Ab initio study of the optical properties of Si-XII

Brad D. Malone,[*] Jay D. Sau, and Marvin L. Cohen

Department of Physics, University of California—Berkeley, Berkeley, California, 94720, USA

and Material Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

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We present a first-principles calculation of the optical excitation spectrum of Si-XII, a high-pressure, metastable phase of silicon in the R8 structure. Recent calculations of the quasiparticle spectrum have shown Si-XII to be semiconducting with a small, indirect band gap. In this paper we solve the Bethe-Salpeter equation to obtain the optical spectrum of this material. We then compare our calculated optical spectrum with experimental data for other forms of silicon commonly used in photovoltaic devices. These include cubic, polycrystalline, and amorphous forms of silicon. We find that the calculated values of the optical functions relevant to photovoltaic absorption in Si-XII show greater overlap with the incident solar spectrum than those found in these other silicon phases.

The importance of silicon in electronic and photovoltaic devices has stimulated many studies of its electronic properties. While the cubic diamond phase is by far the most commonly studied, silicon has a large number of polytypes. Studies of the structural and electronic properties of these phases can be found in the literature.[1–8] One of these phases, Si-XII, also called R8 because of its rhombohedral unit cell containing eight atoms, is the focus of this paper.

Silicon in the R8 structure can be formed upon decompression from the high-pressure metallic β-Sn phase at ~10 GPa. The R8 structure remains the dominant phase until approximately 2 GPa when the BC8 (Si-III) structure begins to form.[9] First obtained in angle dispersive x-ray powder diffraction experiments,[10] Si-XII has more recently been found in nanoindentation experiments performed on silicon wafers.[11–13] Previous calculations[3,8] found Si-XII to be a semimetal, exhibiting an indirect band overlap within the local-density approximation (LDA) of density-functional theory (DFT). However, recently we have shown that upon inclusion of quasiparticle self-energy corrections within the *GW* approximation,[14–16] this indirect overlap is lifted and Si-XII exhibits an indirect band gap of approximately 0.24 eV at ambient pressure.[8] With the current extensive research being done on silicon-based photovoltaic (PV) devices, the presence of another semiconducting silicon polytype with small band gap motivates an interest in its optical properties. In this paper we present calculations of the optical spectrum of Si-XII with the inclusion of electron-hole interactions. We then compare the obtained optical constants with those found for other forms of silicon.

Accurate calculations of optical spectra from first principles involve the inclusion of electron-hole interactions, which takes the computation beyond the level of a single-particle picture. A calculation of the optical spectrum performed without taking into account the mutual attraction of quasielectron and quasihole excitations can show substantial deviations from experiment. In the calculation of the frequency-dependent dielectric function $\epsilon(\omega)$ this can result in incorrect positions and amplitudes of characteristic peaks.[17] By incorporating the effects of the electron-hole interactions in the same manner as is done in this study, accurate optical spectra have been obtained for a wide variety of materials. Perhaps most relevant to the current study is the fact that for the optical spectra of silicon in the cubic phase, first studied by theorists over 40 years ago,[18] this method reproduces the experimental data[17] to a high degree of accuracy.

The electron-hole interaction results in excitations, characterized by the state $|S\rangle$, that are linear combinations of free quasielectron and quasihole pair configurations:[19]

$$|S\rangle = \sum_{\mathbf{k}} \sum_{v} \sum_{c}^{\text{hole elec}} A_{vc\mathbf{k}}^S \hat{a}_{v\mathbf{k}}^\dagger \hat{b}_{c,\mathbf{k}+\mathbf{Q}}^\dagger |0\rangle, \tag{1}$$

where $\hat{a}_{v\mathbf{k}}^\dagger$ creates a quasihole in state $\mathbf{k}$ and $\hat{b}_{c,\mathbf{k}+\mathbf{Q}}^\dagger$ creates a quasielectron in state $\mathbf{k}+\mathbf{Q}$ following the absorption of a photon with wave vector $\mathbf{Q}$. The electron-hole excitations represented by $|S\rangle$ and their energies Ω_S can be calculated by solving the equation of motion for the two-body Green's function using the Bethe-Salpeter equation (BSE) (Ref. 20):

$$(E_{c,\mathbf{k}+\mathbf{Q}}^{\text{QP}} - E_{v\mathbf{k}}^{\text{QP}})A_{vc\mathbf{k}}^S + \sum_{\mathbf{k}'} \sum_{v'} \sum_{c'}^{\text{hole elec}} \langle vc\mathbf{k}|K^{eh}|v'c'\mathbf{k}'\rangle A_{v'c'\mathbf{k}'}^S$$
$$= \Omega_S A_{vc\mathbf{k}}^S. \tag{2}$$

