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Effect of Illumination Temperature on Thermally Stimulated Current Spectrum of $TlInS_2$

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Abstract

The effect of pre-illumination on both thermally stimulated current and photocurrent spectra of TlInS2 crystal is investigated. The increase in the photosensitivity of the crystal by several orders of magnitude together with the appearance of a new peak in the thermally stimulated current spectrum are observed as a result of the pre-illumination process. The filling of the traps, especially the sensitizing centers, during the pre-illumination is found to be the most favourable physical mechanism to explain the results.

1. Introduction

A large number of investigations published in the literature reveal that the thermally stimulated current (TSC) [1], photocurrent (PC) and photoluminescence (PL) characteristics of various crystals are strongly dependent on illumination conditions. Various models are used to explain the effect and some of them are based on the photochemical reaction (PCR) process [2-5]. According to the PCR model, the creation or destruction of various local centers in the forbidden gap of a semiconductor is possible during heat treatment under illumination.

In this work, we report the results of investigations of the TSC and PC of the layered semiconductor $TlInS_2$ which are greatly influenced by temperature and dose of pre-illumination. The results are discussed by considering the important role of the sensitizing

centers [6] in $TlInS_2$.

2. Experimental

The samples used in this study are $TlInS_2$ crystals with high resistivity ($> 10^{11}\Omega$.cm at 300 K) grown in an evacuated quartz ampoule by the use of modified Bridgman method. Because of the Van der Waals interlayer bonds, the crystals are easily cleaved into plates parallel to the layers. The cleaved surfaces of the samples are mirror like and do not require any subsequent treatment. These crystals are grown in the laboratory of the Institute of Physics of Azerbaijan Academy of Sciences and all the measurements are carried out in the TSC laboratory in the Physics Department of Middle East Technical University. The measurements are performed on the samples in the direction perpendicular to the layers. The electrodes are formed by evaporation of gold with thickness of 2000 Å on to the front and back faces of each sample (6 x 6 x 0.5 mm^3) parallel to the layers. The electrode on the front face of the sample is formed with a window having 3 mm diameter in the center to allow for the surface illumination. Thin copper wires are attached to the electrodes by indium soldering. The samples are annealed at $\sim$ 340 K for 2 hours in a vacuum of 0.1 Pa before their use, in order to avoid adsorbates on the surfaces.

The TSC measurements are carried out in the temperature interval between $\sim$ 90 K and 300 K at a constant heating rate of 0.1 Ks^{-1} by the use of a liquid nitrogen cryostat and a temperature controller. The temperature is measured with an accuracy of 0.1 K. The data are collected at a temperature increment of 0.2 K and stored during the measurements in an IBM compatible personal computer through a Keithley-DAS8 A/D converter which facilitated the precise data collection and ease of the data processing.

A light from a tungsten halogen light source of 50 mW/cm^2 with an appropriate interference filter allowing the photon energy close to the band gap of $TlInS_2$ is used for the TSC measurements. The photocurrent spectra are obtained at a constant temperature of 90 K and the data are collected at a wavelength increment of 1 nm in the range between 300 nm and 700 nm. The data of the photocurrent are corrected for the wavelength dependence of the intensity of the incident light. Both TSC and photocurrent spectra are obtained under an applied dc bias of 30 V.

3. Results and Discussion

As in the usual procedure of measurement of a TSC, the spectra shown in Fig.1 are obtained following the illumination of the sample for periods from 30 seconds to 5 minutes with a constant intensity of light having wavelength of $\sim$ 5200 Å at a temperature of $\sim$ 90 K. To keep the same initial conditions for TSC measurements, the sample is always cooled down from 300 K to 90 K in dark. The trapping parameters of $TlInS_2$ were presented in our previous paper [7] and low values of the capture cross sections were found for majority of the traps which were explained by considering the discommensurations in the commensurate ferroelectric state [8] of the crystal at temperatures lower than 200 K. The commensurate-incommensurate phase transition point is well registered in the TSC

spectra at $\sim$ 199 K and the TSC increases monotonically as the behaviour of the dark current at temperatures higher than $\sim$ 200 K [9].

