Urbach-Martienssen's tail in layered ternary semiconductor TlGaS$_2$

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Abstract

Dependence of the absorption coefficient on the photon energy and temperature near the fundamental absorption edge was measured for layered single crystal TlGaS$_2$. The exponentially increasing absorption tail was explained as an Urbach-Martienssen's (U-M's) tail for TlGaS$_2$ samples in the 10-340 K temperature range. The characteristic Urbach's parameters such as steepness parameter $[\sigma(T)]$ and Urbach's energy $[(E_u = k_B T/\sigma)]$ were determined. Analyzing the temperature dependence of these parameters based on the general models, which takes into account the possible role of several different types of disorder, we conclude that the absorption process in the fundamental absorption edge for TlGaS$_2$ is the result of the superposition of at least two different mechanisms; one is related to the phonon induced microfields and the other results from structural and thermal disorders.

Key Words: Optical characterization; Urbach rule; layered semiconductors; TlGaS$_2$.

1. Introduction

Layered ternary crystals with chemical formula TlBX$_2$, B=Ga or In and X=S, Se or Te, have been increasingly interesting due to their structural properties and potential applications in optoelectronics [1]. Their quasi-two dimensionality, structural anisotropy and phase transition, optical and photoconductive properties, and other features attract investigators in an effort to acquire a better insight in the physics of these compounds [2]. In view of its possible applications in optoelectronic devices in the visible range, a great deal of attention has been devoted to the study of the structural, electrical and photoelectrical properties [3-5]. Although there are many valuable works on this compound, no information on the band structure of TlGaS$_2$ has been established due to the

several polytype modifications. So, investigation of the fundamental absorption edge can provide extensive information on the band structure of crystals, impurity and disorder effects, and the character of electron-phonon interactions as well as about the existence of excitons and their role in the absorption mechanism.

In the present study, Urbach-Martienssen's (U-M's) tails in the optical absorption (OA) spectra of TlGaS$_2$ single crystals were investigated. Through the temperature dependence of the steepness parameter $[\sigma(T)]$ and Urbach's energy $[E_U(T)]$, it can be deduced whether the band gap fluctuations associated with structural and thermal disorder or the crystal phonons have the major influence on the absorption process.

2. Experiment

TlGaS$_2$ monocrystals were grown by using a modified Bridgman-Stockbarger method, from a stoichiometric melt of starting materials sealed in evacuated ($\approx 10^{-6}$mbar) and carbon coated quartz ampoules with a tip at the bottom, in our crystal growth laboratory. The light yellow colored samples exhibited good optical quality and were easily cleaved along the (001) plane, perpendicular to the optical c-axis, from the ingot. Samples with about 5x5 mm^2 area and 10-500 μm of thickness of TlGaS$_2$ used in this work were freshly and gently cleaved along the cleavage plane with a razor blade from the ingot and no further polishing and cleaning treatments were required because of the natural mirror-like cleavage faces. The absorption spectra of the samples in a direction close to the normal to the layers were taken by means of a computer controlled Perkin-Elmer Lambda 2S UV/Vis. spectrometer with 190-1100 nm wavelength range. The wavelength accuracy was ± 0.3 nm at the deuterium peak 651.1 nm. The sample temperature was varied from 10 to 340 K by a modified and computer controlled Leybold-Heraeus Variotemp HR1 model temperature controller with an accuracy of ± 0.2 K. The extrapolating line of U-M's tail was drawn by the least-squares fitting method within the spectral region where the product αd was larger than unity to neglect the term attributed to the internal reflection.

3. Experimental Results and Discussion

An exponentially increasing absorption edge (AE) in a number of insulators including ionic crystals, semiconductors, and organic crystals obeys the following empirical expression [6]:

$$\alpha = \alpha_0 \ \exp\left[(E - E_0)/E_U\right]. \tag{1}$$

Where, $E = \hbar\omega$ is the photon energy, E_0 is comparable to the band gap energy and E_U is an inverse logarithmic slope of absorption coefficient. Equation (1) implies that logarithms of α plotted as a function of E can be approximated by a straight line in energies just below the fundamental AE. The extrapolations of those lines for various

temperatures usually converge at a point (E_0, α_0) called as "converging point." This empirical rule was found by Urbach [7] for silver halides (indirect band-gap) and established by Martienssen [8] for alkali halides (direct band-gap). Therefore it is called "Urbach's rule" or "Urbach-Martienssen's rule," and the absorption tail obeying this rule is known as "Urbach-Martienssen's (U-M's) tail."

