# OPTICS
# AND LASER PHYSICS

# Ultrathin GeTe Crystal in a Strong Femtosecond Laser Field: Manifestation of a Quantum Size Effect

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The behavior of a thin-film GeTe crystal induced by intense femtosecond laser pulses ($\lambda = 0.8$ µm) has been studied using a pulsed electron diffractometer. The sample is an annealed 20-nm GeTe film on a copper grid with a carbon coating. It has been found that laser ablation results in the formation of an ultrathin GeTe crystal (assumingly, GeTe monolayer) with a high radiation resistance. Possible reasons for the detected nanosize effect are discussed.

## 1. INTRODUCTION

IV–VI chalcogenide compounds have stable phase states, which allow their application in nonvolatile storage devices based on a controlled change in the degree of ordering of their structure [1, 2]. A high contrast between crystalline and amorphous states with significantly different physical properties in phase memory materials opens the possibility of their wide applications [1, 2]. A controlled and, particularly important, reversible phase transition can be induced by different (thermal, electrical, or laser) pulses [1–4]. As follows from [1, 2], the use of ultrashort laser radiation is promising. In this direction, some aspects of an ultrafast athermal (nonthermal) change in the structure were previously demonstrated in the thin-film phase memory material $Ge_2Sb_2Te_5$ (GST) [5–7]. The authors of [8] recently performed a complex study of transformations in an amorphous 230-nm GST sample induced by ultrashort laser pulses and detected a transition from the Rayleigh–Plateau instability to the thermocapillary Marangoni convection preceding the ablation process.

An exclusive phase memory material is germanium telluride, which has one of the simplest crystal structures (the orthorhombic $\alpha$ phase with the space group $R3m$ and the cubic $\beta$ phase with the space group $Fm3m$) [9, 10]. The aims of this work are to perform a transmission electron diffraction study of a thin-film crystal of this compound after the irradiation of the sample by single intense femtosecond laser pulses and to demonstrate the formation of an ultrathin GeTe crystal, which can be of great fundamental and applied importance.

## 2. EXPERIMENT

The experiment was carried out using a compact electron diffractometer described in detail in [11, 12]. This instrument for the detection of structure dynamics is designed to probe a thin-film crystal sample, which is irradiated by femtosecond laser radiation, by short electron pulses in order to implement ultrafast electron diffraction [13]. A necessary condition for this technique is the acquisition of a signal from a sufficiently large number of laser pulses, which in turn requires the reversibility of studied laser-induced phase transitions. This compact electron diffractometer (an oil-free vacuum of $\sim 10^{-7}$ mmHg) can also be used in the "classical" mode to record electron transmission diffraction patterns from thin crystals.

A 36-keV pulsed photoelectron beam ($\sim 10^3$ electron per pulse) was generated by the irradiation of a thin-film gold photocathode by the ultraviolet third harmonic of a master femtosecond Ti:sapphire laser. The diameter of the probe in the region of the sample was about $100$ µm (several times smaller than the characteristic size of the irradiated region) owing to a static magnetic lens. A highly sensitive detection device was constructed from a pair of microchannel plates and

a luminophore screen information from which was read by a CCD matrix.

The sample was a 20-nm GeTe film polycrystal obtained by vacuum thermal deposition on a commercially available copper grid, which had cell size of about 64 μm and was coated with a 15- to 20-nm carbon film (Ted Pella Inc.). The sample was irradiated by *single* intense linearly polarized 50-fs 800-nm laser pulses incident at an angle of 45°. After the end of excitation, the master Ti:sapphire laser was switched to the 1-kHz mode and the sample was probed by the pulsed electron beam for 20 s. Further, the master laser was returned to the single-pulse mode and the energy in a pulse was increased. The maximum energy density in the laser pulse was about 40 mJ/cm$^2$, which was determined by the "ambient" illumination of the detector. The laser irradiation of the same region of the sample was explained by the limited lateral homogeneity of the prepared crystal of several hundred microns.

## 3. RESULTS AND ANALYSIS

The electron diffraction pattern of the 20-nm GeTe crystal is shown in the inset of Fig. 1. A set of contrast diffraction rings indicates a pronounced polycrystalline structure of the sample. Using the known electron diffraction methods [14], we simulated the intensity distribution of diffracted electrons in the detector plane for polycrystallites of the α and β phases of GeTe. Experimental data are presented in Fig. 1a, and the results of the calculation the α and β phases of GeTe are shown in Fig. 1b. At the chosen de Broglie wavelength $\lambda_{dB} \approx 0.064$ Å and the sample−detector distance of ~200 mm, the scattering parameter $s = (4\pi/\lambda_{dB})\sin(\theta/2)$, where θ is the scattering angle, in this experiment was in the range of ~1−6 Å$^{-1}$. The lower bound of this range is determined by the screen region illuminated by the unscattered electron beam and the upper bound is specified by the size of the detector.