The aim of the present work is to study the effect of illumination temperature on TSC spectrum of $TlInS_2$ crystals. The typical results from several measurements are presented here and qualitatively similar results are obtained on different samples from the same batch of the crystal. As can be seen in Figure 1, the intensities of the high temperature peaks increase gradually and eventually reach saturation levels with the illumination dose at 90 K; whereas the intensity of the low temperature peak at $\sim$ 100 K increases at a faster rate. On the other hand, in the low temperature region ($<$ 130 K) the TSC spectra of the sample illuminated at temperatures higher than 90 K is rather different than that of the sample illuminated at 90 K. The TSC spectra of $TlInS_2$ recorded after 5 minutes of illumination at temperatures of 110 K, 115 K and 120 K are shown in Figure 2. As can be seen in this figure, a new TSC peak at $\sim$ 125 K appears in the spectrum as a result of illumination at higher temperatures.

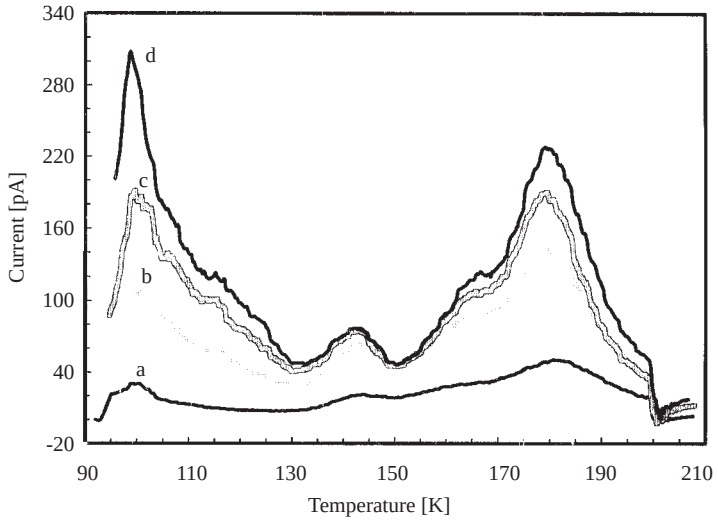

Figure 1. TSC spectra of $TlInS_2$ for illumination at 90 K for (a) 30 seconds, (b) 1 minute, (c) 2 minutes, and (d) 5 minutes.

The following experiment is carried out in order to check the importance of the illuminations at temperatures $>$ 90 K for the TSC spectrum. The sample is first subjected to illumination at 110 K for 5 minutes and then it is cooled down to 90 K and re-illuminated at this temperature for different periods of time from 10 seconds to 5 minutes (Figure 3 (b-d)). The TSC peak at $\sim$ 100 K for the pre-illuminated sample even after 10 seconds of illumination at 90 K has a significantly higher intensity than that for the sample illuminated only at 90 K even for much longer time (Figure 3 (a,b)). Meanwhile, the intensity of the TSC peak at $\sim$ 125 K of the pre-illuminated sample is strongly dependent on the

illumination time at 90 K. For the pre-illuminated sample, the intensity of the peak at $\sim$ 125 K decreases with the dose of illumination for high doses of illumination at 90 K (Figure 3 (b-d)).

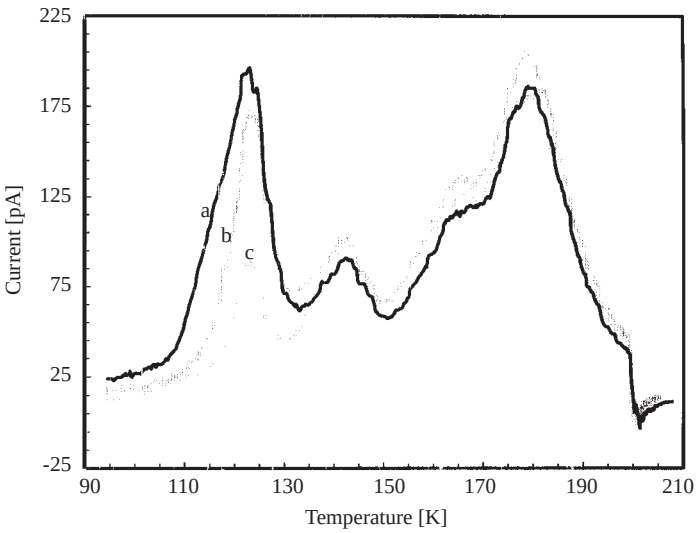

Figure 2. TSC spectra of $TlInS_2$ for illumination at (a) 110 K, (b) 115 K and (c) 120 K for 5 minutes.

