Optical properties of $TlInS_2$ layered single crystals near the absorption edge

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The sample thickness effect on the optical properties of $TlInS_2$ layered crystals has been investigated at room temperature. The absorption coefficient of the samples calculated from the experimental transmittance and reflectance in the photon energy range of 1.10–3.10 eV has two absorption regions. The first is a long-wavelength region of 1.16–1.28 eV. The second region lies above 2.21 eV with a thickness-dependent indirect band gap. The energy gap decreases from 2.333 to 2.255 eV as the sample thickness increases from 27 to 66 μm. The differential spectra of absorption coefficient demonstrates the existence of a thickness-dependent impurity level being lowered from 2.360 to 2.307 eV as sample thickness increases from 27 to 66 μm. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Layered semiconductors have become interesting due to their structural properties and potential optoelectronic applications. Their quasi two-dimensionality, structural anisotropy, optical and photoconductive properties, and other features attract investigators in an effort to acquire a better insight in the physics of these compounds. $TlInS_2$ belongs to the interesting $A^{III}B^{III}C_2^{VI}$ group of dichalcogenide semiconductors. This compound has attracted widespread attention for its structural [1], electrical, photoconductive [1, 2] and holographic properties [3]. Moreover, optical spectra in the region of fundamental absorption [2, 4] and two-photon absorption [5] have been studied.

In our previous papers we have investigated the photoluminescence (PL), the carrier scattering mechanism through Hall effect measurements, and the photoelectronic properties of $TlInS_2$ layered crystals. The PL spectra were studied in the 500–860 nm wavelength range and in the 11.5–100 K temperature range [6]. The study resulted in the observation of two PL bands centered at 2.41 and 1.52 eV. The Hall effect measurements revealed the existence of a set of donor energy levels located at 0.36, 0.28, 0.22 and 0.17 eV in the band gap of the material [7]. The study of temperature and illumination dependencies of the photoelectronic properties demonstrated the existence of the linear, sublinear and supralinear recombination mechanisms at low, moderate and high illumination intensities, respectively [8]. Previously, the absorption and reflection spectra of $TlInS_2$ crystal samples of thickness 3.0 μm [9], 10–20 μm [10–12] and 43 μm [13] were reported. All the data concerned the absorption and/or reflection spectra in the photon energy range above 2.20 eV as a function of temperature.

The aim of this work is to report the detailed information about the variation of the absorption coefficient, the band gap and the impurity energy level of $TlInS_2$ crystals with thickness.

2. Experimental details

$TlInS_2$ polycrystals were synthesized from the high purity elements (at least 99.999%) taken in stoichiometric proportions. The single crystals were grown by the modified Bridgman method. The X-ray diffraction patterns show that these crystals have monoclinic structure with the lattice parameters $a = 1.094$, $b = 1.048$, $c = 1.560$ nm and $\beta = 100.7°$. Samples with mirror-like surfaces were obtained by easy cleavage along the (001) plane, which is perpendicular to the c-axis. Typical sample size was $1 \times 1 \times t$ cm^3. The sample thickness was varied from 27 to 66 μm. The spectral dependencies of the optical transmit-

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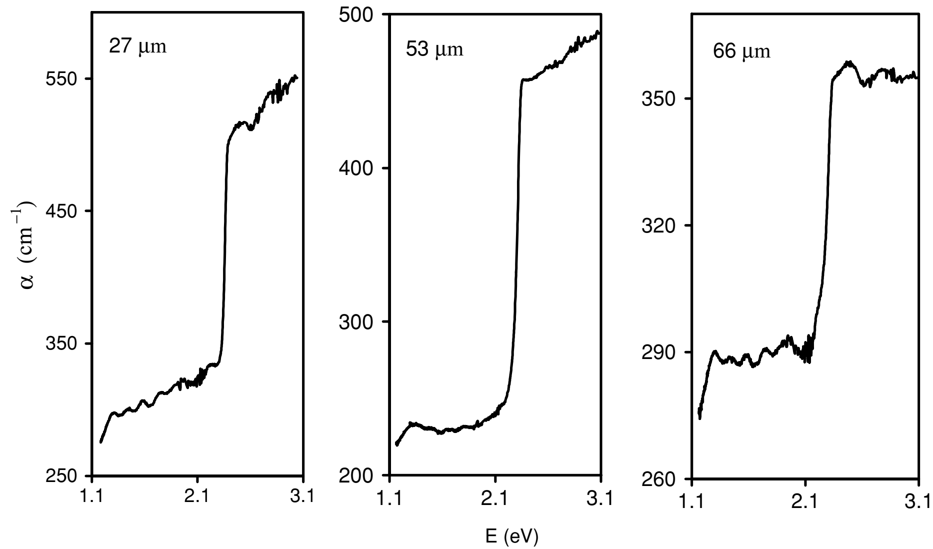

