Terahertz Time-domain Spectroscopy for Ultrafast and Quasi-static Characterizations of Germanium

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Abstract—In this work, we carry out a comprehensive study of charge carrier dynamics in germanium spanning its ultrafast to quasi-static timescales. The study makes use of a continuous-wave (CW) near-infrared (NIR) pump and terahertz (THz) probe beams to realize a CW NIR pumped THz-time-domain spectroscopy (THz-TDS) system with frequency-selective homodyne detection. This enables characterizations of ultrafast charge carrier scattering, while the detection is locked to the THz probe beam, and quasi-static charge carrier recombination, while the detection is locked to the CW NIR pump beam. The ultrafast THz-TDS characterization reveals scatter times of 239 fs for electrons and 204 fs for holes at low pump intensities, which reduce to scatter times of 186 fs for electrons and 159 fs for holes at higher pump intensities. These scatter times give good agreement to the literature mobility of germanium at low intensities and indicate carrier-carrier scattering at higher intensities. The quasi-static THz-TDS characterization suggests that the charge carrier lifetime is dominated by surface states. The manifestation of surface states is gleaned by characterizing germanium samples with varying forms of micro-hole arrays. This reveals lifetimes ranging from 1.5 to 8.6 μs, in good agreement with a linearized model with a surface recombination velocity of 14,200 cm/s. Ultimately, the experimental results from the CW NIR pump THz-TDS system and the applied theoretical models give an accurate depiction of the charge carrier dynamics that evolve in germanium over its ultrafast to quasi-static timescales.

Index Terms—Charge carrier lifetime, charge carrier scattering, germanium, terahertz time-domain spectroscopy.

I. INTRODUCTION

Germanium is a narrow-bandgap semiconductor that has witnessed a rich history [1] and renewed interest as a free-space modulator for terahertz (THz) communications [2], [3], [4]. Germanium is of particular interest for THz modulators owing to its long charge carrier lifetime, which is on the order of hundreds of microseconds [5], allowing it to produce deep modulation. Moreover, germanium has a high carrier mobility, owing to its long carrier scatter times in the hundreds of femtoseconds [6]. This allows carriers to easily migrate to the surface of a modulator, where surface defect states can be used to reduce the carrier lifetime (and realize more rapid modulation) [7], [8]. Nonetheless, the foremost challenge to the characterization and optimization of such germanium-based modulators is the disparate timescales of the underlying charge carrier dynamics, which exhibit scattering on a picosecond timescale [6] and charge carrier lifetimes on a microsecond timescale [3], [5], [9]. The breadth of these timescales makes it challenging to characterize the material. Characterizations of scattering demand time-resolved analyses with ultrashort laser pulses to resolve the ultrafast charge carrier scatter times, whereas characterizations of recombination demand real-time analyses to show the quasi-static charge carrier lifetimes. The challenges are further increased by the low bandgap of germanium, at 0.67 eV [10], which has the photon energies of typical ultrafast pulsed lasers generate energetic charge carriers that relax through a complex network of intra/inter-valley scattering.

To measure the ultrafast charge carrier scatter time and mobility in germanium, a variety of innovative techniques have been introduced for its characterization. Yeh et al. characterized the reflection of mid-infrared probe pulses off germanium following pump excitation [6]. The time- and wavelength-resolved measurements showed charge carrier scattering on an ultrafast picosecond timescale, although quasi-static charge carrier recombination was too slow to be seen. Others have used extreme-ultraviolet probing with near-infrared (NIR) pumping to characterize germanium [11], [12]. This method uses probe beam absorption between states in the valence and conduction bands, which exhibits transient bleaching from pump-induced charge carriers. The technique circumvented the challenge of germanium's low bandgap and revealed charge carrier scattering on a picosecond timescale. Ultrafast charge carrier recombination was characterized for nanocrystalline germanium and found to be on a picosecond timescale [11]. However, this was not possible for crystalline germanium [12].

Several studies have tried to circumvent germanium's low bandgap using THz probing. Grischkowsky et al. used terahertz time-domain spectroscopy (THz-TDS) to investigate the optical properties of intrinsic germanium in the terahertz
The THz spectrum around 1 THz [13]. These optical properties were related to ultrafast scattering and mobility through the Drude model. Here, the low photon energy of the THz probe beam circumvented the challenge of germanium's low bandgap; however, it was unable to measure the quasi-static charge carrier lifetime. In Hebling et al., THz Pump - THz Probe measurements were made on several semiconductors, including weakly-doped germanium [14]. While the system was able to characterize the ultrafast (picosecond) inter- and intra-valley scattering, it was unable to resolve germanium's quasi-static (microsecond) charge carrier lifetime. Finally, Strait et al. studied germanium nanowires using an optical-pump THz-probe system [15]. Ultrafast charge carrier scatter times and charge carrier lifetimes were measured, although the charge-carrier lifetime measurements were only made possible by surface states in the nanowires hastening charge carrier recombination from microseconds to picoseconds.

