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Differentiating Photoexcited Carrier and Phonon Dynamics in the $\Delta$, $L$, and $\Gamma$ Valleys of Si(100) with Transient Extreme Ultraviolet Spectroscopy

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ABSTRACT: Transient extreme ultraviolet (XUV) spectroscopy probes core level transitions to unoccupied valence and conduction band states. Uncertainty remains as to what degree the core—hole created by the XUV transition modifies the measurement of photoexcited electron and hole energies. Here, the Si $L_{2,3}$ edge is measured after photoexcitation of electrons to the $\Delta$, $L$, and $\Gamma$ valleys of Si(100). The measured changes in the XUV transition probability do not energetically agree with the increasing electron photoexcitation energy. The data experimentally confirm that, for the Si $L_{2,3}$ edge, the time-dependent electron and hole energies are partially obscured by the core—hole perturbation. A model based on many-body approximations and the Bethe–Salpeter equation is successfully used to predict the core-hole modification of the final transition density of states in terms of both electronic and structural dynamics. The resulting fit time constants match the excited-state electron thermalization time and the intervalley electron–phonon, intravalley electron–phonon, and phonon–phonon scattering times previously measured in silicon. The outlined approach is a more comprehensive framework for interpreting transient XUV absorption spectra in photoexcited semiconductors.

1. INTRODUCTION

Transient extreme ultraviolet (XUV) spectroscopy offers advantages in terms of temporal resolution and element specificity when compared with visible light and infrared (IR) table top sources.1–5 Unlike traditional visible light and IR transient absorption measurements, the XUV probe pulses created by high-harmonic generation can have attosecond pulse widths.4–6 The XUV probe’s energy range allows core level-to-valence transitions to be measured, with the photoexcited change in absorption containing both electronic and structural dynamics.7 The combination of temporal resolution and probed energy range has led to new insights into the first few femtoseconds of photoexcitation, as well as into the longer timescale dynamics of electronic–phonon and phonon–phonon scatterings.8–14 The same is true for X-ray transient absorption studies performed using X-ray free electron lasers and synchrotrons.15–20

Interpreting photoexcited dynamics from the differential X-ray absorption measurement is challenging because of the core—hole, which is the positive charge left in the core level by the core-to-valence XUV probe transition. Whereas the localized core—hole wave function is beneficial because it imparts structural information onto the X-ray absorption spectrum, in doing so, the core—hole potential also modifies the final transition density of states (DOS).21–23 The change in the final transition DOS masks the energy of photoexcited electrons and holes, sometimes obscuring direct measurement of their time-dependent energies. As a result, the ground-state X-ray absorption spectrum and any photoexcited changes seldom match the expected effects in visible and IR measurements of the same material.24–26 In the case of localized valence orbitals, such as in the 3d transition metals, the core–hole interaction is strong enough that only the photoexcited change in the elemental oxidation state can be measured.27–30

Recent reports suggest that the core–hole effect in covalent semiconductors with delocalized valence electrons, such as Ge and Si, is negligible enough that the electron and hole energies can be measured as a function of time over a broad XUV energy range.31–34 It remains less clear if the transient XUV spectra can be used to distinguish the occupation of nondegenerate valleys in semiconductor band structures. It also remains unknown whether the unique electron–phonon scattering pathways that thermalize photoexcited carriers between and within each valley can be quantified.
In this paper, the differential absorption of the Si L2,3 edge is measured following visible light excitation to the Δ, L, and Γ valleys of silicon. The changes in the XUV absorption at the critical points do not agree with the expected energies of photoexcited carriers because of core–hole effects. A previously reported model is based on the Bethe–Salpeter equation (BSE) with density functional theory (DFT), simplified by several many-body approximations, is tested for analyzing the electron energies within the core–hole perturbation. By fitting the BSE–DFT model to the experimental data, the electron energy, optical phonon population, and acoustic phonon populations are extracted for the Δ, L, and Γ valleys of silicon. The results suggest that transient XUV spectroscopy of the Si L2,3 edge can be used to resolve different carrier and phonon scattering pathways, but only if the excited-state XUV absorption is analyzed in terms of all electronic and structural contributions.

