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Photoacoustic Pulse Generation in $TlGaSe_2$ Layered Crystals

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Direct time- and space-resolved measurements of laser pulse induced photoacoustic pulses (PAP) in layered $TlGaSe_2$ crystal are presented. It is found that under layer plane excitation PAP can be generated by quite low laser fluences in contrast to isotropic solid crystals. The PAP amplitude is proportional to laser fluence but it is independent of actual injected free carrier concentration. The PAP propagates across layers and is multiply reflected from surfaces with small dispersion with 6 μs decay time. A fine splitting of the PAP is explained by an actual thickness difference due to crumble off layer planes. Tentative explanation of PAP generation mechanism, which is different from ordinary thermoelastic process, is presented.
Keywords: layered chalcogenides, photoacoustic effect, sound generation.

INTRODUCTION

The ternary compound $TlGaSe_2$ belongs to the class of layered crystals and consists of alternating two separated layers within the elementary crystal cell [1]. The layer is composed of covalently bonded four units of $GaSe_4$ tetrahedra and this composition is twisted by 90 degrees in each second layer plane. X-ray diffraction studies have shown that Tl^+ cations are regularly stacked in the trigonal cavities between two layers providing a neutrality condition of the crystal and weak van der Waals bonding between the layers. By lowering temperature from 120 K to 106 K $TlGaSe_2$ crystal undergoes a second order phase transition from paraelectric to an incommensurate and further to the ferroelectric phase [2, 3]. Investigations of $TlGaSe_2$ crystals received a great deal of attention due to their optical and electrical properties in view of possible application for optoelectronic devises [4]. Recently, we showed that fundamental absorption in $TlGaSe_2$ is determined by weakly allowed direct optical transitions overlapping with indirect transitions [5]. At low temperature direct excitonic band gap is equal to 2.13 eV. The close lying indirect excitonic transitions start above 2.08 eV and depend on a set of assisted phonons.

In this work, we present for the first time the experimental results showing that in $TlGaSe_2$ crystals it is possible to generate strong photoacoustic pulses (PAP) under laser light pulse excitation directed normally to the layer planes, i.e. parallel to crystal **c**-axis. The observed PAP can be generated by rather low light pulse fluences. The generation mechanism of this phenomenon is obviously different from the common thermoelastic stress wave generation process in the isotropic absorbing medium [6].

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SAMPLES AND EXPERIMENTAL DETAILS

Crystal samples used for the investigation were synthesized from the high-purity elements taken in stoichiometric proportions. Large size platelets of a few millimeter thicknesses and of several square centimeters were grown by modified Bridgman method [7]. Crystals showed week *p*-type conduction at room temperature. The stoichiometry of the crystal volume was confirmed by *x*-ray microanalysis [8]. 2 mm – 5 mm thick and wide slabs have been carefully polished on both sides of layers cross cut planes. After polishing, damaged front parts of the sample were cleaved off parallel to the layers. As a result, a rectangular shape and optically homogeneous samples of dimension about $(2 \times 6 \times (0.2 - 0.5))$ mm^3 were obtained.

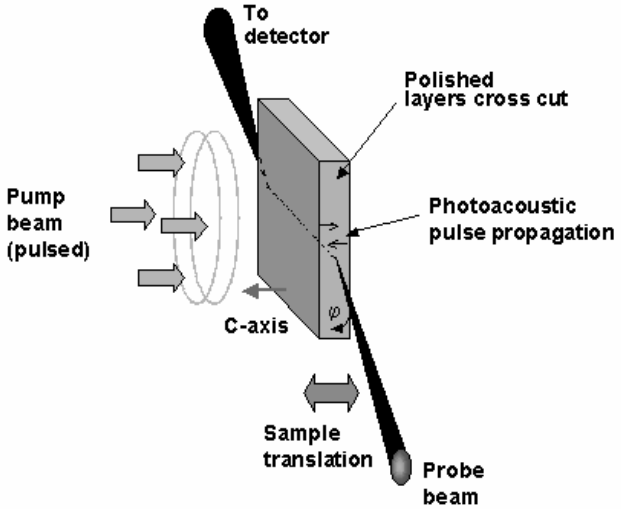

Fig. 1. A key diagram of measurement set-up with pulsed pump beam parallel to **c**-axis of the $TlGaSe_2$ crystal. Note that φ is close to the Brewster angle to minimize multiple reflections of the probe beam. PAP propagation directions are indicated