The quasi-static charge carrier lifetime of germanium can be measured by implementing a modulation measurement technique such as the one demonstrated by Chen et al. for electrical modulation of free-space propagating THz waves [2], or the ones demonstrated by Wen et al. or Alius et al. for optical modulation of free-space propagating THz waves [4], [16]. This method measures the depth of modulation at increasing modulation frequencies to gauge its roll-off with respect to frequency. We show in this work that the frequency at which modulation depth falls off is directly related to charge carrier lifetime. This charge carrier lifetime measurement technique lends itself well to integration with the THz-TDS system described in [13] due to its use of a THz probe beam, which functions as a broadband pulse.

In this work, we carry out a comprehensive study of charge carrier dynamics in germanium for THz modulators spanning its ultrafast to quasi-static timescales. The study utilizes an experimental setup that is a hybrid of two established measurement techniques: THz-TDS [13] and THz modulation measurements [2], [4], [16]. The setup applies a continuous-wave (CW) NIR pump beam (from THz modulation measurements) and pulsed THz probe beam (from THz-TDS) in a CW NIR pumped THz-TDS system that uses frequency-selective homodyne detection. The detection is locked to the THz probe beam to characterize ultrafast charge carrier scattering and is locked to the CW NIR pump beam to characterize quasi-static charge carrier recombination. The advantage to the proposed method over conventional THz-TDS is the ability to photoexcite charge carriers in the sample and analyze the spectral response induced by these carriers, though this does require the sample to be semiconducting. The advantage to the proposed method over conventional pump-probe systems is its ability to make quasi-static (microsecond) charge carrier lifetime measurements without a kilometre-long delay line, although ultrafast (picosecond) measurements must be inferred by fitting the spectral results to a model as opposed to directly measuring them as is done in pump-probe systems.

The mechanism behind charge carrier recombination is studied by measuring the effects that surface modification has on the charge carrier recombination time. The ultrafast experimental results are fit with the Drude model to extract charge carrier scatter times, while the quasi-static results are fit with a modulation rate model to extract the charge carrier lifetime. The charge carrier lifetime is then modified through surface texturing and the results are contrasted to a linearized model of surface recombination to extract the surface recombination velocity of germanium. It is concluded that the scatter times of electrons and holes are comparable to that predicted by mobility calculations at low pump intensities, although they do decrease as carrier-carrier scattering becomes more pronounced at high pump intensities. It is also concluded that the charge carrier lifetime in germanium is 97 μs without surface modification, but this decreases rapidly to 1.5 μs with the increasing presence of surface states due to surface recombination.

II. EXPERIMENTAL SETUP

The proposed work uses a THz-TDS system with a CW NIR pump beam that photo-generates charge carriers in germanium and a THz probe beam whose transmission through the germanium is subject to the charge carriers. Fig. 1 shows a diagram of the experimental setup. The THz-TDS system is seeded by an ultrafast pulsed laser (Spectra Physics, Mai Tai HP), which outputs 100 fs pulses at 780 nm with a repetition rate of 90 MHz, shown as red beams in the figure. This pulsed laser beam is split into two arms, one of which is delayed using a motorized delay line and incident on the THz emitter with an average power of 1.5 W (the rightmost red beam), while the other is incident on the THz detector with an average power of 10 mW (the leftmost red beam). The THz emitter is a custom GaAs photoconductive emitter with electrodes designed for broadband emission, while the detector is an electro-optic detector based on a <110>-cut ZnTe crystal and polarization-sensitive optics, identical to THz-TDS systems used by others [15]. This produces and detects broadband THz probe pulses between 500 GHz and 2.5 THz, shown as the yellow beam in the figure. The intrinsically doped germanium samples, having an orientation of (111), a thickness of δ = 325 μm, and a resistivity of 50 Ω-cm (corresponding to an intrinsic carrier density of 2×10^{13} cm^{-3} for both electrons and holes), are placed into the focus of the THz probe beam, which is about 2 mm in diameter. These samples are then pumped by a CW NIR laser (Newport, LQD980-220E), which outputs a maximum power of 220 mW at 980 nm at a maximum modulation frequency of 100 MHz, shown as the purple beam in the figure. The THz probe beam is modulated by switching the bias field of the photoconductive THz emitter at an angular frequency of ωpr, which gives a sinusoidal variation in the amplitude of the THz beam. This allows for higher probe frequencies, and thus less signal distortion by ambient noise, than conventional mechanical chopping. The CW NIR pump laser is amplitude modulated using an external TTL signal producing square wave modulation at an angular frequency of ωpp.

