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Abstract

The phonon-assisted interband optical absorption spectrum of silicon is calculated at the quasi-particle level entirely from first principles. We make use of the Wannier interpolation formalism to determine the quasiparticle energies, as well as the optical transition and electron-phonon coupling matrix elements, on fine grids in the Brillouin zone. The calculated spectrum near the onset of indirect absorption is in very good agreement with experimental measurements for a range of temperatures. Moreover, our method can accurately determine the optical absorption spectrum of silicon in the visible range, an important process for optoelectronic and photovoltaic applications that cannot be addressed with simple models. The computational formalism is quite general and can be used to understand the phonon-assisted absorption processes in general.

The phonon-assisted absorption of light in materials is an important optical process both from a fundamental and from a technological point of view. Intraband light absorption by free carriers in metals and doped semiconductors requires the additional momentum provided by the lattice vibrations or defects, while phonon-assisted processes determine the onset of absorption in indirect-band-gap semiconductors (Fig. 1). Moreover, the value of the direct band gap in silicon (3.4 eV[1]) is large and precludes optical absorption in the visible. However, silicon is a commercially successful photovoltaic material because of the indirect optical transitions that enable photon capture in the spectral region between the indirect (1.1 eV[2]) and direct band gaps.

Despite their importance, at present, only a very limited number of first-principles studies of phonon-assisted optical absorption spectra exist. Ab initio calculations of direct optical absorption spectra including excitonic effects have already been performed for Si and other bulk semiconductors [3] and the underlying methodology is presently well established [4, 5]. Phonon-assisted absorption studies are more involved, however, and the associated computational cost is much higher than the direct case. The calculation of the indirect absorption coefficient involves a double sum over $\boldsymbol{k}$-points in the first Brillouin zone (BZ) to account for all initial and final electron states. In addition, these sums must be performed with a very fine sampling of the zone to get an adequate spectral resolution. The computational cost associated with these BZ sums is in fact prohibitive with the usual methods. Phonon-assisted absorption calculations have been done for the special case of free-carrier absorption in semiconductors[6], where the carriers are initially limited to a region near the Γ point of the first BZ, but a full calculation using brute-force methods for the general case remains beyond the reach of modern computers.

The difficulty of zone-integral convergence can be addressed with the maximally-localized Wannier function interpolation method[7]. Using this technique, the quasiparticle energies[8] and optical transition matrix elements[9] can be interpolated to arbitrary points in the BZ at a minimal computational cost. Moreover, this interpolation method has been generalized[10] to obtain the electron-phonon coupling matrix elements between arbitrary pairs of points in the first BZ.

In this Letter, we developed a first-principles computational method, based on a Wannier-Fourier interpolation formalism, to calculate the phonon-assisted optical absorption spectra of materials from first principles and applied it to the case of interband absorption in sil-

icon. The calculated spectra near the absorption onset are in very good agreement with experimental results for a range of temperatures. Moreover, we were able to reproduce the absorption spectrum in the energy range between the indirect and direct band gaps (1.1 – 3.4 eV), a spectral region that cannot be accessed by standard model calculations. This region covers the entire visible spectrum and is important for optoelectronic applications. The computational formalism is quite general and can be used to predict and analyze the phonon-assisted optical absorption spectrum of any material.

To calculate the phonon-assisted absorption coefficient, we use the Fermi's golden rule expression[6, 11]:

$$
\alpha(\omega) = 2\frac{4\pi^2 e^2}{\omega c n_r(\omega)}\frac{1}{V_{\text{cell}}}\frac{1}{N_{\boldsymbol{k}}N_{\boldsymbol{q}}}\sum_{\nu ij\boldsymbol{k}\boldsymbol{q}}|\boldsymbol{\lambda}\cdot(\boldsymbol{S}_1 + \boldsymbol{S}_2)|^2
$$
$$
\times P\delta(\epsilon_{j,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega \pm \hbar\omega_{\nu\boldsymbol{q}}),
\tag{1}
$$

where $\hbar\omega$ and $\boldsymbol{\lambda}$ are the energy and polarization of the photon and $n_r(\omega)$ is the refractive index of the material at frequency ω. The generalized optical matrix elements, $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$, are given by

