AC Photoconductivity Measurements of $TlInS_2$ Single Crystals

I.M. Ashraf[a], A. Salem[b,*] and M.J. Al-Salah[c]

[a]Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia

[b]Solid Sate Lab., Physics Department, Faculty of Science, South Valley University, Qena, Egypt

[c]College of Science and Arts, Najran University, Saudi Arabia

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$TlInS_2$ single crystal belonging to the group $A^{111}B^{111}C^{v1}$ gets a great attention nowadays due to its electrical and optical properties, which make it a good candidate for photoconductivity applications. In the present study, the dependence of the AC-photoconductivity of $TlInS_2$ single crystal on the chopping frequency was investigated by plotting $(\Delta\sigma/\Delta\sigma_{st} - \omega)$ versus the chopping frequency (15–300 Hz). The effect of different parameters including temperature (77–300 K), applied voltage (10–70 V), and light intensity (1000–7000 lx) on the dependence of AC-photoconductivity on the chopping frequency was studied. The results indicated that the AC-photoconductivity decreases with the increase in the chopping frequency regardless of the values of the effecting parameters (temperature, voltage, and light intensity). Due to its properties, $TlInS_2$ single crystals represent a promising material for using in photodetector and radiation visualizer employed in recording information in optical devices. Moreover, these materials are suitable for solar batteries due to its ability to generate appreciable quantity of electrical power from sun radiation.

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1. Introduction

The chalcogenides compound formed from elements of group III and VI in the periodic table are very important due to their practical applications in different fields, such as electronic devices, refrigerating materials, photovoltaic detectors, and optical devices [1]. In the last few years, there has been great interest in the investigation of physical properties of layered ternary crystal with chemical formula $TlMX_2$ (M = Ga, In, X = Se, S, Te). Thallium chalcogenides belong to the monoclinic system, and their space group is C_2/C at room temperature. The lattice of these crystals consists of alternating two-dimensional layers arranged parallel to the (001) plane [2].

$TlInS_2$, which is a member of this class of crystals, is a semiconductor with an indirect band gap of about 2.28 eV at room temperature [3]. Previous studies [4] showed that there were two forms of $TlInS_2$ — the high temperature polymorph (β) and the low temperature one (α). β-$TlInS_2$ is characterized by a yellow-orange color and melting point of about 1050 K, while α-$TlInS_2$ is characterized by a blackish color and a melting point of about 870 K. Serious disagreement exists in the literature concerning the structure of $TlInS_2$. It has been described only as monoclinic, tetragonal, or hexagonal [5]. In all the cases, the crystallographic c-axis is reported to be almost perpendicular to the cleavage plane between the layers. Adverse to the earlier studies, Alekperov and Nadzhafov [6, 7] investigated the crystallographic parameters for different poly types of $TlInS_2$. They found five crystal modifications of the $TlInS_2$. Four of them (monoclinic, triclinic, tetragonal, and orthorhombic) crystallize in the layered (triclinic and monoclinic) or chain-and-layered (orthorhombic and tetragonal) structure, while the fifth crystallizes in the hexagonal system. The lattice parameters c of these poly types differ from ≈ 15 to 120 Å, whereas a and b parameters ($a = 10.980$ Å and $b = 10.90$ Å for $c \approx 15$ Å). Slight change occurred only with increasing c. Aydinli et al. [8] showed from the photoluminescence (PL) spectra of $TlInS_2$ crystal in the 500–860 nm wavelength and in the temperature range 11.5–100 K that the PL intensities of the A and B bands reduce with increase of temperature. Rapid thermal quenching of the A band is observed above $T = 35$ K indicating the presences of a shallow impurity. This behavior is attributed to a shallow acceptor level located at 0.02 eV above the valence band in p-type $TlInS_2$.

Badr et al. [9] recently investigated the photoelectric properties of $TlInS_2$ layered single crystal, where the transmittance and reflectance spectra of $TlInS_2$ crystals were measured in the photon energy range 1.96–2.46 eV over the temperature range 77–300 K. The type of optical transition was marked and found to be an indirect allowed one. Optical properties of $TlInS_2$ layered single crystals have been studied by El-Nahass et al. [10]; absorption spectra of thin layers of $TlInS_2$ crystals are used to study the energy gap and the inter band transitions of the composition in the energy region 2–2.4 eV. Shim et al. [11] studied the light figure spectroscopy techniques in spectral range 400–700 nm in temperature

*corresponding author; e-mail: aasalem@kku.edu.sa

interval 80–350 K. As a whole, the obtained results allow for a conclusion that in-commensurate spatial modulation with correlation length at the nanoscale was contributing to biaxial anisotropy of $TlInS_2$ to a level of 10^{-3} versus 10^{-4} for basic lattice. A remarkable increase of the birefringence at photon energies approaching energy gap (2.4 eV) was observed [12] to be a good illustration of the fact that band gap exaction transitions in $TlInS_2$ at room temperature are allowed in $E \parallel c^*$ and forbidden in $E + c^*$ orientation, respectively.

