodnictwa po stanach zlokalizowanych, znajdujących się w wąskich zlokalizowanych stanach w pobliżu poziomu energii Fermiego. Wartość energii aktywacji oszacowano z dokładnością do 0,02 eV. Wyznaczono wartości gęstości stanów zlokalizowanych, jak i rozkład energii na wymienionych stanach. Dodatkowo w różnych temperaturach oszacowano średnią odległość pomiędzy stanami zlokalizowanymi.

1. Introduction

The group of ternary compounds possessing a formula $TlB^{III}C^{VI}_2$ (B=In, Ga, C=S, Se, Te), have very strong anisotropic layered structure. They are characterized by a well pronounced anisotropy. Their are characterized by anisotropic features defined by their crystalline structure [1]. The interest to their exploration is caused by their possible use as polarizers, filters and IR modulators [2, 3]. Moreover, using the $TlInSe_2$ and $TlInTe_2$ it was manufactured ultra-fast photoresists and detectors of X-ray illumination [4-10]. In particularly using $TlInSe_2$ single crystals there were explorer electrical, photoelectrical properties, which allow applying them as X-ray dosimeter. In the ref. [11] an influence of Ag, Cu and Au on electroconductivity properties of the $TlInSe_2$ was studied.

For the further their modification in the desired directions we have carried out cationic substitution of the corresponding ternary compounds $TlInSe_2$. Earlier we have carried out investigations of optical, structural and photoelectrical features [12-15] of the crystals based in the $TlInSe_2$.

In the present work we have performed studies of transport and photoinduced features for solid state alloys $Tl_{1-x}In_{1-x}Ge_xSe_2$ (x=0.1; 0.2), which are created in the system $TlInSe_2$–$GeSe_2$.

2. Experimental

The titled crystals were grown by Bridgman-Stockbarger method in vertical two-zone furnace. The melt of the crystals were moved along the fixed gradient of the furnace [16]. Te such grown crystals had layered structure and were easy cleaved by the mirror stacking planes. They were in a form of parallelepipeds. The crystalline surfaces were mirror-like which allows to use them without any additional treatment.

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The Ohmic contacts were deposited on the fresh cleavage by melting of In on the opposite faces. The measurements of the temperature dependences were conducted at fixed current within the temperature range 100 K …300 K. Thermoregulation were performed by thermo regulator system UTRECS K41. The accuracy of temperature stabilization was equal to about ±0.1 K. The current measurements were done by electrometer Keithley 6514.

The transport properties were explorer within a framework of Mott theory [17-18]. The dark electroconductivity and concentration of the shallow levels (N_t) were evaluated following the expressions presented in the ref. [18].

3. Results and discussion

The single crystals of $Tl_{1-x}In_{1-x}Ge_xSe_2$ are high Ohmic semiconductors with p-type conductivity. The deep acceptor cationic vacancies near the bottom of the valence band form hole type of conductivity. With increasing of x from 0.1 up to 0.2 the conductivity type the conduction type remains the same due to lower content of the doping Ge atoms with respect to the stoichiometric vacancies and other structural defects. The high concentration of V_{Tl}, is caused by partial occupation by Tl atoms of the crystallographic site position *4a* as well as by statistical replacement o the in atoms by Ge atoms in the positions *4b* [16] . Additional some role begins to play a presence of other defects, which cause disturbance of the long range ordering for the perfect crystalline positions [17]. This one leads to occurrence of additional levels within the energy gap which do the solid state alloys compounds more close to the disordered materials. Their physical properties are substantially different with respect to the long-range ordered crystals. This is clearly seen in the Urbach edge [3, 15]. During the processes of charge transfer there exists a temperature dependence of v $\sigma(T)$ which may be presented in the coordinas In $\sigma - 1/T$ by straights with different activation energies correspond to different transport origins [18].

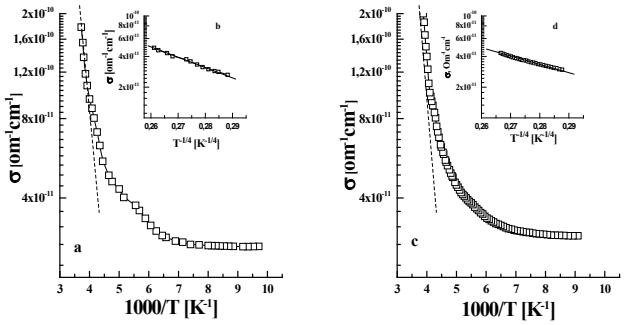

Fig. 1. Temperature dependence of dark electroconductivity for crystals $Tl_{1-x}In_{1-x}Ge_xSe_2$: a, b x = 0.1; c, d x = 0.2

The temperature dependences of the dark electroconductivity are show in the Fig. 1. For crystals $Tl_{1-x}In_{1-x}Ge_xSe_2$ at x=0.1 (a, b) and x=0.2 (e, d), in the coordinates Arrenius (Fig. 1 a, c) and in Mott coordinates (Fig. 1 b, d), respectively. Following the Fig. 1 (a, c) for the temperature range 240–300 K for the both figures one can observe exponential dependences. The evaluated activation energies for this temperature range were equal to 0.33 and 0.29 eV for the crystals with x=0.1 and x=0.2, respectively. The exponential coefficient value σ_0 in this range following the Mott rule [18] corresponds to excitation of carriers near the Fermi level E_F into localized states in the tails of valence band. With increasing x activation energy is decreased due to decrease of energy distances between the defect sub-band and localized states.

