

PII S0038-1098(96)00294-3

OPTICAL AND PHOTOELECTRICAL PROPERTIES OF THE TlGaS₂ TERNARY COMPOUNDN. Kalkan*, J. A. Kalomiros, M. Haniyas⁺ and A. N. AnagnostopoulosSolid State Physics Section 313-1, Aristoteles University of Thessaloniki, GR- 54006
Thessaloniki*Physics Department, Faculty of Science, University of Istanbul, TR- 34459, Istanbul
⁺TEI of Chalkis, GR- 34100, Chalkis*(Received 26 March 1996; accepted 7 May 1996 by G. Bastard)*

Absorption and photoconductivity spectra of thin TlGaS₂ layers are used to study the fundamental and other transitions of TlGaS₂ in the energy region 1.0-3.0 eV and in the temperature range 10-300 K. One of the peaks resolved by photoconductivity measurements corresponds to the excitonic peak registered in the absorption spectrum of this compound. The temperature dependence of the critical energy and of the broadening parameter of this excitonic peak are presented. Most of the rest photoconductivity peaks are related to transitions from localized levels to the conduction band. Copyright © 1996 Elsevier Science Ltd

Keywords: A. semiconductors, D. optical properties, photoconductivity

1. Introduction

2. Experimental

TlGaS₂ belongs to the interesting group A^{III}B^{II}C₂^{VI} of chalcogenide semiconductors. It possesses a pronounced layered structure and crystallizes in a monoclinic lattice ($a = b = 10.40 \text{ \AA}$, $c = 15.17 \text{ \AA}$, $\beta = 100^\circ$) with group symmetry C_{2h}^6 [1-3]. Among published results we take exception to Raman and IR spectra [1,4] and to measurements of the optical absorption in the region of the fundamental absorption edge [5-7]. No information on the electronic band structure of TlGaS₂ has been reported [8].

In spite of the availability of the above results, the localized states present in the energy gap of TlGaS₂ have not been studied extensively, yet. The purpose of the present work is to examine the optical and photoelectrical properties of TlGaS₂ in the energy region 1.0 - 3.0 eV and in the temperature range 10 - 300 K. As a result of this study we derive the distribution of the localized levels present in the energy gap, along with an exciton state in the vicinity of the fundamental optical transitions.

TlGaS₂ single crystals were grown by direct melting of high purity stoichiometric amounts of their constituent elements, in vacuum sealed ($< 10^{-5}$ Torr) silica tubes. A detailed description of the growth is given in Ref [9]. The resulting layered crystals present easy cleavage and natural mirror-like surfaces. Their dimensions are about $5 \times 5 \times 0.5 \text{ mm}^3$ and their color is yellow. Very thin samples were obtained by successively peeling off the crystals.

To check the morphology of them and to control their composition, an examination was carried out using a Scanning Electron Microscope (SEM) of Jeol and an attached X-rays microprobe analysis unit. In Fig. 1 SEM-micrographs are shown, clearly displaying the layered structure of TlGaS₂. In Fig. 2 typical microanalysis results are displayed.

Photoconductivity measurements were performed with a Zeiss double prism monochromator (SMP2), in the

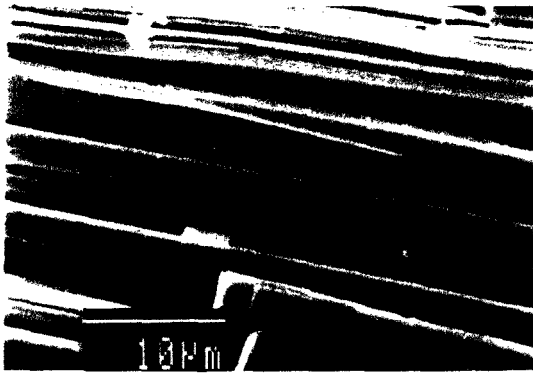


Fig.1: SEM-micrograph of the grown $TlGaS_2$ crystals. The layered structure is obvious.