In the present study, $TlInS_2$ single crystals was prepared by a new local technique called modified Bridgman–Stokbager method. In addition, photoconductivity (PC) for $TlInS_2$ single crystals was studied. The voltage, light intensity, and temperature dependences of carrier lifetime are reported and analyzed as results of the AC-PC measurements.

2. Experimental

$TlInS_2$ single crystal has been crystallized by the Bridgman technique [13]. $TlInS_2$ was prepared from high-purity (99.999%) thallium, indium, and sulphur as initial components. The ratios of components are 13.6256 g of thallium (43.221%), 11.4868 g of indium (36.437%), and 6.413 g of sulphur (20.342%). The modifications were studied by fusing the constituent elements into an evacuated (10^{-6} Torr) silica tube of 1.5 cm diameter and 20 cm in length. The crystal structure of the grown compound was investigated by using X-ray diffraction method at room temperature. The dynamics of the AC-photoconductivity was studied from its frequency dependence. A symmetric square light pulses were used for exciting the specimen under study with aid of a filament tungsten lamp of 1000 W. An optical system consisting of two convex lenses was used to collimate the incident light on the specimen. A variac transformer was connected to the tungsten lamb to control the intensity of the incident illumination on the specimen. To gain symmetric square light pulses, a mechanical chopping system was used, which consists of two parts: one of them is an ac stable motor (220 V) with which a dual aperture copper wheel makes symmetric square light pulses i.e. the incident light is interrupted by passing through the apertures of the rotating disc. The other part of the chopping system is a digital chopper controller with which the chopping frequency for the incident illumination is varying. A simplified representation of this circuit suggests that the specimen under study ($TlInS_2$ single crystals) is connected in series with DC power supply (by which the value of the applied voltage could be adjusted) and a suitable load resistance. Also, electrometer is connected in series for measuring the current. The diversity across the load resistance R due to the modulated AC-photoconductivity observed on a double beam oscilloscope, and could be measured by means of a valve microvoltmeter.

3. Results and discussion

3.1. Structural characteristics of $TlInS_2$ single crystals

The crystal structure of the grown crystal was investigated by X-ray diffraction (XRD) analysis at room temperature, using a modern automated and computerized diffractometer with Cu K_α radiation ($\lambda = 1.54$ Å). The XRD analysis results of $TlInS_2$ crystal in the powder form are shown in Fig. 1.

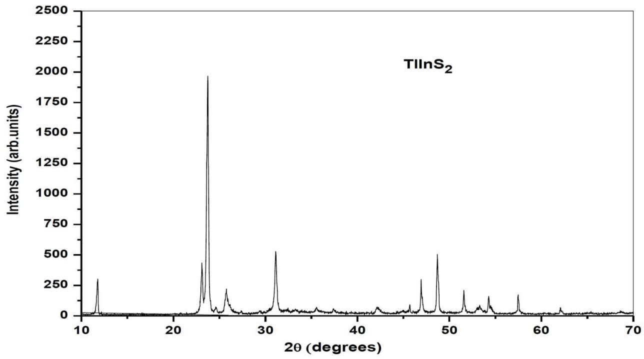

Fig. 1. XRD pattern of $TlInS_2$ single crystals.

3.2. AC-photoconductivity of $TlInS_2$ single crystals

The dynamics of the AC-photoconductivity for $TlInS_2$ single crystals are reported as results of the frequency dependence of the AC-photoconductivity for these crystals. The AC-photoconductivity measurements were carried out by plotting ($\Delta\sigma_\sim/\Delta\sigma_{st} - \omega$) versus the chopping frequency (ω) in the ranges from 15 to 300 Hz, where $\Delta\sigma_\sim$ is the AC-component of the AC- photoconductivity, $\Delta\sigma_{st}$ shows its fixed state and ω is the chopping frequency. Figure 2 clarifies the results of the AC-PC measurements for $TlInS_2$ single crystals in the temperature range from 77 to 300 K. This experiment was carried out