This is caused by a fact that the broadening of defect sub-band is increased doe to increasing defect content, which is confirmed by references [3, 15]. Following the ref. [20], for alloys possessing donor defects (Ge_{In}) and acceptors (V_{Tl}), the Fermi energy is situated within the forbidden gap which forms the maximal density of electron states. So, one can say that the established above activation energies correspond to energy positions of acceptor levels.

During decreasing temperature one can observe continuous decrease of activation energy evaluated from electroconductivity. Temperature dependence of electroconductivity which is characterized by monotonous decrease of electroconductivity in the Mott coordinates (In σ versus $T^{-1/4}$) is presented in the Fig. 1 (b, d). One can see that experimental points within the 145–215 K and 150–210 K temperature range are good fitted for these coordinates. This one allows to assume that for the titled crystals charge transfer along the layers is performed due to jump conductivity of charge carriers thorough localized states which are situated in the narrow band near the Fermi level [19]. In this case the electroconductivity is described by Mott expressions.

Following the slope of the In σ versus $T^{-1/4}$ it was established T_0, which were equal to 8.8×10^5 K and 5.6×10^5 K for x=0.1 and 0.2 respectively. Assuming that the localization radius is equal to typical radius if the bound exciton for crystals $A^{III}B^{III}C_2^{VI}$ (a=20Å) [21], we have evaluated density of localized states near the Fermi energy near the Fermi level (N_F): 2.65×10^{19} $eV^{-1}cm^{-1}$ and 4.18×10^{19} $eV^{-1}cm^{-1}$ for x=0.1 and x=0.2, respectively.

The relatively huge magnitude of N_F obtained for the studies crystals confirms on their close features to amorphous semiconductor with respect to energy structure. The anisotropy of the chemical bonds for the layers structures favors an occurrence of much kind of defects in the range of the layer's stacking, impurities, vacancies and dislocations. This one leads to disturbances of the crystalline periodical long range ordering, occurrence of localized states.

We have defined the lengths of jumps R for charge carriers through the localized states near energy Fermi at different temperatures. It was established that for x=0.1 at T=145 K, R=66 Å, and at T=215 K, R=60 Å. The average jumping length for the given temperature range is equal to R_{cp}=63 Å, which is all most 3 times higher than average distance between the localized carrier's centers (a=20Å). For x=0.2 at T=150 K, R = 59 Å at T=210 K, R=54 Å. The average distance of the jumps for the temperature range 150-210 K was equal to R_{av}=56.5 Å, which is al most 2.8 times higher then the average distance between the localized carrier's distances.

One can see that with decreasing temperature the average jump's distances is increased. This fact is explained by an enhanced probability enhancement for higher distances, which

are energetically more close to the localized center's positions [21].

Applying the same approach we have estimated distribution of the trapping levels near Fermi level (ΔE) and concentration of shallow levels (N_t) (see TABLE 1).

TABLE 1
The average jump length distance and distribution of the localized states for $Tl_{1-x}In_{1-x}Ge_xSe_2$.

$Tl_{1-x}In_{1-x}Ge_xSe_2$	T [K]	R [Å]	ΔE [meV]	N_t [cm^{-3}]
***x*=0.1**	145	66	62	1.65×10^{18}
	215	60	84	2.22×10^{18}
***x*=0.2**	150	59	57	2.38×10^{18}
	210	54	73	3.06×10^{18}

Following the obtained results the cationic substitution for $Tl_{1-x}In_{1-x}Ge_xSe_2$ favors enhanced degree of disordering and leads to increasing content of localization electronic states. So in the temperature range 145…210 K for the titled samples there is observed a jumping conductivity with the varying jump length through the localized states near Fermi level. At T<145 K the conductivity of the crystals is independent on temperature. This one confirms a fact that at T<145 K there is observed non-activation jumping conductivity.

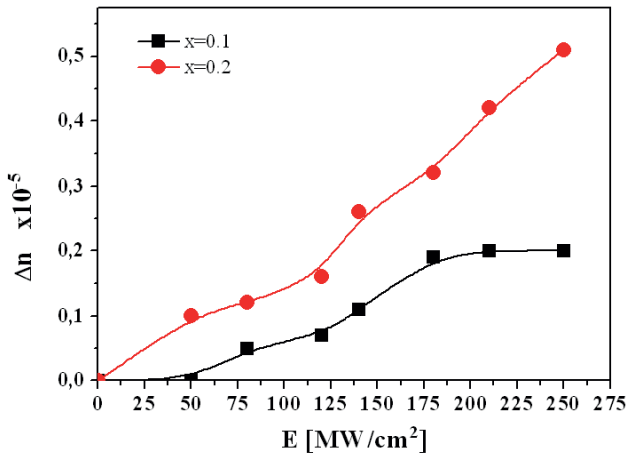

Fig. 2. Dependence of birefringence versus photoinduced power density

To *x*=0.1 these changes are almost two times stronger, which confirm the obtained transport data. Confirm the presented models we have studied the photoinduced birefringence of the two crystals at wavelength 2 μm (see Fig. 2).

4. Conclusions

Following the obtained by us experimental results it was established that for the solid state alloys $Tl_{1-x}In_{1-x}Ge_xSe_2$ during decreasing temperature from 300 up to 240 K the conductivity by conduction band is carried out by thermoexcitaton of impurity carriers with activation energies ~ 0.33 eV and 0.29 eV for x = 0.1 and 0.2, respectively. With the further decrease of temperature there is observed monotonous decrease of activation energy. In the temperature range 145<T<215 K the electroconductivity of the titled crystals is performed by jumps through the localized states near the Fermi level. One can say about the jumping conductivity with varied jump's length, which with the further decrease of temperature becomes non-activated.

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