Strong Photoacoustic Pulses Generated in TlGaSe$_2$ Layered Crystals

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Abstract. Periodic deflections of infrared probe beam in TlGaSe$_2$ crystal after its lateral excitation by laser pulse with photon energy near the band gap are observed. Such deflections arise from travelling of the acoustic pulse within sample which, in turn, is produced by optical pump pulse through photoacoustic effect. The photoacoustic pulse is generated within thin region near the crystal excited face, much shorter then the light penetration depth. In the case of volume excitation photoacoustic pulse is also generated in the region near back face as well. Tentative explanation of the generation mechanism is discussed.

1. Introduction

The photoacoustic effect was widely used in the past years to study transient expansion of heated surfaces, generation of the coherent acoustic phonons and detection of the sound velocity in various media [1-5]. Recently, we have reported the phenomenon of strong photoacoustic effect in layered TlGaSe$_2$ crystals generated by weak (0.01 mJ/cm$^2$) nanosecond laser pulses [6,7]. It was shown that the amplitude of the acoustic pulse is 10 times higher when exciting pump beam is parallel to c-axis of the crystal than in the case when it is perpendicular to c and that the generation region of the acoustic pulse is in close proximity to the excited face even for volume excitation. These results are in contradiction with usual thermoeleastic mechanism of stress generation [1,4,5].

In this paper we describe some more experimental conditions resulting in acoustic wave packet generation in TlGaSe$_2$ crystals, which help to elucidate the observed phenomenon. Finally, we describe some assumptions of the acoustic pulse generation mechanism.

2. Experiment

TlGaSe$_2$ crystals were grown by modified Bridgman method from high purity elements taken in stoichiometric proportions. The structure of the samples was studied by x-ray microanalysis [8]. Samples in the form of 2-5 mm thick slabs were carefully polished on both sides of the layers cross cut planes. The pump-probe technique with orthogonal geometry of beams crossing was used with tunable wavelength 2.2 ns pump pulses. A free carrier absorption (FCA) signal and sharp oscillations induced by probe beam deflections caused by acoustic wave propagation through the probed area was detected using cw 1.3 μm focused probe beam. More details of the measurement technique can be found elsewhere [6-8].
3. Results and discussion

The four time profiles of probe signal are presented in Fig. 1 (a) where pump pulse is incident at starting time of 70 ns on the TlGaSe$_2$ layer plane (||c, see inset). A sharp rise of FCA signal is detected for the volume absorption with excitation of 2.101 eV photons. For the excitation with surface absorption (2.254 eV) free carriers are not generated at the probe depth of 145.9 µm. The first superimposed acoustic pulse is observed with a certain delay after pump pulse. The delay is caused by time needed for the acoustic pulse with longitudinal sound velocity of $2.5 \times 10^5$ cm/s to reach the depth at which the probe beam transmits sample [3,6]. When the acoustic pulse pass through the probe area the sudden deviation of the probe beam occurs due to the change in the refractive index. The probe signal can either increase or decrease according to which half of the probe beam cross-section between two lenses is shaded (see inset to Fig. 1 (a)). Hereafter, the acoustic pulse reaches the back face of the crystal and reflects from it due to acoustic mismatch of the sample and surrounding medium (vacuum). As one can see in Fig. 1(a) in all cases the polarity of induced signal of pulse travelling in backward direction remains the same. The reason of this is that the compression/tensile pressure sequence in the pulse changes its phase after reflection from the free surface [4,5]. This means that the direction of probe deflection is always oriented towards back face and is in the plane of pump-probe beams. We can monitor repetitive sequences of the probe signal oscillations up to 100 reflections with negligible signal dispersion in a few hundred micrometers thick samples [7]. That demonstrates the high quality of surfaces obtained by cleaving the TlGaSe$_2$ samples. Fig. 1 (b) shows that relative deflection signal amplitude ($\Delta I/I$) correlates with the absorption coefficient at the band edge of TlGaSe$_2$ and almost linearly increases with pump pulse fluence. As displayed in the inset, laser fluences for the acoustic pulse generation can be as low as 0.01 mJ/cm$^2$.

Figure 1. (a) Signal of the probe beam transmitted through TlGaSe$_2$ crystal at 295 K, subsequent to pump pulse exciting crystal from lateral side at 70 ns. The pump photon energies are indicated. Upper and lower curves are obtained by shadowing half of the probe beam cross-section between two lenses from the side of excited face and from the opposite side, respectively, as shown in the inset. (b) The magnitude of the acoustic oscillation $\Delta I/I$ (large squares) normalized to constant pump photon number as a function of energy $h\nu$ in comparison with the corresponding absorption spectra (small dots). Dependences of $\Delta I/I$ vs pump pulse fluence for the point indicated by arrow is shown in the inset.

