Ab initio study of electron and phonon coupling in silicon

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Abstract: We have studied electron-phonon coupling in silicon and its relation to hot carriers thermalization. The calculation of electron-phonon and phonon-electron interactions in silicon was obtained from first-principles density functional theory and many-body perturbation theory. Electron and phonon relaxation times were calculated subsequently. Moreover, the results showed that silicon exhibits a relatively wide phononic band gap along the symmetry line $X-W$, which prevents the Klemens mechanism leading to a phonon bottleneck effect. As demonstrated, phonon-electron interactions can play an important role in mitigating the electron thermalization along this symmetry line. This work shade light on the importance of including the phonon-electron interactions in the ab initio approach for future semiconductor materials engineering.

1. Introduction

Semiconductor materials used in photovoltaic (PV) cells have the property of releasing their electrons under the influence of solar energy. In this process, photons strike electrons and create an electron-hole pair. Afterward, the electron (hole) undergoes an inelastic scattering with phonons and relaxes to the conduction (valence) band edge, releasing energy as heat to the crystal lattice\textsuperscript{[1, 2]} in a process called thermalization. Therefore, solar energy is partially converted into heat, causing efficiency degradation due to the increase in cell temperature\textsuperscript{[3]}.

Thermalization dynamics are very important to understand the efficiency degradation in semiconductors and to advance material technologies in this field. Electron-phonon (e-ph) interactions are the origin of the electron thermalization, where the electron creates a phonon at the cost of some of its energy\textsuperscript{[4]}. A semiclassical approach using Monte Carlo simulation was performed to describe the e-ph interactions\textsuperscript{[5]}, however, this approach has used some empirical parameters to fit experimental data.

A study was made to understand deeply these e-ph interactions by Bernardi et al.\textsuperscript{[6, 7]}, who developed an accurate ab initio approach based on the density functional theory and many-body perturbation theory to calculate the electron relaxation time, and applied it to silicon and gallium arsenide semiconductors. Computed electron relaxation times were in agreement with the experimental data.

The previous studies\textsuperscript{[6, 7]} did not take into consideration ph-e interactions that can play an important role in thermalization dynamics. This work is an attempt to fill this lack, by
including ph-e interactions in the ab initio approach used by Bernardi et al. [6, 7], and apply it to investigate the relaxation time of electrons and phonons in silicon (Si).

2. Computational methods

Ab initio calculations were performed on a unit cell Si with a lattice parameter of 5 Å. Electronic band structure calculations were carried out within density functional theory (DFT) [8] using the Quantum ESPRESSO code [9], with a local density approximation (LDA) [10] for the exchange-correlation functional [11]. Norm-conserving pseudopotentials were used [12], and the kinetic energy cutoff was set to 80 Ry for wave functions. Phonon calculations were performed within density functional perturbation theory (DFPT) [13]. The EPW code [14] was used to calculate the electron and phonon self-energies, arising from electron-phonon interaction.

The carrier relaxation time is determined by:

\[ \tau = \frac{[\text{Im}(\Sigma)]^{-1}}{2} \tag{1} \]

Where \( \text{Im}(\Sigma) \) is the imaginary part of the carrier self-energy.

The electron self-energy is calculated as:

\[ \Sigma^{\text{el-ph}} = \sum_{q,\nu} \omega_{q\nu} g^{\text{el-ph}}(k, q)|^2 \left[ \frac{\epsilon_{\nu,q} + \partial q^V}{\epsilon_{\nu,q} - \omega_{\nu,q} - i\eta} + \frac{\epsilon_{\nu,q} + 1 - f(\epsilon_{\nu,q} + \omega_{\nu,q})}{\epsilon_{\nu,q} - \omega_{\nu,q} - i\eta} \right] \tag{2} \]

And the electron relaxation time describing the e-ph interaction is given by:

\[ \tau_{\text{el-ph}} = \frac{[\text{Im}(\Sigma)]^{-1}}{2} \tag{3} \]

On the other hand, the phonon self-energy is calculated as:

\[ \Sigma^{\text{ph-el}} = \sum_{\epsilon_n, k} \omega_{\epsilon_n,k} g^{\text{ph-el}}(k, \epsilon_n)|^2 \frac{f(\epsilon_{\epsilon_n,k}) - f(\epsilon_{\epsilon_n,k+q})}{\epsilon_{\epsilon_n,k} - \epsilon_{\epsilon_n,k+q} - \omega_{q\nu} + i\eta} \tag{4} \]