2. RESULTS

2.1. State-Filling Contributions. The band structure of Si along the L–Γ–Δ path is shown in Figure 1a. The band structure is calculated using DFT (see Supporting Information section 2 for details). The arrows for the photoexcitation energies in Figure 1a are corrected for the underestimated band gap of the DFT calculation to give the proper conduction band energy offsets. As the photoexcitation energy is increased, carriers are promoted to valleys at different k-space positions in the band structure. For 800 nm excitation, an indirect transition is possible to the Δ, valley. For 500 nm excitation, an indirect transition is possible to the L, valley. For 266 nm excitation, a direct transition is possible near the Γ, valley in the Γ–X direction. In each case, the photoexcited carriers will eventually thermalize to the conduction band edge (Δe) by inter- and intravalley electron–phonon scatterings. The electrons and holes then recombine by Auger and nonradiative recombination.

The Si L2,3 edge XUV transition occurs by the promotion of an electron from the Si 2p core level to the unoccupied states in the s- and d-character valence and conduction bands. The Si 2p core level is localized and therefore has a flat dispersion in k-space. For a given energy, the probability of the Si L2,3 transition is the sum of overall dipole-allowed transitions across k-space at that energy. After visible light photoexcitation, the change in the Si L2,3 edge absorption should represent the change in the occupation of the unoccupied states probed. The XUV transition probability will decrease at energies for which electrons have been photoexcited; the XUV transition probability will increase at energies for which photoexcitation leaves behind a photoexcited hole. These changes in the differential absorption are referred to as state-filling effects. Measuring the state-filling in the XUV spectrum should resolve the photoexcited carrier energy and relaxation pathways as a function of time.

The core–hole created in the Si 2p core level, however, obscures the state-filling effects. More specifically, the core–hole potential distorts the final transition DOS from the ground-state band structure of Si, as shown in Figure 1b. In Figure 1b, the experimental XUV absorption (pink area), which has been deconvoluted for the 0.6 eV L2,3 spin orbit splitting, is compared to the partial s + d DOS calculated using DFT (light gray area). The core–hole-corrected DOS, calculated using the BSE–DFT method, is shown as the dark gray area. The critical points of the ground-state band structure are indicated by dashed pink lines. Only when the core–hole effects are included by the BSE do the critical points align with the major peaks of the experimental XUV absorption. Please note that the notation for the critical points is different from the notation for the L2,3 X-ray edge.

To experimentally demonstrate the core–hole distortion of the state-filling, the excited-state differential absorption spectra are shown in Figure 2a–c for photoexcitation with 800 nm (Δe), 500 nm (L1), and 266 nm (Γ1) light, respectively. The experimental differential absorption spectra are calculated as the logarithm of the pump-on over the pump-off spectra. Figure 2a–c is plotted as color maps on a logarithmic time axis up to 200 ps, with the blue shade corresponding to increased absorption and the red shade corresponding to decreased absorption relative to the ground state. The yellow shade represents no excited-state change from the ground-state XUV absorption. Further experimental details are given in Supporting Information section 1.

Immediately after 800 nm excitation, a decrease in absorption (red) is measured at 100–102 eV, centered between the Δ, and the L1 critical points, whereas increased absorption (blue) is measured at all other energies between 98 and 105 eV. For 500 nm excitation, the measured decrease in absorption (red) begins at the L1 critical point and spans halfway to the L3 critical point. For 266 nm excitation, the measured decrease in absorption (red) is again centered between the Δ and L1 critical points, but its appearance is...
delayed in time by several hundred femtoseconds from the pump pulse. For each excitation wavelength, an increase in absorption (blue) is measured at energies below the Si L2,3 edge core-to-valence transition onset energy of 99.8 eV. The transition onset energy should correspond to the conduction band minimum at the Δ1 point; the valence band is then located at \( \sim 98.7 \) eV for the 1.1 eV band gap of silicon.