$$
\boldsymbol{S}_1(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{\boldsymbol{v}_{im}(\boldsymbol{k})g_{mj,\nu}(\boldsymbol{k},\boldsymbol{q})}{\epsilon_{m\boldsymbol{k}} - \epsilon_{i\boldsymbol{k}} - \hbar\omega + i\Gamma_{m,\boldsymbol{k}}},
\tag{2}
$$
$$
\boldsymbol{S}_2(\boldsymbol{k},\boldsymbol{q}) = \sum_m \frac{g_{im,\nu}(\boldsymbol{k},\boldsymbol{q})\boldsymbol{v}_{mj}(\boldsymbol{k}+\boldsymbol{q})}{\epsilon_{m,\boldsymbol{k}+\boldsymbol{q}} - \epsilon_{i\boldsymbol{k}} \pm \hbar\omega_{\nu\boldsymbol{q}} + i\Gamma_{m,\boldsymbol{k}+\boldsymbol{q}}},
\tag{3}
$$

and correspond to the two possible paths of the indirect absorption process (Fig. 1). They are determined in terms of the velocity ($\boldsymbol{v}$) and electron-phonon coupling (g) matrix elements, as well as the real ($\epsilon_{n\boldsymbol{k}}$) and imaginary ($\Gamma_{n\boldsymbol{k}}$) parts of the quasiparticle self-energies. The factor P accounts for the carrier and phonon statistics,

$$
P = \left(n_{\nu\boldsymbol{q}} + \frac{1}{2} \pm \frac{1}{2}\right)(f_{i\boldsymbol{k}} - f_{j,\boldsymbol{k}+\boldsymbol{q}}).
$$

The upper (lower) sign corresponds to phonon emission (absorption).

The Kohn-Sham eigenvalues were calculated within the local density approximation (LDA)[12] to density functional theory using a plane-wave pseudopotential approach[13] with a kinetic energy cutoff of 35 Ry. The ground state charge density was determined on a BZ grid of 14×14×14 $\boldsymbol{k}$-points. Quasiparticle energies within the GW approximation for the self-energy operator[14] were determined on a 6×6×6 grid and interpolated throughout the BZ through the use of the maximally-localized Wannier function formalism[7]. We

included 34 electronic bands in the coarse-grid calculation and extracted 26 Wannier functions, which reproduce the LDA bandstructure 10 eV below and 30 eV above the Fermi level. The interpolated quasiparticle band structure of silicon is shown in Figure 1. The indirect (1.3 eV) and direct (3.3 eV) quasiparticle band gaps are in good agreement with previous calculations[14] and experiment. The same formalism has been used to interpolate the velocity matrix elements[4, 9], including the renormalization required [15] after the GW corrections. The real (ε_1) and imaginary (ε_2) parts of the dielectric function and the refractive index due to direct transitions, required in Eq. 1 to determine the absorption coefficient, were also determined at the quasiparticle level for a range of photon frequencies. Lattice dynamics are calculated using density functional perturbation theory[16]. The electron-phonon coupling matrix elements are calculated on the same coarse grid of electronic points, while the dynamical matrices and phonon-potential perturbations are calculated on a 6×6×6 grid of momentum-space vectors[10] and interpolated for arbitrary pairs of points in the first BZ using the EPW code[17]. For the calculations of the velocity and electron-phonon coupling matrix elements we used the LDA wave functions, because their overlap with the GW-corrected ones is better than 99.9%[14].

Phonon-assisted optical absorption in indirect-band-gap semiconductors occurs for photons with energies greater than the indirect band gap minus (plus) the energy of the phonon absorbed (emitted) to assist the transition. The onset of indirect absorption is calculated over a wide range of temperatures in bulk silicon through Eq. 1 and the results are shown in Fig. 2. Each curve displays a characteristic knee, arising from the different energy onsets of the phonon-absorption and phonon-emission terms, which becomes smoother with increasing temperature. The calculated data are in good agreement with experimental results[18] for all temperatures measured. For these calculations, we used fine grids of 40×40×40 for the $\boldsymbol{k}$ and $\boldsymbol{q}$ sums in Eq. 1, respectively. These fine grids yield converged optical spectra with an energy resolution of 14 meV, which is quite small and necessary to resolve the fine features near the absorption onset. Although the experimental data near the edge can be fit with simple parameterized forms[18], to our knowledge they have not been calculated entirely from first principles previously.