We apply the BSE within the framework described by Rohlfing and Louie,[17] in which a DFT calculation for the electronic ground state is used, together with a calculation for the electron self-energy within the *GW* approximation to obtain the quasiparticle spectrum. The BSE is then solved yielding the correlated electron-hole excitations $|S\rangle$ and their energies Ω_S. Once the states describing the excitations and their associated energies have been solved for, it is then possible to evaluate the optical spectrum.

In our solution of the BSE in Eq. (2) we have included the highest 11 valence bands ($v = 6-16$) and the lowest 12 conduction bands ($c = 17-28$). The electron-hole interaction was calculated for 216 $\mathbf{k}$ points in the Brillouin zone. We then used an interpolation scheme[17] to obtain the matrix elements on a finer mesh of 1000 $\mathbf{k}$ points in the Brillouin zone. This fine mesh is not symmetric with respect to the Brillouin zone, but rather is shifted off the high-symmetry directions to
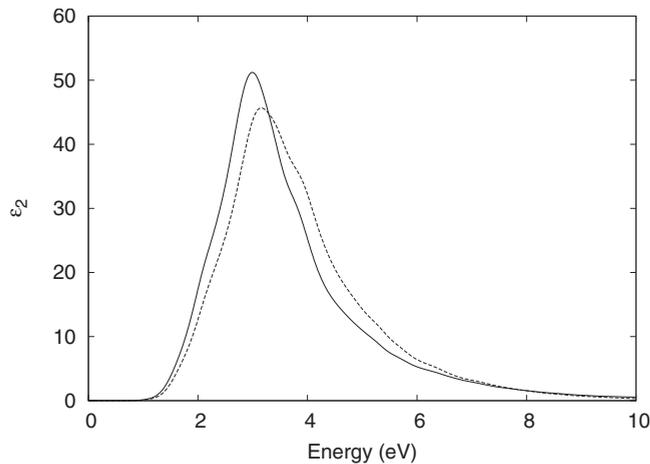
FIG. 1. Calculated imaginary part of the dielectric function of Si-XII. The solid line (dotted line) is with (without) the inclusion of electron-hole interactions.

obtain a finer sampling of the spectra. An artificial Lorentzian smearing of 150 meV is included in these calculation to account for the finite sampling of the Brillouin zone.

Once the BSE is solved, the imaginary part of the dielectric function, $\epsilon_2(\omega)$, is calculated from

$$\epsilon_2(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_S |\vec{\lambda} \cdot \langle 0|\vec{v}|S\rangle|^2 \delta(\omega - \Omega_S). \quad (3)$$

In the above expression $\vec{\lambda}$ is the polarization of the incident light and $\vec{v}$ is the single-particle velocity operator. In the absence of electron-hole interactions, Eq. (3) reduces to the following expression involving photon-induced vertical transitions between the independent electron and hole states:

$$\epsilon_2^{(0)}(\omega) = \frac{16\pi^2 e^2}{\omega^2} \sum_{v,c} |\vec{\lambda} \cdot \langle v|\vec{v}|c\rangle|^2 \delta(\omega - (E_c - E_v)), \quad (4)$$

where the superscript is used to distinguish the fact that electron-hole interactions are not included.