Qualitatively, the measured changes in absorption in Figure 2a–c appear to correspond with state-filling. An increase in absorption (blue) from the photoexcited holes is expected around the valence band energy (\( \sim 98.7 \) eV) for each photoexcitation wavelength. For 800 nm (Figure 2a), electrons are excited to the Δ1 valley, so a decrease in absorption (red) at the Δ1 critical point is expected. In Figure 2b, photoexcitation with 500 nm light to the L1 valley is expected to decrease absorption (red) at the L1 critical point. For 266 nm photoexcitation, electrons are excited to the Γ1 point, which is dipole-forbidden for the Si L2,3 edge, so an initial decrease in absorption will not be measured. Instead, a delayed decrease in absorption at the Δ1 critical point is observed on the several hundred femtosecond timescale as the Γ′–X intervalley and then intravalley electron–phonon scattering thermalize the excited carrier distribution.

Although the measured differential absorptions qualitatively match the state-filling, several experimental observables cannot be explained without including the effects of the core–hole perturbation. First, an increased absorption (blue) is measured at energies higher than the L1 critical point for all excitation wavelengths, as well as below the L1 critical point for 500 nm excitation. In a purely state-filling interpretation, the increase in absorption at these energies would have to unphysically correspond to holes being created in the already unoccupied states. Second, for 800 nm photoexcitation, the decreased absorption (red) increases in center energy with time toward the \( L_1 \) critical point between the 100 fs and 2–4 ps lineouts. For 500 nm photoexcitation, the decreased absorption increases in width toward the Δ1 critical point but does not decrease in center energy on the same timescale. In both cases, photoexcited carriers thermalize through electron–phonon scattering during this timescale. Any state-filling contribution should therefore decrease in energy and width. This is in disagreement with the XUV probe-measured differential absorption. Finally, on close inspection, the measured decrease in absorption is not energetically aligned with the energy of the photoexcited carriers for each wavelength.

The discrepancy between the expected state-filling effects and the core–hole-modified differential XUV absorption is further illustrated in Figure 2d–f. Figure 2d–f compares the core–hole-corrected, theoretically predicted differential absorption from state-filling effects (colored areas) to the experimental differential absorption measured immediately following photoexcitation (black line). The predicted blocking of the XUV transitions by photoexcited electrons is shown as a red area, whereas the predicted opening of new transitions by holes is shown as a blue area. For 266 nm photoexcitation, the thermalized electrons at the Δ1 point (red) and the initially photoexcited carriers in the Γ1 valley (pink) are shown. The theoretically predicted state-filling effects are calculated using the experimental excitation density and the core–hole-modified DOS, as corrected for the dipole-allowed transition amplitudes. For example, the magnitude of the state-filling is lower for electrons photoexcited to the \( L_1 \) critical point because the dipole-corrected DOS is larger at this energy. The magnitude of the state-filling is also lower for holes in the majority p-characterized valence band.

The core–hole-perturbed state-filling and experimental lineouts in Figure 2d–f confirm that the measured decrease (increase) in absorption from state-filling does not energetically...
95% confidence intervals on the experimental data. The lineouts in (d–f) are averaged over the four nearest timepoints.

2.2. Other Electronic and Lattice Contributions. After photoexcitation, a range of electronic and structural changes occur at the Si L2,3 edge on the timescale from femtoseconds to hundreds of picoseconds. The electronic changes can be summarized as renormalization of the band gap, changes in excited-state broadening, and state-filling effects. The anharmonicity of any phonons excited by electron–phonon and phonon–phonon scatterings, as well as the photoexcited screening of the Si–Si bonds, result in structural changes. To approximate the possible core–hole-modified electronic and structural effects, the model of ref 33 is employed, as outlined in Supporting Information section 2. As shown in Figure 3 and discussed below, inclusion of other electronic and structural effects, in addition to the state-filling effects, leads to a better theoretical description of the XUV transient absorption spectra.

In Figure 3d–f, the experimental excitation density is used to estimate the screening of the XUV transition, the excited-state broadening, and the state-filling effects. These changes are included in the BSE–DFT calculation of the ground-state XUV absorption by energetically shifting the conduction band edge, changing the carrier density in the plasmon frequency of the Drude–Lindhard broadening model, and including the change in occupation of the core–hole-modified DOS. The excited-state carrier distribution is modeled as a Gaussian with width 0.3 eV, corresponding to the experimental broadening, and with an initial energy determined by the photoexcitation energy. Structural effects are included by best fitting a range of equilibrium lattice expansions and strains to the residual experimental differential absorption that is not predicted by the electronic effects. The spectra are best fit by structural contributions from a [100] lattice deformation and an isotropic lattice expansion (denoted as 111 for convenience in figures). Other combinations of biaxial and triaxial strains could not fit the spectrum.

