

# Carrier mobility of silicon by sub-bandgap time-resolved terahertz spectroscopy

# TIMOTHY J. MAGNANELLI 🕩 AND EDWIN J. HEILWEIL<sup>\*</sup> 🕩

Nanoscale Device Characterization Division, Physical Measurement Laboratory, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA \*edwin.heilweil@nist.gov

**Abstract:** Low density charge mobility from below bandgap, two-photon photoexcitation of bulk silicon (Si) is interrogated using time-resolved terahertz spectroscopy (TRTS). Total charge mobility is measured as a function of excitation frequency and fluence (charge carrier density), cut angle, and innate doping levels. Frequency dependent complex photoconductivities are extracted using the Drude model to obtain average and DC-limit mobility and carrier scattering times. These dynamic parameters are compared to values from contact-based Hall, above bandgap photoexcitation, and comparable gallium arsenide (GaAs) measurements. Mobilities are shown to increase beyond Hall values at low carrier densities and are modestly higher with increasing dopant density. The former occurs in part from below bandgap photoexcitation exhibiting abnormally small (faster) scattering times, while both reflect unique conduction characteristics at lowest (>  $2x10^{12}$  cm<sup>-3</sup>) carrier densities achieved through photodoping.

# 1. Introduction

Thorough understanding of electrical conduction and mobility of charge carriers that traverse semiconductor materials underlies their efficacy in intricate electronic devices. Previous studies examined carrier behavior of silicon as a function of dopant level or preparation using contactbased Hall measurements. [1–5] Hall methodology assesses charge mobility in semiconductor crystalline materials for use as transistors, sensors, and parts of devices in which conduction occurs across a surface or specific path. [6] These evaluations incur several drawbacks including limitations in establishing satisfactory electrical contact with the semiconductor, distortions to the local structure of the sample following contact application, and enhanced sensitivity to electrically shorted (preferentially conducting) pathways rather than homogeneously across the material. [7] If the semiconductor is intended for use in a photovoltaic device or other application in which conduction of the entire material layer is critical, a non-contact method will provide more accurate, unbiased, and relevant bulk conduction information. A prime example of non-contact conductivity methodology is time-resolved terahertz (THz) spectroscopy (TRTS).

Using TRTS, one can "photo"-dope a semiconductor by exciting a resonant transition with an ultraviolet (UV), visible, or near-infrared (NIR) pump pulse to generate a well understood and empirically calculatable density of charge carriers. The penetration depth, excitation fluence, and charge yield efficiency (assumed to be 100% for inorganic crystalline semiconductors) factor into this tunable charge carrier density. Coupling a THz probe into a photoexcited region integrates over all conduction pathways within that subset interaction volume. A previous study examined Si and GaAs with above bandgap photoexcitation, and yielded substantial insight into variations in total charge mobility as a function of dopant level, carrier density, and some level of variability in pump wavelength. [8] Conductivity calculations account for the limited penetration depth of the photoexcitation source, i.e., these materials and excitation conditions fall within the thin film limit. [8,9] TRTS provides an improvement upon the specific and surface/shorted and contact-influenced conduction pathways of Hall measurements, though the technique incurs losing the (direct) distinction between p- and n- type materials and charge carriers (i.e., hole and electron behavior). [7,8]

Above bandgap TRTS in these materials produces relatively thin photoexcited active volumes near the material's surface. This approach induces carrier interactions that are more susceptible to surface defects and do not wholly reflect the characteristics of the entire bulk material. Because either method is limited in the uniformity with which it reflects the bulk or interior semiconductor conductivity, we employ a more recent adaptation of TRTS using below bandgap, two-photon photoexcitation. [10] When applicable, sub-bandgap (two-photon) excitation circumvents the remaining problems of limited sub-domains and defects. Two-photon cross sections are normally substantially lower than their one-photon counterparts, but by using high peak power excitation, carrier photo-population at near uniform density throughout the entire thickness of the crystalline semiconductor is achieved, in turn lowering the carrier density detection threshold by a few orders of magnitude. This last advantageous property is illustrated by the scaled penetration depths for silicon excited at various pump energies in Fig. 1(a). [11]



**Fig. 1.** (a) Penetration depths of various pump energies into a typical Si wafer shown to scale. 3.10 eV excitation penetrates ca. 100 nm (omitted). (b) Band structure diagrams for Si and GaAs shown to scale energetically. Colored arrows represent the energy above the valence band for each excitation energy considered in this work (1.03 eV, 1.55 eV, 2.07 eV, and 3.10 eV as green, red, yellow, and blue respectively). Each lobe represents a different type of electron (conduction band) or hole (valence band) and dashed lines indicate the energetic minima of each band or energies reached via 1.55 eV and 2.07 eV (equivalently the two-photon absorption of 1.03 eV) photoexcitation pulses.

Precedence exists for employing the two-photon TRTS technique, having been accomplished in our lab with the experimental set-up described previously. [10] There, two-photon cross sections (ß) of five III-IV and II-VI semiconductor materials were determined using the z-scan method and combined with TRTS to compare above to below bandgap photogenerated carrier mobilities. Most of the materials (except cadmium sulfide) showed more than a two-fold increase in mobility for below bandgap compared to above bandgap photoexcitation. [10] Herein, we conduct a similar analysis of Si (and GaAs) but with emphasis on varying the pump frequency, fluence, and sample properties (e.g., dopant-level and cut angle) to evaluate mobility at the lowest carrier densities accessible.

Thurber et al. described the mobility of holes [1] and electrons [2] in chemically doped pand n-type silicon wafers as a function of innate carrier density. They found that the mobility generally increases with decreasing carrier density but plateaus at sufficiently high (>  $10^{19}$  cm<sup>-3</sup>) and low (<  $10^{14}$  cm<sup>-3</sup>) densities. Above bandgap TRTS measurements described previously largely confirmed this trend, but only reached densities as low as  $\approx 10^{15}$  cm<sup>-3</sup>. [8] Two-photon absorption allows us to attain lower densities than above bandgap excitation and comparable ones to the lowest chemically doped samples ( $\approx 10^{13}$  cm<sup>-3</sup> and  $10^{12}$  cm<sup>-3</sup> for Si and GaAs), albeit with significantly more reliability and uniformity.

An adaptation of the band structure diagrams of Si and GaAs is highlighted in Fig. 1(b), illustrating the energetic locations of each applicable conduction band accessible by the employed

excitation. [12,13] These reflect the potential for observing the effect on the charge carrier dynamics for a selected photoexcitation energy. We investigate several excitation energies to determine the roles of excess energy above the bandgap, accessibility of different conduction bands, and orientation of the delocalized dipole and band to the crystal lattice in influencing charge carrier dynamics.

