Photo - Induced Current Transient Spectroscopy of $TlInS_2$ Layered Crystals Doped by Er, B and Tb Impurities

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The photo-induced current transient spectroscopy (PICTS) has been utilized to study electrically active defects in $TlInS_2$ single crystals doped by Er, B and Tb. Eight traps with activation energies lying in between 0.21 to 0.55 eV have been detected. The origin of these traps is discussed.

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The investigation of defects in layered ferroelectrics -semiconductors is of significant interest related to the expected application of these materials in high sensitive UV photo detectors, and to a possibility to examine ferroelectric phase transitions in the presence of defects' activity[1)]. As far as a ferroelectric-semiconductor is concerned, research technique applied to semiconductors to study defect levels is becoming less effective for the uncontrollable activity of the intrinsic electric fields caused by ~~a~~ domain structure of the crystals. The photo-induced current transient spectroscopy (PICTS)[2)] that is a kind of DLTS technique in which light excitation is used to fill the traps is considered to be more appropriate to the case. Here we present the results of PICTS studies of the $TlInS_2$ single crystals which were doped by erbium and terbium as well as non-active "usual" boron impurity[3)] for the first time to our knowledge.

Single crystals of $TlInS_2$ have been grown by the Bridgman – Stockbarger method from a stoichiometric melt of the starting materials sealed in evacuated (10^{-5} Torr) silica ampoule with a tip at the bottom. The doping was performed by introducing the relevant portions of Er, B or Tb (0.1 at. %) into a cell with preliminarily synthesized $TlInS_2$. The obtained $TlInS_2$ crystals were of *p*-type with hole concentration about 10^{13} cm^3 at room temperature. Typical size of the investigated samples was 2 x 4 x 1 mm^3. The photocurrent measurements were performed along the in-layer-plane directions of the samples with indium contacts soldered to lateral sides of the samples. The excitation light beam with $h\upsilon$ = 2.15-2.30 eV that corresponds to the maximum photoresponse was normal to the layer plane of the samples. The photon flux density at the sample surface was of 10^{14} $cm^{-2}s^{-1}$. The experimental set-up was described in detail elsewhere.[4)] The point-wise accumulation and averaging was carried out across 64 realizations of photoresponse decay containing 2000 samplings located at the fixed time interval $\Delta t = 5 \cdot 10^{-5}$ s. The registration of photoresponse

decays was performed over the temperature range 78 -330 K with a temperature step of 1 K. The temperature change was performed with a heating rate of 2 K/min. For the photoresponse transient analysis we used a conventional DLTS technique using a rectangular lock-in weighting function.

The typical PICTS spectra obtained on doped samples are shown in Fig. 1. Eight distinct traps recharging processes have been detected in the 100-300 K temperature range. Corresponding maxima are marked by vertical arrows and labels assigned to the traps. Regular shift of the temperature positions of these maxima allows to associating them with charge carrier emission from the traps filled at photoexcitation. The Arrhenius plots for the detected traps are presented in Fig. 2. The characteristics of traps are shown in Table I. We proposed that the detected traps are acceptor-type since traps of majority carriers are observed for the most part in high - resistivity semiconductors with a wide band gap.[5)]

The most prominent feature of the low temperature spectra of doped crystals was the signal from BTE43 trap. This maximum was also clearly observed in the spectrum of a sample doped by boron on a wing of more intensive maximum B5. It means that this trap has a native origin The temperature dependence of the photocurrent is shown in Fig. 3. It is seen, that thermal activation of photosensitivity is observed for BTE43 trap. This effect is more pronounced in erbium and terbium doped samples and corresponds to a hole trap. We assume that this defect is caused by indium vacancy just the same as acceptor-like gallium vacancy (V_{Ga}) is registered in more investigated GaSe crystals independent of crystal doping.[6,7)]

Observation of recharging of the traps marked as B3, B5, B6 and B7 only in the boron-doped samples indicates that they have impurity origin. Interesting that the B5 trap recharging is detected in the vicinity of transition temperatures from ferroelectric to

incommensurate phase at 201K, and from incommensurate to normal phase at 216K. On the other hand, the photosensitivity of a boron-doped sample changes insignificantly in the temperature region of B5, B6, B7 peaks, whereas for samples doped by rare earth they decrease considerably (see fig. 3). The photoresponse magnitude of these samples is less than that for $TlInS_2$:B by two orders of magnitude. It is also necessary to take into account, that in this temperature region the photoresponse of the investigated samples included a significant additional noise component connected with electric instability, typical of this crystal. Thus, we have no opportunities to judge about the connection of B5, B6, B7 with boron impurity at the present stage. We can conclude only, that B3 trap is due to boron impurity. The TE2 and TE54 traps are probably connected with dopant atoms as they are detected only on samples doped by rare earths.