The predicted differential absorption is compared to the measured differential absorption at three key timescales in Figure 3d–f. The fit parameters for the three timescales and each excitation wavelength are summarized in Table 1. Immediately following photoexcitation (bottom panels in Figure 3d–f, 100 or 300 fs), the differential absorption is best fit for the 800, 500, and 266 nm excitations by a carrier density of $1.5 \pm 0.1 \times 10^{20}$, $1.7 \pm 0.1 \times 10^{20}$, and $0.9 \pm 0.1 \times 10^{20}$ carriers/cm$^3$, respectively. For 266 nm excitation, the carrier distribution is taken to be thermalized to the $\Delta_1$ point by 300 fs. A [100] lattice expansion of $0.3 \pm 0.05$, $0.5 \pm 0.05$, and $0.06 \pm 0.02$% is required for the 800, 500, and 266 nm excitation, respectively. For 500 nm excitation, an isotropic expansion of $0.07 \pm 0.01$% is also fit. An isotropic expansion is not fit for 800 or 266 nm excitation within a $\pm 0.01$% error. Major discrepancies between the fit and measured differential absorptions occur at the critical points that are not accurately captured in the ground-state absorption model.
Table 1. Nonlinear Fit Carrier Densities and Lattice Expansions

<table>
<thead>
<tr>
<th>Excitation Wavelength</th>
<th>Carrier Density (x10^19/cm^3)</th>
<th>100 Expansion (%)</th>
<th>111 Expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 nm (ΔL)</td>
<td>1.5 ± 0.1</td>
<td>0.3 ± 0.05</td>
<td>0.0 ± 0.01</td>
</tr>
<tr>
<td>500 nm (L)</td>
<td>1.7 ± 0.1</td>
<td>0.5 ± 0.05</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>266 nm (Γ)</td>
<td>0.9 ± 0.1</td>
<td>0.06 ± 0.02</td>
<td>0.00 ± 0.01</td>
</tr>
</tbody>
</table>

“Fit quantities are for an average of four times around the time indicated. A 100 expansion denotes an expansion along the [100] direction, whereas 111 expansion denotes an isotropic expansion along each axis. 300 fs for 266 nm excitation.

At 2−4 ps after photoexcitation (shown in the middle panel in Figure 3d–f), the experimental differential absorption is best fit for 800, 500, and 266 nm excitation by a carrier density of 1.5 ± 0.1 × 10^20, 1.0 ± 0.1 × 10^20, and 0.5 ± 0.1 × 10^20 carriers/cm^3, respectively. The electrons are taken to be thermalized to the Δt point for each excitation wavelength. The fitted [100] lattice deformation decreases from the 100 fs value for all excitation wavelengths. The fit values decrease from 0.3 ± 0.05 to 0.05 ± 0.03% for 800 nm photoexcitation, 0.5 ± 0.05 to 0.13 ± 0.04% for 500 nm photoexcitation, and 0.06 ± 0.02 to 0.00 ± 0.03% for 266 nm photoexcitation. A lattice expansion of 0.06 ± 0.01 and 0.02 ± 0.01% is fit for 800 and 266 nm excitation, respectively. For 500 nm excitation, the lattice expansion coefficient decreases from 0.07 ± 0.01 to 0.04 ± 0.01%. The change in the isotropic lattice expansion coefficient could correspond to the anharmonicity of acoustic phonons excited by intravalley electron–phonon scattering as well as phonon–phonon decay processes.39−41 This assignment is supported by the decay of the [100] lattice deformation component, which is attributed to either the excited optical phonon population or the anisotropy of the carrier distribution. Given this expansion is faster than the acoustic velocity, it is most likely a combination of volume-preserving deformations or disordering.12