Figure 1 Spectral dependence of absorption coefficient of $TlInS_2$ for samples with different thickness.

tance and reflectance of the samples at room temperature in the photon energy range of 1.10–3.10 eV were handled using Hewlet Packard UV-VIS spectrophotometer.

3. Results and discussion

The spectral dependencies of the transmittance (T) and reflectance (R) of $TlInS_2$ crystals are being recorded for samples of different thickness, t, in the incident photon energy range (E) of 1.10–3.10 eV. The absorption coefficient, α, is related to T and R through the relation [14]

$$T = (1 - R)^2 \exp(-\alpha t). \tag{1}$$

Representative data of the spectral response of the absorption coefficient for different values of t are illustrated in Fig. 1. The value of absorption coefficient of $TlInS_2$ crystals increases in two main regions. In the long-wavelength absorption region $(1.16 \leq E \leq 1.28$ eV$)$, α is observed to increase moderately up to 1.28 eV. The second sharp absorption region relates to an incident photon energy range of ∼2.21–2.40 eV. Above 2.40 eV, absorption coefficient continues increasing smoothly.

The differential absorption spectra of $TlInS_2$ crystals, $d\alpha$, were then executed and illustrated in Fig. 2. It is seen from Fig. 2, that there exists intensive peak located at the energy position $E_1 = 2.360$ eV. This peak is observed to shift toward lower energy values as the sample thickness

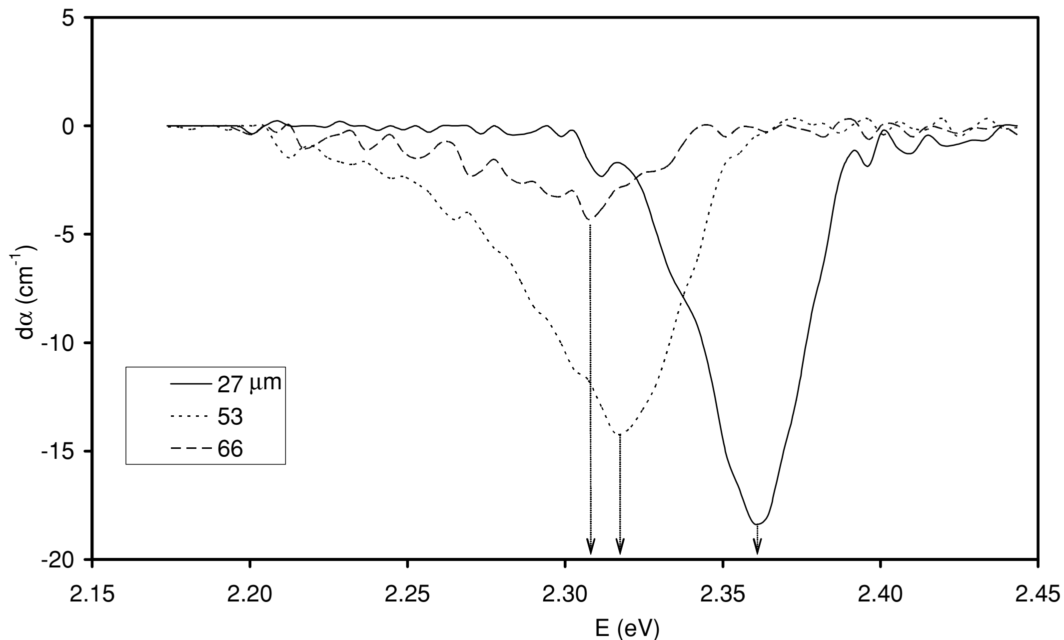

Figure 2 Dependence of $d\alpha$ on the photon energy at 300 K for $TlInS_2$ crystals.