Detection is carried out using frequency-selective homodyne detection, which makes measurements at an
angular reference frequency of \( \omega_{pp} \), in two configurations depending on whether ultrafast or quasi-static measurements are to be made. The first configuration, which is for ultrafast measurements, has the THz probe beam modulated at an angular frequency of \( \omega_{pr} \) and the CW NIR pump beam unmodulated with \( \omega_{pp} = 0 \), i.e., the yellow beam in the figure is directly modulated by the green THz emitter and the purple beam is not. In this configuration, the frequency selective homodyne detection system measures at the angular frequency of the THz probe beam. This effectively gives a THz-TDS measurement of the sample in the presence of the CW NIR pump beam. Two measurements must be made to determine ultrafast material properties, one with and one without the CW NIR pump beam incident on the sample. The second configuration, which is for quasi-static measurements, has the THz probe beam unmodulated with \( \omega_{pr} = 0 \) and the CW NIR pump beam modulated at an angular frequency of \( \omega_{pp} \), i.e., the purple beam in the figure is directly modulated and the yellow beam is indirectly modulated by the purple beam after the sample). In this configuration, the frequency selective homodyne detection system measures at the angular frequency of the CW NIR pump beam. This effectively measures the modulation in THz signal induced by the CW NIR pump beam. This change is dependent on the angular frequency of the CW NIR pump beam and decreases with increasing frequency. Table I summarizes the corresponding frequencies and measured parameters for each configuration. The measurements include electron scatter time, \( \tau_{se} \), hole scatter time, \( \tau_{sh} \), charge carrier density, \( N \), charge carrier lifetime, \( \tau_c \), and surface recombination velocity, \( S \). It should be noted that the homodyne detection described here requires that the repetition rate of the ultrafast pulsed laser be much faster than the reference frequency to simplify the separation of these two effects by filtering during detection. Otherwise, narrow-band filtering is required to separate effects from the ultrafast pulsed laser and the reference frequency when both are on the same order of magnitude. While this experimental setup is used in this work to measure the properties of germanium, it can also be used to measure other semiconductor materials with ultrafast scatter times and quasi-static charge carrier recombination times, such as intrinsic silicon.

### Table I

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Ultrafast Configuration</th>
<th>Quasi-Static Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW NIR pump frequency, ( \omega_{pp}(2\pi) )</td>
<td>DC</td>
<td>500 Hz – 500 kHz</td>
</tr>
<tr>
<td>THz probe frequency, ( \omega_{pr}(2\pi) )</td>
<td>40 kHz</td>
<td>DC</td>
</tr>
<tr>
<td>Reference frequency, ( \omega_{ref}(2\pi) )</td>
<td>40 kHz</td>
<td>500 Hz – 500 kHz</td>
</tr>
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It must be emphasized here that this measurement system only measures relaxed charge carriers due to the continuous nature of the CW NIR pump beam. As a result, the ultrafast scatter times measured in the first configuration are for electrons at the bottom of the L valley and holes at the top of the heavy and light hole bands in the valence band. Although the CW NIR pump beam excites charge carriers with excess kinetic energy, these carriers relax within a few picoseconds [12] and remain in their relaxed state until recombination occurs several hundred microseconds later. Consequently, the density of hot carriers is negligible compared to density of relaxed carriers, and the results in this work reflect the dynamics of relaxed charge carriers. A simple diagram of germanium’s band structure is shown in Fig. 2(a) indicating the occupancy of charge carriers within the band structure.

![Fig. 1. A schematic of the experimental setup is shown. The THz emitter and detector, the CW NIR pump laser, and the sample are denoted. The red beam incident on the THz emitter and detector is a 100 fs, 780 nm pulsed beam, the yellow beam is the broadband THz pulse, and the purple beam is the 980 nm CW NIR pump beam. In the first configuration, which is for ultrafast measurements, the yellow THz beam is directly modulated at an angular frequency of \( \omega_{pr} \), while the purple CW NIR pump beam is unmodulated, i.e., \( \omega_{pp} = 0 \). In the second configuration, which is for quasi-static measurements, the purple CW NIR pump beam is directly modulated at an angular frequency of \( \omega_{pp} \), while the yellow THz beam is unmodulated by the emitter, i.e., \( \omega_{pr} = 0 \), but is externally modulated by effects induced in the germanium sample by the CW NIR pump beam.](image)

### III. Theory

The measured properties in both configurations are driven by photo-generated charge carriers in the sample. These charge carriers are generated by the CW NIR pump beam and subsequently affect the phase and absorption of the co-incident THz electric field. The photo-generated charge carrier density, \( N(e_{pp},t) \), that is probed in the germanium as a function of time, \( t \), evolves according to the rate equation

\[
\frac{dN(e_{pp},t)}{dt} = \frac{G_{op}}{A_0 \delta} \left( 1 + \sum_{k=1}^{\infty} \frac{4 \sin(\omega_{pp}(2k-1)t)}{\pi(2k-1)} \right) - \frac{N(e_{pp},t)}{\tau_r}.
\]  

