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Laser-induced periodic surface structures formation and reversible crystallization in amorphous $Ge_2Sb_2Te_5$ thin films as a result of femtosecond irradiation

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Abstract. Femtosecond laser structuring opens for chalcogenide semiconductor $Ge_2Sb_2Te_5$ new perspectives in photonics applications due to wide change of its structural and optical properties in such processing. We studied laser-induced modification of amorphous $Ge_2Sb_2Te_5$ thin films on silicon substrates. The investigations show that periodic relief formation is accompanied by phase transitions to the fcc crystalline phase and back. Furthermore, the irradiated $Ge_2Sb_2Te_5$ samples demonstrate optical transparency in the near infrared region. The examined structures are interesting for further studies as a base of new memory devices which may possess optical anisotropy and be integrated into fiber optics applications.

Keywords: $Ge_2Sb_2Te_5$, femtosecond laser processing, laser-induced periodic surface structures, reversible phase transitions

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Материалы конференции
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Лазерно-индуцированное формирование поверхностных периодических структур и обратимая кристаллизация в аморфных тонких пленках $Ge_2Sb_2Te_5$ как результат фемтосекундного облучения

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Аннотация. Фемтосекундное лазерное структурирование открывает для халькогенидного полупроводника $Ge_2Sb_2Te_5$ новые перспективы использования в приложениях фотоники благодаря широкому изменению его структурных и оптических свойств при такой обработке. Нами исследована лазерно-индуцированная модификация тонких аморфных пленок $Ge_2Sb_2Te_5$ на кремниевых подложках. Исследования показывают, что периодическое формирование рельефа сопровождается фазовыми переходами в ГЦК-кристаллическую фазу и обратно. Кроме того, облученные образцы $Ge_2Sb_2Te_5$ демонстрируют оптическую прозрачность в ближней инфракрасной области. Рассмотренные структуры представляют интерес для дальнейших исследований в качестве основы новых запоминающих устройств, которые могут обладать оптической анизотропией и быть интегрированы в волоконно-оптические приложения.

Ключевые слова: $Ge_2Sb_2Te_5$, фемтосекундная лазерная обработка, лазерно-индуцированные поверхностные периодические структуры, обратимые фазовые переходы

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Introduction

The laser-induced periodic surface structures (LIPSS or “ripples”) based on $Ge_2Sb_2Te_5$ (GST225) promise large perspectives in the development of novel memory technologies and reconfigurable nanophotonic devices [1]. Usually, LIPSS have the period which is comparable to the wavelength of acted radiation and is significantly less than the laser spot diameter. Optical anisotropy in the visible and near-infrared ranges may emerge in such structures [2]. This is a promising way to encode information, especially in the case of GST225 processing via femtosecond laser irradiation when rewritable phase transitions to the crystalline phase are possible [3]. The significant difference between the optical properties of amorphous and crystalline phases of this material [4] makes a considerable contribution to optical anisotropy. Therefore, currently of great interest is the simultaneous LIPSS formation and phase transitions in amorphous GST225 thin films induced by femtosecond laser irradiation, including reversible phase transitions.

Thus, in this work we have irradiated thin GST225 films by femtosecond laser pulses to simultaneously fabricate LIPSS on the surface and achieve crystallization of GST225 and then investigated structural and optical properties of the modified samples.

Materials and Methods

Initial thin amorphous GST225 films with the thicknesses of 130 nm were deposited on dielectric substrates by magnetron sputtering of a crystalline target (ACI Alloys). Subsequent irradiation was provided by femtosecond laser system Avesta (wavelength $\lambda = 1250$ nm, pulse duration $\tau = 135$ fs, repetition rate $\upsilon = 10$ Hz). The laser fluence F varied from 0.05 to 0.15 J/cm^2. The

focused laser spot diameter was $D = 120 \pm 10$ μm. The samples were irradiated at normal incidence while moving continuously in one direction along the laser polarization at various speeds. As a result, single scanlines with the number of overlapping laser spots N_s from 3 to 750 were formed on the sample surface. Additionally, based on the results obtained for the single scanlines, a square 3x3 mm^2 area was fabricated in a raster mode for the pulse number $N_s = 150$ and step between scanlines $\Gamma = 100$ μm, for optical properties investigation.

