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Characterization of optical quality of GaSe:Al crystals by exciton absorption peak parameters

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Abstract The paper reports a first growth of the Al-doped GaSe crystals by modified technology with heat field rotation. These crystals shown from 2 to 3 times lower absorption coefficient at the maximal transparency range to that in crystals grown by conventional Bridgman technology. Possibility of the identification of optimal doping level in grown crystals by analysis of shape of the exciton absorption peak and intensity of the absorption shoulder at the transmission edge was demonstrated. The optimal doping can be attributed to the concentration of Al in the growth charge between 0.02 and 0.05 at.%. The result of the identification is confirmed by frequency conversion experiments: CO_2 laser SHG and optical rectification of fs pulses.

1 Introduction

Layered GaSe belonging to point group symmetry $\bar{6}m2$ is known from 1934 [1] but for the first time was applied for frequency conversion only in 1972 [2]. It is still in wide use in laboratory mid-IR [3] and THz [4, 5] nonlinear devices due to extreme physical properties: (1) a broad band transparency from 0.62 to 18 μm and further to ≥50 μm, (2) a large second-order nonlinearity of 54 pm/V in mid-IR [3] and 24.3 pm/V in THz [6] range, (3) a high damage threshold [7] and (4) a high thermal conductivity of 0.16 W/° K along growth layers [3]. The layered structure renders GaSe among extremely anisotropic crystals with as high birefringence as $B = 0.35$ at 10.6 μm [2] and 0.79 at 1 THz [8] that allows phase matching for both type I and type II processes almost all over the transparency range.

But the layered structure leads to the weak mechanical properties including very low hardness and easy cleavage along {0001} plane [9]. Another unfavorable effect is the existence of four (ε, δ, β and γ) polytypes, which may be found in one GaSe crystal. These circumstances, together with the presence of point defects (mainly Ga vacancies) and micro precipitations, limit the optical quality of available crystals. So, application of pure GaSe crystals in out-of-door optical systems is suppressed.

On the other hand, GaSe matrix easily accepts impurities. Appropriate doping of GaSe with isovalent elements: Al [10], S [11, 12], In [13, 14], Te [15, 16] and Er [17] significantly strengthens the structure and improves optical quality, and something modifies other physical properties mainly due to decreasing of the point defects and stacking faults. As a result, the doped crystals demonstrate improved frequency conversion efficiency and allow exploitation in field optical systems [18]. However,

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overdoping degrades optical quality and finally leads to destruction of the lattice structure [19]. Thus, some optimal doping level should exist. Direct search of optimal concentration by conventional spectroscopic measurements is very complicated due to low optical losses of GaSe in the range of maximal transparency (absorption coefficient $\alpha \leq 0.1$–$0.2\ \mathrm{cm}^{-1}$). So, one should use some indirect technique for identification of optimal concentration of the dopant. That was done for S [12] and In-doped [14] GaSe crystals by comparison of frequency conversion efficiency. In the case of Te-doping the parameters of phonon absorption spectra were considered [20]. The proposed method of the characterization through parameters of phonon absorption peaks included two stages: (1) recording of the well resolved phonon absorption peaks of GaSe crystals with a set of doping concentration, (2) selection of a sample with maximal phonon peak intensity and narrowest spectral bandwidth. Dopant content of the selected sample is considered as optimal one that was then confirmed by efficiency of SHG and/or optical rectification experiments. But to apply this method one needs quite rare, complicated and expensive facility.

In this study we propose the recording of exciton absorption spectra and intensity of the absorption shoulder at the transmission edge by widespread and cheap UV–visible absorption spectrophotometer to identify optimal doping. Selection of optimally doped crystal can be carried out by choosing a crystal with: (1) maximal intensity and narrowest spectral bandwidth of exciton absorption peak, (2) maximal spectral gradient of the absorption edge, and (3) minimal absorption shoulder at the transmission edge. It can be proposed that impurity local levels in defected pure and over doped GaSe screen the interaction of free electrons and holes that results in weaker exciton bonding. That in turn has to result in lower intensity of the exciton absorption peaks and less inclined absorption edge, as well as extended spectral bandwidth. Besides, wings of the local impurity levels can increase absorption shoulder at the transmission edge [10].