For the first term on the right-hand side, \( G_{op} \) is the optical generation rate in electron-holes pairs per unit time, \( \delta \) is the thickness of the germanium, which is assumed to be much less than the diffusion length, and \( k \) is an integer for the series expansion of the square-wave in parentheses. The constant \( A_0 \) is the effective (diffusion broadened) spot size of the charge carrier distribution. It is assumed to be independent of the charge carrier density in this work. Kannegulla et al. present a
similar expression including diffusion since they were interested in the spatial distribution of charge carriers [3]. However, since this work is not sensitive to the spatial distribution of charge carriers given that $\Delta\phi$ is larger than the THz spot size, a rigorous treatment of diffusion is neglected for simplicity. For $\phi_{0p} = 0$, this term realizes CW photogeneration, with homodyne detection at $\omega_{ref} = \omega_{pr}$ giving an ultrafast THz-TDS characterization of charge carrier scattering. For $\phi_{0p} > 0$, this term realizes square-wave photogeneration, with homodyne detection at $\omega_{ref} = \omega_{pp}$ giving a quasi-static THz-TDS characterization of charge carrier recombination. For the second term on the right-hand side, $\tau_{r}$ is the charge carrier lifetime. This charge carrier lifetime yields a steady-state solution for the charge carrier density of

$$N(\omega_{pp}, t) = \frac{G_{pp}\tau_{r}}{A_{d}\delta} \left( 1 + \sum_{k=1}^{\infty} \frac{4}{\Delta(2k-1)} \cos(\omega_{pp}(2k-1)t - \Delta t_k) \right)^{2},$$

(2)

where $\Delta t_k = \pi - \arctan(1/(\omega_{pp}\tau_{r}(2k-1)))$ is the phase between the photo-generation and ensuing charge carrier density.

The photo-generated charge carriers modulate the propagation characteristics of the THz probe beam as it passes through the germanium. The nominal complex refractive index of the germanium, $\tilde{n}(\omega) = n(\omega) - jk(\omega)$, then has its refractive index, $n(\omega)$, change by $\Delta n(\omega, \omega_{pp})$ and its extinction coefficient, $k(\omega)$, change by $\Delta k(\omega, \omega_{pp})$, given THz radiation with an angular frequency of $\omega$ and a free-space wavevector magnitude of $k_0 = \omega/c$, where $c$ is the free-space speed of light. Such changes can be defined by the Drude model [17] as perturbations to the electric susceptibility from electrons and holes, via

$$\tilde{\chi}_e(\omega_{pp}, \omega, t_d) = \frac{-q^2N(\omega_{pp}, t)}{\varepsilon_0\varepsilon_r\omega(\omega - j(1/\tau_{ce}))}$$

(3a)

$$\tilde{\chi}_h(\omega_{pp}, \omega, t_d) = \frac{-q^2N(\omega_{pp}, t)}{\varepsilon_0\varepsilon_r\omega(\omega - j(1/\tau_{ch}))},$$

(3b)

respectively, where $q$ is the electronic charge, $\varepsilon_0$ is the permittivity of free space, $m_0^* = 0.12m_e$ and $m_h^* = 0.21m_e$ are the effective masses for conductivity [13] of electrons and holes, respectively, with $m_e$ as the electron rest mass, and $\tau_{ce}$ and $\tau_{ch}$ are the scatter times of electrons and holes, respectively. The hole susceptibility is considered here in addition to the electron susceptibility because the hole mobility is comparable (to within a factor of two) to the electron mobility. For expository purposes, the variables' arguments state the relevant Fourier conjugate pairs for the quasi-static THz-TDS characterization of charge carrier recombination, $\omega_{pp}$ and $t$, and the ultrafast THz-TDS characterization of charge carrier scattering, $\omega$ and $t_d$, where $t_d$ is the THz time-delay. Such perturbations to the electric susceptibility are linked to the change in refractive index, $\Delta n(\omega_{pp}, \omega, t_d)$, and extinction coefficient, $\Delta k(\omega_{pp}, \omega, t_d)$, through the complex dielectric function $\tilde{\varepsilon} = \varepsilon_1 - j\varepsilon_2$, where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the dielectric function, respectively. This relationship is given by

$$\tilde{\varepsilon} = \sqrt{\varepsilon_1 - j\varepsilon_2} = \sqrt{\tilde{n}(\omega)^2 + (\tilde{\chi}_e(\omega_{pp}, \omega, t_d) + \tilde{\chi}_h(\omega_{pp}, \omega, t_d))}$$

(4)