energy region 1.0 - 3.0 eV. All samples used in photoconductivity experiments were cleaved from the same crystals also used for the optical measurements. Two indium vacuum evaporated contacts were found to be ohmic and of low resistance. This was proved by the four point-contacts instrumentation. The distance between the electrodes was much greater than the thickness of the samples, thus providing homogeneous distribution of the applied voltage. Care was taken to achieve uniform illumination of the surface area between the two parallel contacts. The uniform excitation over the whole volume of the crystals was provided by choosing the appropriate thickness d , so that the condition $\alpha d \approx 1$, where α is the absorption coefficient, held over the whole spectral region. All measurements were performed with an applied voltage of 50 V, in the ohmic region of the corresponding current- voltage characteristics. The photocurrent was measured with a Keithley electrometer. The samples were mounted on the copper cold-finger of a cryostat that enabled measurements in the region 90 -

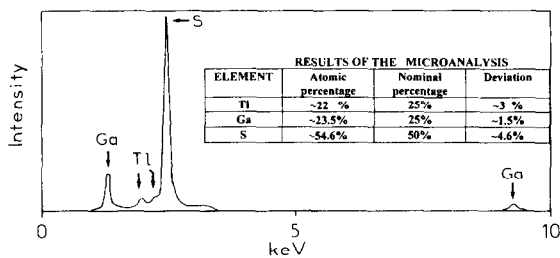


Fig. 2: The X-rays spectrum of the $TlGaS_2$ crystals and as an insert typical microanalysis results for the grown $TlGaS_2$ crystals.

300 K under a vacuum of 10^{-5} Torr. All samples used in the present study were found to exhibit p -type conductivity, as proved by the thermal EMF-method (see also [10]).

Transmission measurements were performed in the energy region 1.0 - 3.0 eV using a double beam monochromator with a resolution of 0.2 nm at 400 nm. A Helium closed-cycle cryogenic system enabled measurements in the temperature range 10-300 K, while the temperature was stabilized within ± 1 K. The cryostat consists of a metallic chamber with high quality quartz windows. During the measurements the vacuum in the cryostat was better than 10^{-7} Torr.

3. Absorption and Photoconductivity Measurements

Transmission measurements were used to determine the absorption coefficient of this compound. Averaging over multiple reflection effects, the values of transmission are given by the formula

$$T \approx (1 - R)^2 e^{-\alpha d} \tag{1}$$

Where R and α are the reflectivity and the absorption coefficient, respectively, and d is the thickness of the sample. The thickness d of the specimen was found using the interference effects present in the long wavelength region of the spectrum. To find the absorption coefficient from the measured transmission spectra we use eq. (1), neglecting the reflectivity R in this region according to Ref. [3].

The low values of the absorption coefficient indicate

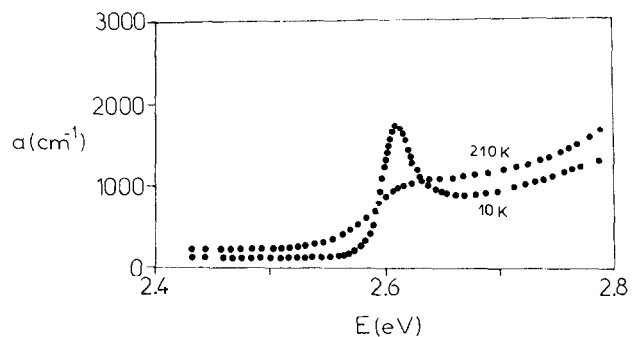


Fig. 3: Typical spectra of the absorption coefficient at two representative temperatures, 210 and 10K. The excitonic peak present at low temperatures vanishes with increasing temperature.

that the absorption edge is due to forbidden transitions. It should be noted that in the case of very thin samples ($d < 8\mu$) no absorption edge is evident. If samples of suitable thickness are used ($20\mu < d < 50\mu$) the absorption edge is transformed at low temperatures into a fine exciton peak. Fig. 3 shows two typical spectra of the absorption coefficient of TlGaS_2 at 10 and 210 K in the spectral region 2.4 - 3.1 eV. Proper evaluation of the absorption curve of Fig. 3 yields a room temperature value of the forbidden direct gap about 2.644 eV, while the room temperature indirect gap is found at approximately 2.41 eV. The direct and indirect gaps were found to decrease with increasing temperature, in accordance with Refs. [11] and [12]

For a further analysis of the observed peaks we produced the second derivative spectra of the absorption coefficient vs photon energy. The structures of the spectrum due to singularities are thus enhanced and a more detailed analysis of the transitions becomes possible. The second derivative of the absorption coefficient was calculated using spline functions that smoothed without distorting the line shapes.