In this paper, the two-photon photoinduced conductivity of an assortment of room temperature, un-doped, n-, and p-doped Si wafers cut along different crystallographic axes using 1200 nm (1.03 eV, below bandgap) excitation is presented. We characterize the frequency dependent real and imaginary conductivities and empirically derive charge carrier densities to extract the total (electron plus hole) charge carrier mobility. Si samples are contrasted with GaAs, which has a different band structure (Fig. 1(b)) and approximately an order of magnitude higher charge carrier mobility. Ultrafast TRTS with electro-optic gated detection sampling of THz probe radiation is well established and utilized as our primary tool of investigation [14].

## 2. Experimental

Several silicon and gallium arsenide samples were evaluated with all properties described in Table 2 of the Appendix. Most of the analyses were conducted on undoped (resistivity > 6000  $\Omega$ cm) <100> and <111> Si wafers from University Wafer [15] and an undoped <100> GaAs from Wafer Technology Ltd. [15] labeled with batch numbers Si\_2018, Si\_3094, and GaAs\_4234, respectively. Additional samples were investigated to isolate the effect of dopant level and are described more specifically in the Appendix. Approximate refractive indices and penetration depths for Si and GaAs samples at the photoexcitation wavelengths used in this study were taken from the literature and included in the Appendix. [11,16,17] ß values (two-photon absorption provided by an optical parametric amplifier (OPA) and an amplified Ti:Sapphire system. ß values determined for each sample and their 95% confidence intervals (CIs) are described in the Appendix and agree with previous reports. [18–21]

The generic set-up and specific details of the ultrafast methodology were described previously. [8,22] However, in order to ensure that  $E_0$  and  $\Delta E$  were phase locked (rather than examined with serial delay scans), a double lock-in procedure was added to the instrument. Briefly, time-dependent and frequency-resolved THz spectra (TDS) were collected by iteratively blocking the THz probe and photoexcitation pump pulses via optical choppers running at 500 Hz and 250 Hz, respectively. The optical probe delay was swept relative to output gate pulses with a translation stage. Interference with the THz probe at a detection crystal was measured as voltages by a matched pair of photodiodes and sampled by two lock-in amplifiers locked to the repetition rate of each chopper. This extracts the full time-dependent E-field waveform of the THz probe pulse with the gate pulse for a fixed pump-probe time delay (20 ps for this study). Complex Fourier Transform (FFT), splitting, and scaling the signals between the two lock-in amplifiers simultaneously provided the frequency-dependent unexcited spectra, E<sub>0</sub>, and the change in each spectrum resulting from photoexcitation,  $\Delta E$ . Four excitation wavelengths, 1200 nm, 800 nm, 600 nm, and 400 nm (i.e., 1.03 eV, 1.55 eV, 2.07 eV, and 3.10 eV energies) were used to photoexcite Si and GaAs below (1200 nm) and above (400 nm to 800 nm) their bandgaps of 1.11 eV and 1.43 eV, respectively. [23] Though 1.03 eV is within 0.1 eV of the Si bandgap, several samples were analyzed with power dependent excitation and found to exhibit over 90% two-photon power dependence in each case as detailed in the Appendix. Example time and frequency-dependent FFT spectra collected for Si\_3094 are also included in the Appendix as Figs. 7(a) and 7(b) to illustrate typical datasets. The employed probe-gate time delays were selected to omit secondary reflections of the THz probe pulse originating from the ZnTe detection and generation crystals and the sample.

Details of the specific fitting procedures, calculations, and error propagation not described here are also found in the Appendix. Complex conductivities were extracted via Eq. (1), where the photoinduced permittivity,  $\hat{\eta}(\omega)$ , can be related to the sum of its ground state permittivity,  $\hat{\varepsilon}(\omega)$ , and the perturbation introduced as photoinduced conductivity,  $\Delta\hat{\sigma}(\omega)$  as functions of the angular frequency ( $\omega$ ) and including the vacuum permittivity  $\varepsilon 0$ . [24]

$$\hat{\eta}(\omega) = \hat{\varepsilon}(\omega) + \frac{i\Delta\hat{\sigma}(\omega)}{\varepsilon_0\omega} \tag{1}$$

After extracting the complex conductivity  $(\Delta \hat{\sigma}(\omega))$  and applying additional equations, (Appendix, Eqs. (7), (8), and (9)), the real and imaginary parts were simultaneously fit to the Drude model. [25] Si charge carriers deviate from Drude-like behavior at sufficiently low (< 10<sup>17</sup> cm<sup>-3</sup>) or high (> 10<sup>19</sup> cm<sup>-3</sup>) charge carrier densities; [26] since the Drude model is most accurate in describing metals rather than semiconductors, Cole-Cole and Cole-Davidson corrections were tested for improvement of frequency-dependent fits to the observed conductivities. [26,27] Though inclusion of these parameters yielded marginally improved fits, the close similarities between including and omitting the Cole-based corrections justified their omission. The Drude Model is shown as Eq. (2).

$$\Delta\hat{\sigma}(\omega) = \frac{\Delta N q^2}{m^*} * \frac{\tau}{(1 - (i\omega\tau))}$$
(2)

Here,  $\Delta N$  represents the photoinduced charge carrier density, q the elementary charge, and  $\omega$  the angular frequency. Each set of complex conductivity data can be fit to the Drude model as a function of two specific physical parameters related to charge conduction  $(\Delta \hat{\sigma})$ , the DC-limit of the real conductivity  $(\Delta \sigma_{DC} = \Delta \hat{\sigma}(0) = \Delta Nq^2/m^*)$  and the scattering time of the charge carriers  $(\tau)$ .  $\Delta N$  can be determined from the excitation fluence and penetration depth so the weighted harmonic mean of the charge carrier effective masses (m\*) can also be extracted. Uncertainties were determined using a nonlinear least squares algorithm, propagated in quadrature, and represented as 95% CIs in the error bars of associated plots. [28] The most straightforward way to determine charge carrier mobility relative to the frequency dependent conductivity is to use Eq. (3) in the DC limit ( $\mu_{DC}$ ,  $\omega \to 0$  THz).

$$\Delta \sigma_{DC} = e \Delta N(\mu_{e^-} + \mu_{h^+}) = e \Delta N \mu_{DC}$$
(3)

Here, the photoinduced change in conductivity is equivalent to the product of the number density of charge carrier pairs ( $\Delta N$ ) and the sum of electron and hole (or all present carrier) mobilities ( $\mu_{e^-} + \mu_{h^+}$ ). To compare to previously measured above bandgap mobilities determined using the thin-film limit approximation, [8] this expression was extended to frequency-dependent mobilities beyond the DC limit. By determining  $\Delta N$  from excitation conditions, applying Eq. (3) to calculate mobility at each frequency and calculating a weighted average over these values, we can determine the integrated mobility for charge carriers observed with TRTS ( $\mu_{THz}$ ) that is directly comparable to the previous above bandgap study of Si and GaAs. [8] Finally, a sigmoidal Caughey-Thomas curve, presented as Eq. (4), can be fit to the density dependent trends in  $\mu_{DC}$ , as shown previously for Si and GaAs. [29,30]

$$\mu = \frac{\mu_{max} - \mu_{min}}{1 + \left(\frac{N}{N_{ref}}\right)^{\alpha}} + \mu_{min} \tag{4}$$