To implement THz-TDS characterizations of ultrafast charge carrier scattering or quasi-static charge carrier recombination, the CW NIR pump beam is applied to the germanium with frequency-selective homodyne detection system referenced to the respective THz probe beam or CW NIR pump beam. The voltage signal generated by the THz probe beam is recorded at each step in TDS time-delay, $t_d$, averaged over a duration of $T$ in the domain of time, $t$, and Fourier transformed in the domain of time-delay, $t_d$, to give a Fourier spectrum of

$$V(\omega_{pp}; \omega) = \frac{V_0(\omega)e^{-j\Delta n(\omega_{pp}, \omega, t_d)\delta}}{\tilde{n}(\omega)r(t_d)\Delta n(\omega_{pp}, \omega, t_d)\delta} e^{-j\Delta k(\omega_{pp}, \omega, t_d)\delta}$$

(5)

where $V_0(\omega)$ is the Fourier spectrum of the voltage signal when the CW NIR pump beam is off, $\mathcal{F}\{\cdot\}$ denotes the Fourier transform, and $\mathfrak{R}\{\cdot\}$ denotes the real component. In the integrand, the first factor arises from frequency-selective homodyne detection at the reference frequency, $\omega_{ref}$, the second factor arises from sinusoidal modulation of the THz probe beam at the frequency $\omega_{pp}$, and the third factor arises from the amplitude and phase characteristics of the germanium following square-wave modulation by the CW NIR pump beam at the frequency $\omega_{pp}$, via changes in refractive index, $\Delta n(\omega_{pp}, \omega, t_d)$, and extinction coefficient, $\Delta k(\omega_{pp}, \omega, t_d)$. These latter changes are not included in the transmission coefficient at the beginning of this factor as they yield only small perturbations to the nominal complex refractive index, $\tilde{n}(\omega)$.

Applying (5) to the first measurement configuration, which has the CW NIR pump beam modulated at an angular frequency of $\omega_{pp} = 0$ and the THz probe beam is modulated at $\omega_{pr}$, allows the characterization of the ultrafast charge carrier scattering in germanium. The frequency selective homodyne detection system is set to measure the same frequency as the THz probe beam, $\omega_{ref} = \omega_{pr}$. The voltage signal is measured with the CW NIR pump beam off and on, and the results are transformed into Fourier spectra of $V_{0}(\omega)$ and

$$V(\omega_{pp}; \omega) = V_0(\omega)e^{-j\Delta n(\omega_{pp}=0, \omega, t_d)\delta} e^{-j\Delta k(\omega_{pp}=0, \omega, t_d)\delta},$$

(6)

respectively. The measured spectra for $V_{0}(\omega)$ and $V(\omega_{pp}=0; \omega)$
are inserted into this equation to extract the changes in refractive index, \( \Delta n(\omega_p=0; \omega) \), and extinction coefficient, \( \Delta \kappa(\omega_p=0; \omega) \), and these results are fit to the Drude model via (2), (3), and (4). Such fitting yields values for the volume of the charge carrier distribution, \( A_0 \delta \), charge carrier lifetime, \( \tau \), and scatter times of electrons and holes, \( \tau_{s,e} \) and \( \tau_{s,h} \), with corresponding mobilities of electrons and holes being 

\[
\mu_e = q \tau_{s,e} / m_e^* \quad \text{and} \quad \mu_h = q \tau_{s,h} / m_h^* ,
\]

respectively.

Applying (5) to the second measurement configuration, which has the CW NIR pump beam modulated with a square-wave at an angular frequency of \( \omega_p \) and the THz probe beam modulated at an angular frequency of \( \omega_p = 0 \), allows for the quasi-static characterization of the charge carrier lifetime in the germanium sample. The frequency selective homodyne detection system is set to measure the same frequency as the CW NIR pump beam, \( \omega_{\text{ref}} = \omega_p \). The square-wave modulation on the charge carrier density maps itself onto changes in the refractive index and extinction coefficient. Such mapping can be modeled by linearizing (4) and (5). In addition, measurements for each sample at various pump angular frequencies are normalized under the assumption \( \omega_p \tau \ll 1 \). This normalization removes any pump-frequency-independent error in the amplitude that would have resulted from linearization, leaving only pump-frequency-dependent error in the amplitude. This pump-frequency-dependent error must be carefully considered in the linearization of (4) but is of less concern in the linearization of (5). The linearization of (4) is applied to its square root function via Taylor series expansion, which assumes 

\[
\tilde{\kappa}_e (\omega_p=0; \omega_{\text{ref}}, \omega, \tau_{s,e}) + \tilde{\kappa}_h (\omega_p=0; \omega_{\text{ref}}, \omega, \tau_{s,h}) \\
\ll \bar{n}(\omega)^{1/2} .
\]

