

Parameterization of photobleaching and photodarkening *in-situ* kinetics in thermally deposited GeSe₂ thin films

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Abstract

Thermally evaporated chalcogenide glass thin films are known to be highly photosensitive revealing both metastable and transient photoinduced changes of optical transmission at the fundamental absorption edge region. *In-situ* kinetics of metastable photobleaching and transient photodarkening as well as following light-off relaxations for as-deposited GeSe₂ thin films were studied and fitted with the stretched exponential function. Dependences of kinetic parameters β and τ on film thickness, temperature, sample prehistory and wavelength of light irradiation were analyzed. The obtained results were discussed within existing approaches to mechanisms of photoinduced kinetic phenomena and structural relaxation in glasses.

Introduction

Photoinduced optical effects in thermally evaporated chalcogenide glass (ChG) thin films have been extensively studied for several decades due to their unique sensitivity and ability to switch between different metastable (irreversible) and/or transient (reversible) states under exposure by applicable light radiation [1-4]. The photosensitivity of ChG thin films have been utilized in numerous applications such as optical memory [2], photonic switching and computing [4,5], nano- and micro-lithography [6]. However, the usefulness of materials are restricted by the complexity of their accompanied electronic, atomic and phase transformations, as well as noticeable drift of the controlled optical parameters during irradiation and post-irradiation relaxation.

Parameterized *in-situ* studies of photoinduced optical effects in ChG thin films allow for identification of their metastable and transient components and exploration of their kinetic features at different conditions of irradiation and sample's prehistory. It was shown previously [7-11] that fitting the kinetic behavior of different induced (including photoinduced) and relaxation-related processes in these materials with stretched exponential function (SEF)

$$y = A_0 + A_1 e^{-\left(\frac{t}{\tau}\right)^\beta}, \quad (1)$$

where τ and β represent the effective response time and dispersion parameter, respectively, is an appropriate tool to quantify the experimental data providing valuable information on correlation of both parameters with specific mechanisms of the responsible structural transformations.

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Stoichiometric GeSe₂ thin films obtained by thermal evaporation from the bulk are suitable model objects to study photoinduced effects in ChG thin films. Long-term kinetics of photoinduced shifts of the optical absorption edge under exposure with bandgap or super-bandgap light, studied earlier [12-14], revealed metastable photobleaching (PB), e.g. shift of the absorption edge towards higher energies, for as-deposited films. Such metastable changes can be partially reversed by prolonged annealing at temperatures just below their glass transition temperature T_g . An opposite effect, photodarkening (PD), was observed upon exposure of these thin films pre-annealed at below- T_g temperatures for prolonged period of time [12,14]. Additionally, reversible transient PD was observed for all thin films in numerous ON/OFF cycles of irradiation [12-14]. Despite the obvious importance of these data, there is still a significant gap related to the parameterization and detailed analysis of the observed effects.

In this paper, we study kinetic behavior for both, the metastable PB (PD in the pre-annealed films) and transient PD effects, in thermally deposited GeSe₂ thin films and analyze how the respective kinetics, specifically the τ and β parameters in the SEF (1), depend on film thickness, temperature, prehistory and wavelength of light irradiation.

Experimental

Two sets of experiments have been performed to parameterize photoinduced effects in thermally deposited GeSe₂ thin films.

For the first one, the amorphous GeSe₂ thin films were thermally deposited onto silica substrates from a crushed bulk glass of the same stoichiometry using the planetary thermal evaporator UP-858 (Tesla Corporation) to target thicknesses of 200 nm and 500 nm. The films were removed and stored in darkness and room temperature. During measurement, the films were placed into a small temperature controlled sealed chamber filled with argon to avoid oxidation, with two optical windows transparent to visible light. The setup allowed for the *in-situ* measurement of optical transmission spectra (StellarNet Inc. fiber-optic spectrometer) at different temperatures during exposure by 447 nm laser light (~ 180 mW/cm²), which corresponds to the GeSe₂ band gap energy [15,16]. The *in-situ* transmission measurements of irradiated films at given temperatures were taken only after stabilization of temperature-induced optical effects. Some films were pre-annealed at the temperature just below glass transition. This set of experiments included kinetics of photoinduced change of optical transmission of the as-deposited films in dependence on temperature, film thickness and pre-annealing.

Another set of experiments to study the kinetics of photoinduced changes of optical transmission of the as-deposited films in dependence on light energy was carried out using 200 nm GeSe₂ films deposited on silica substrates (MBraun thermal evaporator). The thin films were stored in darkness and vacuum until the measurements started. The *in-situ* kinetics of the optical transmission spectra were taken in air using AvaSpec-ULS2048XL-2-USB2 dual channel fiber optic spectrometer for the thin films exposed to ThorLabs high-power (~ 90 mW) LEDs of different wavelengths (385, 455, 590, 780 and 1550 nm). For both experiments, the changes of optical transmittance vs time of exposure $\Delta T(t)$ in the absorption edge region at the wavelength corresponding to the initial 25% transmittance was extracted using appropriate software. The SEF parameters τ and β were derived from $\Delta T(t)$ kinetics using OriginLab software non-linear fit.