In this equation,  $\mu_{max}$  and  $\mu_{min}$  define the limiting low and high carrier density mobility, N<sub>ref</sub> the inflection density, and  $\alpha$  the slope of the fit. Parameters extracted for Si can be compared to the combination of independent hole and electron values determined previously. [29]

# 3. Results and discussion

#### 3.1. Effects of excitation energy and fluence (i.e. carrier density) on mobility

Initially, we seek to address whether the total mobility of electron and hole carriers plateaus at lower attainable carrier densities than previously observed. [1,2,8] Fig. 2(a) shows the average mobilities,  $\mu_{THz}$ , determined for several photoinduced carrier densities populated by two-photon excitation of Si\_2018 and contrasting to previously determined, above bandgap mobilities. [8] The utility of below bandgap excitation lies in photoexciting charge carriers homogeneously throughout the entire sample thickness, permitting measurement of transient carrier densities over two orders of magnitude lower than above bandgap excitation. Within error, the total measured mobility levels off as the carrier density falls below  $5 \times 10^{14}$  cm<sup>-3</sup>, suggesting that carriers behave independently of one another once spaced sufficiently far apart. This result agrees with the Hall findings [1,2,8] and the anticipated low-density limit of the Drude model and indicates that the system behaves as expected when viewed by this metric.



**Fig. 2.** Total charge mobility of Si\_2018 determined by (a) averaging across all THz frequencies ( $\mu_{THz}$ ) and (b) extrapolating to the DC limit ( $\mu_{DC}$ ) using the Drude model from Eq. (2) and fit with a Caughey-Thomas curve from Eq. (4). The results are plotted as a function of pump energy (color) and photoinduced carrier density. Data points for 3.10 eV and 1.55 eV excitation in (a) are taken from previous work. [8] Error bars represent 95% CIs of the associated mobility.

An alternative method for determining the mobility from the Drude model involves extrapolating the frequency dependence to the DC limit (zero probe frequency). Figure 2(b) shows mobility determined using Eq. (3) with below (1.03 eV) and above bandgap (1.55 eV, 2.07 eV, and 3.10 eV) excitation energies. The photoinduced response from above bandgap excitation behaves as anticipated, having mobility that increases steadily with decreasing carrier density. The discrepancy between the low density 3.10 eV and high density 2.07 eV excitations arises from nonlinear THz probe response in the latter and potential error in the assumed penetration depth of the former. The qualitative agreement of the three lower energy data sets and effective fit by a Caughey-Thomas curve (parameters included in the Appendix, Table 4) support the  $\mu_{DC}$  trend observed for low carrier densities accessible through two-photon excitation.

A noteworthy difference occurs for below bandgap excitation between the trends seen in  $\mu_{THz}$  (Fig. 2(a)) and  $\mu_{DC}$  (Fig. 2(b)):  $\mu_{DC}$  increases more substantially (a factor of 2 compared to 1.3) and almost monotonically with decreasing carrier density below the density by which  $\mu_{THz}$  plateaus. The trend towards higher mobilities at lower densities in  $\mu_{DC}$  suggests that carriers are increasingly mobile below the anticipated ranges observed by  $\mu_{THz}$  and reported previously. [1,2,8] This discrepancy must arise from variation in the frequency-dependent complex conduction from below bandgap excitation as a function of carrier density (i.e., pump fluence). For further clarification, we investigated the frequency-dependent conduction by varying the two-photon excitation fluence.

7226

#### Optics EXPRESS

Figure 3(a) shows the normalized frequency-dependent spectra of the real conductivity for 1.03 eV excitation at carrier densities shown in Figs. 2(a) and 2(b). The smooth traces represent the Drude model fit from Eq. (2) applied to each set of real and imaginary (not shown) conductivities simultaneously. The absolute conduction decreases  $\approx$  linearly with decreasing carrier density as anticipated. The normalized spectra are displayed to highlight narrowing of the frequency dependence, such that the real conductivity decreases more rapidly at high frequencies, with decreasing  $\Delta N$ .  $\mu_{THz}$ , proportional to the average mobility across the THz spectrum, will then decrease relative to the corresponding  $\mu_{DC}$  as the density decreases. In this representation (Fig. 3(a)), the latter have been set relative to one to clearly observe this trend. The conduction spectral narrowing results from an increase in scattering time which would be anticipated as the carrier density decreases. Alternatively, increased scattering times signify more delocalization of the charge carriers and increased lower frequency THz absorption. For each excitation energy considered (1.03 eV, 1.55 eV, and 2.07 eV), this trend occurs consistently from high (HF) to low (LF) excitation fluence cases shown in Fig. 3(b).



**Fig. 3.** Normalized frequency dependence of the real photoinduced conductivity of sample Si\_2018 when excited at (a) different 1.03 eV photoexcitation fluences (i.e., carrier densities) and (b) the highest and lowest fluences of each excitation frequency. In (a), the progression flattens as  $\Delta N$  (carrier density) increases from  $1.5 \times 10^{13}$  cm<sup>-3</sup> (red) to  $1.2 \times 10^{15}$  cm<sup>-3</sup> (purple). In (b) 1.03 eV, 1.55 eV, and 2.07 eV excitation (green, red, and yellow, respectively) at high (circle/solid line) and low (square/dashed line) fluences.

The trend between different excitation energies in Fig. 3(b) exhibits an unexpected shift in slope of the frequency-dependence when going from above (1.55 eV) to below bandgap (1.03 eV)eV) excitation, i.e., HF and LF 1.03 eV progressions are noticeably flatter than both their 2.07 eV and 1.55 eV counterparts. Since the different excitation energies have different penetration depths into the sample, the generated carrier densities (for HF or LF) are different by  $\approx 1.5$ orders of magnitude. In accordance with a physical interpretation of the Drude model, we anticipate the scattering time  $\tau$ 's (proportional to the slopes of each spectral progression) to follow the trend,  $\tau_{1.03 \text{ eV}} > \tau_{1.55 \text{ eV}} > \tau_{2.07 \text{ eV}}$ . Instead, we observe  $\tau_{1.55 \text{ eV}} > \tau_{2.07 \text{ eV}} > \tau_{1.03 \text{ eV}}$ . This sharp disagreement exposes the differing role that below bandgap photoexcitation plays in influencing charge carrier behavior. Specifically, two-photon excitation yields a population of charge carriers that scatter significantly more rapidly than would be predicted based on the photoinduced number density of charge carriers alone. While it is possible that systematic errors could arise from mis-matched overlap of the pump and probe beams (errant signal at low frequencies) and uncertainty of the two-photon absorption cross section ( $\beta$ 's) and beam diameter ( $\Delta N$ ), none of these sources of error appreciably affect the trend seen in  $\tau$ , nor can we identify other systematic errors at work in our experimentation.