In Fig. 1 we plot $\epsilon_2(\omega)$ both with and without the inclusion of electron-hole interactions. The differences between these two curves might be interpreted to arise from the attractive nature of the electron-hole interaction, resulting in the shift of the spectrum to lower energies. This explanation is seen to be incorrect upon the examination of the joint density of states (dotted line) and the density of excitonic states (solid line) as shown in Fig. 2. We have divided the joint density of states by ω^2 to aid comparison with $\epsilon_2(\omega)$. These two density of states are seen to be nearly identical and are not related to each other by a shift in energy. This is not unexpected as the energy scale of the electron-hole interaction is related to the exciton binding energy in the material, which in Si-XII is on the order of meV and is thus small on the scale of our plot. Thus the difference between the interacting and the noninteracting spectrum arises from the constructive superposition of oscillator strengths at low energies and the destructive superposition at higher energy. This is precisely the behavior that has been found in calculations for other semiconductors.[17,21–24]
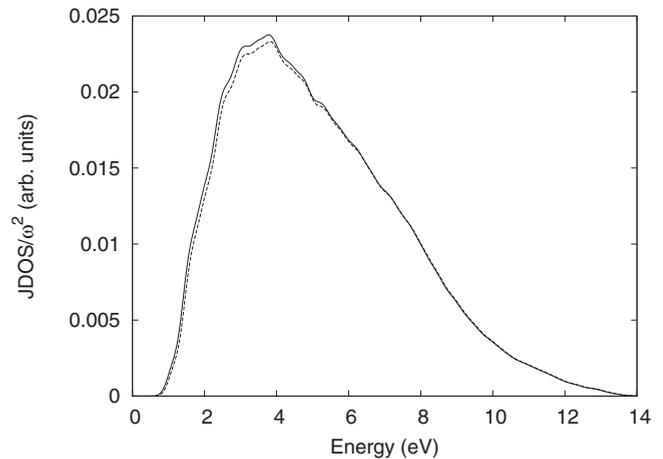
FIG. 2. Calculated joint density of states (divided by ω^2) for Si-XII. The solid line is the density of excitonic states, while the dashed line is joint density of states in absence of the electron-hole interaction.

To facilitate the evaluation of Si-XII as an absorber material in a photovoltaic device we compare the optical constants relevant to photon absorption with some other forms of silicon: amorphous, polycrystalline, and the cubic crystalline phase. These three forms currently dominate the market for photovoltaic modules in commercial applications.[25] In Fig. 3 the imaginary part of the dielectric function of Si-XII has been compared with these other forms of silicon commonly used in solar applications. The measured dielectric functions for these materials are taken from Ref. 26, which are obtained from spectroscopic ellipsometry. The calculated value of $\epsilon_2(\omega)$ for Si-XII clearly has more weight at lower energies. As mentioned previously, this is expected because of the smaller direct quasiparticle gap of Si-XII ($\sim$1.2 eV) compared to that of cubic silicon ($\sim$3.4 eV). This is advantageous for solar applications because the incident photon flux is concentrated at energies less than 3 eV. In Fig. 4 we show the optical absorption coefficient α for these four ma-
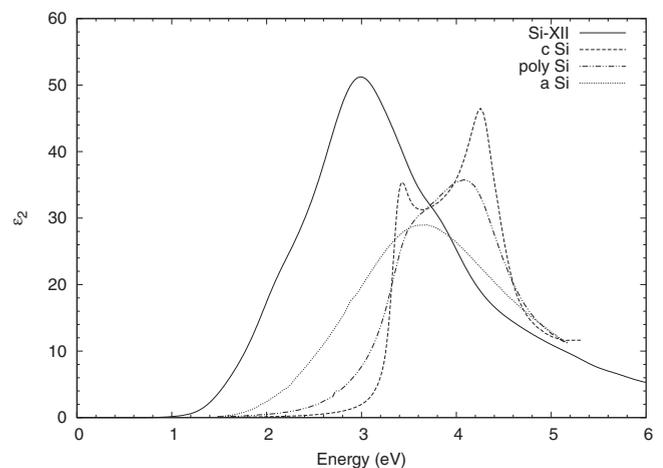
FIG. 3. Calculated $\epsilon_2(\omega)$ for Si-XII along with the experimental values for silicon in the amorphous (a-Si), polycrystalline (poly-Si), and crystalline cubic phase (c-Si). The experimental data is taken from Ref. 26.
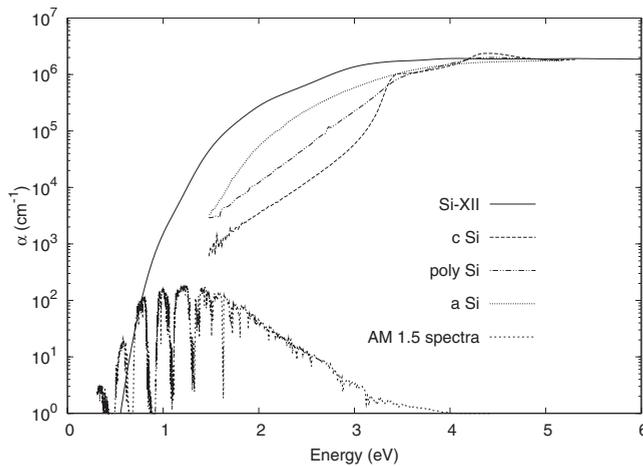
FIG. 4. Optical absorption coefficient α for Si-XII and three other silicon forms commonly used in photovoltaic devices. Shown inset (in arbitrary units and linear scale) is the solar spectral irradiance for AM1.5. The absorption coefficients for *c*-Si, *a*-Si, and poly-Si are experimental and are taken from Ref. 26.

