

Ultrafast electron intervalley scattering and hole dynamics in amorphous and crystalline Ge

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 (Received 8 September 2025; revised 5 February 2026; accepted 27 February 2026; published 21 May 2026)

Understanding the role of holes in energy transport mechanisms and determining electron intervalley scattering times is crucial for optimising Ge-based optoelectronic devices such as transistors, photodetectors, power devices, and light emitters. By employing our recently developed, ultrafast 20-fs resolution ellipsometer, we demonstrate that the absorption (ε_2) in various types of Ge continues to decrease in the first picosecond after optical excitation, proving that the revival of the absorption is limited by the intrabandlike relaxation of holes (near the Γ point), instead of the intervalley scattering of the electrons. The observed decay times depend on the probing photon energies attributed to the different lifetimes of the holes in the light, split-off and heavy-hole bands. With gradually decreasing degree of crystallinity of our single crystalline, semicrystalline and amorphous Ge samples, the recovery times also decrease, which is related to the appearance and intensification of real-space scattering events over reciprocal space scattering. There is excellent correspondence for electron relaxation times for different samples with our two-temperature model, which is thoroughly analyzed via band-structure calculations. Our results contribute to the understanding of the excitation and decay processes in not only crystalline semiconductors, but also semicrystalline and amorphous semiconductors, resolving corresponding debates.

DOI: [10.1103/qkbh-bb3f](https://doi.org/10.1103/qkbh-bb3f)

I. INTRODUCTION

Transient effects of photoexcited carriers in semiconductors cover a broad timescale between femtoseconds (10^{-15} s) and microseconds (10^{-6} s). For the development of photovoltaic or photodetector devices, it is necessary to understand the different mechanisms and their dynamics, and how they depend on the crystallinity of the samples [1]. The dielectric function of a semiconductor determines its absorption, transmission, and reflection properties. More importantly, it is closely correlated with the accessible energy levels for electrons, holes, and phonons [2–5]. Ellipsometry is a surface-sensitive method for optical measurement of the dielectric function in a wide spectral domain extending from the XUV [6] to the THz [7]. Although it is mostly used to perform static measurements, when the ellipsometric principle is combined with state-of-the-art ultrafast laser technology, we can reveal a plethora of relevant ultrafast phenomena by implementing pump-probe ellipsometry [2,3,7,8].

In this work, we used an ultrafast ellipsometric setup with 20-fs time resolution to study Ge samples with different crystallinity. For purely crystalline Ge, theory based

on band-structure considerations predicts the mechanisms and timescales for electron excitation and decay, and these processes have been studied both theoretically and experimentally [2,4,9–12]. In recent years, there has been renewed interest in understanding the details of the conduction band structure and the electron- and hole scattering mechanisms [13–17]. However, for poly- and semicrystalline or amorphous Ge, both of which are highly relevant for practical applications such as power devices, optical sensors, and light emitters, including solid-state lasers and microelectronic circuits, the actual band structure is a subject of debate [18,19]. With all this in mind, our aim was to explore how the dominant decay mechanisms depend on the degree of crystallinity experimentally.

II. EXPERIMENT

A. Sample characterization

1. Sample preparation

To gain detailed insight into the band structures and scattering processes, three types of Ge with different crystalline structures were examined: crystalline Ge, amorphous Ge, and laser-irradiated Ge. For clarification, we do not use the classical band structure picture—which relies on translation symmetry—for amorphous Ge. Rather, we use a picture based on the density of states, which remains valid when considering amorphous materials. Commercially available bulk samples of crystalline wafer-grade Ge were used; 300-nm-thick amorphous Ge films on Si substrate were prepared by thermal deposition from 99.999% pure a-Ge granules with a grain