As seen in Fig. 1, all detected lines can be identified. However, the amplitudes of the detected diffraction peaks noticeably differ from the calculated values. This primarily concerns the diffraction peak at $s \approx 1.8$ Å$^{-1}$. This peak is apparently due to the random coincidence of peaks from the α and β phases of GeTe with the diffraction peak from the carbon substrate. We note that this peak is absent for the unirradiated substrate. The irradiation of the pure substrate by femtosecond pulses leads to the appearance of a peak at $s \approx 1.9$ Å$^{-1}$ characteristic of graphite, one of the allotropic forms of carbon [15], which is apparently due to the graphitization of the substrate caused by its radiation-induced heating. For this reason, we believe that the main contribution to the peak at $s \approx 1.8$ Å$^{-1}$ in Fig. 1a comes from graphite formed in the process of thermal annealing of deposited GeTe, which is necessary for obtaining the crystal film.
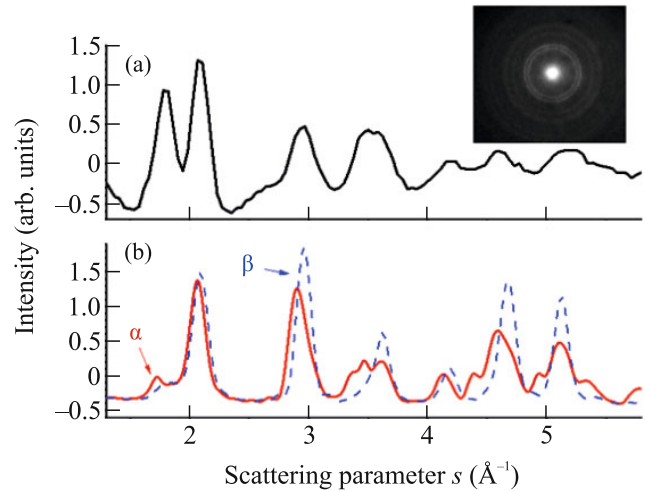


**Fig. 1.** (Color online) Radial distribution of the intensity of electron scattering from GeTe with diffraction maxima according to (a) experimental data and (b) calculation for (solid line) alpha and (dashed line) beta phases. The inset shows the electron diffraction pattern from the 20-nm GeTe crystal film obtained when collecting a signal from $2 \times 10^4$ electron pulses (20-s exposure).

Figure 2 presents the dependence of the integrated intensity of the diffraction pattern, including the signal corresponding to diffuse scattering of electrons, on the fluence of the incident laser pulse *F*. Above the pump fluence $F = F_{thr} \sim F_{abl} \sim 28$ mJ/cm$^2$, we detected a significant ablation-induced decrease in the signal intensity, which indicated a significant decrease in the thickness of the studied sample in the experiment. (The threshold of femtosecond laser ablation for such a phase memory material as the thin-film GST semiconductor studied in [6] is ~30 mJ/cm$^2$, which almost coincides with our measurements for the simpler binary compound, which is also a phase memory material.)

The ultrathin film obtained after ablation evaporation kept the properties of GeTe (which is manifested in the electron diffraction pattern characteristic of this compound (see the right inset of Fig. 2)) and appeared to be resistant to the strong laser field in the range of $F \sim 30-40$ mJ/cm$^2$. According to estimates, the film had a thickness of less than 4 nm. We attribute this behavior of the material to the quantum size effect; i.e., ultrathin, monolayer in limit, structures acquire new properties. In particular, it was shown in [16] that the radiation resistance of a MoS$_2$ monolayer exposed to femtosecond laser pulses is several times higher than that of the bulk semiconductor.

For explanation, we consider the following model. The ablation and laser-induced destruction of a crystal lattice can occur when the density of excited states reaches the critical value. The width of the band gap in thin-film semiconductors $E_C$ increases significantly
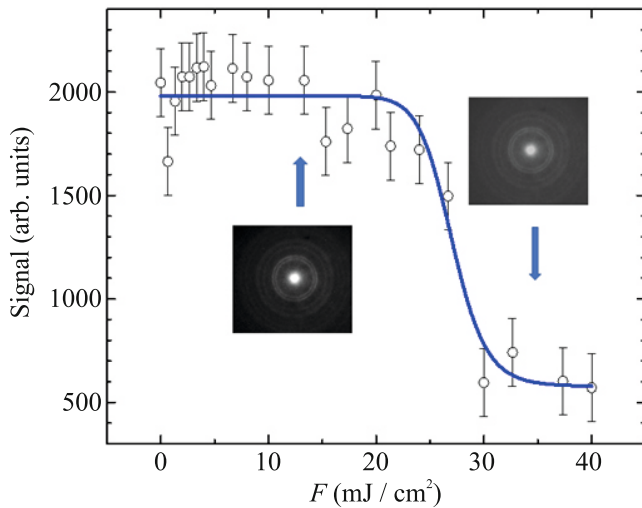
**Fig. 2.** (Color online) Integrated signal on the detector (including the signal corresponding to the diffuse scattering of electrons versus the fluence of laser radiation $F$. The empty circles with error bars are experimental data. The solid line is a sigmoid approximation. The left and right insets show the electron diffraction patterns from the 20-nm GeTe crystal film and from the ultrathin GeTe assumingly monolayer.