terials along with the AM 1.5 solar spectral irradiance[26] to highlight the energies relevant to photovoltaic applications. Silicon in the R8 phase is seen to absorb light more effectively than the other forms of silicon in this energy range. We point out that this result holds in spite of the fact that our calculated values for Si-XII do not include any indirect, i.e., phonon-assisted transitions, whereas the experimental data that it is being compared to does include these transitions. Since the gap in R8 silicon is indirect, we should expect that if these indirect transitions were included in the calculation of the absorption coefficient then R8 would have even more weight in the photovoltaic relevant region of the energy spectrum.

Since Si-XII has a larger absorption coefficient at lower energies, it could in principle allow the use of photovoltaic absorber layers of smaller thickness to be used. This would result in less material being needed for photovoltaic devices of similar absorptive power. This difference can be seen in a calculation of the absorbed energy flux, W, as a function of the length of the absorber material,

$$W(L) = \int_0^\infty (1 - e^{-\alpha(E)L})I(E)dE, \qquad (5)$$

where α is the absorption coefficient, I is the solar spectral irradiance, and L the length of the absorber film. In this expression we have neglected the effects of reflection off the front and back surfaces of the film. The reason for this is that reflection often plays a small role in PV applications because of the use of antireflection coatings, often made of silicon nitride or titanium oxide. A coating of this type applied to a
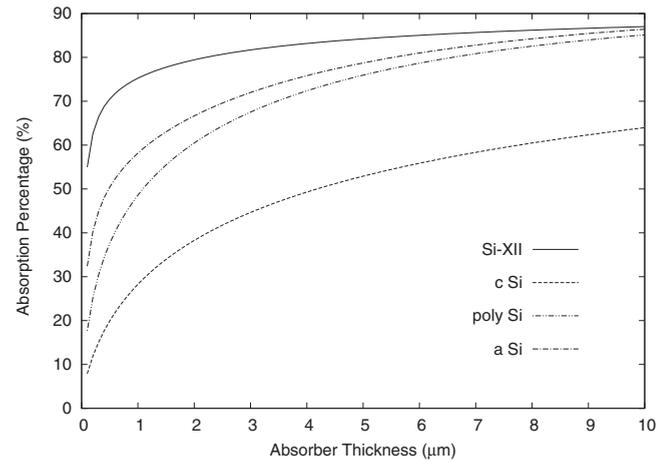
FIG. 5. Percentage of incident energy flux, which is absorbed as a function of film thickness for Si-XII and the other forms of silicon studied. Reflection at the surfaces has not been included.

silicon surface can reduce the percentage of light reflected by the surface from the bare value of ∼30% down to only a few percent.[27] In Fig. 5 we have compared this quantity among the forms of silicon studied. The data has been normalized to the incident energy flux [$L \to \infty$ in Eq. (5)]. Si-XII clearly absorbs a greater fraction of the incident flux with a very marked contrast at small values of the absorber thickness.

In conclusion we have calculated the optical absorption spectrum of the silicon polytype Si-XII (R8) using a first-principles method, which is based on the *GW* approximation to solve for the independent particle quasiparticle spectrum followed by a solution of the Bethe-Salpeter equation to account for electron-hole interactions. We find that the imaginary part of the dielectric function, $\epsilon_2(\omega)$, in addition to the absorption coefficient $\alpha(\omega)$, shows greater overlap with the solar spectrum than three other silicon forms used for comparison. These silicon forms are the cubic, amorphous, and polycrystalline forms, which commonly find use in photovoltaic application. There are of course other features besides absorption which are relevant to determining the efficiency in a photovoltaic device. One of these is the band gap, which places an upper bound on the open-circuit voltage V_{oc}. The small, indirect band gap of Si-XII of ∼240 meV might then limit its efficiency when used for photovoltaic applications.

*bmalone@civet.berkeley.edu

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