The structural properties of initial and modified samples were studied by scanning electron microscopy (SEM; Carl Zeiss Supra 40) and Raman spectroscopy (Horiba Jobin Yvon HR800) at 488 nm excitation, as well as energy-dispersive X-ray (EDX) spectroscopy (Tescan Vega 3). Optical properties were defined via ellipsometry data analysis in the range 300–2000 nm (Horiba Uvisel 2). The type of phase transitions observed in the modified film was analyzed via the two-temperature model (TTM) calculations [5].

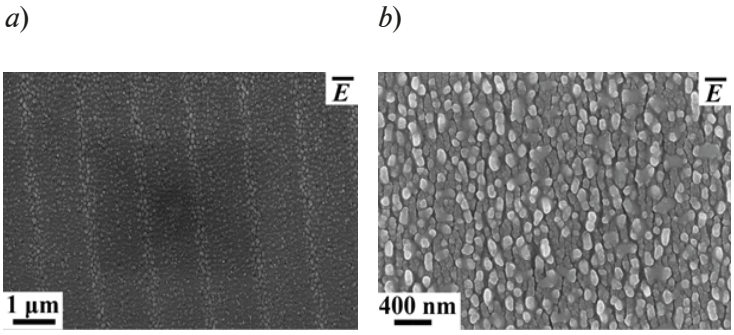

Fig. 1. SEM images of GST225 thin film, irradiated by the N_s=150 (*a*) and N_s=750 (*b*) laser pulses

Results and Discussion

According to SEM data the LIPSS formation on the samples irradiated with $F = 0.10 \pm 0.02$ J/cm^2 occurs at N_s=150 and higher values. Observed ripples period Λ varied from 1150 to 1350 nm, which is close to the wavelength of modifying laser pulses λ (Fig. 1,*a*). In all cases the gratings are directed orthogonally to the laser polarization. Such characteristics of the surface relief commonly indicate its formation mechanism as a result of interference between surface plasmon-polaritons and incident laser radiation [6]. In case of semiconductors such as GST225, the surface electromagnetic waves can be excited due to the transition of the near-surface layer to metal-like state, which means the dielectric permittivity of the irradiated material changes the sign from the positive to the negative one due to the intensive photoinduced generation of free charge carriers.

With the further increase of the $N_s \geq 300$ another LIPSS type was observed on the irradiated surface, in a form of ordered elongated clusters with the period $\Lambda = 130 \pm 30$ nm (Fig. 1,*b*). The orientation of obtained clusters is also perpendicular to the laser polarization. The clusters possess the longitudinal size in the range of 50–200 nm and the transversal size about 50 nm. The formation of such LIPPS is most likely explained by the thermo-capillar effects at the times which exceed pulse duration [7].

Raman spectroscopy indicated that surface modification of amorphous GST225 thin films induced by femtosecond laser pulses is accompanied by reversible phase transitions (Fig. 2). The Raman spectra of non-irradiated GST225 areas (N_s=0) shows the wide broadband at the range of 110–200 cm^{-1} due to the short-range crystallographic order of the amorphous phase (Fig. 2,*a*) [8]. The band consists of several lines near 125, 140, 158, 190 and 270 cm^{-1} which correspond to the A_1 $GeTe_{4-n}Ge_n$ (n = 1,2) corner-sharing tetrahedra, Sb_2Te_3 pyramids, A_{1g} hexagonal $GeTe_{4-n}Ge_n$ (n = 1,2), A_1 $GeTe_{4-n}Ge_n$ (n = 1,2) edge-sharing tetrahedra and F_2 $GeTe_4$ mode vibrations [8].