**Fig. 3.** (Color online) Scheme of the optical excitation of the bulk and single-layer GeTe crystal through the one- and (2FA) two-photon absorption processes at a wavelength of 800 nm (a photon energy of 1.55 eV).

with a decrease in their thickness $d$. The correction caused by the quantization of accessible excited states in ultrathin structures usually is $\Delta E_C \sim d^{-2}$ (this dependence is obtained because $p \sim \Delta p \sim \hbar/\Delta x \sim 1/d$; consequently, $\Delta E_C \sim p^2 \sim 1/d^2$) [17].

Bulk germanium telluride is an indirect-band-gap semiconductor with a narrow band gap (narrower than 1 eV), whereas the GeTe monolayer is an indirect-band-gap compound with an optical band gap of about 1.8 eV [18]. Since the photon energy in our laser beam is 1.55 eV, single-photon absorption prevails for multilayer GeTe, whereas the GeTe monolayer can be excited only through two-photon absorption, which occurs with a much lower probability (Fig. 3). Correspondingly, the radiation resistance of the ultrathin GeTe crystal under the experimental conditions within this model is much higher than that of the bulk semiconductor, which is confirmed by the results of the experiment. When the thickness of the GeTe film decreases to a monolayer, it becomes transparent at a wavelength of 0.8 μm and, thereby, ablation evaporation is completed.

## 4. CONCLUSIONS

To summarize, the 20-nm-thick GeTe crystal has been exposed to single intense femtosecond 800-nm pulses with the in situ electron probing of the formed structure. We have detected the ablation of GeTe and ha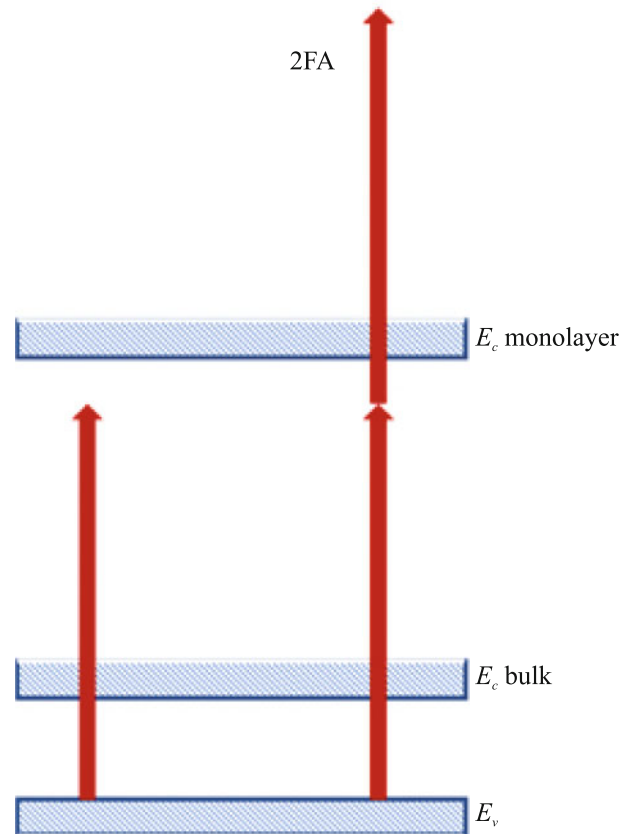ve determined its threshold at the fluence of the laser pulse $F_{abl} \approx 28$ mJ/cm$^2$. The ultrathin GeTe layer obtained at $F = F_{thr} \approx F_{abl}$ is certainly identified in the electron diffraction pattern characteristic of the crystal state of GeTe and is resistant to the strong femtosecond laser field in the fluence range of $F \sim 30$–40 mJ/cm$^2$.

The manifestation of the quantum size effect has been revealed and the GeTe monolayer crystal has been assumingly formed as a result of controlled ablation evaporation. The results obtained in this work are of particular interest first for the possible miniaturization of memory devices to extremely small sizes. Second, the calculation of electron diffraction patterns in the kinematic approximation disregarding multiple scattering of electrons in the sample becomes correct. Indeed, kinematic theory is applicable only to very thin crystals because of strong elastic and inelastic scattering of electrons [19, 20]. Foundations of dynamic theory were developed for thick samples [21], but its application to the analysis of experimental data is complicated because it is difficult to take into account all interactions of electrons with the sample under study [19]. The proposed approach allows

a much simpler interpretation of electron diffraction data.

No convincing evidence of a light-induced phase transition from the crystal to amorphous state in the GeTe thin-film crystal in the strong 50-fs laser field has been obtained. This transition possibly requires longer laser pulses, which is a subject of separate studies. In particular, reversible phase transitions were induced in a 100-nm GeTe film in [22, 23] by nanosecond laser radiation.

## FUNDING

## CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

## OPEN ACCESS

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