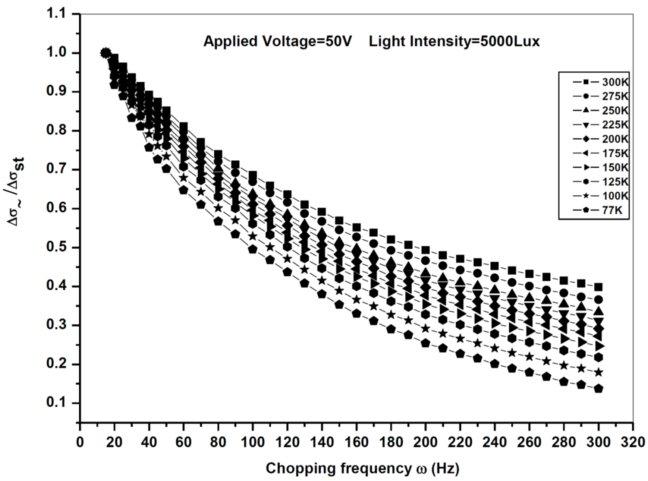

Fig. 2. The frequency dependence of AC-PC for $TlInS_2$ single crystal in the temperature range from 77 to 300 K.

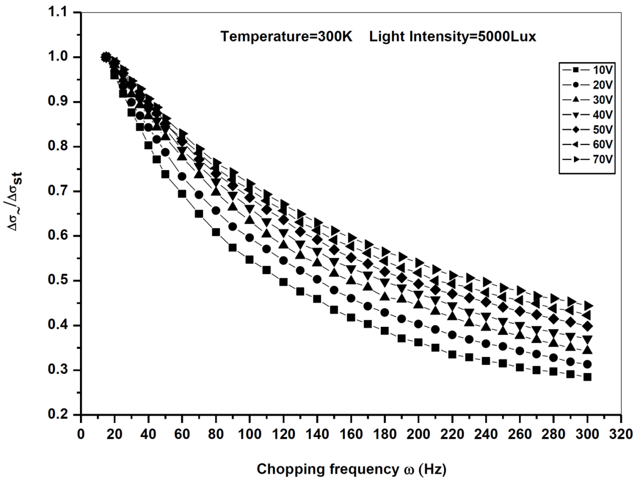

Fig. 3. The frequency dependence of AC-PC for TlInS$_2$ single crystal at different values of the applied voltage.

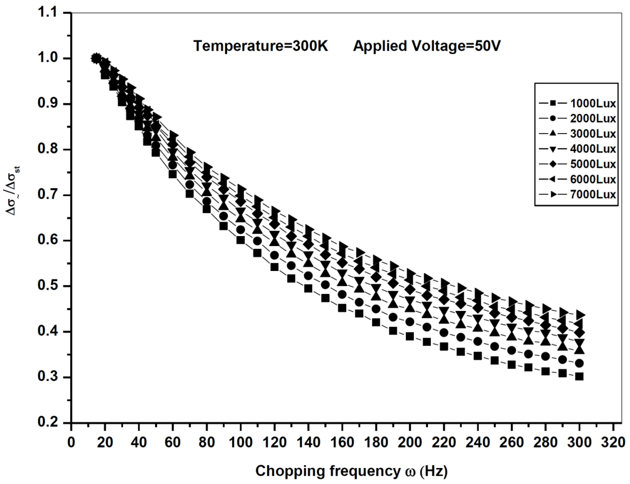

Fig. 4. The frequency dependence of AC-PC for TlInS$_2$ single crystal at different values of the light intensity.

for TlInS$_2$ single crystals by using an applied voltage of 50 V and 5000 lx of the light intensity was used for the excitation process. The attitudes of the curves are similar and have a general shape for all the temperature ranges under study. Figure 3 symbolizes the results of the AC-PC measurements for TlInS$_2$ single crystals, respectively with different values of the applied voltage. The frequency dependence results of the AC-photoconductivity for TlInS$_2$ single crystals in the chopping frequency from 15 to 300 Hz were measured at different values of the applied voltage (from 10 to 70 V) with fixed values of both temperature (300 K) and light intensity (5000 lx). Figure 4 describes the frequency dependence results of the AC-PC at different levels of illumination for the studied TlInS$_2$ single crystals that were measured in the light intensity ranges from 1000 to 7000 lx for TlInS$_2$ crystals. These experiments were carried out with fixed values of both the temperature and the applied voltage (300 K, 50 V). The AC-photoconductivity in all the above experiments decreases with the increase in the chopping frequency in the whole ranges of investigated frequency. Generally, the photo decay curves can be described empirically by the following function [14]:

$$\frac{\Delta\sigma_{\sim}(\omega)}{\Delta\sigma_{st}} \propto A\exp(-C\omega\alpha). \qquad (1)$$

The parameters C and α are independent of illumination intensity (I), voltage (V), and temperature (T), while the parameter A increases with increasing L, V, and T. This practical form is called the extended exponential. The rate of change is initially rapid but becomes slower as chopping frequency progresses. For a better understanding of the dynamic of charge carriers, it will be appropriate to discuss the dependence of the photo decay on the main effective parameters: frequency, temperature, bias voltage, and light intensity.