Raman measurements were taken on Horiba Xplora Raman microscope using 785 nm laser excitation. The photoinduced structural changes were studied *ex-situ* on freshly prepared thin films and films exposed for 200 min with light from 532 nm laser of low intensity (0.25 mW).

Results and Discussion

The characteristic PB observed as a high-energy shift of optical absorption edge in the as-deposited GeSe₂ films when exposed to 385 nm high power LED light in air for 6 hours, is illustrated on Fig. 1. Usually, at these exposure conditions, we observe some minor changes in the optical transmission of thin films associated either with known photoinduced volume changes [17] or/and surface modifications (photooxidation [18], photovaporization [19], etc.). In the present study, we are interested in the *in-situ* kinetics of photoinduced changes of optical transmittance in the absorption edge region, specifically changes observed at the fixed wavelength corresponding to the 25% transmittance at the beginning of irradiation. At this level, the photoinduced changes are already quite significant but still not influenced by interference fringes appropriate to the optical transmission region. For as-deposited GeSe₂ films, such irreversible metastable photoinduced changes are associated with photostructural transformations such as bond breaking and switching accompanied by structural relaxation [12].

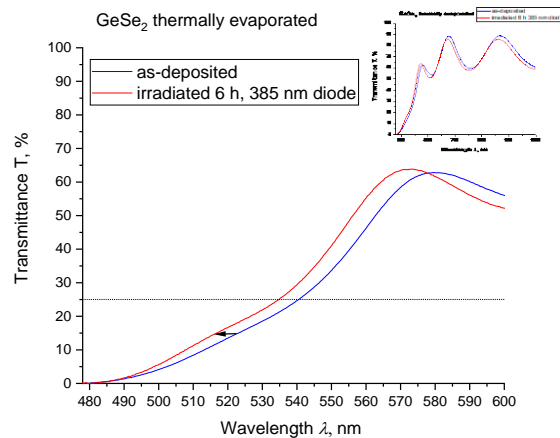


Fig. 1. Verification of typical PB behavior for as-deposited GeSe₂ films under irradiation with bandgap or super-bandgap light.

The kinetics of photoinduced effects have been extensively studied in As-based thermally-evaporated films pre-annealed at below- T_g temperatures [20,21]. It was reported that the fitting function describing the respective kinetics were different for various photoinduced phenomena. The purely single-exponential dependence with $\beta=1$ in Eq. (1) was validated for the kinetics of photoinduced volume changes, while the kinetics of defect creation was characterized by SEF with $\beta < 1$ [20]. More complex dependence was revealed for the kinetics of PD, characteristic for As-based films, where $\beta=1$ if the exposure light completely penetrates through the film and $\beta < 1$ for thicker films if the exposing light is totally absorbed inside the sample. The exponential behavior of the PD in ChG thin films was also reported by Ke. Tanaka [22].

At the same time, sporadic available data on kinetics of photoinduced optical effects in Ge-based films [12,13], while insightful, do not provide detail quantitative analysis of β and τ parameters in the fitting function. The kinetic curves for metastable and transient photoinduced room-temperature changes observed in the optical transmittance of as-deposited GeSe₂ films taken in two different ways are shown in Fig. 2. The black graph (thinner one, left Y axis) shows high energy shift of the wavelength position $\Delta\lambda$ matching to the 25 % level of transmittance and the bold red graph (right Y axis) relates to the photoinduced change of optical transmittance ΔT at constant λ corresponding to 25% transmittance at the beginning of irradiation. Both curves confirm some specific features previously noted by other authors [12,13], such as immediate short-lived

PD (see insert in Fig. 2) followed by prolonged PB and additional self-bleaching (SB) caused by switching OFF the exposure source and subsequent PD when the light excitation is ON again. For the sake of adequate parameterization, we use the $\Delta T(t)$ kinetics directly derived from the raw optical transmission measurements.