The linearization of (5) is applied to its exponential functions via Taylor series expansion, though the normalization in the quasi-static analysis reduces the linearization error to below 1.5% for most scenarios in this work. This gives a tractable solution (before normalization) for the Fourier spectrum in the form of

\[
V(\omega_{\text{ref}}; \omega) \approx \frac{4\bar{n}(\omega) v_n}{(\bar{n}(\omega) + 1)^2} \left( \frac{e^{-k_p(0)} - e^{-k_p(\omega)}}{1 + (\omega_p \tau)^2} \right) \\
\left( -k_p \Delta \kappa(\omega_{pp}=0; \omega) \delta - jk_p \Delta n(\omega_{pp}=0; \omega) \delta \right) . \tag{7}
\]

Note that the Fourier spectrum magnitude, \(| V(\omega_{pp}=\omega_{\text{ref}}, \omega) |\), seen here rolls off to 1/\( \sqrt{2} \) of its zero-frequency value when the CW NIR pump beam modulation frequency is \( \omega_p = 1/\tau \). Thus, \(| V(\omega_{pp}=\omega_{\text{ref}}, \omega) |\) can be curve-fit to define the charge carrier lifetime, \( \tau \).

IV. RESULTS

The characterization of ultrafast charge carrier scattering in germanium was carried out using the first measurement configuration with the CW NIR pump beam unmodulated, \( \omega_p = 0 \), and the THz probe beam modulated at a frequency of \( \omega_p/2\pi = 40 \text{ kHz} \). The reference for homodyne detection was locked to the THz probe beam such that \( \omega_{\text{ref}} = \omega_p \). Fig. 2(b) shows the resulting THz-TDS time-domain waveforms with the CW NIR pump beam on and off. It is apparent here that the CW NIR pump beam reduces the amplitude of the THz probe beam significantly and greatly distorts the phase. To quantify such changes, the waveforms are Fourier transformed to spectra of \( V(\omega_{pp}=0; \omega) \) and \( V(\omega) \), and the spectra are inserted into (6) to compute the change in refractive index, \( \Delta n(\omega_p=0; \omega) \) and change in extinction coefficient, \( \Delta \kappa(\omega_p=0; \omega) \). Fig. 2(c) shows experimental results for the refractive index, \( n(\omega) + \Delta n(\omega, \omega_p=0) \), with \( n(\omega) \approx 4.0 \), versus frequency, \( \omega(2\pi) \), and theoretical results from curve-fitting via the Drude model at two different pump intensities. Fig. 2(d) shows experimental results for the extinction coefficient, \( \kappa(\omega) + \Delta \kappa(\omega, \omega_p=0) \), with \( \kappa(\omega) \approx 0 \), versus frequency, \( \omega(2\pi) \), and theoretical results from curve-fitting via the Drude model at two different pump intensities. The experimental results in Figs. 2(c) and 2(d) are plotted over a range of frequencies allowed by the dynamic range of the THz-TDS system. Dynamic range limits the maximum measurable extinction coefficient, which cuts off experimental results below 1 THz for the high intensity data and 0.5 THz for the low intensity data. Consistency to the Kramers-Kronig relations were verified for all refractive index and extinction coefficient measurements to ensure the integrity of the experimental results. Note that the low intensity results show minor etalon artefacts as oscillations in the frequency domain due to internal reflections in sample. The high refractive index and low loss of unilluminated germanium makes these etalon oscillations more prominent at lower intensities, disappearing due to increasing extinction coefficient when the intensity becomes sufficiently large. While several methods have been proposed to remove such etalon artefacts from refractive index and extinction coefficient spectra [18], it was considered unnecessary in this work given that etalon artefacts in Figs. 2(c) and 2(d) were sufficiently small in amplitude and high in frequency to allow the experimental results to be fit by the slowly evolving trends of the Drude model's theoretical results. Fig. 2(e) shows the dependence of charge carrier scatter time on charge carrier density for a range of charge carrier densities.

For a low pump intensity, with an optical generation rate of \( 1.7 \times 10^{17} \pm 1.7 \times 10^{16} \text{ carriers/s} \) and corresponding to the crosses and solid lines in Figs. 2(c) and 2(d), the Drude model fits to the experimental data yield an equal carrier density for both electrons and holes of roughly \( 1.3 \times 10^{15} \text{ cm}^{-3} \), with charge carrier scatter times of \( \tau_{s,e} = 239 \text{ fs} \) for electrons and \( \tau_{s,h} = 204 \text{ fs} \) for holes. These scatter times give mobility values of 

\[
\mu_e = q \tau_{s,e} / m_e^* = 3510 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \text{for electrons and}
\]

\[
\mu_h = q \tau_{s,h} / m_h^* = 1710 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \text{for holes} .
\]

These mobilities are slightly lower than the literature mobility values of 

\[
\mu_e = q \tau_{s,e} / m_e^* = 3900 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \text{for electrons and}
\]

\[
\mu_h = q \tau_{s,h} / m_h^* = 1900 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \text{for holes} .
\]