In this study, we used the pump-probe technique with orthogonal geometry of pump and probe beams. The prepared sample is placed in optical cryostat with the crystal **c**-axis directed to the front window. As shown in Fig. 1, the front sample face is homogeneously excited with 2.5 ns (width at half-maximum amplitude) pulses from a tunable wavelength optical-parametric-oscillator, which is pumped by Nd:YAG laser. The pulse repetition rate is 40 Hz and the maximum laser fluence is 2.5 mJ/cm^2 per pulse. Photoinduced signal is detected using 1.3 μm or 1.54 μm focused infrared probe beam directed from the lateral side, i.e. carefully aligned along the crystal layers. The probe beam is *p*-polarized and strikes the sample surface at the angle of incidence close to the Brewster angle, φ, to avoid multiple reflections. The actual resolution is limited by probe beam focusing, its wavelength and is to some extent depended on the sample width [9, 10]. In the current measurements probe beam diameter was of about 20 μm. Using micrometer translation of the cryostat it is possible to chose the position of the probe beam with 1 μm precision. Photoinduced signal is recorded using a fast optical receiver connected to a digital oscilloscope with 1 ns sampling resolution. The signals are averaging over 500 traces in order to attain sufficient signal-to-noise ratio. Further details of measurement technique can be found in Refs. [9, 10].

RESULTS AND DISCUSSION

Fig. 2 shows absorption transient $\Delta\alpha(t)$ of the probe beam at the depth position of 140 μm. The sample at 295 K is excited by 570 nm pump wavelength with fluence of 1.7 mJ/cm^2. The corresponding pump photon energy exceeds the band gap by about 100 meV and the absorption coefficient of the pump light is equal to 270 cm^{-1} [5]. At time moment immediately after pump laser pulse, $\Delta\alpha$ rises steeply above 0.1 cm^{-1} by means of band-to-band free carrier photogeneration. Then excess carrier density decays gradually. We have shown recently that Auger recombination dominates the beginning part of the recombination decay [7]. The following stage of exponential decay in a few next microseconds is caused by carrier recombination through deep centers.

As can be seen from Fig. 2, rather narrow oscillations are superimposed along the main absorption trace. The period of oscillations is proportional to the sample thickness. The detailed measurements at various depths [11] have given unambiguous evidence that the first oscillation arises in a close proximity to the excited surface. Then it travels across the sample thickness with the speed of acoustic waves $2.6\cdot10^5$ cm^2/s. This is consistent with the value found in literature [12]. Such results suggest a photoacoustic effect: the pump laser beam impinges on the sample inducing a strain which generates longitudinal acoustic pulse (coupled Lamb modes [13]). In our case, since the laser spot is wide – 2.5 mm in diameter, the acoustic modes exhibit a plain PAP traveling across the sample thickness. After passing to the other side, PAP is reflected from the back surface due to acoustic mismatch of the crystal and surrounding vacuum [6]. In this way, periodic modulation of material density arises by compression and expansion in the probed crystal volume, i.e. each time when PAP is passing in the forward and backward direction. The sequence of oscillation is indicated by arrows in Fig. 2. Detail investigation have shown that corresponding response of the probe beam is associated with cumulative changes of the absorption $\Delta\alpha$ and refractive index Δn. For the probing geometry shown in Fig. 1, oscillation is mainly caused by temporary probe beam deflection due to change of refractive index.

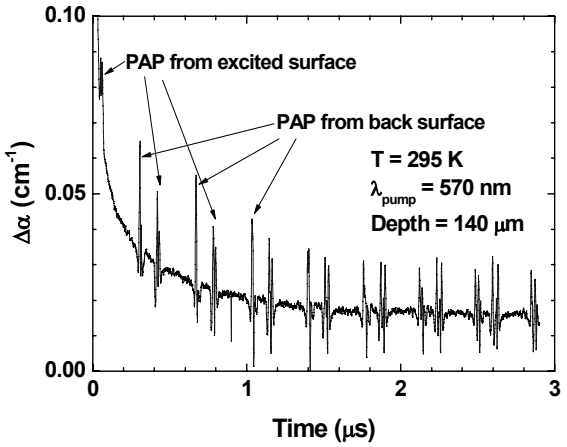

Fig. 2. Absorption decay in $TlGaSe_2$ sample excited at $t = 0$ by 570 nm pulse with pulse fluence of 1.7 mJ/cm^2 at 295 K and probed with 1.3 μm at the depth 140 μm from the front sample face

In the following figures we present detail investigation of the observed phenomenon. For any pump wavelength PAP amplitude linearly increases with intensity of the pump beam. In Fig. 3 quantum energy of the excitation (pump wavelength 580 nm) exceeds the band gap by 50 meV. In this case oscillation can be distinguished at rather low fluence of 0.6 mJ/cm^2.