To clarify further, we present the fluence dependent scattering times extracted from fitting the Drude model, Eq. (3), for all four excitation energies and plot them as a function of carrier

**Research Article** 

density in Fig. 4(a). An abrupt discontinuity is found as the excitation energy transitions to below bandgap whereby the scattering time decreases by a factor of  $\approx 3.5$ .



**Fig. 4.** (a) Scattering times ( $\tau$ ) for samples Si\_2018 (<100>, circles) and Si\_3094 (<111>, squares) as for different pump energies and (b) The DC-limit conduction for Si\_2018 at each pump energy, both as functions of carrier density. Green, red, yellow, and blue represent 1.03 eV two-photon, and 1.55 eV, 2.07 eV, and 3.10 eV one-photon, excitation energies, respectively. The dashed line in (b) represents a power law fit through all four sets, indicating a common trend in  $\Delta\sigma_{\rm DC}$  despite the discontinuity in  $\tau$ . Error bars represent 95% CIs and are not visible in (b).

We conjectured that this offset in scattering time occurs in response to switching between crystalline orientation and possible preference for exciting into the conduction band along the X ( $\approx$  <100>) and L ( $\approx$  <111>) axes based on one- and two-photon absorption selection rules, respectively. We then sought to query whether the observed difference in  $\tau$  was linked to differing geometries of accessible conduction band states in Si (Fig. 1(b)) and if shifting the orientation of the excitation dipole/quadrupole from along the <010> axis to the within the plane of the <111> axis would have an impact.

To test these possibilities, we performed 1.03 eV and 2.07 eV excitation measurements of an undoped silicon sample cut along the <111> axis (Si\_3094) for direct comparison to the <100> cut Si\_2018 sample and extracted scattering times. These results are included in Fig. 4(a) and show near overlap between the <111> (squares) and <100> (circles) datasets, with the gap between bridging 1.03 eV and 2.07 eV scattering times decreasing only slightly. This comparison confirms that the excitation-dependent shift in scattering time occurs regardless of the cut angle of the Si crystal and an inconsequential dependence on the relative orientation between photoexcitation and crystal geometry.

Figure 4(b) shows the DC conduction ( $\sigma_{DC}$ , at v = 0) of each Si\_2018 data set plotted with both axes on logarithmic scales to visualize all three excitation regimes together (despite orders of magnitude difference in respective carrier densities). Employing a power law, as described by Eq. (5), fits the combined data sets very well ( $r^2 = 0.991$ ), indicating that the overall conductivity (and similarly mobility) exhibits no discernible shift by switching from one- to two-photon excitation amongst these datasets.

$$\sigma_{DC}(S/m) = 9.72 * 10^{12} * \Delta N^{0.83}(cm^{-3})$$
<sup>(5)</sup>

A slight vertical discrepancy is apparent between the overlapping 3.10 eV and 2.07 eV excitation data, though the primary takeaway from this analysis is that 1.03 eV excitation is consistent in terms of conduction with other excitation frequencies. Precluding the conclusion that below bandgap excitation causes a difference in photoinduced conductivity, the shift in scattering times still poses an interesting curiosity and may be related to a change in relative types of charge carriers (e.g., effective masses) that make up the photoinduced population. Exploring this

possibility remains an ongoing investigation. Inconsistencies between the respective directional polarizations of the photoexcitation pump and THz probe were considered as a potential cause. However, no discernible conduction anisotropy at any excitation frequency, nor anisotropic trends in frequency-dependent conduction of 1.55 eV photoexcitation were observed, suggesting that different polarization orientations are not a factor. We next investigated whether this phenomenon was unique to Si (or an indirect material of similar band structure) by comparing it to GaAs.

# 3.2. Comparison to gallium arsenide

Gallium arsenide is a direct bandgap semiconductor with a geometrically similar crystal structure, but different electronic band structure, compared to silicon (Fig. 1(b)). GaAs is known to be significantly more conductive than silicon due to its higher electron mobility. [8] By comparing a prototypical, low-doped GaAs sample to previously discussed Si results, we distinguish between carrier mobility at the lowest photoinduced carrier densities and the excitation dependence of carrier scattering times for above versus below bandgap excitation. Figures 5(a) and 5(b) show  $\mu_{DC}$  and  $\tau$  as a function of carrier density for GaAs\_4234, similarly presented in Figs. 2(b) and 4(a) for Si\_2018, respectively. The extracted mobility values are found to be approximately an order of magnitude larger than for Si. As GaAs is a direct bandgap semiconductor with some initial relaxation and charge recombination, the determined carrier density was scaled by ratio of the integrated TRTS signal at the experimental pump probe delay (20 ps) relative to the peak signal (a ratio of approximately 0.9).



**Fig. 5.** Extracted (a) DC-limit mobility ( $\mu_{DC}$ ) and (b) carrier scattering times ( $\tau$ ) for GaAs\_4234 photoexcited above bandgap (3.10 eV/blue, 2.07 eV/yellow, and 1.55 eV/red) and below bandgap (1.03 eV/green). These values can be compared to the Si\_2018 results in Figs. 2(b) and 4(a), respectively. A fit to a Caughey-Thomas curve, Eq. (4) is applied to the combined data in (a) as the dashed line. Error bars (95% CIs) are included with smaller ones obscured by the points shown.

The mobility determined using below bandgap excitation is generally smaller than (though it begins to approach) the reported value for the Hall mobility of electrons in GaAs at comparable densities, specifically  $\approx 9000 \text{ cm}^2/\text{V} \cdot \text{s}$  at room temperature and  $10^{14} \text{ cm}^{-3}$  carrier density. [31] Similar to Si, GaAs shows a monotonically increasing mobility with decreasing carrier density that does not plateau (as expected) in the lowest density regime and approaches/exceeds that of the Hall mobility progression. [31] The data appears split between two trends (1.55 eV and 3.10 eV vs. 1.03 eV and 2.07 eV) that are not readily fit by a Caughey-Thomas curve as for the Si progression. This presumably arises from error in the mobilities of the 2.07 eV dataset and nonlinear THz probe response from high fluence 1.03 eV excitation, as the 1.55 eV and 3.10 eV datasets exhibited excellent repeatability (< 10% deviation).

Interestingly, the scattering times from Fig. 5(b) also show a disconnect between the lowest energy above bandgap and highest energy below bandgap carrier density regimes. The

nonlinearities arising from increasing attenuation of the THz probe may be responsible for the falloff in scattering times at higher carrier densities (particularly 2.07 eV excitation), but comparing the low-density limit for each excitation frequency reveals a lower scattering time for below bandgap (1.03 eV, 0.14 ps) than above bandgap excitation (all < 0.20 ps). It is also possible that since GaAs has a much higher intrinsic mobility than Si that the anticipated low-density plateau regime occurs below  $10^{12}$  cm<sup>-3</sup> [30] which is inaccessible *via* the Hall approach.