2 Experimental

Synthesis of stoichiometric GaSe was performed according to the steps described in details in Ref. [21]. Then synthesized polycrystalline material was reloaded to the growth ampoules with addition of from 0.01 to 2 at.% elementary Al 99.95. After charging, the sealed off ampoules were heated up to 1000 °C and kept during several days in order to dissolve the aluminium. The last step was a slow unseeded crystallization by the modified Bridgman technique with a heat field rotation in the melt. Details on the design of modified Bridgman furnace may be found in Ref. [22].

The samples were cleaved along the (0001) layers from as-grown ingots (Fig. 1); no additional treatment or surface polishing were made. Due to the difficulties in determining the real concentration of Al in the crystals, the direct meauserements of dopant distribution are not available, and the crystals were labbled by the charge composition. However optical measurements show quite uniform distribution of properties in the samples from one boule. Visual control has shown that GaSe:Al($\leq$0.5 at.%) were suitable for nonlinear applications. Al micro precipitations especially in the end part of the boules were observed in GaSe:Al($\geq$0.2 at.%). Structure defects undoubtedly appear at the doping level of $\geq$0.5 at.% of Al. The physical properties including some optical properties of pure GaSe and GaSe:Al (0.01, 0.05, 0.2, 0.5, 1, 2 at.%) crystals have been described in comparison elsewhere [23].

UV–visible transparency spectra were recorded by Cary 100 Scan (Varian Inc.) spectrophotometer: wavelength range 190-900 nm, spectral resolution $\Delta\lambda = 0.2$–4 nm, wavelength deviation ±1 nm.

3 Results and discussion

In difference to data in Ref. [10], no long-wave shift of the short-wave absorption end is observed. It is likely due to optimized and identical sample thicknesses, higher

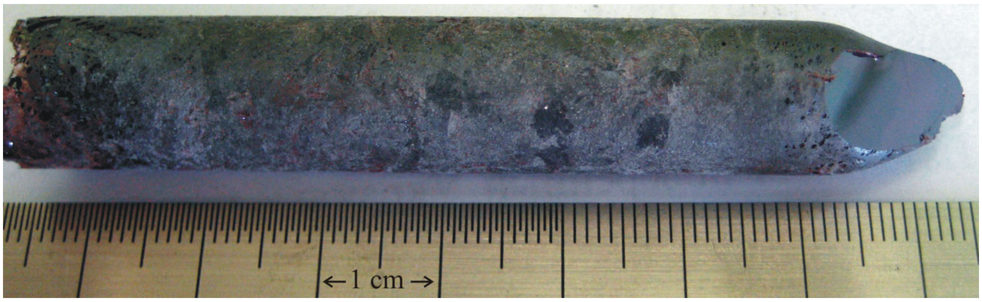

Fig. 1 As grown GaSe:Al (0.05 at.%) with the cleaved surface along (0001)

uniformity and optical quality of the crystals grown by the modified growth technology with. In average, studied crystals were characterized by at least from 2 to 3 times lower absorption coefficient in the maximal transparency range to that in the pure GaSe crystals grown by the conventional Bridgman technology.

It was found that optimal sample thickness for exciton spectra measurement is within from 20 to 50 µm. Such thickness excluded interference patterns due to large exciton absorption coefficient of about 2000 cm^{-1} for pure GaSe in accordance with our and known [24, 25] data, and close value for Al-doped crystals. Selected thickness well-kept one pass absorptivity (production of the absorption coefficient and the crystal length) above 50 that leading to a small power of the reflected beam that exclude interference with the reflected beam. On the other hand, reflectivity was well within the spectrophotometer specification limit of 1,000. Representative exciton absorption spectra for various concentrations are presented in Fig. 2. The curves for GaSe:Al(0.2, 0.5 at.%) are corrected for non-selective (within the spectral range shown) scattering losses caused by Al precipitations.