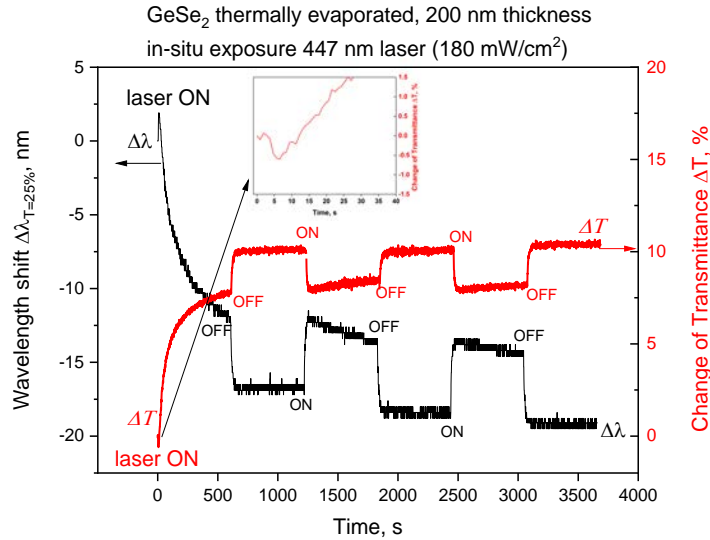


Fig. 2. *In-situ* room-temperature $\Delta\lambda$ PD (PB) kinetics (left vertical axis) and photoinduced changes of optical transmittance ΔT at constant λ (right vertical axis) for as-deposited GeSe_2 films (200 nm thick) irradiated by bandgap laser light in ON/OFF cycles.

When considering PD or PB kinetics in the as-deposited ChG thin films it is necessary to take into account that the metastable part (when the light exposure is just ON) is in fact a combination of irreversible and reversible contributions. Similarly, the transient part also results from overlapping of reversible and irreversible effects (to the less extent, though, if close to the saturation regime). This means that comparison of fitting parameters for as-deposited and pre-annealed films, where the transient component can be easily separated, is not quite reliable. It is evident that precise fitting of such kinetics requires complex function comprised of a sum of two SEF related to metastable and transient effects (similar approach was explored recently by Barik et al. [13]). However, the number of fitting parameters in this case is too high and, consequently, the fitting results are ambiguous. That is why we decided to fit experimental curve separately for irreversible and transient parts. As a result, we got precise fitting data and analyzed them having in mind as many mechanisms as possible.

To address thickness dependence of the β value for the kinetic curve reported for As-based ChG thin films [20] and explore if the same conclusions can be applied to the metastable PB and transient PD in GeSe_2 films, we prepared samples of 2 different thicknesses (200 nm and 500 nm). According to Fig. 3, a noticeable portion (around 7 %) of 447 nm laser light with energy little above the GeSe_2 bandgap is still transmitted through the 200 nm film, while the light is completely absorbed in the 500 nm film. The former film (having 200 nm in thickness), according to the earlier studies [20,22], is good candidate to observe purely exponential behavior of PD.

Kinetic curves of photoinduced changes of optical transmittance $\Delta T(t)$ for as-deposited GeSe_2 films of both thicknesses exposed in argon atmosphere to the 447 nm CW laser light ($\sim 180 \text{ mW/cm}^2$) are shown in Fig. 4. The first conclusion, which could be clearly drawn for the reported conditions of exposure, is the increase in the magnitude of photoinduced effects (both metastable

and transient ones) with film thickness. Thus, the number of affected structural units is definitely crucial in this case. The data from Table 1 show that there is no significant difference between β values (~ 0.7) for the metastable component of the photoinduced effect (PB during the first cycle of exposure of the as-deposited film) in the films of both thicknesses. However, the time constant τ rises almost 3 times (from 73 s to 203 s) with increased thickness (from 200 nm to 500 nm), showing that time needed for saturation of photoinduced changes is determined by amount of the substance affected. The β values obtained for metastable PB are remarkably close to $3/5$, the value introduced by Phillips in his axiomatic diffusion-to-traps model [7] for relaxation available for all channels equally activated. Therefore, we assume that bandgap light exposure activates all possible relaxation channels in the as-deposited films. So, in the case of metastable PB, the observed SEF dependence is most probably determined by dispersive character of complicated relaxations occurring under photoexposure in highly defective non-equilibrium amorphous matrix. The nature of this dispersive mechanism does not depend on the film thickness as constant β value suggests, but its time constant τ , which shows a strong dependence on thickness, testifies to the dependence on a number of sites activated by light in different layers below the exposed surface.

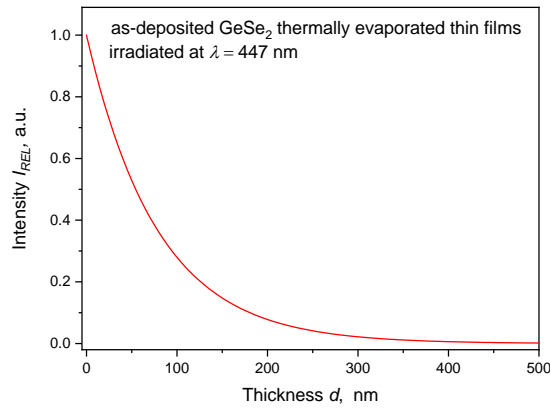


Fig. 3. Thickness dependence of I_{out}/I_{in} for as-deposited GeSe_2 film under 447 nm laser irradiation.