At 150 ps after photoexcitation (top panels in Figure 3d–f), the experimental differential absorption for each photoexcitation wavelength converges to a similar spectrum. Below 101−102 eV, there is an increase in absorption (blue); above 101−102 eV, there is a decrease in absorption (red). The lineouts at 150 ps can be fit to a carrier density of 0.1 ± 0.1 × 10^20, 0.8 ± 0.2 × 10^20, and 0.2 ± 0.1 × 10^20 carriers/cm^3 for 800, 500, and 266 nm excitation, respectively. The electrons are again assumed to be thermalized to the Δt point. A [100] lattice deformation is not required to fit the experimental data within the ±0.1% error. An isotropic lattice expansion of 0.16 ± 0.02, 0.15 ± 0.03, and 0.10 ± 0.02% is required for 800, 500, and 266 nm excitation, respectively. The decreased carrier densities are indicative of Auger recombination.33 The increased lattice expansions are indicative of the thermalizing phonon bath and the lattice becoming heated.31,39−41 The cross-over energies between the areas of increased and decreased absorption vary slightly between the excitation energies in the top panels of Figure 3d–f, as does the amplitude of the increased absorption at the L1 critical point. These changes are not captured by the model, suggesting that the final lattice distortion cannot be completely described by the three lattice distortions that were tried, namely [100], [110], and [111] lattice distortions.

2.3. Interpretation of Spectra Including Core−Hole Effects. Using the model of section 2.2, the best fits of the experimental differential absorptions can be decomposed into the amplitudes of the different electronic and structural effects (Figure 4). In this manner, the spectral features of the experimental differential absorption can be assigned. Immediately following photoexcitation (Figure 4a), the increase in absorption below the transition edge is primarily from broadening and renormalization (gray area), matching ref 33.
The state-filling from holes (blue area) and structural changes (orange area) play more minor roles. The excited-state renormalization and broadening create a large below-edge differential absorption because the red shift of the XUV spectrum increases absorption at energies where absorption was previously not possible. For energies between the $\Delta_1$ and $L_1$ critical points, the measured decrease in absorption is caused by an equal mixture of all four effects. The state-filling from electrons (red area) cancels with the broadening and renormalization (gray area) near the $\Delta_1$ point. This explains why the state-filling component for electrons does not energetically align with the measured decrease in absorption unless all core–hole perturbations of the final state are approximated. At energies above the $L_3$ critical point, the differential absorption is a positive amplitude mixture of broadening, renormalization, and structural components.

As the photoexcitation energy is increased, the center energy of the state-filling component increases immediately following photoexcitation (top to bottom panel in Figure 4a). In the model used, the broadening and renormalization from the core–hole are unchanged as the excitation energy changes because they only depend on the carrier density. Comparing the 800 and 500 nm panels in Figure 4a, the change in the differential absorption between the $\Delta_1$ and $L_1$ critical points is because of the change in the electron state-filling energy. The increased center energy of the photoexcited electrons for 500 nm excitation shifts the decreased absorption feature to the $L_1$ critical point. However, this shift in the center energy for 500 nm excitation also decreases the cancellation at the $\Delta_1$ point, effectively increasing the absorption. The structural components also contribute to the measured differences in absorption around these critical points. Therefore, when core–hole effects are included, the measured differences between 800 and 500 nm photoexcitation are related to the difference in state-filling, but the decreased absorption cannot be assigned only to the excited electron energy.

By 150 ps after photoexcitation (Figure 4b), all carriers are thermalized to the $\Delta_1$ point, and Auger recombination has decreased the photoexcited carrier density. This is evidenced by a reduced magnitude of the positive differential absorption at energies below the $L_1$ critical point. At energies above the $L_1$ critical point, the predicted differential absorption is dominated by the isotropic expansion from the heated lattice. At the $\Delta_1$ critical point, the lattice expansion and state-filling components have a similar amplitude but opposite sign. This cancellation is why the decreased absorption signature in Figure 3a–c disappears on a timescale faster than expected for recombination.