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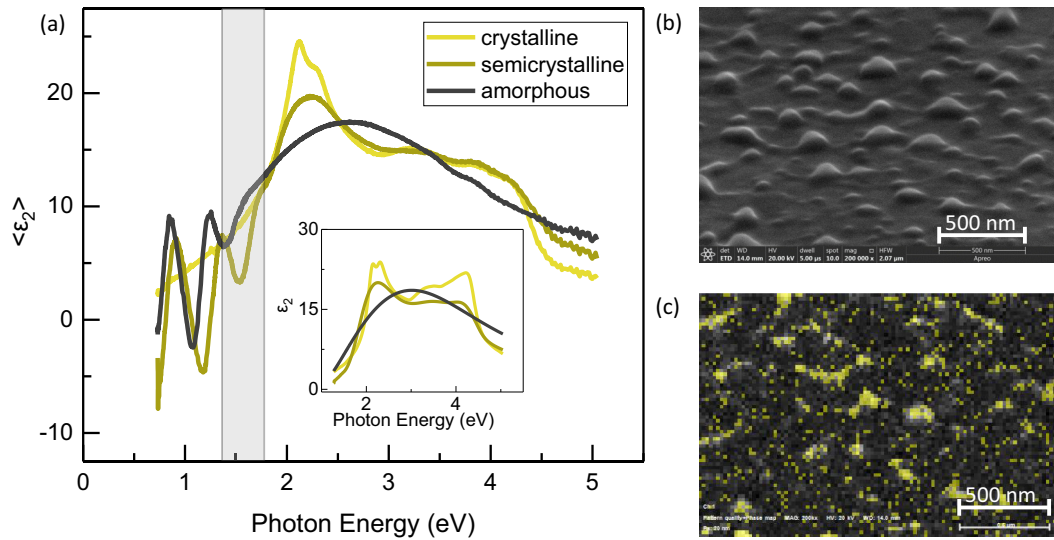


FIG. 1. (a) Pseudodielectric function of the three investigated Ge samples. The highlighted area shows the spectral range of the ultrafast ellipsometer setup. Inset: Imaginary part of the dielectric function from ellipsometric modeling. Periodic oscillations below 1.5 eV are explained in the main text. (b) Scanning electron microscope (SEM) image of the laser-irradiated Ge. (c) Electron backscatter diffraction (EBSD) image of the laser-irradiated Ge sample [same as in (b)]. Yellow spots correspond to crystalline phases.

size of 2–8 mm at an initial pressure of 1×10^{-5} mbar and a growth rate of 0.5 nm/s. The crystallization of amorphous Ge films by laser irradiation is a well-known process [20]. In our case, nanosecond Nd:YAG (1064-nm) laser radiation was absorbed in an amorphous Ge film (the same as our a-Ge films used in this study), resulting in its melting. During the cooling of the film, the growth of crystallites and crystal phases took place. To find the optimal irradiation parameters for crystallization, we systematically varied the pulse energy and the number of pulses. The diameter of each treated area was 4 mm. Based on a static ellipsometric study, 14 mJ of laser energy (223 mJ/cm^2 energy density) and 128 shots resulted in most crystalline Ge structure.

2. Comparison of the Ge samples

Figure 1(a) shows the imaginary part of the dielectric function of our three Ge samples measured by an SE-2000 spectroscopic ellipsometer manufactured by Semilab Inc. In ellipsometry, we measure the change in the polarization state of light upon reflection from the sample under study, which can be characterized by two ellipsometric angles, called Ψ and Δ , corresponding to the relative amplitude and phase change of the reflected light. Through the Fresnel equations these quantities correlate with the real (ϵ_1) and imaginary (ϵ_2) parts of complex dielectric function. We can use a direct inversion to retrieve ϵ_1 and ϵ_2 from an ellipsometric measurement if we assume that the sample is a semi-infinite, isotropic, homogeneous bulk material. This results in the pseudodielectric function. This function is called “pseudo” because the aforementioned assumption is often not true (e.g., thin films, multilayers, and anisotropy). Thus, the result is not the actual material’s dielectric function, but rather a convenient representation of the data [see Fig. 1(a)]. For more complex systems, a modeling procedure must be carried out that takes the structure of the samples into account [21]. For

bulk crystalline Ge, this means considering only the native oxide layer, but for laser-irradiated and amorphous layers, the optical properties of the layers had to be modeled as well, as detailed in Sec. II of the Supplemental Material [22].

Figure 1(a) shows both the pseudo-optical properties of the investigated Ge materials and their actual dielectric function. In the pseudodielectric function curves, below 1.5 eV, both laser-irradiated and amorphous Ge have periodic oscillations in their spectra. Such oscillations are related to the interference of the probe beam due to the layered nature of the material. Their presence allows the determination of film thicknesses and band gaps [21,28]. Otherwise, the main characteristics are very similar for pseudo- and the actual dielectric functions. In the case of crystalline Ge, the ϵ_2 spectrum shows the well-known interband critical-point-related characteristic peaks [29,30]. These peaks are not observed for the amorphous film [31], but appear in the ϵ_2 spectrum of the laser-irradiated film, which serves as a measure of the degree of crystallization of the film.