In addition to the absorption onset, we are interested in the phonon-assisted absorption spectrum in the energy range between the indirect and direct band gaps, covering the visible range. This spectral region involves transitions between valence and conduction band states
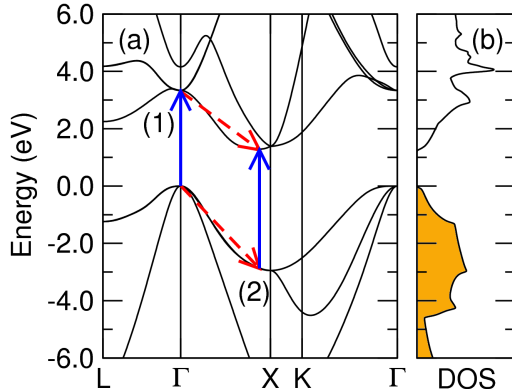
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FIG. 1. (a) Quasiparticle band structure of silicon calculated within the GW approximation and interpolated with the Wannier formalism. The arrows indicate the lowest-energy phonon-assisted optical absorption processes across the indirect band gap. Solid lines denote optical transitions, while dashed lines correspond to electron-phonon scattering events. The two terms, S_1 and S_2, of Eq. 1 are represented by paths (1) and (2) respectively. (b) Density of electronic states versus the quasiparticle energy. The density of states of the occupied bands has been highlighted.

away from the band extrema and, as a consequence, cannot be modeled with simple parameterized forms. On the contrary, because of the large number of electronic states and phonon modes involved, first-principles calculations are the only computational tool that can access this spectral region. The interpolation of the *ab initio* quantities within the Wannier-Fourier formalism makes the calculation feasible on modern computers. The calculated spectra with an energy resolution of 30 meV (Fig. 3) converge with zone-sums of $24 \times 24 \times 24$ electronic and $24 \times 24 \times 24$ phonon points. The imaginary part of the electron self-energy for the intermediate electronic states was set to a constant value (100 meV). However, the calculated data are not very sensitive to the particular value of the quasiparticle lifetime for photon energies in this spectral region.

To facilitate comparison with experiment, the theoretical absorption spectra of Figs. 2 and 3 have been rigidly shifted to the left along the energy axis by 0.15–0.23 eV in order to match the onset of the experimental absorption curves. This shift is needed to account for the numerical difference between the calculated and experimental band gap, and for finite-temperature effects on the quasiparticle energies which we have not considered explicitly. Although the GW method is the most accurate first-principles computational formalism for the calculation of quasiparticle properties presently available, it typically yields abso-
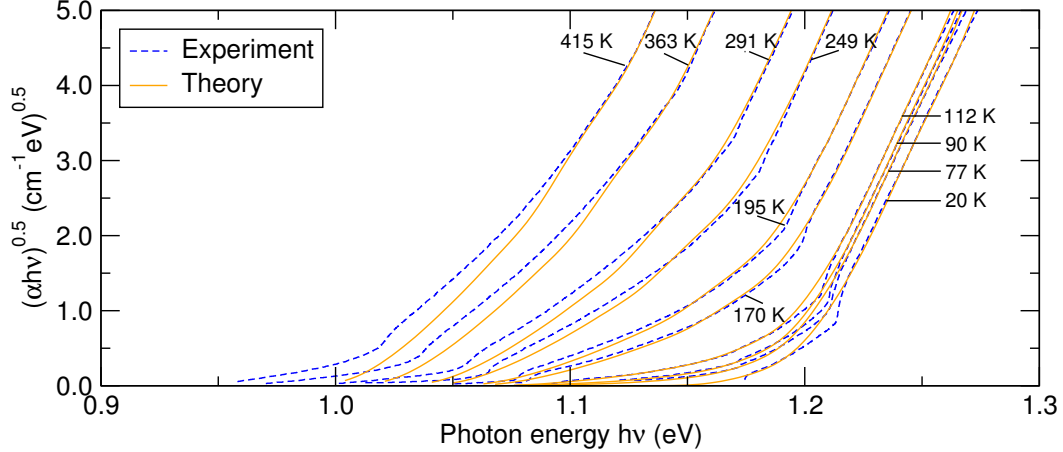
FIG. 2. Onset of the phonon-assisted optical absorption in silicon, as a function of photon energy and temperature. The theoretical results (solid lines) are in good agreement with experiment (dashed lines). Experimental data are from Ref. 18. The theoretical curves have been shifted horizontally to match the onset of the experimental spectra.
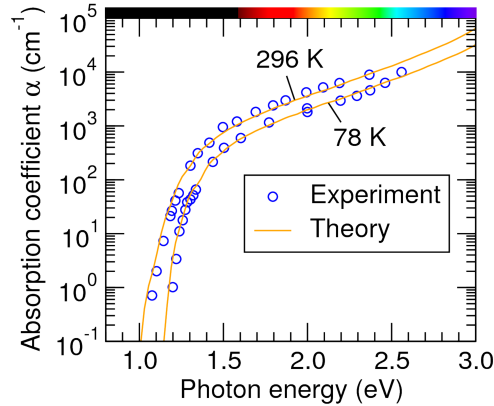