Fig. 4 shows the temperature variation of the critical energy for the excitonic peak. Only a very small temperature dependence is observed and it is mainly confined in the low temperature region, up to 50 K. In this region the energy threshold of the transitions increases slightly with increasing temperature. Above 50 K the temperature coefficient of the energy threshold is nearly constant. The negligible temperature dependence

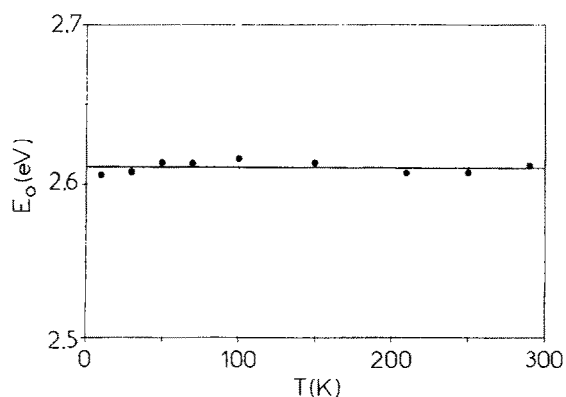


Fig. 4: The temperature variation of the critical energy for the excitonic peak. The full line represents a least square fit.

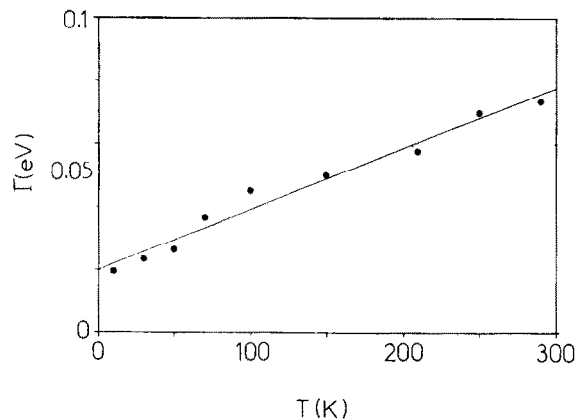


Fig. 5: The broadening of the excitonic peak as a function of the temperature. The full line represents a least square fit with eq. (2), $\Gamma_L = 0.0199$ eV and $\gamma = 1.926 \times 10^{-4}$ eV / K].

of the critical energy of the observed excitonic peak is in contrast with the behaviour registered in other ternary layered compounds [13,14], but in very good agreement with the results obtained for the very similar layered compound TlGaSe_2 , [15]. In most other cases the critical energies are strongly temperature dependent, decreasing with increasing temperature. In the high temperature region this dependence is parabolic and can be described taking into account the electron-phonon interaction and using a Bose-Einstein statistical factor for phonons [16]. In order to interpret the dependence of Fig.4 one should consider in addition a positive term to account for the lattice dilatation. It should be also noted that several members of the $\text{A}^{\text{III}}\text{B}^{\text{II}}\text{C}_2^{\text{VI}}$ group, like TlInTe_2 and TlInSe_2 exhibit a positive overall temperature dependence of the energy gap [9].

The broadening of the excitonic peak is shown in Fig.5 as a function of the temperature. For the overall description of these data we use an expression of the form

$$\Gamma(T) = \Gamma_L + \gamma T \quad (2)$$

with $\Gamma_L = 0.0199$ eV and $\gamma = 1.926 \times 10^{-4}$ eV / K.

Next, we tried to determine the binding energy of the exciton line. For this purpose we use a model for the absorption coefficient in the region of the electron-hole interaction, given in [17] and also described in [13].

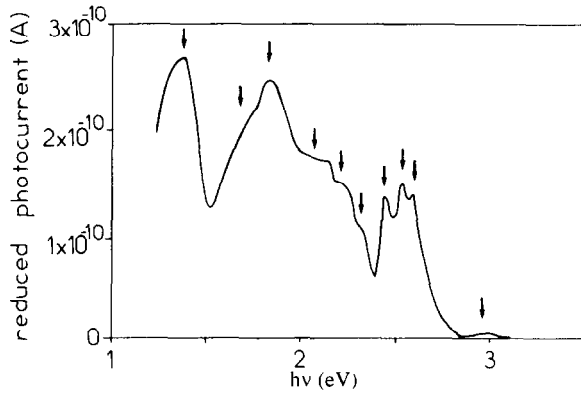


Fig. 6: Reduced photocurrent spectrum at 300K.

