**First-Principles Study of Charge Carrier Dynamics with Explicit Treatment of Momentum Dispersion on Si Nanowires along <211> crystallographic Directions**

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***ABSTRACT***

*The ground state structure, optical properties and charge carrier dynamics of silicon nanowire (SiNW) grown in <211> crystallographic direction is studied as a function of wavevector using density functional theory. This nanowire can be used as fundamental unit of nanoelectronic devices. The optical properties are computed under assumption of momentum conservation. The on-the-fly non-adiabatic couplings for electronic degrees of freedom are obtained along the ab initio molecular dynamics nuclear trajectories, which are used as parameters for Redfield density matrix equation of motion. By investigating the photo-induced process on this nanowire, it is shown that high-energy photoexcitation relaxes to the band gap edge within 75 ps. The results of these calculations help to understand the mechanism of electron transfer process on the Si nanowire.*

**INTRODUCTION**

Photoinduced nonradiative dynamics [1]is a key process in silicon nanostructures.[2] Silicon nanowire (SiNW) is a unique and special class of semiconductor due to its intrinsic properties such as one dimensionality, high surface-to-volume ratio, and biocompatibility.[3] The development of SiNW is a good choice due to its compatibility with existing silicon-based technology.[4] Moreover, SiNW has many promising applications in optoelectronic devices, transistors, lasers and solar cells.[5-6] It is important to determine carrier lifetime[7-8] of SiNW with axial arrangement of p-n junctions [9] to assure that the excited state can be processed in a useful way. The computational modeling of the hot carrier relaxation in molecules and nanostructures stakes on allowing for energy flow between electronic part and nuclear part and partitioning the total energy between them, going beyond Born-Oppenheimer approximation.[10] Quantum part of kinetic energy of nuclei is assessed through on-the-fly nonadiabatic coupling.[1] This small coupling is taken into account in terms of time dependent perturbation theory, affecting the orthogonality of Kohn-Sham orbitals and introducing change in occupation numbers of those orbitals [11-13].

Optical and electronic properties of bulk silicon and silicon nanostructures depend on momentum of charge carriers. As an example, energy of a carrier may depend on momentum asquadratic dependence weighted by inverse of effective mass of a carrier or in a more complicated way. Matrix elements of both electron-to-photon and electron-to-phonon interaction as well as energy offsets of initial and final state in all nonequilibrium processes substantially depend on value of the momentum or wavevector of charge carriers. These trends and dependencies attract attention for both, application-based necessity and fundamental importance. This paper introduces computational approaches to address this challenge.

Sampling of the Bloch state is a necessary minimum for considering periodicity and nonzero momentum in achieving electronic structure data, for frozen geometry and in equilibrium. Present work reports methodological steps and preliminary results representing influence of k-vector distribution onto nonequilibrium processes induced by photoexcitation of nanostructure.

There are some successful computational methods for electronic relaxation is depending on the concept of surface hopping between potential energy surfaces.[14] Molecular dynamics trajectory is a competent approach for calculating the electron-to-lattice coupling in semiconductors.[15]

On the basis of density functional theory (DFT), there is an approach to combine Redfield theory of electron relaxation with on-the-fly coupling of electrons-to-lattice.[16] In this research, the electronic structure and optical properties of SiNW along <211> direction is calculated using DFT. Additionally, wavelength of maximum absorption, oscillator strength at that wavelength and exciton lifetime are also calculated.[17]

**THEORY**

The electronic structure was obtained by density functional theory (DFT)[18] followed by determining the initial positions of ions by constructing a model of the atomic structure. The Vienna Ab-initio Simulation Package (VASP)[19] has been used to perform calculations of self-consistent DFT equations whereas the main equation is fictitious one-electron Kohn–Sham equation [20]

(1)

Where the first term represents the kinetic energy, the second term describes potential energy, and corresponds to the orbital energy for the set of one-electron orbitals,.[21]

We use VASP software to solve equation (1) in which valent electrons are treated explicitly while core electrons are described with pseudopotentials [22]. All calculations were done on the basis of plane waves and the kinetic energy cutoffs for the wave function was used 500 eV. The functional for the electron–electron interaction energy was chosen according to Perdew–Burke–Ernzerhof procedure (PBE-functional)[23] which follows generalized gradient approximation.

The density of states was determined by the following equation:

(2)

The optical absorption spectra were calculated by using the equation below:

(3)

Where, is the partial absorption spectrum and

is the partial oscillator strength, computed in terms of matrix elements of transition dipole Overall absorption reads , under

The computational procedure for non-radiative relaxation includes three steps, each of which follows or breaks Born-Oppenheimer approximation (BOA) as follows: (i) adiabatic molecular dynamics trajectory is computed within BOA; (ii) on-the-fly nonadiabatic coupling matric elements are computed according to equation (4)

and quantify the level of fulfilment of breaking down of BOA.

(iii) dynamics of populations of electronic states, pursued by eq. (5) manifests the consequence as shown in what follows of nonadiabaticity, where electronic degrees of freedom dissipate energy into nuclear degrees of freedom.