And the phonon relaxation time describing the ph-e interaction is given by:

\[ \tau_{\text{ph-el}} = \frac{[\text{Im}(\Sigma)]^{-1}}{2} \tag{5} \]

In Eq. 2 and Eq. 4 the electron-phonon matrix elements are given by:

\[ g^{\text{el-ph}}(k, q) = \langle \psi_{\epsilon_n,k+q} | \hat{\epsilon}_{\nu,q} V | \psi_{\epsilon_n,k} \rangle \tag{6} \]

With \( \psi_{\epsilon_n,k} \) the electronic wave function for band n, wave-vector k and eigenvalue \( \epsilon_{\epsilon_n,k} \) , \( \hat{\epsilon}_{\nu,q} V \) the derivative of the self-consistent potential associated with a phonon of wave-vector q, branch index v and frequency \( \omega_{q\nu} \cdot f(\epsilon_{\epsilon_n,k}) \) and \( f(\epsilon_{\epsilon_n,k+q}) \) are Fermi occupations, and \( \omega_{k,q} \) are weights of k-points and q-points, respectively.

The electronic states were calculated self consistently using DFT over a uniform grid of 6×6×6 k-points, then the vibrational states using DFPT over a uniform grid of 6×6×6 q-point grids. Subsequently, the EPW framework [14] transforms the quantities needed to evaluate the e-ph self-energy into the Wannier representation [15, 16] on a finer grid of 20×20×20 k and q points. Finally, the carrier relaxation time was calculated using Eq. 3 and Eq. 5.
In this work, electron-electron (e-e) interactions are neglected, due to their slight contribution to the electron relaxation time compared to e-ph interactions. This assumption is justified based on the results obtained by Bernardi et al. [6]. They showed that the phonon emission processes from e-ph interactions dominate the electron relaxation time.

3. Results and discussion

The electronic band structure with the electron relaxation time in Si along high-symmetry directions with Fermi level set at 0 eV are depicted in Fig 1. As observed, the electron relaxation time depends highly on the band and k directions. Also, the symmetry line X-W exhibits the longer overall relaxation time compared to the other symmetry lines. This is related primarily to the few energy bands and the separation between them along this direction, which restricts the electron possible states transitions leading to phonons emission.
Therefore, the rate of e-ph interactions along the X-W direction is relatively weaker resulting in longer relaxation time of the order of ~ 10fs.

The phonon dispersion with the phonon relaxation time in Si along high-symmetry directions is shown in Fig 2. The dispersion relations result in two modes of phonons, specifically, the acoustic and optical modes corresponding to a zero and non-zero frequency at the Brillouin zone center, respectively. We observed that the phonon lifetime in Si is uniform and exhibits a weak dependence on q directions, except at the optical branch of the Brillouin zone center and the symmetry line X-W where the phonon lifetime drops dramatically.

This result can be explained by the phonon bottleneck effect [17], which occurs whenever a large phononic band gap exists between the optical and acoustical modes, preventing optical phonons (OP) from decaying into two lower energy acoustical phonons (AP) (OP → 2AP) in a process known as Klemens decay [18]. The conservation of energy will prevent the Klemens mechanism, as long as the phononic gap energy is greater than the highest acoustic phonon energy.

The phononic band gap is nearly absent in Si (Fig. 2), and the Klemens mechanism is strongly present. Except along the X-W direction, where we observed the presence of a relatively wide phononic band gap between optical and acoustical branches, hence slowing the decay of hot phonons. Consequently, the ph-e interactions will take place, increasing the probability of electrons reabsorbing hot phonons.

Hot phonons along the X-W direction with a lifetime of the order of ~ 10fs can contribute effectively to the reheating of electrons by optical phonon absorption. As discussed, the X-W direction minimizes the difference between electron and phonon lifetime, making the extraction of electrons appreciable within silicon thin films along this direction.

4. Conclusion

Thermalization dynamics were investigated in silicon, through the calculation of electron and phonon relaxation times along high symmetry directions. The electronic band structure in silicon depicts few energy bands relatively separated along the X-W direction. Besides, the phonon dispersion reveals the presence of the phonon bottleneck effect along this direction. As a result, the electron and phonon relaxation times are comparable along the X-W direction (~ 10fs), allowing the reabsorption of hot phonons by electrons. These results suggest that including phonon-electron interactions in the ab initio analysis allows for a better understanding of thermalization dynamics in silicon and emphasizes the significant role of phonon-electron interactions in engineering semiconductor materials.
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