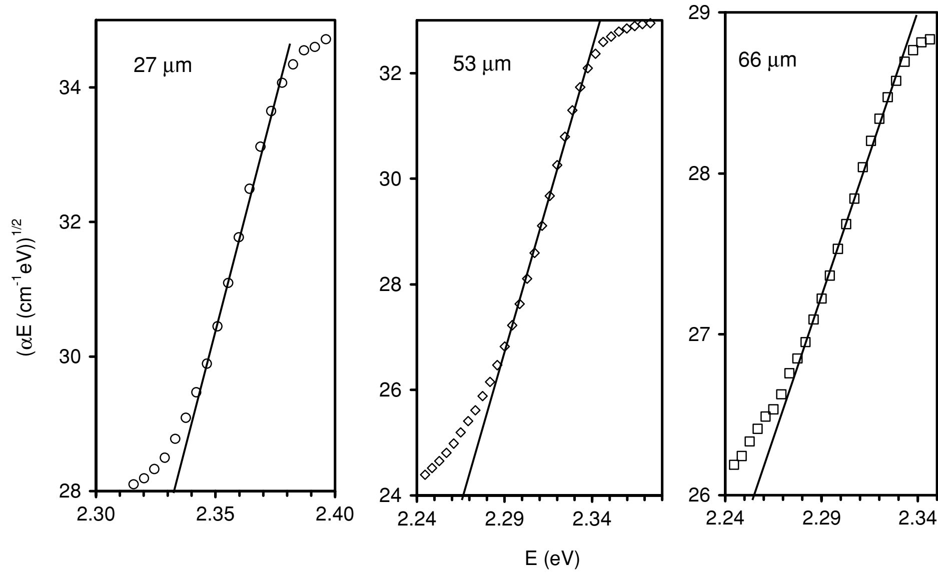

Figure 3 Plots of $(\alpha E)^{1/2}$ versus E for $TlInS_2$ crystals of various thickness in the energy region of 2.24–2.40 eV.

increases. The position of this peak is 2.360 eV for $t = 27\ \mu$m, 2.316 eV for $t = 53\ \mu$m and 2.307 eV for $t = 66\ \mu$m. The observed peak may be assigned to an impurity level existing in the band gap of $TlInS_2$ crystals.

To find out the character of optical transition in the crystals under study, we have analyzed the absorption coefficient spectra in the energy region of 2.24–2.40 eV, where sharp increase in α is observed, using the relation [14]

$$\alpha E = B(E - E_g)^n \tag{2}$$

where B is a parameter that depends on the transition probability, E_g is the band gap of the material and n takes the values of 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The plots of $(\alpha E)^2$, $(\alpha E)^{2/3}$, $(\alpha E)^{1/2}$ and $(\alpha E)^{1/3}$ as a function of E were then checked. The plot of $(\alpha E)^{1/2}$ versus E gave a straight line fit. The best plots are illustrated in Fig. 3. The intercepts of the plots illustrated in Fig. 3, which represent the indirect allowed band gap (E_g^i), shift toward lower energy positions as the sample thickness increases. The values of E_g^i and E_1 are presented in Table I.

Since the thickness-dependent energy values of E_g^i and E_1 are calculated by two different methods, there is a need to check, weather E_g^i —calculated from Equation 2—could be observed in the numerically executed derivative—illustrated in Fig. 2— or not. For this purpose the first and second derivatives of Equation 2 were

TABLE 1 Optical parameters of $TlInS_2$ crystals for different thickness samples

t (μm)	E_g^i (eV)	E_1 (eV)
27	2.333	2.360
53	2.268	2.316
66	2.255	2.307

evaluated. The second derivative of Equation 2 takes the form,

$$\frac{d^2\alpha}{dE^2} = \frac{(n-1)(n-2)E^2 + 2(n-2)EE_g + 2E_g^2}{E^3}(E - E_g)^{n-2}. \tag{3}$$