From Fig. 2 it comes that maximal intensity and minimal spectral bandwidth of the exciton absorption peak as well as maximal inclination of the absorption edge and minimal absorption coefficient at its shoulder are owned by GaSe:Al(0.02 at.%) and GaSe:Al(0.05 at.%) crystals. Thus, optimal doping can be attributed to from 0.02 to 0.05 at.% of Al that is quite in coincidence with the data in Ref. [10]. CO_2 laser SHG experiment similar to that in [10] and optical rectification experiment similar to that in [26] also fully confirmed it. It can be proposed that low optimal level is due to the fact that Al does not form AlSe compound and solid solution crystals $Ga_{1-x}Al_xSe$ cannot exist. At higher Al content in the growth charge the interstitials, interlayer intercalated atoms and precipitations drastically decrease the optical quality of the crystals. During the analyses, attention has to be paid to possible effect of the electronic structure modification on the absorption spectra for such kind of crystals [27]. In the result, even decreased absorption in the maximal transparency range can be caused significantly by this reason. Detailed description of the possible effect can be found in Refs. [28–30].

However, achieved results differ from many known data that, in particular, demonstrate permanent decreasing in the inclination (spectral gradient) of the short-wave absorption end with the increment of doping level [19, 25]. We proposed that it is due to overstepping of optimal doping levels. For instance, optimal S-doping roughly estimated in Ref. [12] through SHG efficiency as between 2 and 3 wt% cannot be compared with data in Ref. [25] for 1.04, 2.22, 4.6, 5.85, 7.17 wt% S-doped GaSe due to high gradient in the doping in both cases. On the other hand, optimal Te-doping estimated by parameters of phonon absorption peaks was shown to be in the range 0.07–0.38 wt% [20] is in a good agreement with 0.085–0.17 wt% reported in [26] because enough well overlapped doping concentrations. Thus, it can be proposed that, new sets of doped GaSe crystals with decreased step of the dopant concentrations have to be grown and studied in details to explain available discrepancies.

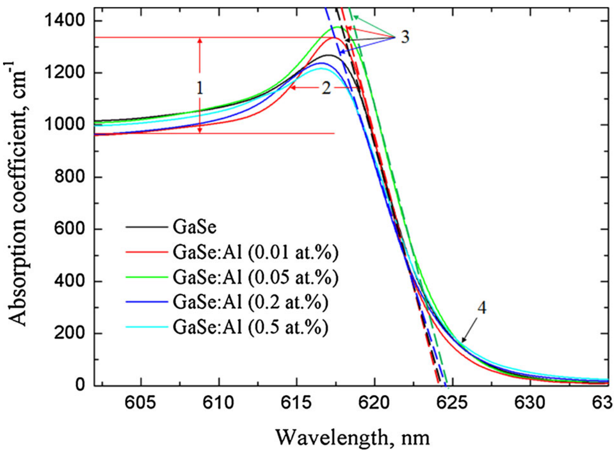

Fig. 2 Short-wave absorption spectra for Al-doped GaSe crystals: 1 and 2 are the exciton *peak* intensity and bandwidth for GaSe:Al(0.01 at.%), respectively; 3 are the approximations of the short-wave edges for: GaSe—the *black line*, GaSe:Al(0.01 at.%)—the *red line*, GaSe:Al(0.05 at.%)—the *blue line*, GaSe:Al(0.2 at.%)—the *green line*; 4 are the absorption shoulders at the *bottom* of the diagrams

4 Conclusion

For the first time Al-doped GaSe were grown by modified Bridgman method with heat field rotation. It was established that they possess at least from 2 to 3 times lower absorption coefficient in the maximal transparency range to that grown by conventional vertical Bridgman technology. Exciton absorption spectra were for the first time carefully studied in details using commercial UV–visible spectrophotometer. It was demonstrated that determination of the optimal doping can be carried out by choosing a crystal with: (1) maximal intensity and narrowest spectral bandwidth of exciton absorption peak, (2) maximal spectral gradient of the absorption end, and (3) minimal absorption at the absorption end plateau. The results achieved were confirmed by both mid-IR SHG and optical rectification (THz generation) experiment.

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