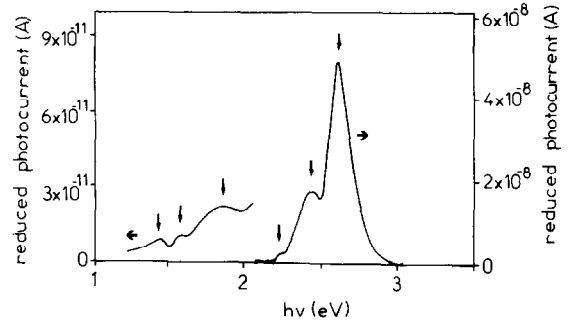


Fig. 7: Reduced photocurrent spectrum at 90K.

According to this expression the absorption coefficient is given in terms of the exciton binding energy and broadening. Numerical fitting of the experimental values of α in the region of the exciton line produces a value of the binding energy $E_b = 34$ meV, almost constant for all temperatures. The broadening of the exciton line is found within the experimental error of the values given in Fig.4.

In the following, the results of the photoconductivity measurements are presented. Figs. 6 and 7 show the photocurrent, reduced to the same number of incident photons for all wavelengths, as a function of the energy and at temperatures 300 and 90 K. Several peaks in the curves of these figures can be observed. Their energy positions below the conduction band, at 300 and 90 K, are listed in table I.

4. Conclusions

In this work the levels present in the gap of the ternary layered compound $TiGaS_2$ were studied by optical absorption and photoconductivity measurements. Some remarks should be made comparing the peaks of the photoconductivity and the absorption spectra:

a. The photoconductivity peaks at 2.61eV (300K) and 2.62 eV (90K), seem to correspond to the excitonic peak registered at 2.61 eV also in the absorption spectrum at low temperatures. It has to be mentioned here that this peak is more pronounced in the photoconductivity spectra at 90K, as expected for excitons. It weakens in both kinds of spectra at higher temperatures.

b. The photoconductivity peaks at 1.38eV (300K) and 1.40eV (90K) have to be ascribed to some shallow acceptor level. The adjacent peak at 1.70eV is also found by electrical measurements in darkness to correspond to an acceptor level located at 1.68eV below the conduction band [18], while the peak at 1.83eV was also detected by similar measurements at 1.85eV in Ref. [19].

c. The photoconductivity peaks at 2.07eV and 2.22eV correspond to an indirect transition and to a transition to the mentioned excitonic level, respectively, from an acceptor level located 0.37eV above the valance band, as detected by similar measurements in Ref. [18]. The peak at 2.30eV seems to correspond to a direct transition from the same acceptor level.

d. The photoconductivity peaks at 2.41eV (300K) and 2.43eV (90K) are most probably related to an indirect gap located at 2.45-2.46 eV, according to Refs. [5,7].

TABLE I [All values in eV]

300K	1.38	1.70	1.83	2.07	2.22	2.30	2.41	2.54	2.61	2.96
90K	1.40	1.70	1.81	-	2.22	-	2.43	-	2.62	-

e. The peak at 2.54eV (300K) has to be related to some shallow donor. This last peak is fully covered by the strong excitonic transition at 90K.

f. The photoconductivity peak at 2.96eV seems to be related to some phonon assisted higher interband transition. This assumption is corroborated by the fact that this peak vanishes at 90K.

g. Finally, it has to be mentioned here, that according to the microanalysis results (insert in Fig. 2) the grown crystals most probably contain more S than indicated by

the formula TlGaS₂, either in the form of nanoclusters or in the form of extra GaS layers. This fact may smooth the absorption curves and add some photoconductivity structures.

Acknowledgement - Two of us N.K. and A.N.A. acknowledge financial support from NATO-CRG 950014. Thanks are also due to the personnel of the SEM facility of the Aristotle University for its help.

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