Setting the values of n as 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively, and finding the roots of $\frac{d^2\alpha}{dE^2} = 0$ for each value of n, it is possible to determine weather $\frac{d\alpha}{dE}$ has local minimum and/or maximum or not. Substituting the second derivative roots and singularities into the equation,

$$\frac{d\alpha}{dE} = \frac{(n-1)E + E_g}{E^2}(E - E_g)^{n-1}, \tag{4}$$

one can easily check the increasing and decreasing points of Equation 4. As could be seen from Equation 2–4 there is a singular point at $E = 0$, but this point is not considered, since the applied energy values are greater than 1.10 eV.

For $n = 2$, $\frac{d^2\alpha}{dE^2} = \frac{2E_g^2}{E^3}$ and no roots other than $E = 0$ exist. Thus, the second derivative test fails and one should refer to the first derivative test. Substituting $n = 2$ into Equation 4 and finding its roots as $E = 0$, $E = E_g$ and $E = -E_g$, it is easily observable that at these roots/singular points, the main function reported in Equation 2 could have local minimum at $E = E_g$, local maximum at $E = -E_g$ and does not exist for $E = 0$. For this reason, the local minimum, which is observed in the first derivative plot (Fig. 2), could not be assigned to the band gap of the material.

For $n = 1/2$, Equation 3 reveals four real roots being $E = 0$, $E = E_g$, $E = 0.58\,E_g$ and $E = -4.58\,E_g$. The test of these roots gave four singular points in the first

derivative. The latter result indicates that one could find singularity for $E = E_g$ in $\frac{d\alpha}{dE}$. This root was assigned to the fundamental band gap of the material, because it is the only root, which is located at $E = E_g$.

For $n = 3$ and $n = 3/2$, three singularities and one local minimum for the roots $E = E_g$ (for $n = 3$) and $E = 1.46\,E_g$ (for $n = 3/2$) were calculated. However for these two n values the plots of $(\alpha E)^{1/3}$ and $(\alpha E)^{2/3}$ as a function of E does not linearly fit the experimental data.

The above reported analysis indicated that the experimentally observed local minimum E_1 in the differential spectra of $TlInS_2$ single crystals could only be assigned to an additional energy value in the band gap of the material, which we refer in our discussion to impurity level.

As could be seen from Table I, there is a systematic decrease in the energies of indirect band gap and impurity level E_1 with sample thickness increment. This behavior may be associated with the influence of various factors such as structural parameters, presence of impurities, deviation from stoichiometry, and lattice deformation [15–17]. Increasing the sample thickness increases the impurity concentration in the layered crystals. The increase in the impurity concentration causes shrinkage in the band gap known as the band gap narrowing effect [18, 19] and shifts the impurity energy level deeper in the band gap (with respect to the fundamental energy gap). In addition, the band gap decrement with thickness increment may be explained by referring to the fact that the lattice deformation of the crystal decreases by increasing its thickness. Allakhverdiev *et al.* [20] have studied the lattice deformation effects on the band gap of $TlInS_2$ single crystals and reported the existence of two deformation potentials being parallel and perpendicular to the crystal layer. The nature of the behavior of the perpendicular deformation potential was attributed to the peculiarities of the band structure of layered crystals. According to the band structure calculations [21], interlayer interaction leads to splitting of the top of the valence band and the bottom of the conduction band of a layered crystal. Under deformation, when the interlayer distances decrease, splitting increases and leads to a decrease of the band gap E_g. On the other hand, E_g increases when intralayer distances decrease. Thus, the final change of band gap depends on two competitive contributions having opposite signs.

4. Conclusions

In this work the effect of sample thickness on the optical energy gap of $TlInS_2$ crystals was studied. The sample thickness was varied from 27 to 66 μm. The transmittance and reflectance spectra wre recorded in the photon energy range of 1.10–3.10 eV. The spectra contained two absorption regions. The indirect allowed transition gap in the second absorption region varied from 2.333 to 2.255 eV as the sample thickness increases from 27 to 66 μm. The differential spectra of the samples contained a singular point, which related to impurity level being lowered from 2.360 to 2.307 eV with thickness increase.

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