Raman analysis of the crystallinity degree for the local regions in Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films after laser exposure at different parameters

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Abstract. The evaluation of the crystallinity degree for the local regions in Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} (GST) thin films after phase state transformation by laser pulses at 405 nm wavelength was analyzed using the Raman spectroscopy. The modes of laser radiation for controlling the reflectivity and transmissivity at 1550 nm telecommunication wavelength of the local regions in the GST film were established. The results obtained make it possible to implement the method of the completely optical control of the multilevel modulation of the optical signals for the integrated optics devices.

1. Introduction
PCM (Phase Change Memory) materials with phase state transformations are successful in this regard, in particular, chalcogenide glassy semiconductors, Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} material (GST). GST has a fast and low-energy phase transition. The sizes of the GST active regions are limited (~1 μm) by the wavelengths of the used laser radiation. Such active regions can be integrated into waveguide paths comparable to these sizes. This will allow good levels of integration, miniaturization, and performance in integrated optic and network-on-chip systems [1, 2]. In addition to the amorphous and crystalline phase states, there can be additional intermediate states due to the presence of partially crystalline and amorphous nanosized fractions of the material. Controlling the ratio of the fractional composition of GST opens wide possibilities in fine-tuning of its optical parameters, but at the same time, it requires studying the processes that occur when laser radiation is applied to the GST material. The ratio of amorphous and crystalline fractions in the bulk of the material is characterized by the crystallinity degree. The aim of this work is to study the crystallinity degree of the local regions of the GST film to select the optimal modes of laser exposure for the phase state transformations in the GST material.

2. Methods and materials
The GST thin film with the thickness of 24 nm were deposited by magnetron sputtering. The measurement setup (see figure 1) was used that allowed to carry out investigations using methods of Raman spectroscopy, atomic force microscopy (AFM), optical microscopy, photometry, laser modification. The phase state of the local regions of the GST film (see figure 2a) was changed from crystalline to amorphous phase state by the pulsed laser with 405 nm wavelength, with the focused spot diameter of about 1 μm, pulse durations from 5 to 30 ns and energy exposure from 2 to 4 nJ/μm\textsuperscript{2}. The radiation of 405 nm wavelength was used due to its high absorption by GST. The crystallinity degree was estimated from the Raman spectra (see figure 3) in the same way as in the work [3].
Raman spectra and AFM scans were obtained using the Ntegra-Spectra probe nanolaboratory (NT-MDT SI, Russia). Photometry of the local regions was used to measure the reflectivity and transmissivity of the film at 1550 nm wavelength.

![Figure 1. Structure of the measurement setup.](image)

3. Estimation of the film crystallinity degree

Estimation of the fraction of amorphous phase in the local range of the GST film volume is characterized by the crystallinity degree \( C \). The crystallinity degree \( C \) of the material can be estimated by Raman spectroscopy as follows. Intensity of the Raman scattering from the local region of the GST film can be estimated by Raman spectroscopy as follows. Intensity of the Raman scattering from the local region of the GST film is equal to [3]:

\[
I_{m,n} = 8 \times 9^{-1} \pi \omega^4 c^{-4} N I_0 \sum_{\rho,\sigma} \left| (\alpha_{\rho,\sigma})_{m,n} \right|^2,
\]

where \( I_0 \) is intensity of the incident laser radiation; \( \omega \) is a frequency of the scattered light; \( \alpha_{\rho,\sigma} \) is a polarization tensor component with indices \( r \) and \( s \); \( m \) and \( n \) are initial and final electronic states of the molecule; \( c \) is a velocity of light; \( N \) is a number of scatterers in the focal volume.

The number of scatterers changes from \( N_C \) to \( N_A \) in the focal volume due to the amortization of the crystalline film, which influences the intensity of the Raman peaks. In this case following equations can be obtained:

\[
I_C = K N_C I_0 \xi_C,
\]

\[
I_A = K N_A I_0 \xi_A,
\]

where \( I_C, I_A \) are intensities of the Raman scattering from the local regions of GST film for the amorphous and crystalline phase states, respectively.
Crystallinity degree is expressed as follows:

\[ C = N_C \left( \frac{N_C + N_A}{I_C} \right)^{-1} = I_C \left( I_C + I_A \xi_C \xi_A^{-1} \right)^{-1}. \]

(6)

4. Results and discussion

Figure 2 shows AFM images of local regions in the GST film irradiated by the pulsed laser with 405 nm wavelength and various energy exposure. Figure 3 shows Raman spectra in local regions showed by numbers from 1 to 11 in figure 2a.

**Figure 2.** AFM images of the local regions in the GST film irradiated by the laser with various energy exposure from 2.92 nJ/μm² (No. spectra 1, crystalline local region of GST film) to 3.26 nJ/μm² (No. spectra 11, amorphous local region of GST film) (a), energy exposure of 3.26 nJ/μm² (b), energy exposure of 3.57 nJ/μm² (c).

**Figure 3.** Raman spectra local regions in the GST film irradiated by the laser with various energy exposure from 2.92 nJ/μm² (No. spectra 1) to 3.26 nJ/μm² (No. spectra 11).
The evaluation of crystallinity degree showed that amorphization of the crystalline GST film is observed when exposed to laser with a wavelength of 405 nm at pulse energy exposure of 3.26 nJ/μm$^2$ (see figure 2b), with pulse duration of 10 ns. Film ablation is observed (see figure 2c) at pulse energy exposures greater than 3.4 nJ/μm$^2$. The conclusion about film ablation was made from the change in the GST film thickness in the local region using the AFM method. The GST film thickness without ablation was 24 ± 2 nm; during ablation, the thickness changed to the thickness of 0 ± 2 nm.

The change of the spectra from 1 to 11 (see figure 3) obtained after irradiation of local region in the crystalline film at 405 nm wavelength with radiant exposures from 2.92 to 3.26 nJ/μm$^2$ is due to the evolution of the crystallinity degree. Measurement of the reflectivity and transmissivity for 1550 nm radiation for the local regions of GST films with different crystallinity degree showed the change in these optical properties (see table 1), which allows multilevel amplitude modulation of an optical signal with a modulation depth of 45%.

Obtained values of the energy exposure allow selection of the operation modes of the GST film for the reflection and transmission of 1550 nm radiation in specified ratios. As can be seen table 1, it is possible to perform separation of radiation, partly block it or let it pass.

Table 1. Change of the optical properties of local GST regions.

| No. | Raman spectra | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  |
|-----|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|     | Energy exposure for 405 nm, nJ/μm$^2$ | 2.92| 2.95| 2.99| 3.02| 3.06| 3.09| 3.13| 3.16| 3.19| 3.23| 3.26|
|     | Crystallinity degree                  | 0.98| 0.83| 0.62| 0.58| 0.55| 0.59| 0.61| 0.50| 0.41| 0.29| 0.04|
|     | Reflectivity for 1550 nm              | 0.57| 0.55| 0.54| 0.51| 0.48| 0.46| 0.41| 0.35| 0.32| 0.27| 0.23|
|     | Transmissivity for 1550 nm            | 0.23| 0.26| 0.29| 0.32| 0.36| 0.38| 0.43| 0.49| 0.53| 0.6 | 0.68|

5. Conclusion

Thus, it was found that the change in the energy exposure of a laser pulse irradiation leads to the change of reflectivity, transmissivity, due to the evolution of the crystallinity degree. These results demonstrate the possibility of multilevel modulation of the optical signal at the 1550 nm wavelength and make it possible to establish the optimal modes of laser radiation at the 405 nm wavelength to initiate the phase state transformations of the GST material with necessary crystallinity degree.

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