The steepness parameter $\sigma(T)$, which characterizes the steepness of the straight line near the AE, is expressed empirically as a function of temperature [6-8]:

$$\sigma(T) = \sigma_0 \left(\frac{2k_B T}{h\nu_p} \right) \tanh \left(\frac{h\nu_p}{2k_B T} \right), \tag{2}$$

where σ_0 is a temperature-independent but material-dependent parameter being inversely proportional to the strength of the coupling between excitons and phonons [6].

The OA spectra just below the excitonic resonance energy is shown in Fig. 1 as a function of temperature for TlGaS$_2$. Logarithms of α increase linearly with increasing photon energy between 10-340 K in the range of α= 20-100cm^{-1} absorption coefficients and all extrapolations converge at $(E_0, \alpha_0) = (2.62$ eV, $3.8\text{x}10^2$ cm$^{-1})$. Figures 2, 3 show the steepness parameter $\sigma(T)$ and $E_U(T)$ by open circles as a function of temperature. To compare the $\sigma(T)$ data with theoretical values, the steepness parameter $\sigma(T)$ was estimated using Eq. (2). The solid line in Fig. 2 represents the best fitting curve to the experimental data with σ_0=0.58 and $h\nu_p$= 26±1 meV parameters calculated using Eq. (2). This $h\nu_p$ value is comparable with the value of measured by earlier IR studies [9].
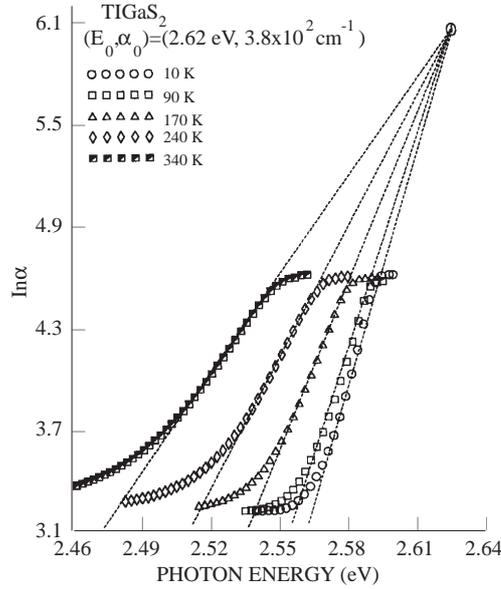
Figure 1. Optical absorption (OA) spectra for TlGaS$_2$ as a function of temperature.
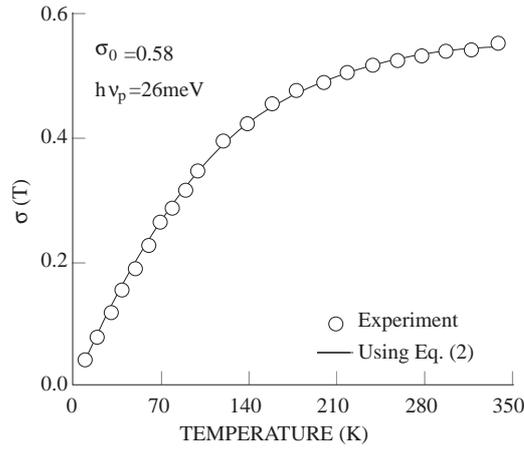
Figure 2. The steepness parameter $\sigma(T)$ as a function of temperature for TlGaS$_2$. The solid line represents a fitting curve using Eq. (2).
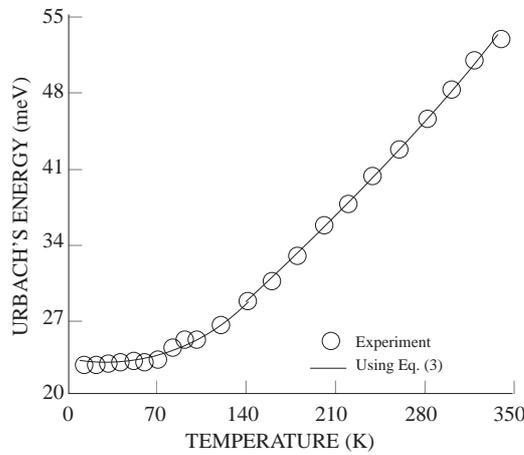
Figure 3. The Urbach's energy as a function of temperature for TlGaS$_2$. The solid line represents a fitting curve using Eq. (3).

We have analyzed our results within the frame work of the three most widely cited theoretical models: To explain the U-M's tails many theoretical studies were performed but there is still no accepted unique explanation. The most widely cited theories are those of Sumi and Toyozawa and further developed by Schreiber and Toyozawa (S-T) [10], Skettrup [11] and Dow and Redfield (D-R) [12].