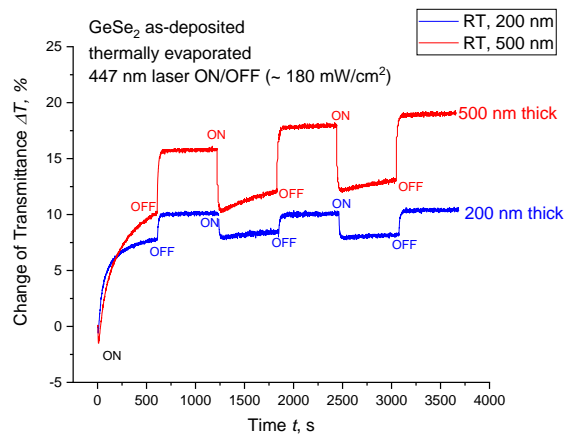


Fig. 4. Kinetics of photoinduced changes of optical transmittance $\Delta T(t)$ at $\lambda=535$ nm for as-deposited GeSe_2 films of different thicknesses irradiated (ON/OFF cycles) by 447 nm laser light in argon atmosphere.

Numerous previously reported structural explanations for the metastable part of the kinetic curve were mostly based on photoinduced transformation of homo-bonds Ge–Ge and Se–Se in the as-deposited films into hetero-bonds of Ge–Se type [12] accompanied by structural relaxation. Our Raman data (Fig. 5) advocate the structural changes when the bandgap light destroys polymeric (140 cm^{-1}) and fragmentary (312 cm^{-1}) Se chains [23], edge-shared (ES) $\text{GeSe}_{4/2}$ tetrahedra (215 cm^{-1}), as well as Ge– $\text{Se}_{4-n}\text{Ge}_n$ ethane-like units (170 cm^{-1}) [24]. Increase in the concentration of corner-shared (CS) $\text{GeSe}_{4/2}$ tetrahedra in dimers or short chains (268 cm^{-1}) [24] was observed instead. No changes were detected for the symmetric stretch vibration of CS $\text{GeSe}_{4/2}$ tetrahedra at 199 cm^{-1} or some type of Se structural unit with Raman band at 242 cm^{-1} [24].

Table 1. SEF parameters for the kinetic curves of photoinduced change of optical transmittance $\Delta T(t)$ for as-deposited GeSe_2 films of different thicknesses irradiated in ON/OFF cycles by 447 nm laser light

Thickness ↓	Switching ON						Switching OFF					
	β			τ , sec			β			τ , sec		
	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd	1 st	2 nd	3 rd
	ON*	ON [†]	ON [†]	ON*	ON [†]	ON [†]	OFF [†]	OFF [†]	OFF [†]	OFF [†]	OFF [†]	OFF [†]
200 nm	0.69	1.00	0.88	73	6.8	5.3	0.83	0.97	0.74	8.5	11	8.1
	± 0.01	± 0.11	± 0.09	± 1	± 0.5	± 0.4	± 0.06	± 0.10	± 0.06	± 0.5	± 1	± 0.6
500 nm	0.70	0.88	0.72	203	6.5	6.5	0.76	0.71	0.76	9.1	11	10
	± 0.01	± 0.04	± 0.08	± 2	± 0.2	± 0.3	± 0.02	± 0.07	± 0.02	± 0.3	± 1	± 1

* – metastable; [†] – transient

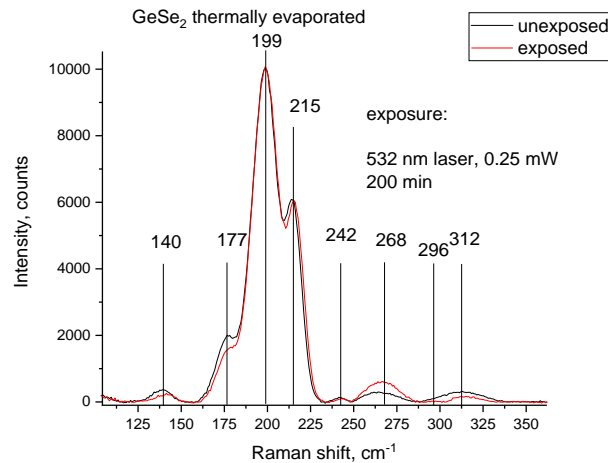


Fig. 5. Raman spectra of as-deposited 200 nm GeSe_2 film irradiated *ex-situ* by 532 nm laser light.

