Saturable absorption of Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$ quaternary solid solutions

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Abstract. Nonlinear light absorption in variously thick films of Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$ quaternary solid solution crystalline grown on sapphire substrates by means of MOCVD [1] was investigated. We measured the transmission coefficient of laser pulses through samples as a function of the incident laser radiation intensity. A pulsed Nd$^3+$: YAG laser was used as a source of laser radiation (wavelength $\lambda$=1064 nm, duration of pulses $\tau\approx$ 35 ps, pulse repetition period 7 ns). The nonlinear absorption in Bi$_{1.25}$Sb$_{0.75}$Te$_{1.65}$Se$_{1.35}$ films was observed starting from the saturation intensity $I_{sat}\approx$ 50 MW/cm$^2$. The data can be explained by a process of filling states in a quantum well [2]. We have not observed the nonlinear absorption in two of the investigated films and, moreover, these films were destroyed at a high radiation intensity. An earlier work [3] demonstrated a change in the type of conductivity of a semiconductor film to metallic at a high radiation intensity. Since metal films are known to be destroyed at high radiation intensities, this phenomenon can explain the destruction of the investigated films. It was also found that a nonlinear change of the transmission of quaternary solid solutions can occur only for compositions with a Sb content of about 2 times less Sb than Bi, and the film thickness should not exceed 12 nanometers.

1. Introduction

The search for and study of new saturable absorbers with distinctive optical properties and suitable for specific tasks are among the most important issues in fiber-optic photonics. Saturable absorbers are used for passive mode-locking in fiber-optic lasers [4-6]. Up to now, semiconductor mirrors with a saturable absorber (SESAM), graphene, and carbon nanotubes have been the most actively studied and introduced into industry among various saturable absorbers. However, these absorbers are known to have a number of disadvantages. For example, SESAM has a narrow wavelength range (usually several tens of nanometers) in which absorption occurs, and its production is expensive and labor-intensive (nevertheless, these mirrors are widely used in laser systems). In carbon nanotubes, the problem of the narrow absorbent wavelength range is solved due to the specifics of the nanotube growth process when nanotubes of different diameters are formed. However, the dispersion of nanotube diameters usually leads to large additional losses that are not related to the absorption of radiation by nanotubes. Graphene, unlike carbon nanotubes, has a zero band gap, which makes it possible to use it as a broadband absorber in the range from 800 nm to 2200 nm. However, the modulation depth of graphene transmission is small (typically 1.3-2% for a single layer). Therefore, the main efforts of researchers were aimed at finding new materials that do not have these shortcomings.
Nowadays much attention is paid to the study of films of bismuth and antimony chalcogenides (Bi$_2$Te$_3$, Bi$_2$Se$_3$, Sb$_2$Se$_3$) because of their nonlinear optical properties, which can be used to create saturable absorbers [4]. Chalcogenides of bismuth and antimony are narrow-gap semiconductors (with a bandgap less than 0.3 eV) with a rhombohedral (tetradyymite) crystal structure. These materials have the following advantages over other previously studied saturated absorbers: a low saturation intensity, damage resistance at a high radiation intensity, a large modulation depth of transmission, absorption of radiation in a wide spectral range, and reasonable cost of production. A combination of these advantages makes Bi and Sb chalcogenides one of the most promising materials for practical application as saturable absorbers for passive mode-locking in fiber lasers.

In this paper, we present the results of the investigation of saturable absorbers based on thin films of Se$_x$Bi$_{2-x}$Sb$_x$Te$_{3-y}$Sey solid solutions grown by MOCVD on (0001) sapphire substrates. This method of growth makes it possible to control optical parameters of films and exactly reproduce the parameters of passive mode-locking in fiber lasers, in contrast to the method of depositing chalcogenide nanocrystallites from solutions and then forming a saturable absorber in a polymer, which is poorly reproducible and acceptable only for demonstration. The MOCVD method also enables growth of both thin films of complex compounds on different flat surfaces and a homogenous film on a side-polished and/or tapped surface of a fiber, which cannot be achieved using magnetron or laser ablation [7].

2. Experimental details

Rhombohedral films of Se$_x$Bi$_{2-x}$Sb$_x$Te$_{3-y}$ were grown on Al$_2$O$_3$ (0001) substrates with a thin buffer layer of ZnTe in a horizontal quartz reactor at atmospheric pressure of hydrogen. The ZnTe buffer layer was grown for passivation of free bonds of the substrate, which prevent the formation of continuous films that grow through the Van der Waals mechanism. More details about the growth of Se$_x$Bi$_{2-x}$Sb$_x$Te$_{3-y}$ films are presented in [1,8]. The surface and total thickness of the films obtained by growing were studied using atomic force and electron microscopy. We used an energy dispersive X-ray spectrometer to determine the elemental composition of the films. Some characteristics of the investigated films are given in table 1.

| Sample Code | Thickness ZnTe buffer layer, nm | Realized composition | Growth time, s | Calculated thickness | Transmission at 1064 nm |
|-------------|-------------------------------|---------------------|----------------|---------------------|-----------------------|
| TI607       | 16                            | Bi$_{1.25}$Sb$_{0.75}$Te$_{1.65}$Se$_{1.35}$ | 40             | 12                  | 0.16                  |
| TI610       | 6                             | Bi$_{0.64}$Sb$_{1.36}$Te$_{1.8}$Se$_{1.2}$ | 22             | 7                   | 0.50                  |
| TI614       | 6                             | Bi$_{1.33}$Sb$_{0.67}$Te$_{1.24}$Se$_{1.76}$ | 80             | 24                  | 0.13                  |