3. Crystallinity of the laser-irradiated Ge film

To confirm the crystallization of the laser-irradiated Ge film, we performed electron backscatter diffraction (EBSD) measurements [Fig. 1(c)]. The yellow spots on the resulting EBSD maps indicate the presence of the crystalline phases. Compared with the SEM image in Fig. 1(b), it can be seen that the dropletlike surface structures show the crystalline properties, while the host material is still amorphous. Throughout the paper, we will refer to this structure as “semicrystalline Ge.” Based on the EBSD map, the crystallinity ratio of the laser-irradiated films was $\sim 15\%$.

B. Experimental setup

As a next step, we performed time-resolved ellipsometric measurements with our femtosecond pump-probe

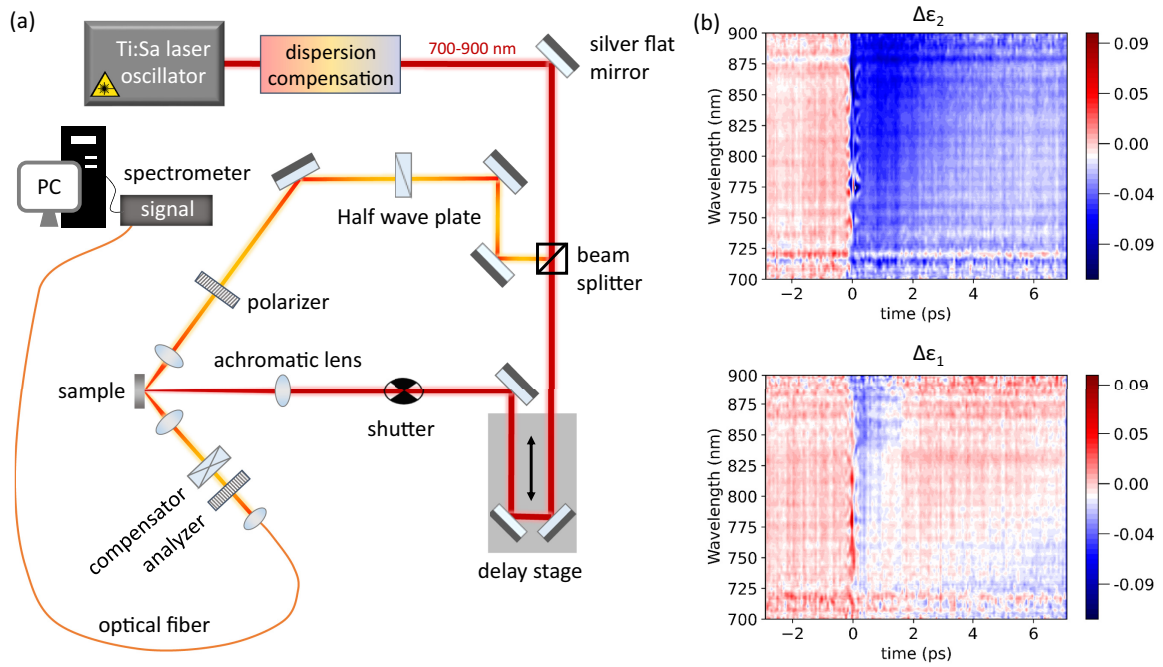


FIG. 2. (a) Experimental setup of the ultrafast ellipsometer. (b) 2D transient $\Delta\epsilon_1$ and $\Delta\epsilon_2$ maps.

spectroscopic ellipsometer. In this setup, the light source is a Ti:sapphire laser oscillator (Spectra-Physics Element 2) delivering ~ 10 -fs pulses centered at 810 nm, with a repetition rate of 80 MHz and a spectral bandwidth exceeding 100 nm full width at half maximum.

As indicated in the scheme [Fig. 2(a)], the femtosecond laser beam is split into two parts: the pump (80%) and probe (20%) beams, respectively. These two beams have identical spectral characteristics.