The more commonly used theory developed by S-T ascribes the exponential shape of the absorption coefficient to the coexistence of free excitons and momentarily localized

self trapped excitons. In this case, the excitons after being created interacts with the surrounding phonons through their deformation potential. The behavior of the excitations in the lattice is primarily defined by the character of its chemical bond and this model is predominantly applicable to highly ionic crystals, such as alkali halides [13]. Thus, it seems that the self trapping model of exciton is not proper to apply our results as the chemical bond in TlGaS$_2$ has largely covalent character. So we postpone further investigations on this theory.

According to Sketrup's model the U-M's tail is controlled by the amount of structural, thermal or compositional disorder. This disorder influences the width of the exponential tail and E_U have to be introduced by the sums of the contributions of structural $[E_U(X)]$, thermal $[E_U(T)]$ and compositional $[E_U(C)]$ disorder in the sample: $E_U(X, T, C) = [E_U(X) + E_U(T) + E_U(C)]$. Where, $E_U(X)$ and $E_U(C)$ are temperature independent, while $E_U(T)$ will increase with temperature. According to this model, when compositional disorder contribution is neglected as our crystal is not a mixed one, the Urbach's energy can be expressed by

$$E_U(X, T) = [E_U(X) + E_U(T)] = 22.6 + 45 \left(\frac{1}{e^{\Theta_E/T} - 1} \right), \tag{3}$$

where $\Theta_E = 302 \pm 2$ K, the Einstein temperature, is the same manner as the $h\nu_p$ value obtained above. Solid line in Fig. 3 represents the best fitting curve estimated from Eq. (3) of Urbach's energy. It is recognized that the fit using Eq. (3) is quite good agreement with the data. From the right side of Eq. (3), it is seen that in the TlGaS$_2$, the structural disorder component value of about 23 meV is not dominant but comparable with the thermal disorder component value of 31.5 meV at 340 K. Thus, structural disorder contribution to the Urbach's energy must also be considered in addition to the thermal contribution.

According to the D-R model the origin of the U-M's tails is due to the broadening of the exciton absorption band by the microfields present in the lattice. Phonon-induced electric microfields resulted from charged impurities and potential fluctuations due to disorder, and longitudinal optic (LO) or longitudinal acoustic (LA) phonons create new energy states in the forbidden energy gap below the ground state of the $1S$ exciton which enable excitons to tunnel out from their quasi-bound state into the potential through beyond the Coulomb potential barrier, or equivalently, to be ionized and have a part of its wave function free. To investigate the applicability of the D-R theory we have adopted the procedure suggested by Samuel *et al.* [14]. In that work, the influence of the external electric fields F_E causing the internal Franz-Keldysh effect is replaced by the root-mean-square value of the phonon induced electric field F_P, leading to the following expression:

$$E_g(T) \tanh \left(\frac{h\nu_p}{2k_B T} \right) = E_g(0) - E_0 \left[1 - \tanh \left(\frac{h\nu_p}{2k_B T} \right) \right]. \tag{4}$$

Linear dependence of $E_g(T) \tanh (h\nu_p/2k_B T)$ on $1 - \tanh (h\nu_p/2k_B T)$ of the experimental results, as can be seen from Fig. 4, together with temperature dependence of

steepness parameter and Urbach's energy (Figs. 2 and 3) substantiates the validity of these assumption and gives qualitative agreement between the model and the absorption process in TlGaS$_2$ compound as in the case of GaSe [15].
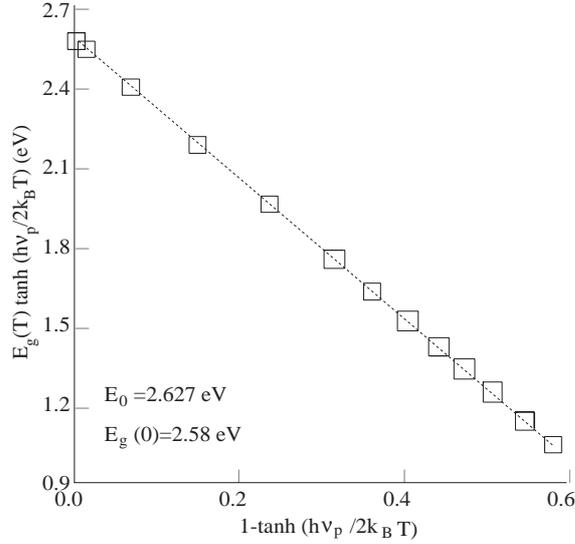
Figure 4. The relationship between $E_g(T)\tanh(h\nu_p/2k_BT)$ and $1-\tanh(h\nu_p/2k_BT)$.

In conclusion, these results reveal that both static structural and dynamic thermal disorders associated with crystal phonons contribute to the U-M's tail within the forbidden gap and hence the absorption below the indirect band gap. Structural disorder, which likely results from the existence of multiple structural defects associated with stacking faults and precipitates of the compound elements in the TlGaS$_2$ lattice.

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