Conversion of Laser Pulse Optical Energy to Photo-acoustic Wave in nm-Scale Layered TlGaSe$_2$ Crystals

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Abstract. Experiments are presented that reveal an efficient optical energy conversion from the visible to the infrared wavelengths range as a result of photo-acoustic response (PAR) after light pulse incites onto the free surface of TlGaSe$_2$ crystal. Excitation was carried out with a tunable wavelength of ns-pulse laser and the PAR was detected laterally with a focused cw-probe. The observed properties can be related to variety of successive factors: high electron-hole-phonon deformation potential, a high factor of refraction coefficient dependency on pressure, the absence of surface recombination and the band filling effect, in relation with low absorption coefficient due to the forbidden direct-band optical transition in TlGaSe$_2$. All these ensure that the acoustic energy remain well confined under a wide pulse power and energy range suggesting that TlGaSe$_2$ is a promising material for dynamic optical energy conversion.

1. Introduction
The ternary compound TlGaSe$_2$ is a dense quasi-two dimensional layered semiconductor with revealed predominantly forbidden electron transitions and a close indirect and direct optical band gaps at $E_G \approx 2.1$ eV resulted from a weak covalent nature of the interlayer bonding [1]. The layer consists of corner linked GaSe$_4$ tetrahedra where Tl atoms lay on straight lines along $a,b$ crystalographic e-axis of trigonal voids between tetrahedra. Layer stacking direction is along the growth $c$-axis and every consequent layer is twisted by 90º in stacking plain. Within the layer prevails strong covalent bonding while between the layers interaction is weak. The structure undergoes sequential phase transitions below RT. Because of this and some other extraordinary properties, TlGaSe$_2$ crystals received a great attention for applications in optoelectronics [1-3]. We present prominent acoustic responses in TlGaSe$_2$ which can be used for pulsed energy conversion in optical circuits. The results are obtained by the method of the time-resolved acoustic wave perpendicular probing. It is based on probe deflection under the perpendicular probe direction to the longitudinal wave propagation on a rectangular semiconductor solid strip. The technique was adopted from acoustic studies in liquids and gasses and is referred as a schlieren optical probe method [4]. The preliminary results have been published in [5].

2. Experimental
The TlGaSe$_2$ samples used for PAR measurements were grown by modified Bridgman method from high purity elements taken in stoichiomteric proportions. Optical quality surfaces parallel to the layers (001) were cleaved mechanically and no additional surface treatment was needed. Perpendicular
lateral surfaces however are not smooth; the edges are crumbled and have a step like layered nature. It must be noted, that the preparation of samples with specular lateral faces was a difficult task. A careful gentle polishing thus was performed along the a (or b) axis which are a natural termination for layer edges [6]. This allowed to form optical quality lateral facets. Rectangular corners were achieved by additional removal of some damaged part by cleavage.

The sample was glued with silver paste to the holder allowing (001) facet excitation along || c direction, while probe beam was directed perpendicularly \perp {\sf c} through the lateral surface, as shown in figure 1. Tuneable pulse laser (Infinity Coherent) used for excitation was of 2 ns pulse duration and of 40 Hz repetition rate. Excitation beam was focused to d = 0.9 mm spot. The narrow probe-beam (from a typical infrared LED) focused to d \sim 7 \mu m penetrated lateral surface. It could be positioned at any distance from the excited surface with 1 \mu m precision [5]. After probe was transmitted throughout the sample, it was collimated with two lenses. A knife edge was inserted between the lenses to block a portion of the beam. This allows detecting a small variation of the refractive index generated by acoustic wave; see more quantitative description of physical principles below. Next, the transmitted probe beam was focused to 0.5 ns rise time InGaAs photo- receiver and the signal trace was observed on 2 GHz oscilloscope and recorded to PC. Typically the 500 traces were averaged to increase the signal-to-noise ratio. The measurements were performed in the vacuum cryostat at room temperature (RT) and at 77 K.

After excitation pulse hits the free surface of the absorbing sample, a fraction of absorbed light energy goes to the generation of acoustic wave. In agreement with earlier studies, we expected completely decoupled mechanisms contributions of electronic stress (d_{CV} \Delta N, where d_{CV} is a plasmaphonon deformation potential and \Delta N is concentration of the excited electrons and holes) and of thermoelastic stress induced in the media. The thermoelastic stress is released as a thermal energy of hot carriers relaxation energy (E - E_G) and by a delayed nonradiative recombination in the plasma [7]. Since the carrier and the heat diffusivity in TlGaSe_2 across the layers are very small we expected identical stress profiles to contribute as a simple sum under our experimental conditions. Assuming that the total stress only depend on depth z, the longitudinal acoustic (LA) strain profile travelling into the sample by sound velocity v_s is expressed by \varepsilon(\eta) \propto (1/\rho V_s^2)[3B\beta \Delta T(0,t) + d_{CV} \Delta N]/F(\eta), where \eta = z - v_s t, V_s is thermal capacity volume, B is the bulk modulus, \beta is the linear expansion coefficient and F(\eta) is a waveform function which has been analytically given by bipolar pressure waveforms with the duration of double optical absorption length (1/\alpha) [8]. The equation predicts that the initial strain polarity on a free surface depends on the sign of d_{CV} and gives rise to the contraction or dilatation stresses accordingly. The predicted pressure wave form is shown in the middle inset of the figure 1.