The probe beam is directed to the sample through a half-wave plate and a polarizer to create a well-defined polarization state in front of the sample, and it is focused on the sample (~ 20 - μm diameter) at 60° angle of incidence. After reflection, the beam is collimated and passed through a compensator (quarter-wave plate) and another polarizer (called analyzer) for proper polarization characterization of the reflected beam, which is needed to perform ellipsometric measurement. The pump beam is passed through a delay line containing a 25-mm-long motorized linear translation stage. This allows us to control the time delay in the 60-ps range with an ~ 20 -fs temporal resolution. The beam is then focused almost perpendicularly onto the sample (~ 40 - μm diameter). We measured 18-fs duration for the probe and 14-fs duration for the pump pulse with D-scan [32,33] at the sample position. The energy density of the pump beam was 13.1 J/m^2 at the surface.

III. RESULTS AND DISCUSSION

A. Transient dielectric function

With this experimental setup, we measure the transient reflection for several compensator azimuth angles, from which the transient dielectric function can be determined as described in Ref. [34]. Unless otherwise stated, we show the transient behavior of the pseudodielectric function below. We will demonstrate that this follows the same time evolution

as the actual dielectric function, while its derivation is more straightforward. Figure 2(b) shows the differential transient $\Delta\epsilon_1$ and $\Delta\epsilon_2$ spectra of crystalline Ge with respect to the first recorded spectrum. An interference pattern can be observed on the maps (striped region) around $t = 0$ ps, which originates from the spatial and temporal overlap of the pump and the probe beam clearly indicating the zero time delay (time zero). Both $\Delta\epsilon_1$ and $\Delta\epsilon_2$ first drop after time zero, and then they slowly rise. This increase in $\Delta\epsilon_1$ and $\Delta\epsilon_2$ is referred to as recovery in the following. The behavior of the recovery is different for different wavelengths and is present in all three types of Ge under study, as shown in Fig. 3 and discussed in detail in the following section.

To receive more insight, three wavelengths (725, 800, and 875 nm) were selected from the transient $\Delta\epsilon_2$ maps and the corresponding pseudodielectric function was plotted as a function of the time delay (Fig. 3). The sudden drop at time zero is clearly observable on these plots as well. Interestingly, for crystalline Ge this drop is not followed instantaneously by the recovery, but the $\Delta\epsilon_2$ values decrease slightly further or remain constant for a while, forming a plateau in $\Delta\epsilon_2$. This section of slower decay or plateau lasts for a few hundred femtoseconds, after which the slow recovery starts. On the $\Delta\epsilon_2$ curves of the semicrystalline and the amorphous sample, the plateau stage is also present except for the shorter wavelength (725 nm), where it is less visible; rather, the recovery starts immediately after the drop with no further decrease. The plateau right after the drop is absent in $\Delta\epsilon_1$ curves (see Fig. S1 in Supplemental Material [22]). To analyze these trends quantitatively, we deduced the characteristic duration of the plateau by visually identifying the end of the sudden signal drop right after time zero and the onset of recovery. These time instants are denoted in Fig. 3. by green vertical lines. For determining the recovery times, we fitted exponential curves to these rising parts of the $\Delta\epsilon_2$ curves. As an example, see