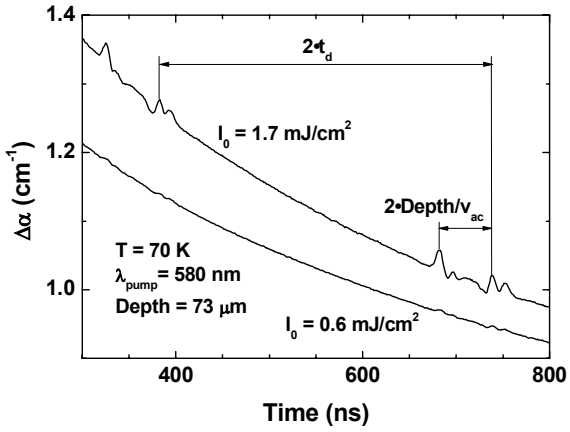

Fig. 3. A fragment of the absorption decay in $TlGaSe_2$ sample excited at $t = 0$. Excitation is provided with 580 nm wavelength of two different fluences, $T = 70$ K. Crystal is probed at the depth of 73 μm. Probe beam wavelength is 1.3 μm, t_d is the time for traveling of PAP from the exited to the back face

In Fig. 4 PAP is monitored for constant laser pulse fluence at 580 nm and 600 nm wavelength. The last one corresponds to quantum energy of 20 meV below the band gap. Due to indirect optical transition with assisted phonons the light absorption coefficient at this wavelength is 50 cm^{-1} [5]. Such low absorption coefficient ensures free carrier absorption all across the sample thickness. This is evidenced by rather high $\Delta\alpha$ values at the probe depth of 189 μm (upper curve in Fig. 4). Therefore, even for bulk like 600 nm excitation the PAP oscillations appear at the same time and have similar shape as for above band gap 580 nm excitation.

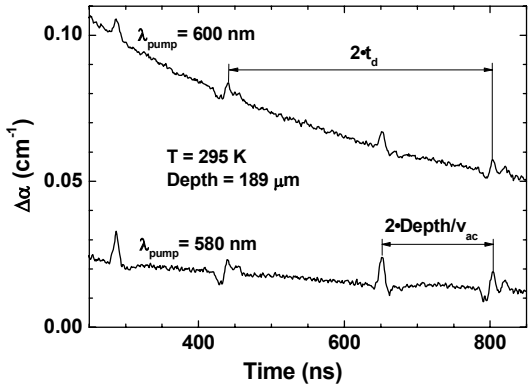

Fig. 4. A fragment of the absorption decay in $TlGaSe_2$. Excitation is provided by different wavelength at 295 K, the depth is 189 μm. Probe beam wavelength is 1.3 μm. t_d is the time for traveling of the photoacoustic pulse from the exited to the back (or vice versa) surface of the crystal, v_{ac} is the velocity of sound in $TlGaSe_2$

Intensity dependences of free carrier absorption and PAP amplitude for pump wavelength 550 nm and probe of 1.54 μm are shown in Fig. 5. No clear correlation between $\Delta\alpha$ and PAP amplitude is perceived in the high injection region. Saturation of $\Delta\alpha$ we tentatively attribute to band filling effect, which reduces free carrier generation ratio. It seems that reduction in pump absorption does not affect the PAP amplitude, which still increases linearly with pump fluence.

Fig. 6 shows fine resolution of PAP oscillations at 70 K and their transformations during time corresponding to more than 60 round trips in the sample. The decay due to free carrier recombination was artificially subtracted in this plot. In Fig. 6 a fine splitting of PAP is clearly visible. Two packages are drifting apart at a constant rate of 3.7 ns per round trip. At the same time the shape of the modulation is not much distorted up to 60 round trips. The doubling effect we explain by an actual difference in the sample thickness due to crumble off of layer planes on the sample back surface. The difference in thickness reaches 9.7 μm. Thus, the time it takes for PAP to travel through the thickness of the crystal is different in two parts of the sample. A rather long lifetime of the PAP allows observing an interference effect of the absorption oscillation when PAP propagating forward and backward meet at the position of probe beam. This can be noticed in Fig. 6 for the 12 – 16 round trips.

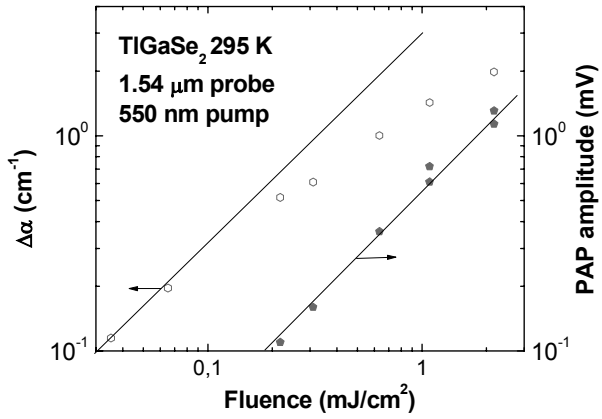

Fig. 5. Intensity dependence of free carrier absorption and PAP amplitude. Excitation is provided with 550 nm pulses. Solid lines indicate a linear increase