The method of a schlieren optical probe provides time-resolved acoustic wave probing based on the probe deflection mode under the perpendicular probe transition to the LA wave propagation [4].

![Figure 1](image.png)

**Figure 1.** A scheme for excitation direction || c in layered TlGaSe_2. Pump pulse excites the surface area and the narrow probe beam penetrates the sample perpendicularly to the longitudinal acoustic wave propagation direction. The insets explain waveforms of the acoustic stress and the PAR response.
schlieren scheme (figure 1) is sensitive due to relatively wide intersection area (~1 mm) between the LA wave and the probe. Also this method has no shear acoustic components. The acoustic stress dilatation and contraction cause the deflection of opposite directions providing the temporal derivative of the refractive index versus strain pressure profile in the transverse plane. The transfer function of refractive index variation vs. pressure [4] can be considered as a simple linear function since the acoustic stress of the LA amplitude is on a milibar level [9]. Important to note that if one would block an opposite side of the probe beam with the knife edge one would get an opposite event registration succession, i.e. the obtained PAR would be of the opposite polarity [5]. In the result section we have adopted PAR as a ratio between the signal amplitude and the ground level as shown in the right inset of figure 1. Majority of performed measurements were obtained with 1540 nm probe, while with 633, 671, 861, 1300 nm probe beams quite similar results arise in TlGaSe₂.

3. Results and discussion

Figure 2 shows PAR echoes in TLGaSe₂ for 6.3 mJ/cm² excitation fluence at different quanta at RT in a 300 µm-thick sample. PAR shapes are of symmetrical form and qualitatively are explained by considering that dilatation and contraction are proportional to deflection angle, as was predicted (see figure 1). We determine that the acoustic wave propagates along the e-axis with longitudinal speed of sound $v_{ac} = 2.63 \cdot 10^5$ cm/s [5,6]. When acoustic wave reaches back side of the sample it reflects and experiences phase shift by $\pi$ which interchanges the contraction-dilatation order of the stress, therefore, PAR propagating backwards appears of the same polarity in the transient (see 2nd PAR instance in figure 2a). The third (3) and fourth (4) PAR are reflections from the front and from the back surfaces, respectively. This process continues for several microseconds (figure 2b) with low dispersion of acoustic energy [4]. That indicates high optical quality (small roughness) of the cleaved surfaces. Under a low excitation quanta (< 2.0 eV) the absorption coefficient is low enough to allow excitation through the bulk of the sample. Then, the PAR signal superimposes on the background shape of free-carrier-absorption. Also, in this spectral range, we observe small PAR generated from the back surface propagating in opposite direction and having opposite polarity. (The PAR depicted in figure 2a as (1’) - generated from the back surface and (2’) is a reflection from the front surface.) This behavior was explicitly investigated in reference [5] showing that, at the specific probe depth positions, PAR signals from the front surface and from the back surface is superimposed and can be virtually canceled.

![Figure 2](image_url)

Figure 2. (a) PAR transients in TlGaSe₂ for various excitation quanta energy for 6.3 mJ/cm² excitation in 300 µm-thick sample. An indexed instant of echoes, namely, 1st is PAR generated on front surface; 2nd – reflection from the back; 3rd – reflection from front surface; 4th – second reflection from front surface. The reflected PAR changes stress polarity, therefore is registered as the same dilatation process. Note that at low energies excitation penetrates whole sample and PAR generation from back surface arises simultaneously which appear of the opposite polarity: 1’ - generated; 2’- reflected. Also free carrier absorption signal is pronounced for 2.0 eV curve. (b) Multiple echoes of PAR maintain constant form in µs-time scale indicating a good optical quality of the cleaved opposite surfaces.
Figure 3. (a) PAR transients for different excitation fluencies at 2.194 eV and at 77 K temperature. (b) PAR increase with increasing laser fluence at different quanta energy at RT and at 77 K. In a wide spectral range PAR show linear growth $\sim F^1$ as given by fitted lines.