For transient PD, which is the ON parts of the ON/OFF cycles (Fig. 4, Table 1), we observe clear decrease in β with thickness from close to 1.0 (single-exponential function) for 200 nm as-deposited film, when significant part of the light is transmitted through the film, to around 0.8 (SEF behavior) for 500 nm film, when light is completely absorbed inside the film. This result is in full agreement with the data for As-based films [20,22] proving exponential character of the PD process if entire film volume is affected by the near bandgap light and decrease of β when film is too thick to effectively transmit the light. The difference in the β value demonstrates that amorphous matrix of the films reacts in different way on specific transient stimulus caused by the light in ON/OFF cycles, and dispersive character of the process develops with thickness. Similar trend of β decrease, although less distinct, is observed for the OFF components (SB) of the transient effect too (Table 1). The magnitudes of the transient ON/OFF effects are larger for thicker films showing a strong dependence on the number of oscillators involved. However, the τ values

do not depend on the film thickness testifying to the governing role of short-range ordering in the mechanisms causing transient PD and following relaxation during the SB process. Though the transient PD has been known for many decades, there are still no commonly accepted mechanism of this effect in ChG, but a number of rational explanations have been proposed. Photoinduced atomic twisting or displacement [22], excitation of lone pair electrons and formation of coordination defects [25], photoinduced expansion and slip motions of charged layers [26] are the most noticeable ones. Independence of τ value on thickness matches all the above mechanisms.

The same value of $\beta \sim 0.7$ for the metastable PB component was found for both film thicknesses (200 nm and 500 nm) when 455 nm LED ($\sim 90 \text{ mW/cm}^2$) was used as an exposure source instead of the 447 nm laser (180 mW/cm^2). This confirms that the β value for the metastable component does not depend on light intensity, but most probably, is determined by cooperative rearrangements of extended structural fragments. At the same time, the kinetic process at lower intensities becomes slower and the difference in the values of time constants τ became bigger (670 s for 200 nm film and 1750 s for 500 nm film). Therefore, we can speculate that time constant τ for metastable PB is defined by light intensity and short-range order structure of the film.

Comparison of the kinetics of photoinduced $\Delta T(t)$ changes for as-deposited GeSe₂ film and the one pre-annealed at below- T_g temperature (Fig. 6) shows opposite signs in the metastable components (PB for as-deposited film and PD for pre-annealed film). The transient PD and SB components demonstrate the same trend, but their magnitudes decrease after pre-annealing, which is in full agreement with previously reported data [12]. The numerical values of β and τ parameters are compared in Table 2. Interestingly, the values for transient effects are not changing noticeably (compare 2nd and 3rd ON and OFF states for as-deposited and pre-annealed films in Table 2). At the same time, pre-annealing leads to a significant decrease of β from 0.70 to 0.38 and more than 3 times increase of τ from 203 s to 669 s for the initial ON state (metastable effect, see 1st ON state in Table 2). Such drop in β can be explained by field-forced relaxation in the pre-annealed film structure, resulting in a β value close to 1/3 [27]. Similarly $\beta \sim 1/3$ values were observed earlier for structural relaxation of Se- and S-rich bulk ChG under bandgap light [28], which is concomitant with an idea that structure of the annealed at below- T_g thin film resembles the structure of bulk glass more than those of the as-prepared one. The only noticeable change in Raman spectrum of GeSe₂ due to pre-annealing is decrease in intensity of the line related to the ethane-like Ge-Se_{4-n}Ge_n units ($\sim 180 \text{ cm}^{-1}$) owing to breaking of Ge-Ge bonds [29]. Therefore, it is plausible to assume, that pre-annealing stabilizes the defect structure of the as-deposited films and reduces the number of modes available for relaxation. Additionally, we have to take into account that exposing the annealed thin film with near bandgap light leads to electronic excitations accompanied by bond switching and topological defects formation, where the lone-pair electrons play dominant role. The increased τ value means that structural changes in the pre-annealed amorphous matrix are slower and more time is needed to reach saturation, as could be expected from a reduced number of relaxation channels.

Temperature dependence of $\Delta T(t)$ changes for as-deposited GeSe₂ films is depicted on Fig. 7. It is well known that photoinduced optical effects obey a decreasing tendency with temperature [1,2]. Thus, it would be reasonable to assume such behavior for the studied *in-situ* photoinduced effects in the as-deposited GeSe₂ films. According to the obtained data, this expectation looks correct for transient PD and SB components, but wrong for the metastable PB. Nevertheless, if we consider our previous conclusion that metastable PB is determined by structural relaxation mainly, the results can be explained by a temperature dependence of relaxation. It was established previously using As₄₀Se₆₀ bulk glass that the magnitude of isochronal structural relaxation first