In summary, Figure 4 shows that the core–hole must be considered to accurately map the spectral changes in the XUV spectrum. This includes correcting the final transition DOS, the renormalization with carrier density, the XUV broadening, and the spectral appearance of structural modes in the XUV spectrum. Within the assumptions of the model used, the features of the >100 ps differential absorption spectrum are attributed primarily to the heated lattice, whereas the initial transient XUV signal is a mixture of electronic and structural effects. Immediately after photoexcitation, the primary differences between the excitation wavelengths occur because of the energy of the photoexcited electrons. Between 100 fs and 2–4 ps, thermalization of the photoexcited electrons and the lattice deformations that result create differences in the measured differential absorption. After 150 ps, the electrons are fully thermalized to the conduction band edge, and the measured differential absorption spectra converge because the primary contribution is the isotropic expansion of the heated lattice. For each photoexcitation wavelength, the differential absorption above the $L_3$ critical point primarily corresponds to structural modes, whereas the differential absorption at energies below the $L_3$ critical point is a mixture of electronic and structural components. These findings are consistent with the analysis of static X-ray absorption in terms of near-edge and far-edge features in synchrotron studies.

3. DISCUSSION

The core–hole effects mean that the features of the experimental differential absorption are not solely assigned to state-filling from the photoexcited electrons and holes (Figure 4). The core–hole perturbation also exaggerates structural changes in the differential spectrum. The model used to predict core–hole effects in this paper is an approximate approach to treating the core–hole perturbation. To test the accuracy of this model, the magnitude of each electronic and structural component was fit as a function of time. This allows the extracted dynamics to be compared to those known from visible light and IR experiments. In this fit routine, the fit parameters are the carrier density and electron center energy as well as the structural components.

The extracted electron state-filling from fitting the experimental differential absorption is shown in Figure 5. For 800 nm excitation, the experimental and excited-state broadenings prevent the thermalization of the electrons from being observed at a resolution better than $\sim$0.5 eV. The amplitude of the state-filling otherwise follows the expected intravalley thermalization and Auger decay timescales. For
500 nm excitation, the photoexcited electrons initially occupy the \( L_1 \) critical point and then relax to the \( \Delta_1 \) valley on the timescale of the electron–phonon thermalization.\(^{37,38}\) The middle panel of Figure 5 shows that the model extracts this trend. A notable feature is the difference in amplitude as carriers fill the smaller joint DOS for the Si 2p transition to the \( \Delta_1 \) versus the \( L_1 \) critical point, as well as when they first scatter in to the \( \Delta \) valley near the \( \Gamma \) point around 10 ps. For 266 nm excitation, a delayed rise is observed in the probed second timescale. On a picosecond timescale, the amplitude of the state-filling decreases, consistent with Auger recombination and thermalization timescales.\(^{33}\) For 266 nm excitation, state-filling is not fit in the \( L \) valleys, consistent with a stronger \( \Gamma-X \) direction than the \( \Gamma-L \) direction intervalley scattering.\(^{35,37,38}\)

The structural components determined by the best fit are shown as a function of time in Figure 6. The squares represent the [100] lattice deformation component, whereas the triangles represent the isotropic lattice expansion component. The extracted amplitudes are fit to a three temperature model (3TM) (solid line) to test if the kinetics of the structural components match the known scattering processes within each photoexcited valley. The 3TM, described in detail in Supporting Information section 3, represents the average intervalley electron–phonon (\( \tau_{e-o} \)), intravalley electron–phonon (\( \tau_{e-o} \)), and phonon–phonon (\( \tau_{o-o} \)) scattering processes. For silicon, the intervalley electron–phonon scattering mostly involves high energy optical phonon modes (e–o), whereas the intravalley scattering mostly involves acoustic phonon modes (e–a).\(^{44-46}\) The 3TM is chosen because it allows for the kinetics of the extracted structural components to be quantified while also accurately modeling the absorption depth, carrier diffusion, and shock wave contributions for the range of excitation wavelengths used in the experiments. The fit coefficients are summarized in Table 2.