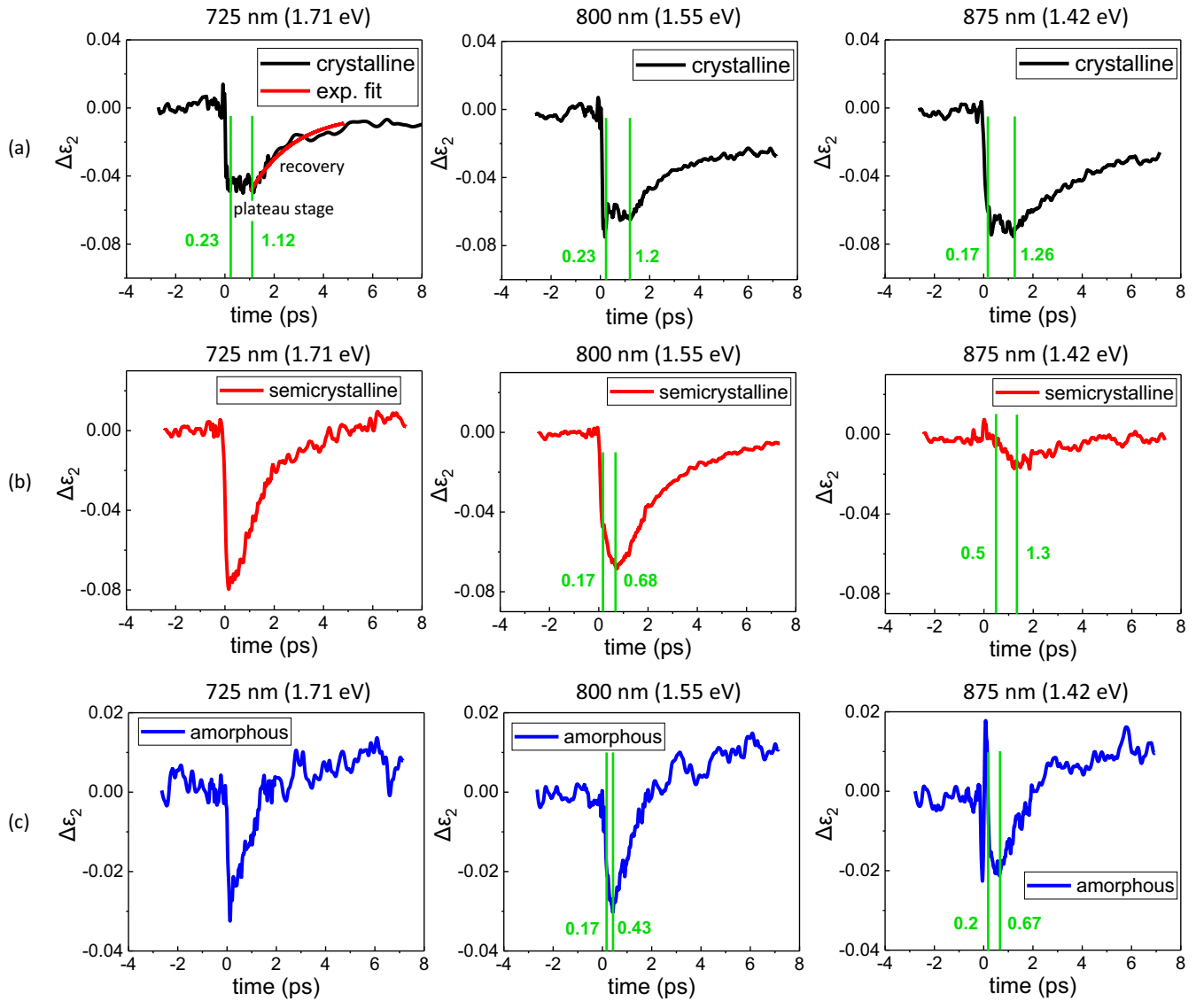


FIG. 3. Constant wavelength sections from $\Delta\epsilon_2$ maps as a function of delay time for (a) crystalline, (b) semicrystalline, and (c) amorphous Ge samples. Vertical green lines show the onset and end of plateau stage in $\Delta\epsilon_2$ explained in the main text.

top left panel of Fig. 3. Note that different parts of the $\Delta\epsilon_2(t)$ curves were not taken at the same temporal resolution: in order to see all details of the plateau region the highest resolution with the smallest time steps (23 fs) was chosen around time zero.

Figure 4(a) shows the duration of the section of slower decay/plateau stages. A relatively long plateau belongs to crystalline Ge, while there is a section of slower decay after the quick drop in semicrystalline Ge. This section could also be identified in amorphous Ge, but it is even shorter here. One can conclude from the figure that the shorter the wavelength is (the larger the photon energy is), the shorter the time duration of section of slower decay/plateau is.

The characteristic times of the slow recoveries resulting from the fitting also depend on the crystallinity and the investigated wavelength. The dependence on wavelength is shown in Fig. 4(b) for all three types of Ge samples. The longest characteristic recovery time belongs to crystalline Ge. As the

crystallinity decreases, shorter times are sufficient for recovery, exhibiting the same trend as the previously discussed section of slower decay/plateau stages.

Note that we showed pseudodielectric functions so far. These quantities do not describe the individual behavior of all Ge materials studied, since semicrystalline and amorphous Ge samples are thin layers on Si substrate. To show that the transient pseudodielectric function still characterizes the transient response of the Ge layers, we performed full ellipsometric modeling determining the transient behavior of the actual dielectric functions of amorphous and semicrystalline Ge, and carried out the same exponential fitting to determine the recovery times (for details, see Sec. II of Supplemental Material [22]). The recovery times of the modeled dielectric functions are present also in Fig. 4(b). By comparing the recovery times of the pseudo- and actual dielectric functions, we concluded that the representation of the data does not affect the observed electron relaxation times.