The Si <111> measurements ruled out the possibility that the observed scattering time discontinuity arises from a geometrical discrepancy between one- and two-photon alignments of the photoexcitation sources to the crystal structure; this assessment illustrates a comparable, discrete step in scattering time but in a different semiconductor crystal, though the magnitude and extent of the phenomena appears to be material dependent. We assert from these findings that observed jump in scattering time occurs from proportional population of different K-space modes (bands) arising from one and two-photon excitation. This would be analogous to molecular excitations through dipole and quadrupole moments, and yields differing linear combinations of charge carriers with different aggregate scattering properties.

We envision three further avenues of study. First, we consider how utilizing this technique would clarify other systems previously studied with below bandgap excitation; namely that other semiconductor materials could be examined for similar density dependent mobility. [10] CdS could also be interrogated to clarify why its below gap mobility was found to be lower than its above gap mobility. [10] Second, we consider ramifications of the Drude model beyond simply extracting scattering times. For instance, it may be possible that differences in the relative sub-populations of charge carriers, arising from the excitation frequency and fluence-dependent photoexcitation, affect the effective masses (m\*'s) observed for equivalent electron and hole carrier densities, though investigation of this concept is beyond the scope of this work. Third, performing lower excitation energy two-photon excitation of Si (at 0.78 eV) would potentially be more selective in exciting only the lower lying electronic bands and will be explored in subsequent studies.



**Fig. 6.** (a) Real total charge mobility, from Eq. (3), for n- and p-doped Si as a function of THz probe frequency. The inset key describes the dopant type and resistivity ( $\Omega$ •cm) for each sample. (b) Average ( $\mu_{THz}$ ) and DC ( $\mu_{DC}$ ) mobility determined for each sample plotted as a function of innate (doped) conductivity (S/m) for p-(red, squares) and n-type (blue, circles) Si samples. The two-photon excitation fluence was set to generate a carrier density of  $\approx 1.2 \times 10^{15}$  cm<sup>-3</sup>. Red and blue dashed vertical lines represent the conductivity at which the doped charge carrier density is approximately equivalent to the photoexcited carrier density for p- and n-type samples, respectively. Total charge mobility is found to nominally increase with increasing dopant level visualized through fits with models for  $\mu_{THz}$  and  $\mu_{DC}$  (green and black dashed lines, respectively). Error bars indicate 95% CIs.

# 3.3. Dependence on intrinsic dopant level

The interactions of electrons and holes are contingent upon the photoinduced charge carrier density and mode of generation but also depend on the presence of n- or p-type dopants (i.e., static charge carriers) within the semiconductor crystalline lattice. We now focus on examining Si samples as a function of intrinsic doping level and the resulting effect on photoinduced charge carrier mobility. Carrier mobility was determined across the THz probe spectrum using Eq. (3) and extrapolating from the DC limit to higher frequencies. This approach yielded the traces plotted in Fig. 6(a) for several doped (mostly <100>-cut) Si samples photoexcited below bandgap (1.03 eV) at constant fluence. The resultant  $\mu_{THz}$  and  $\mu_{DC}$  values are included in Table 1 and plotted as a function of wafer conductivity (the inverse of the reported resistivity) in Fig. 6(b). These values can be compared to the sum of Hall mobilities for both electrons and holes at the total photogenerated carrier density,  $1.2x10^{15}$  cm<sup>-3</sup>, of  $\approx 1820$  cm<sup>2</sup>/V•s. [1,2]

Table 1. Average and DC-limit total mobility determined from conductivity values in Fig. 6(a)	for
fixed $pprox$ 1.2x10 <sup>15</sup> cm <sup>-3</sup> two-photon photo-density (error limits with 95% Cls).	

Dopant Type / Resistivity ( $\rho$ , $\Omega$ •cm), (Name) <sup>a</sup>	$\mu_{THz}$ (cm <sup>2</sup> /V•s)	$\mu_{DC}$ (cm <sup>2</sup> /V•s)
N / 0.1 (736)	1810 +/- 220	2900 +/- 130
N / 1-3 (C2)	1450 +/- 180	2450 +/- 90
P / 1-10 (2020)	1570 +/- 190	2350 +/- 120
N / 11-15 (C3)	1390 +/- 160	1970 +/- 70
P / 10-15 (C4)	1370 +/- 160	2040 +/- 60
N / 10-30 (C1)	1220 +/- 160	1840 +/- 100
None / >10k (2018)	1320 +/- 150	2010 +/- 60
Hall @ $1.2 \times 10^{15} \text{ cm}^{-3}$	18	20

<sup>a</sup>See Appendix Table 2 for sample details.

We find  $\mu_{DC}$  values are greater than those obtained by Hall measurements and previously obtained by above bandgap excitation measurements, while  $\mu_{THz}$  are slightly lower than anticipated from Hall results. [8] The trend of  $\mu_{DC} > \mu_{THz}$  arising from the frequency dependence of the conduction response is once again observed and weakly supports the nominal increase in carrier mobility preceding the plateau at low carrier densities, similar to that in Fig. 2(b). The important distinction for Fig. 6(a) is that we now observe this dependence regardless of the doping level in a lightly to moderately doped regime (0.1 – > 10000  $\Omega$ •cm). Unfortunately, highly doped samples (< 0.01  $\Omega$ •cm), like those studied previously using above bandgap measurements, cannot be interrogated using sub-bandgap excitation. [8] This limitation occurs when, at a thickness to absorb enough 1.03 eV photons to yield a discernible photoconductive signal, the entire THz probe is absorbed by static, non-photoinduced charge carriers, rendering the measurement inapplicable. As an aside, no appreciable correlation is observed between the extracted carrier scattering times ( $\tau$ ) associated with these samples and their dopant level.

Considering Fig. 6(b), the charge carrier mobility appears to slightly increase with decreasing resistivity (or increasing dopant density/conductivity). This trend appears to onset (given limited doped Si samples) when the photoexcited carrier density exceeds that through chemical doping. [12] The dashed line models represent simple fits through the data where mobility (across this lower conductivity regime) is assumed to be linear and directly proportional to conductivity, i.e.  $\mu = \mu_0 + c_1 \sigma$  for some constant mobility  $\mu_0$  and scaling constant  $c_1$ . This functional form is meant to guide the eye rather than represent the physical behavior of the dependence on innate (chemical dopant) conductivity. Initially, we anticipated the opposite trend would occur as higher photoinduced charge carrier density hinders charge carriers from freely moving. However, we

Sample Name	Doping	Resistivity (Ω•cm)	Cut Angle	Thickness (µm)	Supplier <sup>a</sup>	β <sup>b</sup> (cm/GW)	ß 95% CI
Si_2018	undoped	>10000	<100>	277	UW	1.17	0.56 - 1.71
Si_3094	undoped	>6000	<111>	330	UW	1.17 <sup>c</sup>	_
GaAs_4234	undoped	N/A	<100>	320	WT	10.6	9.2 - 12.1
Si_2020	p-type	1-10	<100>	282	UW	1.06	0.45 - 1.67
Si_736	n-type	0.1	<100>	274	UW	1.07	0.72 - 2.08
Si_C1	n-type	10-30	<100>	330	N/A	1.19	0.77 – 1.63
Si_C2	n-type	1-3	<100>	310	N/A	0.99	0.01 - 1.83
Si_C3	n-type	11-15	<100>	541	N/A	0.93	0.44 - 1.39
Si_C4	p-type	10-15	<111>	404	N/A	1.09	0.55 – 1.61

Table 2. Properties of the investigated silicon (Si) and gallium arsenide (GaAs) wafers; ß measured at 1.03 eV.