Fig. 2 presents the case when two opposite surfaces of TlGaSe$_2$ sample are simultaneously excited with the same laser pulse. Then the two acoustic pulses generated near front and back faces traveling towards each other and the reflectings from both surfaces are observed. These pulses are of the
opposite polarity as indicated by numbers in Fig. 2 (see caption, where asterisk marks pulses arriving after reflection). In the middle of the sample the two acoustic pulses coincide and, due to the opposite polarity of them, partly cancel each other. That can be observed at the probe depth of 131 µm.

![Diagram](image)

**Figure 2.** Signal of probe beam transmitted through TlGaSe₂ crystal at three different indicated depths. The pump pulses are directed to the two opposite faces perpendicular to the layer plane. 1(1’) indicate acoustic pulse generated near the front face, 2(2’) indicates acoustic pulses generated near the back face (an asterisk marks pulse after its reflection from the opposite face). At the sample mid position of 131 µm both pulses coincide.

The acoustic wave near the back face is also generated after the volume excitation as shown in Fig. 3 (a) for four different excitation quanta. In Fig. 3 (b) these pulses are presented after subtraction of the smooth FCA signal. It is clear that the polarity of the acoustic pulses remain the same as for the two side’s excitation case presented in Fig. (2). That means that acoustic pulse generated near the back face in fact moves at first towards the back face, changes the sequence of compression/tensile pressure and then after reflection propagates towards the front face. This effect can be attributed to the gradient of pump light intensity and corresponding temperature gradient, which is opposing near the front and back faces as indicated in the inset to Fig. 3 (a).

![Diagram](image)

**Figure 3.** (a) Signal of the probe beam transmitted through TlGaSe₂ crystal at 295 K after excitation in direction ||c with photons of different energies for the one-side volume excitation. (b) The same signals after FCA decay subtraction. 2(2’) indicates acoustic pulse generated near the back face, where asterisk shows this pulse after its reflection in the backward direction from the front face.
The depth resolution in our measurement is limited by the 15 \( \mu \text{m} \) diameter of the probe beam and in addition by the acoustic energy propagation distance within laser pulse duration of about 5.5 \( \mu \text{m} \) [6]. Despite resolution limit, our results clearly note that thermal stress is confined in the sample depth \( \leq 20 \mu \text{m} \), which is much shorter than the light penetration distance, \( 1/\alpha \), as predicted by the linear thermoelastic expansion mechanism of acoustic pulse generation [1,2]. We have checked that such near-surface generation region remains in different TlGaSe\(_2\) samples for any shorter pump wavelength near the band edge and is not changed for the samples obtained from the former slab by its cleavage. Moreover, the acoustic pulses have been observed with other probe wavelength, namely 1.54 \( \mu \text{m} \), 0.861 \( \mu \text{m} \) and 0.633 \( \mu \text{m} \) [6]. All of them yielded results quite similar to that described above.

The anisotropy of the bulk thermal expansion coefficient \( \beta \) of TlGaSe\(_2\) was investigated in [10]. It was shown that in direction perpendicular to crystal layers \( \beta_\perp \) of this semiconductor is 10 times larger then one in layered graphite. Along the layer planes \( \beta_\parallel \), is negative in large temperature range \( T < 140 \text{K} \). However, even such thermal expansion \( \beta_\perp \) is too small to explain the observed photoacoustic effect since the light absorption coefficient near the band gap is rather weak [11]. Moreover, a constant value of \( \beta_\perp \) in a sample cannot explain generation of acoustic pulse near surface.

It can be assumed that mechanism for explanation of the observed phenomenon may be related to two possible physical reasons. Additional enhancement of the thermal expansion coefficient in the interlayer between expanded linear stacking fault defects can occur. In Ref. [9] it was suggested from the studies of \( x\)-ray scattering technique that stacking faults are forming in TlGaSe\(_2\) crystal on average in one of every four double layers. Stacking fault can be extended in rather large area of hundred square microns as we deduced from the sizes of broken lateral terraces in the TlGaSe\(_2\) crystal [8]. The modification of some physical properties of surface layers can also be responsible for the acoustic pulse generation. The TlGaSe\(_2\) crystal elementary cell consists of two alternating layers which are separated by weak Van der Walls forces and are turned through 90° relative to each other. Ti ions are situated in triangular cavities between two layers composed GaSe\(_4\) tetrahedrons. Such configuration at the surface may have quite different thermal expansion properties than in the bulk of the crystal which can provide a source for the strong acoustic pulse generation. High amplitude and low spatial dispersion of the acoustic wave in TlGaSe\(_2\) allows some applications of the observed phenomenon in optical switching from visible to infrared light in telecommunication wavelengths range.

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