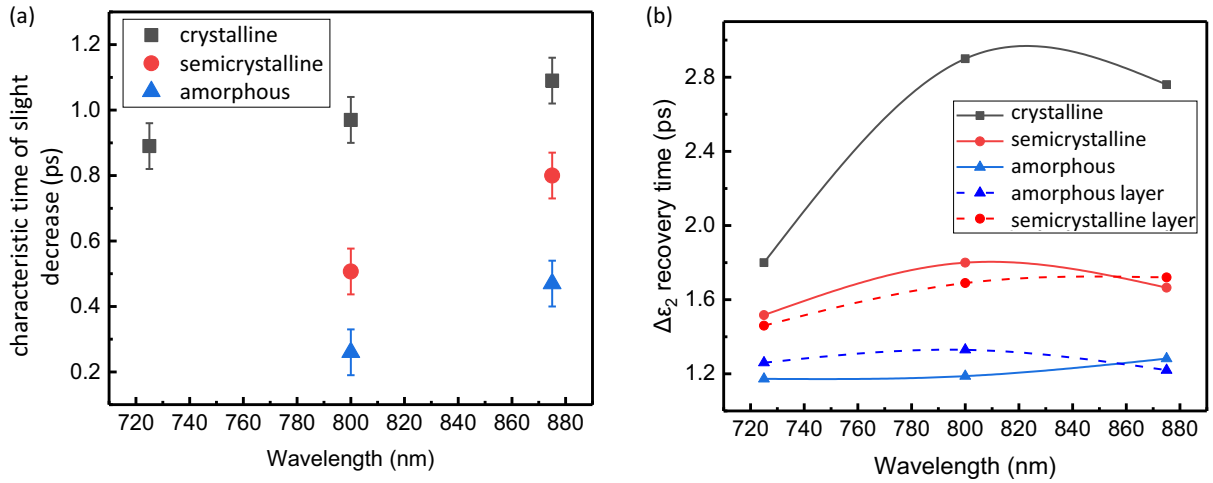


FIG. 4. (a) Duration of the section of slower decay/plateau stages observed for the Ge samples with different crystallinity. The duration of the plateau could be quantified at 725 nm only for crystalline Ge (black square), as shown in the first row in Fig. 3. (b) Characteristic timescales of the recovery of ϵ_2 . Data points connected with solid lines are from direct inversion of the measured data, while data points with dashed lines originate from modeling. Solid and dashed lines are guides for the eye.

B. Theoretical description of relaxation processes

When crystalline Ge is excited by pump pulses with 1.5-eV photon energy, electron-hole pairs are created near the Γ point (the band structure of crystalline Ge is shown in Fig. 5). Electrons are initially excited from the valence band to the slopes of the Γ valley of the conduction band; therefore, they do not arrive at the conduction band's lowest-energy states. They

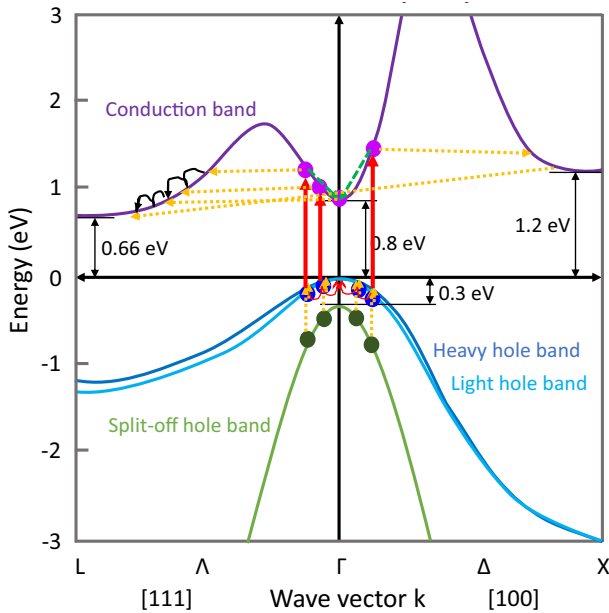


FIG. 5. Band structure of crystalline Ge (based on Refs. [2,10–12]) showing the excitation of electrons (purple dots) from the valence band to the conduction band (red arrows), electron-electron scattering (green), electron intervalley scattering (yellow), and thermalization (black) within the first few picoseconds. Holes (green and blue dots) experience intraband scattering between the heavy hole, light hole, and split-off hole bands (yellow) redistributing the energy within the valence band (red).