After femtosecond laser irradiation, the Raman spectra demonstrate the next transformations. The intensity of narrow peak near 125 cm^{-1}, which corresponds to $Ge_nTe_{4-n}Ge_n$ (n=1,2), increases with the growth of N_s from 3 to 15 (Fig. 2, *a*, *c*) while the line at 158 cm^{-1} decreases in intensity (Fig. 2,*d*). Such behavior may indicate transition to the face-centered cubic (fcc) crystalline phase [8]. The TTM calculations for the $F = 0.1$ J/cm^2 confirm this hypothesis (Fig. 3,*a*). According to the calculations the temperature of electron gas achieves ~$1.4 \cdot 10^4$ K during single

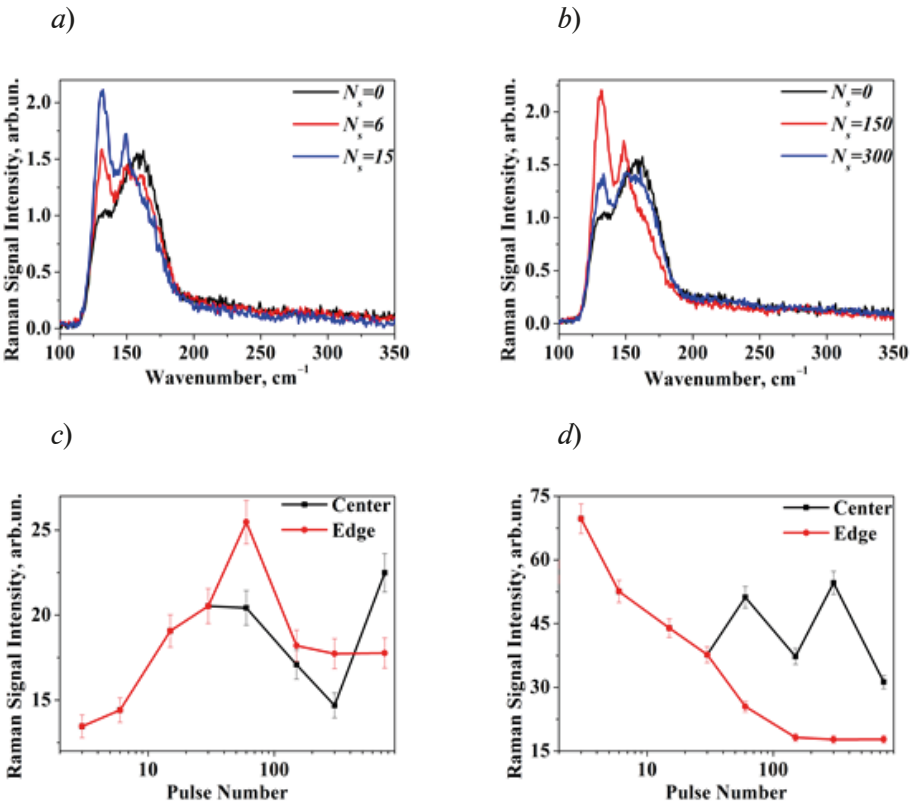

Fig. 2. Raman spectra of non-irradiated GST225 thin film (N_s=0) and samples for N_s=6 and N_s=15 (*a*). Raman spectra of non-irradiated GST225 thin film (N_s=0) and samples for N_s=150 and N_s=750 (*b*). Dependencies of integrated intensities of 125 cm^{-1} (*c*) and 158 cm^{-1} (*d*) line for center and edge of the scanlines on N_s

pulse treatment. The lattice temperature then increases due to the electron-phonon relaxation, and 2 ps after the laser pulse end exceeds the temperature of transition to fcc crystalline phase, which is 410 K. The peak temperature the GST225 lattice achieves during such heating is 480 K.