FIG. 3. Calculated (solid lines) and experimental (circles) absorption coefficient of silicon in the energy range between the indirect and direct gaps, for two temperatures. Experimental data are from Ref. 19. The theoretical spectra have been shifted to match the experimental absorption onset.

lute quasiparticle energies accurate to 0.1 eV. In our particular case, we found that the calculated band gap is also within this error bar larger than the experimentally measured value. We note that no other first-principles method is presently available to guarantee a more accurate result. Moreover, the only temperature dependence we considered in our calculations is for the phonon occupation numbers. However, the quasiparticle energies

themselves are temperature-dependent because of additional finite-temperature effects, such as lattice expansion and electron-phonon renormalization [10, 20–24]. We found that the thermal-expansion correction to the indirect band gap is small and amounts only to a 2.5 meV increase of the LDA band gap as the lattice constant increases from the 0 K to the 400 K value [25], in agreement with Ref. 22. On the other hand, empirical pseudopotential calculations have shown that electron-phonon renormalization effects are stronger and decrease the band gap of silicon by approximately 0.05–0.1 eV for temperatures in the range 0–400 K [22]. We note that the determination of electron-phonon-coupling corrections to quasiparticle energies from first principles is still a subject of ongoing research [23]. The cumulative effects of this electron-phonon band-gap renormalization (0.05–0.1 eV) and the intrinsic accuracy of the GW method (order of 0.1 eV) explain the difference between the onsets of the theoretical and experimental data that we need to take into account when comparing our calculated spectra to experiment. Moreover, this electron-phonon coupling correction to the quasiparticle energies may have an effect on the shape of the absorption spectra near the onset of indirect transitions in Fig. 2.

Although excitonic effects, arising from the electron-hole interaction, are potentially important for optical processes and in general affect the direct absorption spectra even for photon energies far from the absorption edge[4], we found that they are not as important for the case of indirect absorption. Sharp features that appear near the onset of indirect absorption are attributed to excitonic effects[18, 26]. Our calculations, however, are based on quasiparticle theory and do not account for the electron-hole interaction that gives rise to these excitonic features. Nevertheless, the calculated absorption spectra are in very good quantitative agreement with experimental data, pointing to a weaker role of the electron-hole Coulomb interaction for the case of indirect optical transitions. This is probably because the band-extrema wavefunctions in indirect-gap materials are located at different points of the BZ and hence the wavefunction overlap, which determines the magnitude of the Coulomb interaction between them, is small. Therefore, the phonon-assisted spectra can to a large extend be explained at the quasiparticle level of theory, without the need to account for excitonic effects.

The computational formalism we developed is based on first-principles methods and can be used to study the fundamental physics of phonon-assisted absorption in materials in general. It can complement experimental studies to shed light on the microscopic phonon-

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assisted transition mechanisms and address questions that are not accessible by experimental techniques. Moreover, the method can be used to analyze the phonon-mediated optical properties of technologically important materials for optoelectronic applications. E.g., it can investigate the role of phonon-assisted optical processes in silicon photonics, or it can predict the photovoltaic performance of indirect-band-gap materials.

In conclusion, we used a Wannier-Fourier interpolation technique to calculate the phonon-assisted optical absorption spectra of silicon at the quasiparticle level. The calculated spectra are in very good agreement with experimental measurements, both near the absorption onset and in the spectral region between the indirect and direct band gaps for any lattice temperature. The first-principles computational formalism is very general and can be used to study the fundamental physics of phonon-assisted absorption, as well as the phonon-mediated optical properties of optoelectronic materials.

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