<sup>*a*</sup>UW = University Wafer, WT = Wafer Technology [15],

<sup>b</sup>ß's measured at 1.03 eV,

<sup>c</sup>ß not explicitly measured for Si\_3094, assumed equivalent to Si\_2018

interpret this finding to indicate that static charge carriers may provide enhancement to the motion of charged carriers through attractive interactions over prolonged distances more than like charges hinder and deflect local motion. Since TRTS only detects the combined mobilities of holes and electrons, it is not readily discernible how holes and electrons separately contribute to this observation. Interestingly, no substantial difference is observed between p- (squares) and n-type (circles) doping within our limited sample set, though more accurate comparison could be made in subsequent work by analyzing additional and more dispersed dopant level samples.

Our assertion given these two findings is that native dopants may provide a stabilizing force for photoactivated charges produced at very low density, facilitating total charge carrier motion and slightly increasing mobility. This directly contrasts with increasing the photoactivated charge carrier density (i.e., more collisions), and the dopant level comparison of above gap excitation at  $>10^{16}$  cm<sup>-3</sup> densities measured previously. [8] Instead, we appear to observe more efficient conduction networks at low photoexcited carrier densities.

# 4. Conclusions

Contactless measurements of charge mobility in bulk semiconductor silicon and gallium arsenide were conducted using two-photon excitation to generate charge carrier population throughout the entire thickness of each crystalline semiconductor wafer. Below bandgap excitation permits a hundred-fold lower carrier density to be explored than by generic one-photon excitation or Hall techniques. Combining two-photon excitation with a terahertz probe serves as a more accurate method to extract absolute and integrated carrier mobility by minimizing of the impact of surface defects and providing an explicit depth of photoexcitation. Carrier mobility was determined and compared to values previously measured using one-photon excitation and found to be significantly higher than anticipated when extrapolated to the DC conduction limit. More thorough comparison between below and above bandgap photoexcitation methodology revealed consistent trends in overall photoconductivity and carrier mobility despite a sharp shift in carrier scattering time. This observation for both Si and GaAs suggests that the effect is not uniquely due to Si's (indirect) bandgap structure and may be the product of differing selection rules or effective masses for populated carriers.

For constant two-photon excitation fluence, the mobility of photoinduced carriers increases slightly with increasing intrinsic dopant density, likely occurring as a result of stabilization by

oppositely charged dopants. Though at odds with previous reports, these differences indicate that photoinduced carriers behave differently than intrinsically present within an inorganic semiconductor by chemical doping. We hope to explore this trend further by contrasting oppositely doped Si samples at near equivalent doping, or by identifying the tendencies of each type of involved charge carrier as a function of doping in subsequent work. One can also imagine performing the same measurements on thicker samples to extend the analysis to even lower charge carrier densities. Cumulatively, the TRTS measurement approach and corresponding findings unveil a litany of information and potential spectroscopic applications for all-optical exploration of mobility and photoinduced conductive properties of semiconductor materials and substrates.

# 5. Appendix

Two-photon absorption cross sections ( $\beta$ ) were measured by fitting the model described by Eq. (6) to the power dependent, transmitted light through a given silicon or gallium arsenide sample. Here,  $\alpha'$  and  $\beta'$  are the fit parameters ascribed to the combined Fresnel losses/one-photon absorption and two-photon absorption, respectively.  $I_0$  is the incident laser intensity, and d is the sample thickness. The two-photon absorption cross sections reported above ( $\beta$ ) are determined by applying unit conversions, the temporal pulsewidth, and beam spot size to  $\beta'$ . The 1.03 eV excitation pulsewidth was determined *via* autocorrelation and found to have a temporal full width half maximum (FWHM) of 350 fs. These values agree reasonably well with literature values of 1.8 cm/GW for Si [18] and 26-45 and 22 cm/GW for GaAs [14–16] measured using 1200 nm and  $\approx$ 1060 nm picosecond pulses, respectively. [14–16]

$$I = I_0 * 10^{-\alpha'} * \left( 1 - \frac{1}{1 + \beta' dI_0} \right)$$
(6)

The incident beam spot sizes were set to overfill a  $\approx 1.5$  mm to 2 mm diameter iris such that the pump intensity and E<sub>0</sub> probe electric field were reduced to  $\approx 50\%$  and  $\approx 75\%$ , respectively. The incident pump beam size and lateral homogeneity in carrier density ( $\approx 82\%$  edges to center of the beam) were confirmed by imaging the two-photon excitation beam at the sample location onto a Si CCD camera under the same excitation conditions as the TRTS measurements, shown in Fig. 8(a). Approximately 0.3% to 3% (Si) and 1.4% to 20% (GaAs) of the input power was absorbed depending on the dataset yielding < 1.5% (Si) and < 10% (GaAs) longitudinal variation in carrier density for each photoexcited sample. Assuming the 1.03 eV refractive indices of Si and GaAs from Table 3,  $\approx 18\%$  of the beam would be reflected from the back surface back into each sample, yielding  $\approx 3.6\%$  more carriers and negligible population on subsequent passes; this factor has been omitted from this study.

Table 3. Assumed Si and GaAs penetration depths ( $1/\alpha$ , µm) and pump wavelength refractive indices ( $n_1$ ).

Pump Energy, $\lambda$ (eV, nm)	Si 1/α [11]	GaAs 1/ <i>a</i> [16]	Si n <sub>1</sub> [11]	GaAs n <sub>1</sub> [16,17]
3.10 eV, 400 nm	0.09756	0.01484	5.623	4.374
2.07 eV, 600 nm	2.578	0.2071	3.931	3.920
1.55 eV, 800 nm	12.09	0.7432	3.669	3.684
1.03 eV, 1200 nm	_	_	3.522	3.428

Fitting the THz photoconductivity signal ( $\Delta E$ ) as a function of excitation fluence for three Si samples at 1.03 eV yielded  $\geq$  90% two-photon absorption for each dataset. This analysis was done preliminarily to determine how selective 1.03 eV is for two-photon charge carrier generation since it is relatively close to the reported 1.11 eV Si bandgap at room temperature. [23] Samples Si\_2018, Si\_736, and Si\_2020 exhibited 90%, 90%, and 95% two-photon fluence dependence

	• • •			1.50
Sample	$\mu_{max}$	$\mu_{min}$	N <sub>ref</sub>	$\alpha^{a}$
Si_2018	2903	549	$7.8*10^{14}$	0.74
GaAs 4234	6940	2734	7.7*10 <sup>15</sup>	0.75

Table 4. Parameters for Caughey-Taylor curve fits applied to Si\_2018 and GaAs\_4234  $\mu_{DC}$  values.