Figure 3a shows PAR measured at different excitation fluence of 2.194 eV at 77 K. PAR growth is observed over three orders of excitation laser fluence $F$. Experiments were carried out in a wide spectral range 1.75 – 2.7 eV. Wave form remains the same shape though some FWHM narrowing occurs from 18 ns to 8 ns due to absorption depth shrinkage with increasing absorption coefficient approaching 2.7 eV. The growth follows almost a linear dependence ($\sim F^1$) at all spectral range. Few transients on depicted fluencies are shown in figure 3b. The small sublinear add-on we explain by an increase of the thermoelastic stress contribution due to emerging of a fast recombination lifetime component of an order of the laser pulse duration. This component was depicted form free-carrier absorption transient (not shown). The PAR magnitudes of 70 % were reached with no sign of PAR saturation. Moreover, PAR wave form remains undistorted at high excitations at all times. These two facts emerge from predominantly forbidden electron optical transitions and a close indirect and direct optical band gaps resulted from a weak nature of the interlayer bonding in TlGaSe$_2$ [6].

In figure 4a it is shown PAR dependence versus absorption coefficient $\alpha$ (figure 4b) as measured by free-carrier absorption at 77 K [5]. For excitation energy above the indirect exciton edge (2.08 eV) PAR linearly increases with $\alpha$ until the absorption depth reaches acoustic energy delivery depth $1/\alpha = \tau_L \times \upsilon_{ac}$. This is predicted by theory of acoustic response [4] and is called as a condition of proper stress confinement. When absorption depth becomes shorter than the acoustic delivery depth, the PAR begins to decrease. For $1/\alpha << \tau_L \times \upsilon_{ac}$, the theory predicts inverse dependence (PAR $\sim 1/\alpha$) [4]. Both the linear and inverse dependences are shown in figure 4a by fitted lines and the acoustic delivery point at $1.9 \times 10^3$ cm$^{-1}$ is indicated by an arrow. Agreement with theory is quite satisfactory for the above the band gap excitation, i.e. at $\alpha > 40 - 3000$ cm$^{-1}$ (figure 4b). However, higher PAR is observed than the theory predicted for the below band gap excitation at $\alpha < 40$ cm$^{-1}$ (figure 4a). This finding we explain as deviation from the bipolar condition, i.e. the electron concentration is low compared to hole concentration, and as possibility of excess hole dislocation on a different layers on a ns-scale layer near the surface of the crystal [6]. Loose od locality between excess hole and trapped electron can cause additional contribution to PAR similar to the piezoelectric mechanism observed on GaAs (111) surfaces [7].

The deformation potential $d_{CV}$ and refraction coefficient dependence on pressure ($dn/dp$) still are not established by the direct experiments in TlGaSe$_2$. Combination of these factors contribute to high PAR magnitudes and determine the PAR polarity. PAR polarity in TlGaSe$_2$ is certainly opposite than in GaAs [10]. We assume that $dn/dp$ in TlGaSe$_2$ is positive as in layered InSe and GaSe layered crystals. Assuming the same value for TlGaSe$_2$ ($dn/dp = 0.045$) we estimate $d_{CV} \approx 3$ eV in comparison with known value for GaAs $d_{CV} = 10$ eV. Hence high PAR is caused mainly by the large $dn/dp$ value.
The absence of surface recombination, restricted carrier diffusivity across the layers and forbidden optical transitions are the main factors determining linear PAR dependence on carrier injection.

**Figure 4.** (a) PAR as a function of absorption coefficient at 77 K and (b) absorption spectrum obtained by free-carrier absorption [5]. The characteristic indirect exciton at 2.08 eV and two direct ones at 2.12 eV and at 2.36 eV are indicated.

**4. Conclusions**

We have applied a schlieren optical probe method for the detection of LA waveforms in TlGaSe$_2$ plates under perpendicular probe direction to crystallographic c-axis. PAR exhibits symmetric strain pulse generated by coinciding shapes of electronic and thermoelastic stresses because of low carrier diffusion and heat transfer across the crystal layer plain. Such LA pulses propagate millimeter distances in the sample under μs-time range with low acoustic dispersion. PAR is observed from the subband gap excitation spectral range from 1.7 eV (at $\alpha$ ~ 1 cm$^{-1}$) into the above band gap range until 2.7 eV (at $\alpha$ > $5 \times 10^3$ cm$^{-1}$). The PAR echoes remain of the same waveform shape with a linear dependence versus excitation energy up to high value of PAR = 70% for appropriate optical excitation fluence ~ 30 mJ/cm$^2$. The latter property gives rise to the very specific features of indirect-direct band gap nature with mainly forbidden optical transitions. Large PAR can be used for optical light pulse conversion into the infrared wavelength signals and easy acoustical signals integration into an optical circuits.

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