either lose their excess energy via electron-electron scattering within the Γ valley or they undergo intervalley scattering via phonon interactions to reach lower-energy states in the L - and X valleys. The conduction band in Ge has a nearly direct band gap at the Γ point, but the L point in the Brillouin zone has a higher density of states, making it more favorable for electrons. Thus, once electrons reach the L valley, they become thermalized through phonon interactions on a picosecond timescale [2,18,35].

When electrons are excited to higher-energy states, the number of states available for further optical transitions decreases, leading to the sudden drop in absorption (i.e., in the imaginary part of the complex dielectric function) observed at time zero. Energy redistribution via electron-electron scattering within the Γ valley or intervalley scattering of electrons to other parts of the Brillouin zone takes place within 50 fs to a few hundred femtoseconds [2,14]. These processes lead to more empty states around the Γ point, which is expected to cause a rapid increase in absorption, especially for the higher exciting photon energies. Contrary to expectations, in our measurements (probing at the same energy as the pump), the absorption—represented by the transient ϵ_2 —continues to slightly decrease after the sudden drop in some cases. At 1.71 eV, even a plateau can be observed before the relatively slow relaxation. The delayed recovery of the absorption hints at the fact that besides the electrons, hole dynamics should also play an important role in the recovery.

Whereas electrons relax mostly through intervalley transitions, holes experience more intraband scattering near the Γ point, redistributing energy within the valence band. As hole scattering is a slower process [35], the relaxation of electrons to the initial states is delayed for optical transitions with 1.5 eV; this makes the hole dynamics the dominant factor in differential absorption signals [35].

Besides the section of slower decay or plateau of the transient $\Delta\epsilon_2$, we also observed that the plateau is shorter for higher exciting photon energies. Higher photon energies allow for the formation of holes farther from the Fermi level.

These light holes and split-off holes with higher excess energy quickly scatter into the heavy-hole band, which is closest to the Fermi level. Light-hole scattering into the heavy-hole band is faster for higher photoexcitation energies, since the heavy-hole band has higher density of states at higher energies, making transitions more likely. The split-off band population decays quickly due to rapid scattering to the heavy-hole band. This energy dependence of the scattering process results in faster relaxation of the electrons to those initial states that can contribute to the higher photon energy transitions, which in turn explains the shortening of the section of slower decay or the plateau with increasing excitation photon energy. These relaxation processes happen within a few hundred femtoseconds to 1-ps timescale, after which further thermalization and recombination processes continue for several picoseconds or even longer timescales [18,35].

The mechanisms described above apply to the crystalline sample with a well-defined band structure. For samples with amorphous domains (as in the case of our laser-irradiated sample) or with pure amorphous character, the band structure or rather the density of states can be strongly modified with the appearance of defect-related bands and localized states [19]. These not only affect the band gap and the initial excitations but also open up different scattering pathways where the reciprocal space scattering mechanisms are replaced by scattering at real defects. The disappearance of the long-range order leads to a shorter lifetime of the excited carriers and a faster recovery of the absorption properties.

C. Two-temperature model and band-structure calculations

The signal recovery on few-ps timescales [see Fig. 4(b)] can be attributed to purely thermal processes, which can be followed by the two-temperature model (2TM). The model describes the energy transport processes between the electron and lattice systems using coupled differential equations (see Sec. IV in Supplemental Material for more details [22]). These include the temporal and spatial evolution of the electron-hole concentration, and the temperatures of the electron and lattice systems.