increases with annealing temperature after the threshold temperature $\sim 0.7T_g$ has been reached, then achieves maximum and vanishes at close proximity of T_g [30] because of limited amount of enthalpy the glass structure can lose at specific annealing temperature T_a : $\Delta H_\infty = \Delta C_P(T_g - T_a)$, where ΔC_P is the thermal capacity change at T_g [31]. The β parameter was found to be close to 0.6 if the full enthalpy relaxation kinetics collected under annealing at $\sim(0.85-0.95)T_g$ was fitted [32]. The calorimetric T_g of bulk GeSe₂ glass is around ~ 390 °C [16], and it is expected to be $\sim 10-15\%$ lower for the isocompositional thin film [33]. So, the threshold temperature to observe a noticeable dark structural relaxation in the investigated GeSe₂ thin films can be estimated to be within the 100-130 °C range. Before the films are subjected to laser exposure, the GeSe₂ films were heated at various temperatures T (70, 110, 130 or 180 °C) for ~ 12 h to remove the fast-thermal component of structural relaxation. This was done to ensure that changes to the films during exposure were optical in nature, not thermal. Then, laser was first turned ON and the metastable PB effect was recorded. Its magnitude goes through a maximum at ~ 110 °C (Fig. 7), which can be explained by crossing the threshold temperature of structural relaxation. Before and at the threshold temperature, the dark relaxation was very slow (not observable within the chosen time scale) and the laser light accelerated it. After the threshold temperature, the structure already relaxed to some degree (the higher temperature T , the more enthalpy is recovered in the dark) and the turned ON laser can only facilitate (accelerate) a remaining portion of relaxation (whatever was left after thermal relaxation). So, it seems reasonable that maximum in metastable PB effect is observed around $T \sim 110$ °C. According to the Raman data shown on Fig. 5, we can conclude that light accelerates structural relaxation by removing constrains associated with Ge-Ge bonds (their amount decreases after photoexposure).

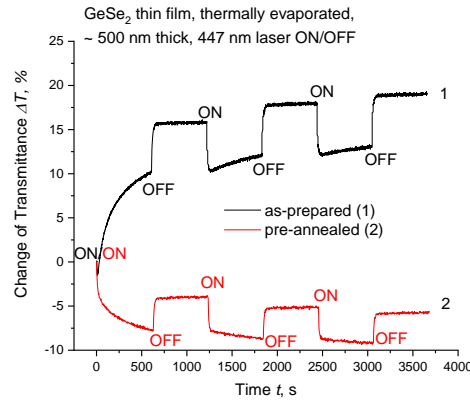


Fig. 6. Effect of pre-annealing on the kinetics of photoinduced change of optical transmittance $\Delta T(t)$ for 500 nm GeSe₂ film irradiated by 447 nm laser in ON/OFF cycles

Table 2. Parameters of SEF for the kinetics of photoinduced optical transmittance changes $\Delta T(t)$ for as-deposited and below- T_g pre-annealed 500 nm GeSe₂ films irradiated by 447 nm light in ON/OFF cycles

Sample ↓	Switching ON						Switching OFF					
	β			τ , sec			β			τ , sec		
	1 st ON*	2 nd ON [†]	3 rd ON [†]	1 st ON*	2 nd ON [†]	3 rd ON [†]	1 st OFF [†]	2 nd OFF [†]	3 rd OFF [†]	1 st OFF [†]	2 nd OFF [†]	3 rd OFF [†]
As-deposited	0.70	0.88	0.72	203	6.5	6.5	0.76	0.71	0.76	9.1	11	10
Pre-annealed,	±0.01	±0.04	±0.03	±2	±0.2	±0.3	±0.02	±0.03	±0.02	±0.3	±1	±1
	0.38	0.95	0.82	669	7.0	5.8	0.80	0.82	0.72	8.4	8.9	7.3
	±0.01	±0.09	±0.12	±155	±0.5	±0.7	±0.04	±0.06	±0.07	±0.4	±0.5	±0.7

* – metastable; [†] – transient

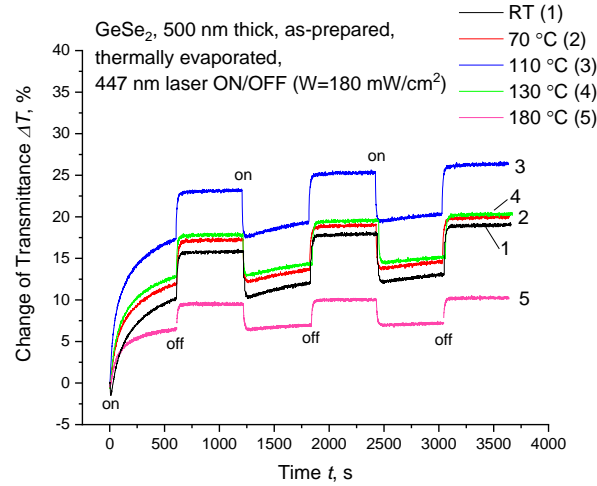


Fig. 7. Kinetics of photoinduced optical transmittance changes $\Delta T(t)$ for 500 nm as-deposited GeSe₂ films irradiated at different temperatures by 447 nm laser light in ON/OFF cycles

The β values of the PB show a weak dependence on the temperature being close to $\beta \sim 0.6 \div 0.7$ (see Table 3), which is in good agreement with previous studies on structural relaxation in arsenic selenides [32]. The τ values decrease with temperature T as one would expect from decrease in the α -relaxation times when approaching T_g [34], showing an anomaly (minimum at 110–130 °C) while crossing threshold temperature. It is worth to mention that while the magnitudes of the transient PD and SB decrease, the increase in temperature does not alter significantly the β parameter.