The general shape of decay curve can be divided into three regions.

1. Low frequency region extending from 15 Hz to 40 Hz: in this region the decay of photoconductivity is rapid with increase in the chopping frequency (ω). This is identical to the case where the allowed exposure time ($1/\omega$) is higher than the carrier lifetime (τ). The band-to-band recombination mechanism is more likely to dominate, since the steady state (before light cessation) is dominated by the same process. This high recombination process depends only on the life time of majority carriers.

2. Medium frequency region of the chopping frequency (ω) from 40 Hz to about 240 Hz: the fall of photoconductivity is not so rapid as in the first region, since the excess density of recombination centers is now decreased.

3. The elevated frequency region, from 240 Hz to 300 Hz: in this region, the decay is nearly frequency independent. In this region, multi trapping is expected, since there is the possibility for more than one trapping in a half cycle. If minority carriers are trapped first, the lifetime of majority carrier will not depend on the density of traps. Due to that, the concentration of trapped carriers builds up until the equal concentration of free electrons give a recombination rate equal to generation rate. At any certain temperature, other than zero kelvin, the recombination rate is considered nearly equal to the thermal generation rate. Therefore, at relatively higher frequencies the deterioration of photoconductivity and its dependence of chopper frequency is very weak, as observed experimentally in the present work.

The lifetime of the charge carriers can be evaluated for each temperature, applied voltage, and light intensity by using the relation [15]:

$$\frac{\Delta\sigma_{\sim}(\omega)}{\Delta\sigma_{st}} = \tanh\left(\frac{1}{4\tau\omega}\right), \qquad (2)$$

where τ is the lifetime of the charge carrier. This can be done by drawing a straight line parallel to the frequency axis at a height 0.76 of the $\Delta\sigma_{\sim}/\Delta\sigma_{st}$ axis (where tanh = 0.76) to intersect the curves at certain points. Then, if straight lines are drawn from these points perpendicular to the frequency axis, they cut off segments of the axis equal to $1/4\tau$ for each curve as in Fig. 5.

The temperature dependence of the AC-photoconductivity measurements results in the effects of temperature on the carrier lifetime for the studied $TlInS_2$ single crystals are described in Fig. 6. These figures suggest that the lifetime minimizes with increasing the temperature in all of the temperature ranges investigated (77 to 300 K).

The reduction in the carrier lifetime in this figure with the increase in temperature could be due to the trapping process [13], and the increase in the carrier concentrations. Using Fig. 7, the effects of applied voltage on the carrier lifetime for $TlInS_2$ single crystals was estimated, and these are presented graphically in Fig. 7. This figure suggest that the values of the lifetime decrease with increase in the applied voltage for all the studied $TlInS_2$ single crystals, which could be due to the trapping process and increase of carrier velocity leading according to the relation [16]:

$$\tau = (vSN)^{-1}, \qquad (3)$$

where S is the capture cross-section of the recombination centres, N is the carrier concentration, and v is the thermal velocity of the carriers ($\sqrt{2kT/m}$).

As results of the light intensity dependence of the AC-PC measurements (see Fig. 8), the effects of the light intensity on the carrier lifetime for $TlInS_2$ single crystals are presented graphically in Fig. 8. This figure suggests that the values of the lifetime decrease with the increase in the light intensity which could be due to that the probability of trapping increases with increase in the intensity of the exciting light [17].

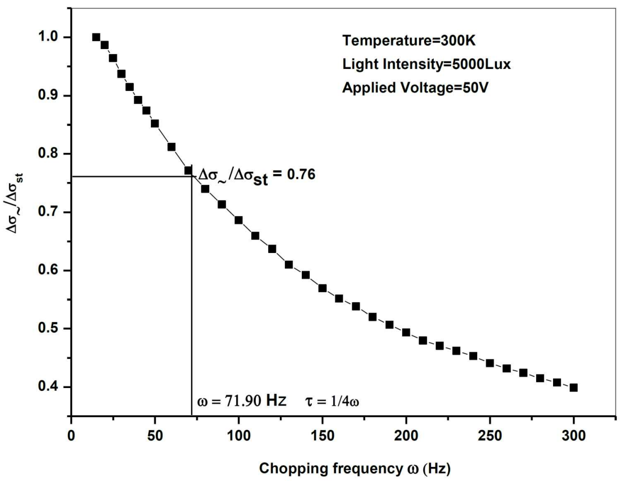

Fig. 5. Determine of carrier lifetime from the AC-PC measurements.