For 800 nm excitation, the structural coefficient amplitudes are fit to time constants of 30 ± 10 fs for \( \tau_{e-o} \), 400 ± 10 fs for \( \tau_{e-o} \), and 470 ± 20 fs for \( \tau_{o-o} \). These time constants match previous reports of silicon’s intervalley scattering time of 20–60 fs,\(^{47,48}\) electron–acoustic phonon scattering time of 500 fs,\(^{39}\) and the 400 fs screened optical phonon lifetime at 1020 carriers/cm\(^3\) excitation.\(^{50}\) For 500 nm excitation, the scattering times are 90 ± 30 fs for \( \tau_{e-o} \), 300 ± 100 fs for \( \tau_{e-o} \) and 600 ± 100 fs for \( \tau_{o-o} \). The 3TM does not include the possibility of two different early timescale structural contributions, resulting in the 100 fs fit error for the intravalley and phonon–phonon scattering times. The intervalley scattering time \( \tau_{e-o} \) correlates well with a mixture of L–L’ intervalley scattering on a 20–100 fs timescale and the slightly slower 100–200 fs timescale of L–X intervalley scattering.\(^{37,38}\) Within the fit error, a similar intravalley scattering time \( \tau_{e-o} \) and a screened phonon–phonon scattering time \( \tau_{o-o} \) are fit at 500 nm as at 800 nm excitation. The intervalley and intravalley scattering times match the thermalization of the electron energy in Figure 6.

For 266 nm excitation, the fit time constants are 110 ± 20 fs for \( \tau_{e-o} \), 570 ± 20 fs for \( \tau_{e-o} \) and 180 ± 20 fs for \( \tau_{o-o} \). The slower intervalley electron–optical phonon scattering time as compared to 500 or 800 nm excitation is consistent with the slower intervalley electron–phonon scattering expected from the smaller \( \Gamma_2-X \) joint DOS.\(^{37,38}\) The longer intravalley scattering time is also consistent with the increased excess energy that must be dissipated after \( \Gamma-X \) intervalley scattering. However, several discrepancies exist in the 3TM fit for 266 nm photoexcitation. First, the 3TM cannot replicate the long timescale kinetics of the isotropic lattice expansion. Second, the phonon–phonon decay time is reduced by several hundred femtoseconds compared to 800 or 500 nm excitation. These trends must be corrected for the 5–10 nm absorption depth of 266 nm light in silicon as follows.\(^{34}\)

![Figure 6. Best-fit lattice expansion coefficients for 800, 500, and 266 nm excitations. The squares correspond to the [100] lattice deformation component. The triangles correspond to the isotropic lattice expansion component. The black solid line corresponds to a fitting of the extracted structural components with a three-temperature model (3TM). The trade-off between the [100] expansion and the isotropic expansion with increasing time is indicative of the switch from carrier thermalization to lattice heating. The 3TM describes this trade-off through fitting the average electron–optical phonon, electron–acoustic phonon, and phonon–phonon lifetimes as reported in Table 2. The dotted line shows the predicted shock-wave contribution from the spatially variant carrier profile. The excitation wavelengths are indicated on the plot, and the error bars correspond to the standard error from a robust nonlinear fit weighted by the experimental uncertainty. The experimental noise level is reflected in the scatter of the data points. The logarithmically scaled time axis is offset by 100 fs for visualization.](image-url)

<table>
<thead>
<tr>
<th>Excitation (nm)</th>
<th>( \tau_{e-o} ) (fs)</th>
<th>( \tau_{e-o} ) (fs)</th>
<th>( \tau_{o-o} ) (fs)</th>
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<tr>
<td>800</td>
<td>30 ± 10</td>
<td>400 ± 10</td>
<td>470 ± 20</td>
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<tr>
<td>500</td>
<td>90 ± 30</td>
<td>300 ± 100</td>
<td>600 ± 100</td>
</tr>
<tr>
<td>266</td>
<td>110 ± 20</td>
<td>570 ± 20</td>
<td>180 ± 20</td>
</tr>
</tbody>
</table>