Additionally, at the values of $N_s > 75$, the 125 cm^{-1} Raman line decreases in intensity compared to the scan line edge (Fig. 2, *b*, *c*). Consequently, in the scan line center the Raman spectra become similar to non-irradiated GST225 thin films for $N_s \approx 300$ and higher. Such behavior can indicate re-amorphization of GST225. Such reversible phase transition is possible due to metastability of fcc crystalline GST225 [9] or rapid quenching of the melted material [10]. The cooling velocity more 10^{10} K/s and heat removal to the surface substrate contribute to the second mechanism of re-amorphization. It should be noted that the stoichiometry of GST225 film is not changed by femtosecond laser irradiation, which is confirmed by EDX spectroscopy data (Table 1).

Table 1

Concentration of Ge, Sb and Te atoms in initial amorphous GST225 thin film (N_s=0), as well as irradiated for the N_s=3, N_s=150 and N_s=750, defined by EDX spectroscopy

N_s	Atomic concentration, %		
	Ge	Sb	Te
0	18.9±1.5	25±3	56±3
3	17.1±1.0	25±1	58±5
150	19.5±1.2	26±2	55±2
750	18.9±0.7	27±1	54±3

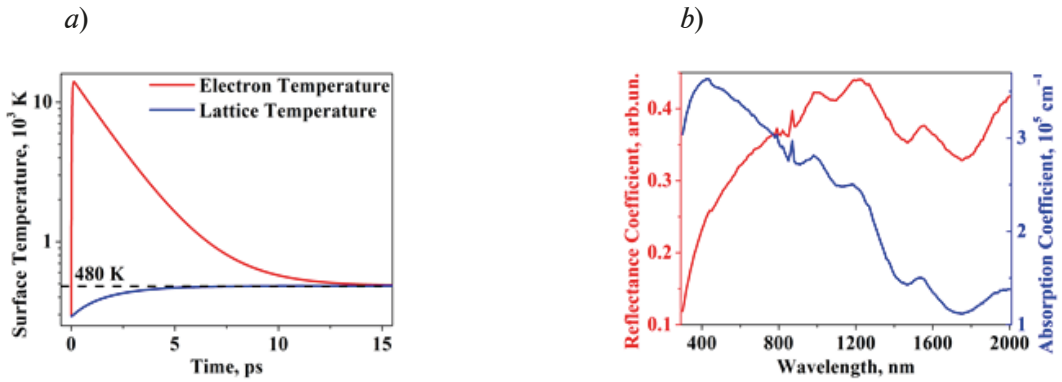

Fig. 3. Simulated surface temperature of GST225 during pulse treatment (*a*); reflectance and absorption spectra of irradiated GST225 sample, defined by ellipsometry data (*b*)

The reflectance and absorption spectra of irradiated GST225 sample are presented in Fig. 3,*b*. The reflectance coefficient grows from the 0.1 to 0.35 with the wavelength increase from 300 to 800 nm. Additionally, it demonstrates oscillations in the range of 800–2000 nm. Such behavior can be caused by the interference in GST225 thin film. On the other hand, the absorption coefficient decreases from $3.5 \cdot 10^5$ cm^{-1} to 10^5 cm^{-1} with the wavelength increase from 400 to 1800 nm. Thus, the studied GST225 films are transparent in the near-infrared range after femtosecond laser treatment and look promising for further studies and the development of new memory devices which may be compatible with the fiber optics applications, among other things.

Conclusion

We observed that surface modification of amorphous GST225 thin films induced by femtosecond laser pulses is accompanied by phase transitions to the fcc crystalline phase and back which is confirmed by Raman analysis and TTM simulations. Additionally, LIPSS with the period close to the laser wavelength were formed on GST225 surface at such treatment and the irradiated films are transparent in the near-infrared range. Therefore, the examined structures are interesting for further studies as a base of new memory devices which may possess optical anisotropy and be integrated into fiber optics applications.

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