<sup>*a*</sup>Values for  $\alpha$  were fit adjusted separately to avoid erroneous parameter convergence.

respectively, as shown in Fig. 8(b). The excitation fluence used for this analysis was ca. 150  $\mu$ J/cm<sup>2</sup>, which is much lower than the maximum excitation fluences used in the main study (> 800  $\mu$ J/cm<sup>2</sup>). These conditions suggest that this effect is lower for the higher fluence data described above. The effect of generating a 5% to 10% subpopulation through one-photon absorption on the low fluence data points were not explored or corrected for in the results presented in this work; this possibility may slightly elevate  $\tau$  or lower  $\mu$  values accordingly. Sample GaAs\_4234 exhibited the lowest proportion of two-photon absorptive character at 78% across the five lowest carrier density measurements. This result is unexpected giving the larger energy gap between the excitation energy and limit of the bandgap and may influence the low-density behavior of GaAs. There is an observed geometric dependence to overall excitation absorption observed as a function of rotating the face of each <100> sample about the incident pump polarization (a C<sub>6</sub> symmetry in absorption). This was accounted for by maintaining consistent alignment of the two-photon pump polarization to the <010> axis.

The photoexcited volume for above bandgap excitation of these samples was assumed to be limited by the surface area of an over-filled iris used to constrict the beam diameter and twice the penetration depth of the pump pulse at the applied wavelength  $(2/\alpha')$ . This value for the penetration depth represents the integrated average depth of penetration by an incident photon. We note this is a systematically different assumption from the previous above bandgap study of silicon. [8] The active volume depth is inversely proportional to  $\alpha'$  and will directly impact the measured photoconductivity ( $\sigma_{DC}$ ) and calculated charge carrier density ( $\Delta N$ ). However, these effects cancel and do not influence the resulting charge carrier mobilities ( $\mu_{DC}$ ) or scattering times ( $\tau$ ). Refractive indices from the literature were used to estimate the amount of pump energy lost due to Fresnel reflection from the sample's front surface. Optical parameters were obtained from external references for Si [11] and GaAs [16,17].

The following equations were used to calculate the change in conductivity starting with Eq. (1) in the Experimental section.  $\varepsilon$  and  $\eta$  are both defined by Eq. (8) though it is written in terms of  $\varepsilon$ .

$$n'(\omega) = 1 + \frac{c}{\omega d} ln(\phi - \phi_0), \ n''(\omega) = -\frac{c}{\omega d} ln\left(1 + \frac{\Delta E}{E_0}\right)$$
(7)

$$\hat{\varepsilon}(\omega) = \varepsilon' + \varepsilon'' : \varepsilon' = n'^2 - n''^2, \ \varepsilon'' = 2n'n'' \tag{8}$$

$$\hat{\sigma}(\omega) = \sigma' + \sigma'' : \sigma' = \varepsilon_0 \omega \ (\eta'' - \varepsilon''), \ \sigma'' = \varepsilon_0 \omega \ (\varepsilon' - \eta') \tag{9}$$

Here, the  $\hat{}$ ,  $\hat{}$ , and " designations represent the complex, real, and imaginary components, respectively, of the refractive index (n), dielectric constant ( $\varepsilon$ ), and conductivity ( $\sigma$ ). c is the speed of light, d the sample thickness,  $\omega$  the angular frequency,  $\Delta E/E_0$  the relative absorption of THz probe radiation (dividing  $\Delta E$  by  $E_0$  from Fig. 7(b)), and  $\phi - \phi_0$  the relative phase shift between ( $\Delta E + E_0$ ) and  $E_0$ , with the latter energy waveforms determined as a function of angular frequency. The above equations permit one to bridge the measurable quantities such as the time-dependent waveforms shown in Fig. 7 to extract changes in conductivity of the form  $\Delta \hat{\sigma}(\omega)$ . As a note, all calculations were computed using these equations and angular frequencies ( $\omega = 2\pi v$ ) though all frequency-dependent plots are shown as ordinary frequencies (v).

Uncertainties throughout the manuscript were determined according to the specific data type, model and application. Where possible, when data/modeling were considered sufficiently linear,



**Fig. 7.** (a) Example TDS and TRTS two-photon (1.03 eV) photoexcited time-dependent sweeps for sample Si 3094 and (b) the corresponding frequency-dependent (real) FFT of the time-domain signals in (a).  $E_i$ ,  $E_0$ , and  $\Delta E$  represent the THz electric field signal passing though air, unexcited silicon, and the difference between excited and unexcited silicon, respectively.



**Fig. 8.** (a) Charge density distribution from 1.03 eV excitation (white  $\rightarrow$  blue colormap) relative to data collection iris (red outline). (b) Fluence dependence of TRTS measured photoconductivity for three silicon samples collected using 1.03 eV two-photon photoexcitation. All Si samples (blue, orange, and green) exhibit >90% two-photon generated carrier population with the GaAs sample (yellow) exhibiting  $\approx 78\%$  overall two-photon absorption character.

values were numerically averaged with standard errors of those averages used to represent confidence intervals (e.g., k = 1.96 type A uncertainty analysis). For nonlinear least squares regression parameters and results, (i.e. to estimate  $\Delta N$ ,  $\tau$ ,  $c_1$ ,  $\sigma_{DC}$ , etc.) the procedure described in detail below was used to obtain nonlinear confidence intervals associated with each parameter. For a given nonlinear least squares regression model, containing n data points and k adjustable parameters, the model was initially optimized using a Marquadt-Levenburg optimization algorithm (starting with a reasonable initial guess) to determine an optimal fit and then treated with the error analysis algorithm below to yield the reported values. Each reported uncertainty associated with a single adjustable parameter was determined by performing an F-test using the following procedure: [28]

- 1. Perturbing the parameter of interest by fixed increments and re-optimizing the remaining parameters at each unique value.
- 2. Calculating the  $\chi^2$  (chi-squared) of each fit relative to the  $\chi^2$  of the optimal fit.
- 3. Assessing the range of  $\chi^2$  values to determine the point at which it exceeds a critical value defined by looking up F(k, n-k) at 95% confidence from an F-distribution table.

4. Individual parameters from the same model were repeated separately.

This procedure results in nonlinear 95% confidence interval with unequal positive and negative error bounds. The approach requires some degree of local linearity, continuity, and unique convergence to parameters of the associated model but is adequate for the Drude and other simple models used in this work.

# Funding

Physical Measurement Laboratory (PML); National Institute of Standards and Technology (NIST); Scientific Technical Research Support (STRS).