These results may be interpreted as follows: The great increase of the intensity of the low temperature TSC peak at $\sim$ 100 K for the pre-illuminated sample may be due to the increase of photosensitivity of the crystal after filling of the traps, especially the sensitizing centers, during pre-illumination. If we suppose that the first TSC peak is associated with the electron traps, then the increase in the intensity of this peak must be due to the longer recombination time with the holes accumulated at the sensitizing centers which act as slow recombination centers. If such sensitizing centers are associated with the TSC peak at $\sim$ 125 K, then it is possible to understand the effect of illumination condition on the appearance of this peak in the spectrum. During the TSC process the electrons thermally released from the electron traps now recombine with holes in the sensitizing centers. Thus, it will be possible to observe the releasing of the holes from the sensitizing centers in the TSC spectrum, if the number of electrons in the electron traps are lower than that of the holes in the sensitizing centers. That is why the peak at $\sim$ 125 K can only clearly appear in the TSC spectrum when the electron traps are empty or only partially filled by a very short period of time of illumination at 90 K following the pre-illumination. For high doses of illumination ($>$ 5 minutes) at 90 K, the recombination of electrons with holes at the sensitizing centers leads to emptying of these centers almost completely and no clear peak at $\sim$ 125 K is apparent in the TSC

spectrum. So, even from the behaviour of the TSC spectrum alone, one can predict the increase of the photosensitivity of the crystal as a result of filling of the traps.

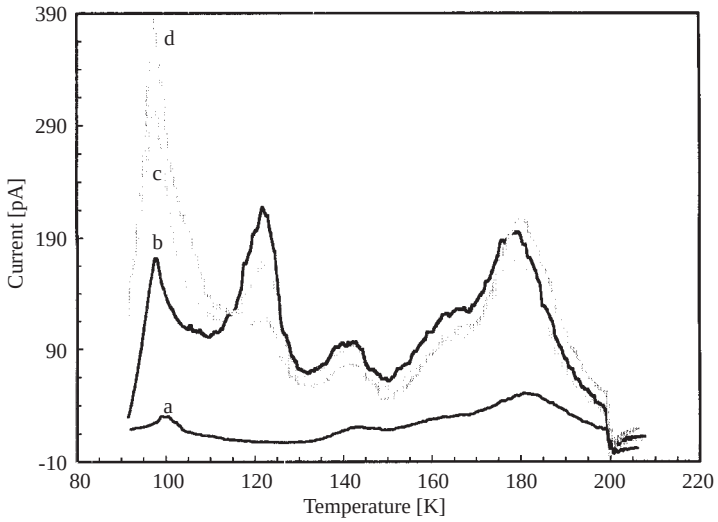

Figure 3. TSC spectra of $TlInS_2$ for illumination at 90 K for 30 seconds only (a). Curves (b), (c), and (d) are for 10 seconds, 30 seconds, and 5 minutes of illumination at 90 K, respectively following pre-illumination at 110 K for 5 minutes.

In order to verify the increase in the sensitivity of the crystal the photoconductivity spectra are studied with and without pre-illumination. The photoconductivity spectrum of $TlInS_2$ without pre-illumination recorded at 90 K reveals very small response without any clear structure for the maximum available intensity of light used in this investigation (Figure 4-a). If however, the sample is subjected to a pre-illumination with light having maximum available intensity at 90 K for 5 minutes, the intensity of the PC in all the investigated spectral region is increased and has a well pronounced peak in the region of direct optical transitions of $TlInS_2$ (Figure 4-b). The intensity of the PC is strongly dependent on the dose of pre-illumination and it decreases with the decrease of pre-illumination dose. The position of the sharp peak in the spectrum is very close to the energy of the free bandgap excitons in $TlInS_2$ [10,11]. Moreover, the high energy peak is also registered in the spectrum. According to the absorption spectrum of $TlInS_2$ crystals [10,11] this peak is attributed to deep excitons. The high values of the PC at energies lower than that of exciton peak may be due to the impurity photoconductivity. The absence of any discrete structure in this spectral region may confirm our previous suggestion [7] that the traps in $TlInS_2$ are closely spaced. The PC response of the pre-illuminated sample at 90 K is reduced considerably when the sample is subjected to a thermal annealing at temperature higher than 90 K. For example, the PC response of the pre-illuminated sample in the whole investigated spectral region is reduced to almost

one third of its original values after the sample had substantially been heated up to 130 K. When the thermal annealing temperature further increased from 130 K up to 190 K, the response gradually decreased and eventually reach below the detectable level under the given measurement conditions. These results also indicate that the most appreciable part of the effect is caused by the traps associated with the peaks below 130 K in the TSC spectra.