A discrepancy attributed to minor carrier-carrier scattering. The standard deviations between the experimental results and the Drude model are 0.015 and 0.014 for the refractive index and extinction coefficient, respectively.
scatter time of germanium is constant for carrier densities below about $1 \times 10^{15}$ cm$^{-3}$ and decreases for higher carrier densities. The calculated electron and hole mobilities for the lowest carrier densities agree with literature mobilities to within 5%. The definition for mobility used here is for static/DC mobility, not high-frequency mobility. This is in line with other THz studies on germanium [3], [4], [13]. The lack of carrier density dependence in the scatter times for germanium at low densities indicates that the dominant scattering mechanism is carrier-phonon scattering. However, at high carrier densities, the results show carrier density dependence in the scatter time indicating that carrier-carrier scattering is beginning to become the dominant scattering mechanism. (In all cases, the undoped nature of the intrinsic germanium samples eliminates the possibility of significant impurity scattering [10].) While the fitted charge carrier densities could be used in (2) to estimate the charge carrier lifetime, $\tau$, such a result would be unreliable. The charge carrier lifetime, $\tau$, and effective (diffusion broadened) spot size, $A_\phi$, appear as an unknown ratio in (2), making it necessary to assume a value for $A_\phi$ to calculate $\tau$. To avoid this problem, the quasi-static characterization is applied next with controlled levels of diffusion.

The characterization of quasi-static charge carrier recombination in germanium was carried out using the second measurement configuration with the CW NIR pump beam applied as a square-wave with its modulation frequency swept over $\omega_{pp}/2\pi = 100$ Hz to 300 kHz, and the THz probe beam unmodulated, $\omega_r = 0$. The reference for homodyne detection is locked to the CW NIR pump beam, such that $\omega_{ref} = \omega_{pp}$, while THz time-domain waveforms are recorded. Each waveform is Fourier transformed and its magnitude spectrum between 500 GHz and 1 THz is extracted to define the Fourier spectrum magnitude of $|V(\omega_{pp}, \omega)|$. Fig. 3(a) shows the experimental magnitudes displayed as markers, versus the CW NIR pump beam modulation frequency, $\omega_{pp}/2\pi$, with theoretical curve-fits from (7) displayed as lines. Results are presented for a 50-mm diameter germanium sample (solid black circles with a solid black line) and a 12.5-mm diameter germanium sample (solid black circles with a dashed black line). The curve-fits for the 50-mm and 12.5 mm germanium samples roll off to $1/\sqrt{2}$ of their zero-frequency values at $\omega_{pp}/(2\pi) = 1/(2\pi \tau) \approx 10.3$ kHz and 75.8 kHz, respectively, suggesting charge carrier lifetimes of $\tau \approx 97$ $\mu$s and 13.2 $\mu$s, respectively. The differing values of $\tau$ seen for the two samples, along with the fact that neither conform to the millisecond bulk charge carrier lifetime measured by others [3], [5], [19], [20], suggest that surface recombination is strongly impacting the charge carrier lifetimes. The effects of surface recombination can be simply modelled using the linear relation

$$1/\tau = 1/\tau_{rb} + SR,$$  \hspace{1cm} (8)

where $\tau_{rb}$ is the bulk charge carrier lifetime, $S$ is the surface recombination velocity, and $R$ is the surface-area-to-volume ratio of the sample [7], [8]. In Fig. 3(a), the surface of the

For a higher pump intensity, with an optical generation rate of $7.0 \times 10^{17} \pm 7.0 \times 10^{16}$ carriers/s and corresponding to the hollow circles and dashed lines in Figs. 2(c) and 2(d), the Drude model fits to the experimental data yield shorter scatter times of $\tau_e = 186$ fs for electrons and $\tau_h = 159$ fs for holes. These shorter scatter times, attributed to significant carrier-carrier scattering, give lower mobility values of $\mu_e = 2730$ cm$^2/$(V·s) for electrons and $\mu_h = 1330$ cm$^2/$(V·s) for holes. The carrier density for the higher intensity curve is equal for both electrons and holes at roughly $5.6 \times 10^{15}$ cm$^{-3}$ giving standard deviations between the experimental results and the Drude model of 0.020 and 0.018 for the refractive index and extinction coefficient, respectively. Note that the inflection seen in the high intensity Drude model in Fig. 2(c) also exists for the low intensity Drude model, although it exists below 500 GHz and cannot be seen in the figure. Fig. 2(e) shows the scatter time for several other pump intensities. Clearly, the
large wafer was left untreated, while the surface of the small wafer was cleaned with boiling water to remove oxide. The literature suggests that the untreated wafer has a surface recombination velocity on the order of $10^3$ cm/s [19], while the wafer treated with boiling water has a surface recombination velocity of $10^4$ cm/s [9]. Given the similar surface-area-to-volume ratios for both wafers, and negligible bulk recombination due to the millisecond bulk recombination time in germanium, the tenfold difference in surface recombination velocities for the two bulk wafers matches the nearly tenfold difference in measured charge carrier lifetime.