Table 3. Parameters of SEF for the kinetics of photoinduced optical transmittance changes $\Delta T(t)$ for as-deposited GeSe₂ films irradiated by 447 nm light in ON/OFF cycles taken at different temperatures

Sample ↓	Switching ON						Switching OFF					
	β			τ , sec			β			τ , sec		
	1 st ON*	2 nd ON†	3 rd ON†	1 st ON*	2 nd ON†	3 rd ON†	1 st OFF†	2 nd OFF†	3 rd OFF†	1 st OFF†	2 nd OFF†	3 rd OFF†
Room temperature	0.70 ± 0.01	0.88 ± 0.04	0.72 ± 0.03	203 ± 2	6.5 ± 0.2	6.5 ± 0.3	0.76 ± 0.02	0.71 ± 0.03	0.76 ± 0.02	9.1 ± 0.3	11 ± 1	10 ± 1
70 °C	0.61 ± 0.01	0.88 ± 0.03	0.83 ± 0.05	152 ± 2	6.1 ± 0.2	6.1 ± 0.3	0.77 ± 0.04	0.75 ± 0.03	0.78 ± 0.03	9.8 ± 0.5	9.5 ± 0.4	9.5 ± 0.3
110 °C	0.54 ± 0.01	0.94 ± 0.06	0.72 ± 0.04	128 ± 1	4.9 ± 0.3	6.0 ± 0.3	0.73 ± 0.04	0.75 ± 0.04	0.80 ± 0.04	7.8 ± 0.4	7.2 ± 0.4	7.6 ± 0.3
130 °C	0.61 ± 0.01	0.75 ± 0.04	0.87 ± 0.06	137 ± 1	5.5 ± 0.3	5.0 ± 0.3	0.79 ± 0.04	0.68 ± 0.04	0.87 ± 0.04	7.2 ± 0.3	6.8 ± 0.5	7.3 ± 0.3
180 °C	0.63 ± 0.01	0.75 ± 0.04	0.76 ± 0.04	98 ± 1	8.0 ± 0.4	7.9 ± 0.4	0.82 ± 0.05	0.88 ± 0.03	0.86 ± 0.05	8.3 ± 0.4	8.3 ± 0.2	10.4 ± 0.5

* – metastable; † – transient

Comparison of the kinetic curves of photoinduced change of optical transmittance $\Delta T(t)$ for 200 nm as-deposited GeSe₂ films irradiated by high power LEDs of different energies (Fig. 8) demonstrates some interesting tendencies for the metastable PB and transient effects. The transient effect has a maximum magnitude when the films are irradiated by light with energy close to the band gap (455 nm LED). It confirms that transient effects are directly related to transition of electrons through the energy gap from top of the valence band (occupied by lone-pair electrons of

chalcogen atoms) to bottom of the conduction band and formation of electron–hole pairs or charged coordination defects. When the light energy is increased (385 nm LED), thermalization of the excited electrons limits formation of the metastable defect pairs. At the same time, the metastable PB is strongest at irradiation energies lower than the band gap (590 nm LED), which also agrees with light dispersion of structural relaxation in bulk germanium selenides [35]. The exposure by photons with energies well below the band gap of the film (the LEDs with wavelengths of 780 and 1550 nm) leads to disappearance of transient effects and the decay of the metastable PB (Table 4).

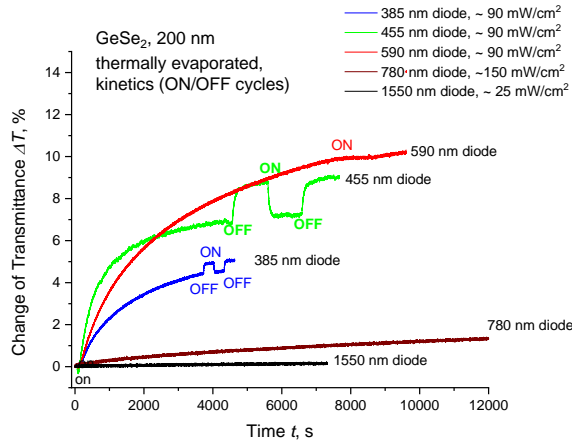


Fig. 8. Kinetics of photoinduced optical transmittance changes $\Delta T(t)$ for as-deposited GeSe_2 thin films irradiated (ON/OFF cycles) by LED light of different energies

The β value of the PB kinetic curve demonstrates a broad minimum within the wavelengths of LED light that are close to the bandgap of the film (Table 4). Similarly, the τ value for metastable PB was found to be lowest when exposed to band gap light. Again, both these results agree well with previously reported data on structural relaxation of Ge-Se bulk glasses under photoexposure with light of different wavelengths [28].