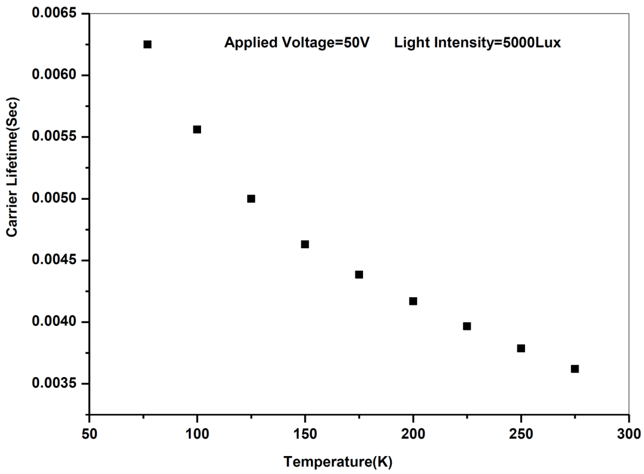

Fig. 6. The temperature dependence of carrier lifetime for $TlInS_2$ single crystal.

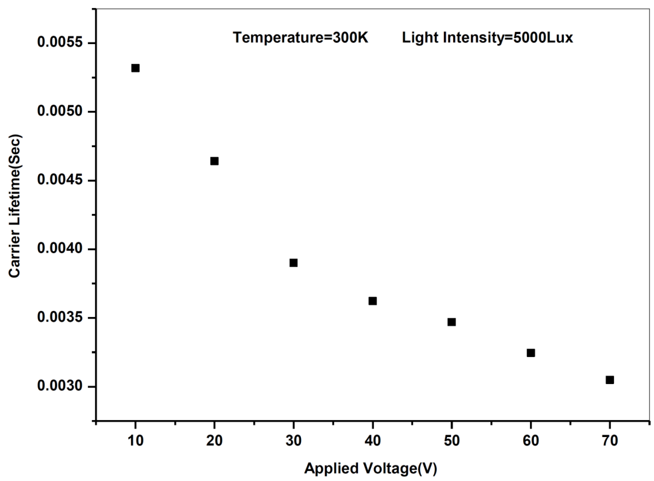

Fig. 7. As in Fig. 6, but for the applied voltage dependence.

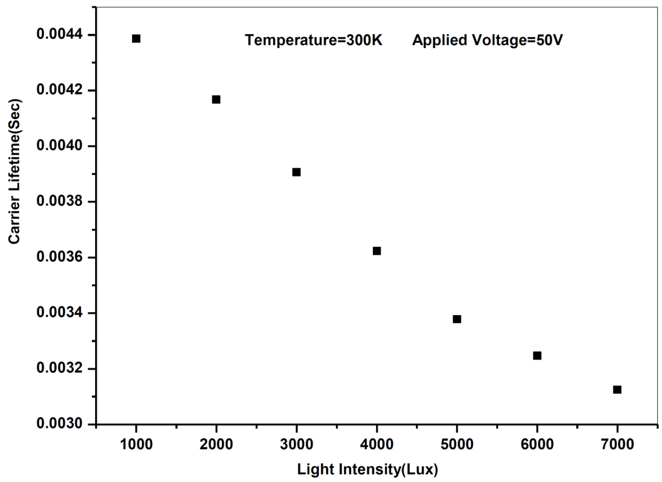

Fig. 8. As in Fig. 6, but for the light intensity dependence.

4. Conclusion

The AC-photoconductivity measurements was carried out in the temperature range from 77 to 300 K by plotting $(\Delta\sigma_{\sim}/\Delta\sigma_{st} - \omega)$ versus the chopping frequency (ω). The effect of different parameters including temperature (77–300 K), applied voltage (10–70 V) and light intensity (1000–7000 lx) on the dependence of AC-PC on the chopping frequency was studied. It was noticed that the AC-photoconductivity decreased with the increase in the chopping frequency in the whole ranges of investigated frequency. The lifetime of the charge carriers for each temperature, applied voltage, and light intensity has been evaluated. The results illustrate that the values of life time depend on the temperature, applied voltages, and the intensity of the light.

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