Thus, traps recharging with thermal activation energies E_t = 0.21 - 0.55 eV were found in ferroelectric - semiconductor $TlInS_2$ by PICTS technique. From comparison of results received on samples with various dopants, it was established that B3 trap with E_t = 0.33 eV is connected with boron impurity. TE2, TE54 traps with E_t = 0.21 and 0.32 eV are connected with rare earth impurities. Interpretation of the trap with E_t = 0.27 eV as native hole trap (indium vacancy) is also proposed.

Acknowledgments

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Figure captions

Figure 1. PICTS spectrums corresponding to emission rate of 80 s^{-1}, obtained for an optical pulse duration of 27.5 ms on the variously doped samples under applied voltage of 9 V. Spectra are normalized to the height of the peak maximum and smoothed by weighted-averaging over 10 temperature points.

Figure 2. The rate of charge carrier emission from traps as a function of temperature with taking into account T^2 correction. Solid lines represent the fitting to experimental data.

Figure 3. Photoresponse of samples as a function of temperature.

Table I. Parameters of traps.

Trap	Temperatures of recharge detection (K)	Tthermal activation energy (eV)	Apparent capture cross section (cm^2)
TE2	100-120	0.21	$4.2 \cdot 10^{-13}$
BT23	114-130	0.23	$1.3 \cdot 10^{-13}$
B3	133-157	0.33	$2.3 \cdot 10^{-11}$
BTE43	147-178	0.27	$1.2 \cdot 10^{-14}$
B5	175-217	0.24	$3.5 \cdot 10^{-17}$
B6	218-239	0.55	$1.2 \cdot 10^{-11}$
B7	244-285	0.48	$2.0 \cdot 10^{-14}$
TE54	272-299	0.32	$1.4 \cdot 10^{-18}$

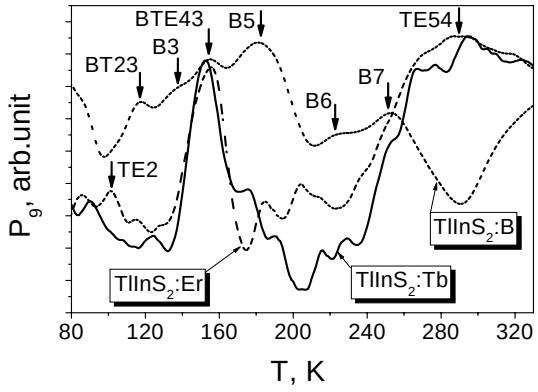
BTE43
B5
TE54
B3
BT23
B7
B6
TE2
TlInS2:B
TlInS2:Er
TlInS2:Tb
Pg, arb.unit
80
120
160
200
240
280
320
T, K

Fig. 1

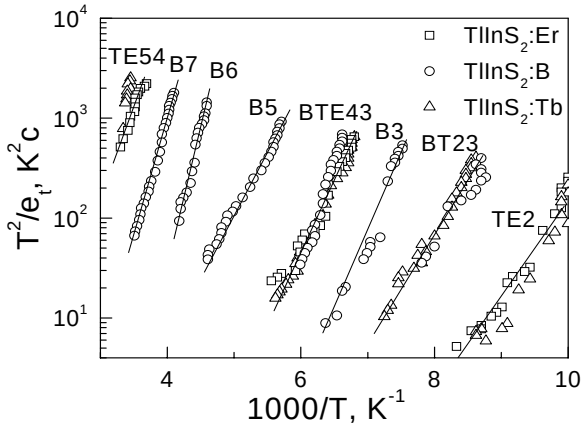
TlInS2:Er
TlInS2:B
TlInS2:Tb
TE54
B7
B6
B5
BTE43
B3
BT23
TE2
T2/et, K2c
1000/T, K-1

Fig. 2

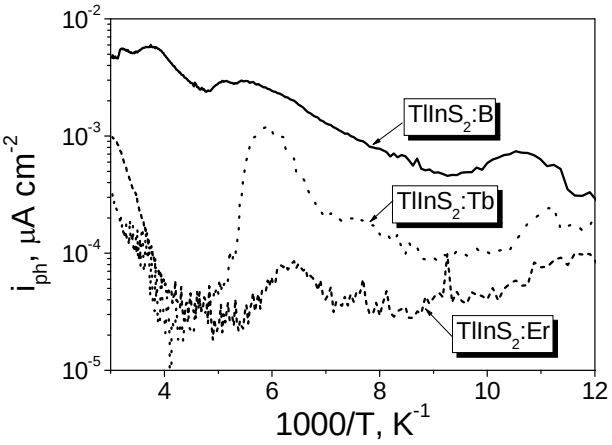
10^{-2}
10^{-3}
10^{-4}
10^{-5}
i_{ph}, μA cm^{-2}
TlInS$_2$:B
TlInS$_2$:Tb
TlInS$_2$:Er
4
6
8
10
12
1000/T, K^{-1}

Fig. 3