Table 4. Quantification of the kinetic curves of photoinduced optical transmittance changes $\Delta T(t)$ for as-deposited 200 nm GeSe_2 films irradiated (ON/OFF cycles) by LED light of different energy

LED wavelength ↓	Switching ON				Switching OFF			
	β		τ , sec		β		τ , sec	
	1 st ON*	2 nd ON†	1 st ON*	2 nd ON†	1 st OFF†	2 nd OFF†	1 st OFF†	2 nd OFF†
385 nm	0.75 ± 0.01	1.00 ± 0.03	1970 ± 13	39 ± 2	0.77 ± 0.02	0.89 ± 0.02	53 ± 1	41 ± 1
455 nm	0.69 ± 0.01	0.80 ± 0.02	670 ± 1	39 ± 1	0.84 ± 0.02	0.91 ± 0.02	74 ± 2	59 ± 1
590 nm	0.70 ± 0.01	-	3341 ± 6	-	-	-	-	-
780 nm	0.77 ± 0.01	-	13675 ± 85	-	-	-	-	-
1550 nm	-	-	-	-	-	-	-	-

* – metastable; † – transient

Therefore, the energy dependence of PB effect for LED light could be explained as follows: the light of above-bandgap energy penetrates primarily the surface layers creating electron-hole pairs and hot electrons in the conduction band, which means that only surface layers actively participate in photostructural transformations. The light of bandgap energy (with 455 nm wavelength) has higher penetration depth compared to the UV light, thus, affecting more sites responsible for the structural relaxation in addition to carrier's excitation responsible for PD effect (more volume of the film is involved). The light with longer wavelengths cannot generate electron-hole pairs, acting only as indirect facilitator of structural re-arrangements through weak two-photon absorption processes, phonon-assisted electronic transitions or inelastic photon scattering, which lead to transitions between different metabasins in potential energy landscape [36]. However, they penetrate the entire volume of the film, which can explain the maximum of metastable PB under exposure by 590 nm light.

The transient PD component does not demonstrate pure exponential behavior under the bandgap light LED exposure (455 nm) as would be expected based on our studies of thickness dependence for 200 nm film with 447 nm laser exposure. Most probably, the line width of the LEDs emission is high compare to 447 nm laser beam. It could result in dispersion of the mechanisms responsible for the transient PD, leading to deviation from single-exponential law.

Conclusions

Application of a stretched exponential function to fit the kinetics of *in-situ* photoinduced optical transmittance changes $\Delta T(t)$ for as-deposited GeSe₂ films taken at different conditions reveal several remarkable features related to β and τ parameters, and are quite different for metastable (PB) and transient (PD and SB) components. The kinetics of metastable PB registered at the bandgap light exposure is characterized by $\beta \sim 3/5$. This value is independent to film thickness and light intensity, and is linked with activation by light of maximum number of relaxation channels. On the other hand, increase of time constant τ with thickness and light intensity (number of photons) demonstrates dependence of the PB on the number of structural sites affected by the relaxation. Alternatively, we observed clear decrease of β parameter for transient PD in films with thickness from ~ 1.0 (200 nm) to ~ 0.8 (500 nm) and independence of τ on penetration depth of the light.

The β value of PB in as deposited GeSe₂ films show weak dependence on the temperature but the τ value decreases with T as expected from drop in α -relaxation times approaching T_g , showing an anomaly (minimum at 110÷130 °C) while crossing threshold temperature for noticeable dark structural relaxation. In addition, temperature does not significantly alter the β values for transient PD and SB, even though their magnitude decreases.

The transient effects (PD and SB) have a maximum magnitude at bandgap irradiation of as-deposited GeSe₂ thin films. The metastable PB is strongest at light energy slightly below the bandgap, which agrees well with the light dispersion of structural relaxation observed in bulk Ge-Se glass. The β and τ values of the PB kinetic curve demonstrate minima for light energy close to bandgap of the film.

Pre-annealing of GeSe₂ films at temperature just below T_g not only reverse metastable PB to PD, but also significantly decreases β from 0.70 to 0.38 (close to the Phillips' 1/3 value) and increases τ for more than 3 times. Similar β values were observed also earlier for structural relaxation of Se- and S-rich bulk ChG under bandgap light exposure.

Raman microscopy data suggest that the structural transformations accompanying the PB in as-deposited GeSe₂ films are caused by destruction of structural fragments with Ge-Ge bonds

(ethane-like units), Se-Se bonds and ES GeSe_{4/2} tetrahedra and increase in concentration of CS GeSe_{4/2} tetrahedra in dimers or short chains.

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