# Acknowledgments

We acknowledge the National Institute of Standards and Technology/National Research Council Research Associateship Program (T. J. M.) and NIST STRS for support. The authors acknowledge discussions with Jared Wahlstrand concerning band structures and Alan Bristow regarding two-photon cross sections ( $\beta$ 's) and Christina Hacker for supplying several Si wafers.

# Disclosures

The authors declare no conflicts of interest.

#### References

- W. R. Thurber, R. L. Mattis, Y. M. Liu, and J. J. Filliben, "Resistivity-Dopant Density Relationship for Boron-Doped Silicon," J. Electrochem. Soc. 127(10), 2291–2294 (1980).
- W. R. Thurber, R. L. Mattis, Y. M. Liu, and J. J. Filliben, "Resistivity-Dopant Density Relationship for Phosphorus-Doped Silicon," J. Electrochem. Soc. 127(8), 1807–1812 (1980).
- F. Schindler, J. Geilker, W. Kwapil, W. Warta, and M. C. Schubert, "Hall mobility in multicrystalline silicon," J. Appl. Phys. 110(4), 043722 (2011).
- T. Bronger and R. Carius, "Carrier mobilities in microcrystalline silicon films," Thin Solid Films 515(19), 7486–7489 (2007).
- 5. F. Szmulowicz, "Calculation of the mobility and the Hall factor for doped p-type silicon," Phys. Rev. B **34**(6), 4031–4047 (1986).
- K. Ellmer, "Hall Effect and Conductivity Measurements in Semiconductor Crystals and Thin Films," in *Characteriza*tion of Materials (American Cancer Society, 2012), pp. 1–16.
- R. Chwang, B. J. Smith, and C. R. Crowell, "Contact size effects on the van der Pauw method for resistivity and Hall coefficient measurement," Solid-State Electron. 17(12), 1217–1227 (1974).
- B. G. Alberding, W. R. Thurber, and E. J. Heilweil, "Direct comparison of time-resolved terahertz spectroscopy and Hall Van der Pauw methods for measurement of carrier conductivity and mobility in bulk semiconductors," J. Opt. Soc. Am. B 34(7), 1392–1406 (2017).
- F. A. Hegmann, O. Ostroverkhova, and D. G. Cooke, "Probing Organic Semiconductors with Terahertz Pulses," in *Photophysics of Molecular Materials* (John Wiley & Sons, Ltd, 2006), pp. 367–428.
- J. K. Wahlstrand and E. J. Heilweil, "Contactless THz-based bulk semiconductor mobility measurements using two-photon excitation," Opt. Express 26(23), 29848–29853 (2018).
- C. Schinke, P. Christian Peest, J. Schmidt, R. Brendel, K. Bothe, M. R. Vogt, I. Kröger, S. Winter, A. Schirmacher, S. Lim, H. T. Nguyen, and D. MacDonald, "Uncertainty analysis for the coefficient of band-to-band absorption of crystalline silicon," AIP Adv. 5(6), 067168 (2015).
- 12. S. M. Sze, Physics of Semiconductor Devices, Second (John Wiley & Sons, Inc., 1981).
- J. R. Chelikowsky and M. L. Cohen, "Nonlocal pseudopotential calculations for the electronic structure of eleven diamond and zinc-blende semiconductors," Phys. Rev. B 14(2), 556–582 (1976).
- 14. M. C. Beard, G. M. Turner, and C. A. Schmuttenmaer, "Terahertz Spectroscopy," J. Phys. Chem. B 106(29), 7146–7159 (2002).
- 15. "Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose,," (n.d.).
- 16. D. E. Aspnes, S. M. Kelso, R. A. Logan, and R. Bhat, "Optical properties of AlxGa1-x As," J. Appl. Phys. 60(2), 754–767 (1986).

#### Vol. 28, No. 5/2 March 2020/ Optics Express 7236

#### Research Article

# Optics EXPRESS

- T. Skauli, P. S. Kuo, K. L. Vodopyanov, T. J. Pinguet, O. Levi, L. A. Eyres, J. S. Harris, M. M. Fejer, B. Gerard, L. Becouarn, and E. Lallier, "Improved dispersion relations for GaAs and applications to nonlinear optics," J. Appl. Phys. 94(10), 6447–6455 (2003).
- A. D. Bristow, N. Rotenberg, and H. M. van Driel, "Two-photon absorption and Kerr coefficients of silicon for 850–2200nm," Appl. Phys. Lett. 90(19), 191104 (2007).
- A. Penzkofer and A. A. Bugayev, "Two-photon absorption and emission dynamics of bulk GaAs," Opt. Quantum Electron. 21(4), 283–306 (1989).
- A. A. Said, M. Sheik-Bahae, D. J. Hagan, T. H. Wei, J. Wang, J. Young, and E. W. V. Stryland, "Determination of bound-electronic and free-carrier nonlinearities in ZnSe, GaAs, CdTe, and ZnTe," J. Opt. Soc. Am. B 9(3), 405–414 (1992).
- C. M. Cirloganu, L. A. Padilha, D. A. Fishman, S. Webster, D. J. Hagan, and E. W. V. Stryland, "Extremely nondegenerate two-photon absorption in direct-gap semiconductors [Invited]," Opt. Express 19(23), 22951–22960 (2011).
- O. Esenturk, J. S. Melinger, and E. J. Heilweil, "Terahertz mobility measurements on poly-3-hexylthiophene films: Device comparison, molecular weight, and film processing effects," J. Appl. Phys. 103(2), 023102 (2008).
- 23. C. Kittel, Introduction to Solid State Physics, 8th Edition (John Wiley & Sons Inc., 2005).
- 24. S. L. Dexheimer, ed., Terahertz Spectroscopy: Principles and Applications, 1 edition (CRC Press, 2007).
- J. Lloyd-Hughes and T.-I. Jeon, "A Review of the Terahertz Conductivity of Bulk and Nano-Materials | SpringerLink," https://link.springer.com/article/10.1007%2Fs10762-012-9905-y.
- R. Ulbricht, E. Hendry, J. Shan, T. F. Heinz, and M. Bonn, "Carrier dynamics in semiconductors studied with time-resolved terahertz spectroscopy," Rev. Mod. Phys. 83(2), 543–586 (2011).
- K. J. Willis, S. C. Hagness, and I. Knezevic, "A generalized Drude model for doped silicon at terahertz frequencies derived from microscopic transport simulation," Appl. Phys. Lett. 102(12), 122113 (2013).
- 28. G. A. F. Seber and C. J. Wild, Nonlinear Regression (John Wiley & Sons, 2003).
- D. M. Caughey and R. E. Thomas, "Carrier mobilities in silicon empirically related to doping and field," Proc. IEEE 55(12), 2192–2193 (1967).
- M. C. Beard, G. M. Turner, and C. A. Schmuttenmaer, "Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy," Phys. Rev. B 62(23), 15764–15777 (2000).
- D. L. Rode, "Chapter 1 Low-Field Electron Transport," in Semiconductors and Semimetals (Academic Press, N.Y., 1975), Vol. 10, pp. 1–86.