To more accurately quantify the relationship between charge carrier lifetime and surface recombination, micro-hole arrays were fabricated in 12.5-mm-diameter intrinsic germanium samples and characterized in terms of their quasi-static charge carrier recombination. The samples were laser-micromilled as square arrays of micro-holes with a diameter, $d$, of 100 μm, and pitches, $a$, of 240, 270, 320, 350, 400, 500, or 650 μm. Surface-area-to-volume ratio was calculated using $R = \pi d/a^2$, giving values ranging from 7 to 55 cm$^{-1}$. All samples were immersed in boiling water to remove oxides from the laser micromill. Fig. 3(a) shows representative experimental and theoretical results for the Fourier spectrum magnitude of three micro-hole arrays: an array with $R = 12.6$ cm$^{-1}$ (hollow red circles with a solid red line), an array with $R = 25.6$ cm$^{-1}$ (hollow red circles with a dashed red line), and an array with $R = 43.1$ cm$^{-1}$ (hollow red circles with a dotted red line). The charge carrier lifetimes of these micro-hole arrays are $\tau = 7.0$, 3.2, and 1.5 μs, respectively. Charge carrier lifetime measurements are made for THz probe frequencies ranging from 500 GHz to 1 THz and the error bars in Fig. 3(a) correspond to the standard deviation in the data over this range. Errors introduced by linearization when deriving (7) for each sample are zero for $\omega_0 \tau < 1$ and increase for $\omega_0 \tau > 1$. For nearly all the data in Fig. 3(a), linearization error is below 1.5%. The exception is the large wafer, which has linearization errors of up to 15%, when $\omega_0 \tau = 10$, due to the large charge carrier density in this sample. While large enough to introduce some linearization error, this large charge carrier density, approximately $5.6 \times 10^{15}$ cm$^{-3}$, is not large enough to affect the charge carrier lifetime of the sample [20]. Clearly, increasing the surface area of the micro-holes hastens surface recombination and decreases the charge carrier lifetime. To illustrate this trend, the reciprocal of the charge carrier lifetime, $1/\tau$, is plotted in Fig. 3(b) (hollow red circles) versus surface-area-to-volume ratio, $R$, for these three samples and six additional samples. A representative scanning electron microscope image of laser micro-milled holes in germanium is shown in the inset of Fig. 3(b). The figure also shows a theoretical curve-fit (solid red line) for the linear relation in (8). The slope of the trendline in Fig. 3(b) gives a surface recombination velocity of $S = 14,200$ cm/s. This velocity agrees with values seen in the literature for germanium surfaces treated with boiling water [9]. The error bars in Fig. 3(b) correspond to the standard deviations in the measured charge carrier lifetimes and were consistently about ±16%.

This leads to the more prominent error bars seen for larger reciprocal lifetimes. This standard deviation makes it challenging to identify an accurate value for the vertical axis intercept, which corresponds to the inverse bulk charge carrier lifetime. The bulk charge carrier lifetime could be assumed to be 100 μs, corresponding to the longest measured charge carrier lifetime in this work. Unfortunately, this is an order of magnitude shorter than literature values for bulk charge carrier lifetime, indicating that some surface effects are still present. Therefore, the inverse bulk charge carrier lifetime of the theoretical fit is set to zero, agreeing with the millisecond charge carrier lifetimes seen in the literature.

### V. CONCLUSION

In conclusion, we have presented a comprehensive study of charge carrier dynamics in germanium. The study made use of a CW NIR pumped THz-TDS system with frequency-selective homodyne detection in two configurations. The first configuration enabled an ultrafast THz-TDS characterization of charge carrier scattering, showing scatter times of 239 fs for electrons and 204 fs for holes at low intensities, and 186 fs for electrons and 159 fs for holes at higher intensities. Such findings were in good agreement with carrier mobilities given in literature for the low intensities, and they indicated heightened levels of carrier-carrier scattering at higher pump intensities. The second configuration enabled a quasi-static THz-TDS characterization of charge carrier recombination, which showed a predominance of surface recombination. The manifestation of the surface states was gleaned by characterizing germanium samples with micro-hole arrays. The samples revealed charge carrier lifetimes ranging from 1.5 to 8.6 μs with good agreement to a linearized model having a
surface recombination velocity of 14,200 cm/s. Ultimately, the CW NIR pump THz-TDS system was effective in capturing the charge carrier dynamics that evolve in germanium over its ultrafast to quasi-static timescales.

REFERENCES


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