"The coefficient values are determined by fitting the 3TM to the structural components extracted from the experimental differential absorption using the BSE–DFT model."
The small absorption depth compared to the sample thickness creates a photoexcited carrier distribution gradient. The spatial carrier gradient excites an acoustic shock wave, which can be modeled using the elasticity equation \( \rho v^2 \frac{\partial^2 u}{\partial z^2} = \rho \frac{\partial^2 u}{\partial t^2} + F(z, t) \) (1)

where \( \rho = 2.328 \text{ g/cm}^3 \) is the density of Si, \( u \) is the displacement, \( v = 8430 \text{ m/s} \) is the longitudinal sound velocity in silicon, \( F(z, t) = \frac{\partial s(z, t)}{\partial z} \) is the source term with the time-dependent stress calculated using the spatial and temporal results of the 3TM. An acoustic shock-wave contribution at this velocity will become noticeable 1 ps after excitation (wave moves ~10 nm) and reach a spatially averaged maximum in 20–30 ps for a 200 nm membrane. As shown by the dotted line in the bottom panel of Figure 6, the acoustic shock wave increases the agreement between the 3TM prediction and the experimental data at timescales longer than 10 ps. It should be noted that the transmission geometry makes the probe interpretation solely in terms of the state-filling effects from the photoexcited electrons and holes. Instead, the core–hole perturbation to the electronic and structural contributions must be modeled. To approximate these many-body effects, the data is analyzed in terms of a ground-state BSE–DFT calculation of the silicon XUV absorption. The BSE–DFT model is used to assign the measured differential absorption features. Immediately after photoexcitation, a mixture of core–hole-modified effects from state-filling, excited-state broadening and renormalization, and lattice deformation is predicted to lead to the measured spectrum. On the hundreds-of-picoseconds timescale, the measured differential absorption is mainly the result of the heated lattice, the effects of which are prevalent in the differential absorption because of the localized core–hole wave function. The validity of the BSE–DFT model is tested by fitting the electron energy as a function of time from the experimental data. When corrected for the possible dipole transitions, the carrier thermalization from the \( L \) and \( \Gamma \) valleys to the \( \Delta \) valley is quantified, but the energetic resolution is limited by the core–hole broadening. The fit kinetics of the structural modes also match the electron–phonon and phonon–phonon scattering times previously reported for the \( \Delta, L \), and \( \Gamma \) valleys of silicon. These results show that transient XUV spectroscopy of the Si \( L_{2,3} \) edge cannot be interpreted without modeling the core–hole perturbation to some degree. The model of ref 33, although approximate, was found to extract the photoexcited dynamics with timescales that match previously reported carrier thermalization pathways.

4. CONCLUSIONS

In conclusion, the transient XUV signal of the silicon \( 2p L_{2,3} \) edge is measured following excitation to the \( \Delta, L \), and \( \Gamma \) valleys. The experimental transient XUV spectra could not be interpreted solely in terms of the state-filling effects from the photoexcited electrons and holes. Instead, the core–hole perturbation to the electronic and structural contributions must be modeled. To approximate these many-body effects, the data is analyzed in terms of a ground-state BSE–DFT calculation of the silicon XUV absorption. The BSE–DFT model is used to assign the measured differential absorption features. Immediately after photoexcitation, a mixture of core–hole-modified effects from state-filling, excited-state broadening and renormalization, and lattice deformation is predicted to lead to the measured spectrum. On the hundreds-of-picoseconds timescale, the measured differential absorption is mainly the result of the heated lattice, the effects of which are prevalent in the differential absorption because of the localized core–hole wave function. The validity of the BSE–DFT model is tested by fitting the electron energy as a function of time from the experimental data. When corrected for the possible dipole transitions, the carrier thermalization from the \( L \) and \( \Gamma \) valleys to the \( \Delta \) valley is quantified, but the energetic resolution is limited by the core–hole broadening. The fit kinetics of the structural modes also match the electron–phonon and phonon–phonon scattering times previously reported for the \( \Delta, L \), and \( \Gamma \) valleys of silicon. These results show that transient XUV spectroscopy of the Si \( L_{2,3} \) edge cannot be interpreted without modeling the core–hole perturbation to some degree. The model of ref 33, although approximate, was found to extract the photoexcited dynamics with timescales that match previously reported carrier thermalization pathways.

**ASSOCIATED CONTENT**

Supporting Information
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Experimental methods, XUV absorption prediction, and 3TM (PDF)

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References