During laser irradiation, the energy is first absorbed by the electron system, leading to the generation of free carriers in semiconductors. Our 2TM simulations showed that after excitation, the free carrier density reaches $2.24 \times 10^{20} \frac{1}{\text{cm}^3}$, the value of which is close to the estimated value of the number of absorbed photons ($2.28 \times 10^{20} \frac{1}{\text{cm}^3}$; see Sec. III in Supplemental Material [22]). The presence of the excited charge carriers changes the transition energies known in literature as band-gap renormalization (BGR). The BGR in our case was smaller than 78 meV (see Sec. III in Supplemental Material [22]), which is negligible compared to our excitation energies. Parallely, due to the e-e interactions, the temperature of the electron system increases on a timescale of a few 10 femtoseconds after excitation. The highest electron temperatures (T_e) are around 3000 K according to our calculations. These results can be compared with electron temperatures calculated from the band-structure picture for crystalline Ge, if we consider the electron transitions belonging to the Γ point taking into account the heavy-hole band (for details, see Supplemental Material [22]). This is a reasonable constraint, since such

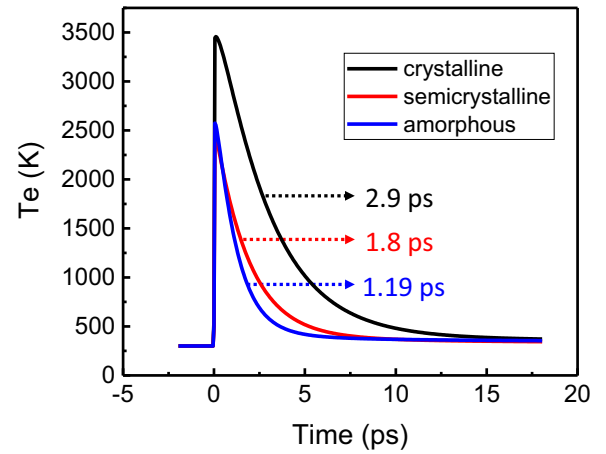


FIG. 6. Relaxation profiles of the electron system temperature for crystalline, semicrystalline, and amorphous Ge, simulated by a two-temperature model.

transitions are expected to make the largest contribution to the electron temperature because optical excitation can be realized for transitions with $\Delta k = 0$, and the density of states is highest in the heavy-hole band.

Thereafter, the energy is transferred to the lattice on a picosecond timescale, heating the material. This thermalization process will determine the recovery times observed in our experiments, since it is the electron system temperature (T_e) which affects most the dielectric properties among the parameters of the 2TM model. The time evaluation of T_e is strongly dependent on the electron relaxation time (τ_{relax}); thus, measured recovery times allow us to estimate the relaxation times for the materials under study. From our simulations, we obtained the following values of τ_{relax} : 2.85 ps for crystalline, 1.75 ps for semicrystalline, and 1.15 ps for amorphous Ge. With these values, the electron temperature dynamics (see Fig. 6) came closest to the measured recovery times of the transient ε_2 [see data points at 800 nm in Fig. 4(b)].

IV. CONCLUSIONS

Our transient ellipsometric data allowed us to identify different stages of relaxation after pumping crystalline Ge, semicrystalline Ge and amorphous Ge with 20-fs time resolution. Our measurements confirm that the process dominating the first ps after excitation is not the intervalley scattering of the electrons, but rather the intraband relaxation of the holes. The photon energy dependence of the decay times results from the different lifetimes of the holes in the light, split-off, and heavy-hole bands. The decreasing recovery times with decreasing crystallinity can be attributed to the dominance of real-space scattering events over reciprocal space (crystal defects) scattering. After a detailed interpretation of the nonthermal processes, electron-lattice interactions were also considered in a two-temperature model, which allowed us to follow how the electron relaxation times decrease with crystallinity. Fast electron relaxations observed for less-crystalline samples are related to short carrier lifetimes, which can be advantageous in improving the response time and bandwidth of a photodetector and enabling increased data

transmission rates. Thus, our time-resolved studies answer a fundamental research question in semiconductor physics and have the potential to contribute to semiconductor device development alike.

ACKNOWLEDGMENTS

We would like to thank Professor Stefan Zollner for fruitful discussions. We would like to express our gratitude to Gergely Samu and Ádám Balog for their assistance with the EBSD measurements at the Institute of Chemistry, University of Szeged. We acknowledge support from National Research,

Development, and Innovation Office of Hungary (Projects No. 137373 and No. TKP-2021-NVA-04), and also the ELI-ALPS (project GINOP-2.3.6–15-2015–00001), which is supported by the European Union and co-financed by the European Regional Development Fund. Z.P. and J.B. received support from a Bolyai Research Scholarship of the Hungarian Academy of Sciences (MTA), BO/00773/24, BO/00686/24, respectively.

DATA AVAILABILITY

The data that support the findings in this article are available from the authors upon reasonable request.

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