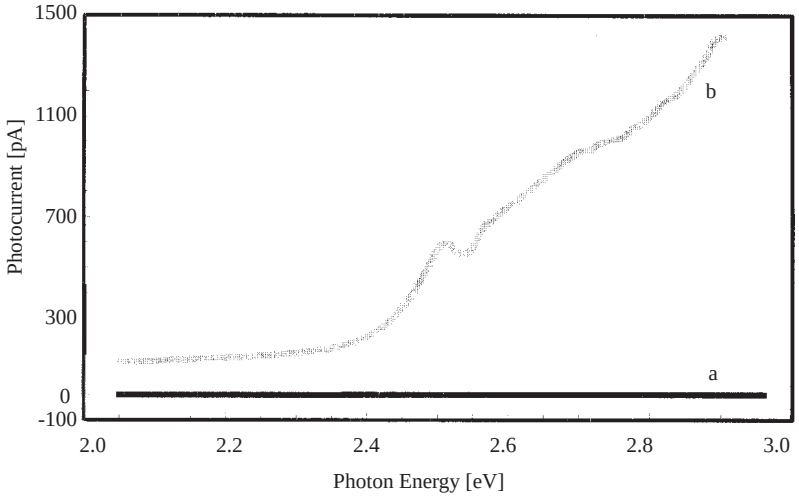

Figure 4. Photoconductivity spectra of $TlInS_2$ obtained at 90 K (a) before and (b) after pre-illumination at 90 K for 5 minutes.

The results show that the maximum increase of the photosensitivity after the pre-illumination is not only due to filling of the sensitizing centers but other traps must also be full. The increase of the photoconductivity alone after pre-illumination may simply be explained as follows: The increased PC observed after the traps are filled must be attributed to either an increased mobility or an increased lifetime of the photogenerated free carriers. Although we have not measured mobilities, we do not expect any appreciable part of this effect due to a change in mobility of the carriers, since no model exists to account for a very large mobilty changes. For example, the mobility should change over three orders of its magnitude to lead such a large amount of increase in the PC response after pre-illumination (Figure 3.b). Therefore, the effect may be attributed primarily to an increase in lifetime of the photogenerated carriers when the traps are filled. The dependence of lifetime of the photogenerated carriers on the trap population may be explained by the mechanism which involves the competition between recombination centers and the traps for the photogenerated carriers [3]. If the traps are empty and the trapping probabilities of all are extremely high, then the lifetime will be very short due to the dominance of the trapping process. When the traps are filled, trapping does not

play a role any longer and the longer lifetime determined by the recombination process dominates. According to this mechanism, the increase in PC only requires a filling of the traps. However, the behaviour of the first two peaks in the TSC spectra suggest that, at least some of the filled traps in $TlInS_2$ play a role as sensitizing centers. The increase in the intensity of TSC peak as well as photosensitivity as a result of pre-illumination has already been established in CdS crystals and the effect is explained by the different center transformation processes [4,5]. These processes include the Auger interaction of the fast recombination centers with donor-acceptor (DA) pairs. The energy released as a result of the recombination of the excited DA pairs is transformed to the electrons located in the sensitizing centers. Thus, it leads to accumulation of the holes in the sensitizing centers. For the realization of such transformation process, the illumination with a specific wavelength is required for a direct excitation of the DA pairs. Besides, the PCR process has a well defined temperature threshold due to its activation character [2,3]. Our results described above do not indicate any possibility of a PCR in $TlInS_2$ crystals at present time.

4. Conclusion

The intensity of the TSC peak at ~ 100 K corresponding to electron traps in $TlInS_2$ crystals can substantially be increased as a result of filling of the centers associated with the peaks at temperatures ≥ 125 K in the TSC spectrum. If the illumination temperature is low enough to fill the electron traps, then the electrons thermally released from these traps will lead to emptying of the sensitizing centers associated with the TSC peak at ~ 125 K by the recombination process. In this case, it will not be possible to observe the ~ 125 K peak clearly in the TSC spectrum. On the other hand, if the illumination temperature allows filling of the sensitizing centers rather than the electron traps, a new peak at ~ 125 K will appear in the TSC spectrum. Hence, at least some parts of the TSC spectrum of the $TlInS_2$ crystal is strongly dependent on the illumination temperature.

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