An experimental setup was created and adjusted to measure the nonlinear transmission of the samples, depending on the excitation radiation intensity (illustrated in figure 1). The output radiation of a Nd$^{3+}$: YAG laser is a train of 15-20 35-picosecond pulses with a time interval of 7 ns between them. The radiation wavelength is 1064 nm. After two prisms, the output laser radiation impinges on a beam-splitting plate, which divides it into two parts. After that, one part of the radiation passes through a delay line, and another part passes through the sample. The radiation has a Gaussian intensity distribution in the cross-section. To correctly estimate the intensity, a diaphragm was installed, the size of which corresponds to the size of the central part of the beam with the highest radiation intensity. After the diaphragm, the laser beam was focused on the sample by a lens ($F = 180$ mm).
3. Results and discussion
The measured dependence of transmission of the Bi$_{1.25}$Sb$_{0.75}$Te$_{1.65}$Se$_{1.35}$ film (sample TI 607) on the intensity of excitation laser pulses is presented in figure 2. The transmission was measured both by increasing and decreasing the intensity of excitation pulses in order to exclude the possible influence of long-lived processes, including thermal ones, on the transmission. Two regions were found where the transmission changed with increasing intensity of laser pulses. In the first region (I) at low intensities (up to 20 MW/cm$^2$) no increase in the transmission was observed. In the second region (II) at intensities of 20-100 MW/cm$^2$ a transmission increase was found. The increase in the transmission can be explained by absorption saturation in the range from 0 to -0.9 eV below the Fermi level in the twofold degenerate valence band (U-band) due to phase-space filling [3]. The transmission increases in absolute value $\Delta T = T - T_0 \approx 4\%$, with a relative change in transmission $\frac{\Delta T}{T_0} \approx 25\%$. Since the time of interband recombination of carriers for Bi$_2$Te$_3$ is 0.5-2 ps [9], we assume the same duration for the investigated quaternary solid solution, and the time of excitation by a laser pulse is 35 ps. The process can be considered stationary. Then, the saturation intensity can be calculated using the formula:

$$T = \exp (-T_m) \exp \left( \frac{-\Delta T}{1 + \frac{t}{t_{sat}}} \right),$$  

(1)

where $T_m = \Delta T + T_0$. 

Figure 1. Diagram of the experimental setup. BSP is the beam splitter plate, D is the diaphragm, L is the focusing lens ($F = 180$ mm), NF is the neutral filters, TI is the sample, MM is the metal mirrors.
Figure 2. The dependence of transmission of a topological insulator on the intensity of excitation laser pulses. (a) $\text{Bi}_{1.25}\text{Sb}_{0.75}\text{Te}_{1.65}\text{Se}_{1.35}$ film (sample TI 607) at low and medium intensities, (b) $\text{Bi}_{1.25}\text{Sb}_{0.75}\text{Te}_{1.65}\text{Se}_{1.35}$ film (sample TI 607) at a high intensity.

For this sample, the saturation intensity is about 50 MW / cm$^2$. The third region (III) at intensities of 100-110 MW/cm$^2$ is characterized by absorption saturation, which can be explained by the competition between the process of phase-space filling of the conduction band, leading to saturation of absorption, and absorption on excited carriers to deeper valence bands, draining the working valence band. Also, this growth of transmission can be explained by a change in the lifetime of carriers with increasing intensity of excitation radiation. As we can see in figure 2 (b), the sample is destroyed at a high intensity (above 150 MW/cm$^2$).

A nonlinear change in transmission for samples TI610 and TI614 (see table 1) have not been observed (figure 3 (a),(b)). At the same time, thermal destruction of these samples, as well as of TI 607 sample, was found at intensities above 150-200 MW/cm$^2$. This can be explained by a significant
conversion of the laser pulse energy into thermal energy due to band structure transformation in the near-infrared (IR) range in the case of high radiation intensity and the initial change of the film type from superconductor to metallic.

**Figure 3.** The dependence of transmission of a topological insulator on the intensity of excitation laser pulses. (a) Bi_{0.64}Sb_{1.36}Te_{1.8}Se_{1.2} film (sample TI 610), (b) Bi_{1.33}Sb_{0.67}Te_{1.24}Se_{1.76} film (sample TI 614).

We also found that there is no nonlinear change in transmission of a thin sample TI 610 with a higher content of Sb at low radiation intensity and for a thicker sample TI 614. This is in contrast to
sample Ti607, where a nonlinear change in transmission was found. This behavior of the dependence was explained by different contents of Sb and different thicknesses of the samples. It was concluded that the nonlinear change in transmission in Bi and Sb quaternary solid solutions can occur only when the composition of these compounds contains approximately 2 times less Sb than Bi, and the thickness does not exceed 12 nanometers.

4. Conclusions
The dependence of transmission on the intensity of laser excitation at a wavelength of 1064 nm was studied for samples of Bi$_{2-x}$Sb$_x$Te$_{3-y}$Se$_y$ solid solutions of different thickness and composition prepared by the MOCVD method. The nonlinearity of transmission was observed. A rapid increase in transmission with an increase in the incident light intensity was explained by the saturation effect associated with phase-space filling and a finite carrier lifetime. The transmission increases by about 4% from the initial value of 16% (with a saturation intensity of about 50 MW/cm$^2$) for the Bi$_{1.25}$Sb$_{0.75}$Te$_{1.65}$Se$_{1.35}$ film. The relative change in transmission ($\frac{\Delta T}{T_0}$) of the Bi$_{1.25}$Sb$_{0.75}$Te$_{1.65}$Se$_{1.35}$ film was about 25%. A nonlinear change in transmission was found for films with a thickness of less than 12 nm. For quaternary solutions, it was found that the Sb content should be about 2 times less than Bi in order for a nonlinear change to occur. It was found that most of the studied samples were thermally destroyed at an intensity of about 0.15 GW/cm$^2$.

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