Among the three steps computational procedure, step (ii) is a combination of VASP and home-grown script, which executes VASP software as subroutine. Step (iii) is a completely new code, specifically designed to take into account nonadiabatic effects away from Born-Oppenheimer approximation. Several additional computational tools for describing phenomena beyond Born Oppenheimer Approximation have been compared in recent review13

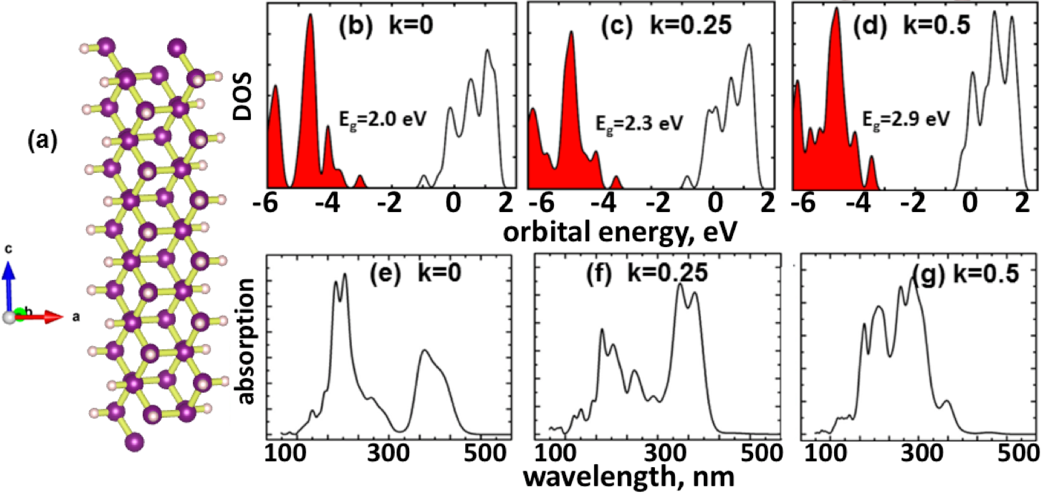
For a specific initial excitation , the time dependence for the density matrix is calculated, where initially an electron is promoted from an orbital a to an orbital b by solving the equation of motion for the reduced density matrix for electronic degrees of freedom

(5)

Where the first term in equation (5) represents either one-electron Fock or Kohn−Sham Hamiltonian and the second term corresponds to dissipative electronic transitions facilitated by thermal fluctuations of the lattice ions through nonadiabatic couplings. In this research, the first term is one-electron Kohn-Sham Hamiltonian. The coefficients of dissipative electronic transition quadratic operator that enter into the equation of motion for the electronic degrees of freedom is obtained from a time average of the autocorrelation function of the electron-to-lattice nonadiabatic couplings .[2]

**RESULTS AND DISCUSSIONS**

The model of Si nanowire grown in <211> crystallographic direction is shown in **Figure 1 (a)**. This SiNW is periodic along c direction. A procedure to generate strain-free nanowire was introduced by Huang et al.. [24] Specifically, the c-axis value was varied until total energy is minimized. We used the vacuum along the directions of a and b to avoid spurious interaction between periodic images.[25] Moreover, hydrogen atoms were attached to all surface Si atoms in order to saturate the dangling bonds.[26] The calculated ground state structure and absorption spectra of SiNW grown in <211> crystallographic direction is shown in **Figure 1** (b)-(g). The bandgap is 2eV, 2.3 eV, and 2.9 eV at k-points 0, 0.25, and 0.5 respectively. It appears that the bandgap is increasing corresponding to higher k-points. The absorption spectra show that strong absorption starts at150 nm for all k-points and continues up to around 400nm.

**Figure 1: (a)** The model of SiNW oriented in <211> crystallographic direction. The Si and H atoms are represented as purple and off white color respectively. **(b)-(d)** The density of states (DOS) and **(e)-(g)** the absorption spectra of <211> SiNW at three different k-points such as **k**=0, **k**=0.25, and **k**=0.5 respectively.

In order to calculate photoexcited dynamics, The Redfield tensor was extracted from DFT calculations. Selected elements of Redfield tensor for three different k-points (**k**=0, **k**=0.25, & **k**=0.5) are shown in **Figure 2** (a) - (c). The nonzero transition along the sub-diagonal line indicates nonradiative transitions mostly occur between the nearest neighbour orbitals . Since density of states (DOS) in conduction band (CB) is greater than that in valence band (VB), the transition probability in conduction band is higher and electron relaxes faster than hole. **Figure 2** (d) – (f) shows the distribution of electron density as a function energy and time with respect to ground-state equilibrium. The red, green, and blue regions present the gain in population (electron), equilibrium value of electronic population, and the loss in population respectively. Initial photoexcitation occurs at on the left-hand side of the plot. Due to change of excitation energies, electrons and holes populate different sequence of states within the valance band and conduction band. Therefore, electron lifetime can vary for each specific initial excitation. Both charge carriers reach their respective band edges after a certain period of time and the expectation value of excitation energy remains constant under an approximation of no recombination. The excitation cooling relaxation rate at three k-points are shown in **Figure 2** (g) - (i). Data in **Figure 2**, panels (g)-(i) demonstrate that rates of non-radiative cooling of charge carriers, electrons and holes depend on value of momentum or wavevector and, for this model lower value of momentum provides quicker cooling . Electrons relax faster than hole as DOS is higher in CB.[27]

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**Figure 2**: Selected elements of Redfield tensor near the band gap for studied <211> SiNW model at **(a) k**=0 **(b) k**=0.25, and **(c) k**=0.5. Change in the distribution of electron density as a function of energy and time with respect to the electronic equilibrium following photoexcitation from **(d)** HO-13 to LU at **k**=0, **(e)** HO-3 to LU+1 at **k**=0.25, and **(f)** HO to LU+23 at **k**=0.5. Summary of the relaxation rates of holes and electrons for a range of initial excitations of <211> SiNW model **(g)** **k**=0 (h) **k**=0.25, and (i) **k**=0.5.

**CONCLUSIONS**

A theoretical and computational investigation of electron dynamics on Si nanowire oriented in <211> crystallographic directions is presented in this work. Electronic and optical properties of this nanowire are calculated using the combination of density matrix method and ab initio electronic structure method. In <211> SiNW, electrons relax faster than holes which can be applicable in potential photovoltaic device.

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