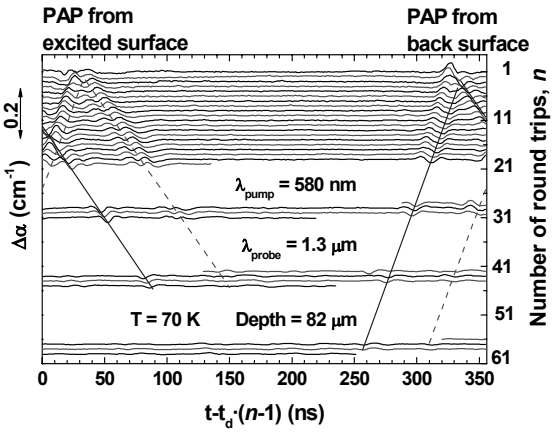

Fig. 6. Time-resolved oscillation changes owing to the PAP propagation at different periods across the sample. Excitation is provided with 580 nm pulses, probed depth is 82 μm, $T = 70$ K. The decay due to free carrier recombination was artificially subtracted. Solid and dashed lines indicate splitting of oscillation, which drift apart at a rate of 3.7 ns per round trip

The magnitudes of oscillation versus time are given in Fig. 7. Above mentioned interference of two packages appears in a narrow time range about 5 μs. Generally, PAP decays exponentially with a rough characteristic time of 6.2 μs. Free carrier absorption decay is also presented in the figure by dashed line. As evident from it, the shape of magnitudes of oscillation coincide with $\Delta\alpha(t)$ decay when $t \leq 7$ μs. In this region both qualities vary more rapidly than exponentially. For $t > 7$ μs the magnitudes of oscillation decrease with time constant less than the FCA decay. It is therefore concluded that magnitude of oscillation is independent of the free carrier concentration.

The common photoacoustic generation process in absorbing medium is related to thermoelastic stress wave. Compression and tensile waves are exact replicas of the absorbed energy density distribution (absorption coefficient of the medium) and are proportional to so called Grüneisen coefficient [6]. This mechanism does not allow

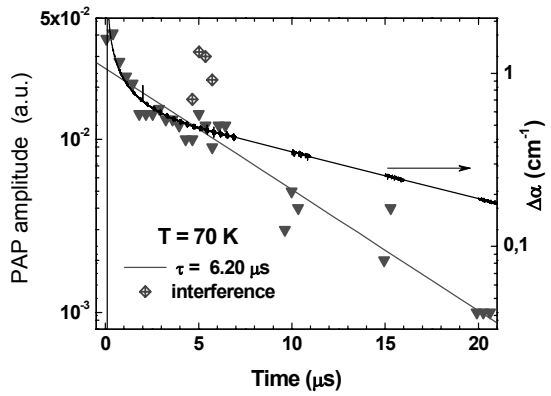

Fig. 7. Decrease of absorption oscillation amplitudes with time at 70 K. The $\Delta\alpha(t)$ decay is also presented

to explain all features of the phenomenon observed in $TlGaSe_2$. For the pure thermoelectric mechanism PAP amplitude must be strictly proportional to the amount of the absorbed energy, which is not the case shown in Fig. 5 at high injection. The PAP duration should increase withdecreasing of absorption that is not observed in Fig. 4 for 600 nm pump wavelength (excitation below the band gap). Comparing the obtained results with data of isotropic semiconductor GaP we found that an order of magnitude larger Grüneisen coefficient should be invoked for explanation of the PAP amplitudes in $TlGaSe_2$. All these features suggest modification of thermoelastic stress generation in layered $TlGaSe_2$. We suggest that amplified thermal expansion in the crystal with common stacking fault defect can explain our observations. According to estimation made for $TlGaSe_2$ in Ref. [14], a stacking fault (a structure displacement of the layer plane along (110)) is occurring approximately ones in every four layer plains. This defect arises because the energy difference of the two positions for the layer sheet stacking differs very little. Thermal expansion of the $TlGaSe_2$ material around an imperfect stacking in our opinion can be responsible for the observed efficient PAP generation in a close proximity to the excited face. Further investigation with shorter picoseconds duration laser pulses, however, is needed to confirm this idea.

CONCLUSIONS

We have reported on the direct time- and space-resolved measurements of oscillations generated in $TlGaSe_2$ due to photoacoustic effect. This phenomenon linearly depends on the laser pulse fluence but do not show evident relation neither to the absorption coefficient of the pump light nor to the injected free carrier absorption. Rather high amplitude of the PAP allows some practical application of the observed phenomenon in optical switching from visible to infrared light in telecommunication wavelength ranges.

Acknowledgements

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