Simulation of optical excitation spectra of semiconductor nanowires within effective bond orbital model

Y.C. Chang [a,b,*], Waleed E. Mahmoud [c,d]

[a] Research Center for Applied Sciences, Academia Sinica, 11529, Taiwan
[b] Department of Physics, National Cheng-Kung University, Tainan, 70101, Taiwan
[c] King Abdulaziz University, Faculty of Science, Department of Physics, Jeddah, Saudi Arabia
[d] Suez Canal University, Faculty of Science, Department of Physics, Ismailia, Egypt

ARTICLE INFO

ABSTRACT

Systematic studies of optical excitation spectra of semiconductor nanowires (including group IV, III–V, and II–VI materials) obtained by using an eight-band effective bond-orbital model (EBOM) are presented. A new set of EBOM parameters are determined which produce good band structures of zincblende semiconductors for the entire Brillouin zone, suitable for modeling the excitation spectra from infrared to ultraviolet. The band structures and optical excitation spectra, including both the interband and intraband transitions (for doped cases) are calculated. The calculations were done with the use of a symmetrized basis functions which transform according to the irreducible representations of the underlying point group. This can improve the computation efficiency by about two orders of magnitude. Thus, the electronic and optical properties of a large class of materials can be simulated.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Recently, nanostructure/polymer composite has been demonstrated to have high potential in organic solar cell application due to its low cost compared to the thin-film silicon technology [1]. These cells can be processed from solution, allowing a simple roll-to-roll printing process, which can lead to large scale production at low cost. The commonly studied organic solar cells use polymers such as polyphenylene vinylene (PPV) mixed with copper phthalocyanine, carbon fullerenes, or fullerene derivatives such as PCBM. Although the energy conversion efficiency of typical organic solar cell using conductive polymers is low ($<10\%$) compared to inorganic solar cells, the efficiency may be improved significantly with the advance in nanotechnology. Furthermore, the mechanical flexibility and disposability of polymer solar cells may have some advantages in certain applications. The main reason for the low energy efficiency of the polymer-based solar cell devices is the lack of absorption in the infrared region (with photon energy below 2 eV), which covers 45% of the solar spectrum. One possibility to improve the performance is to mix some semiconductor nanostructures (such as quantum wires and quantum dots), which can absorb strongly in the infrared, to form a nanostructure/polymer material. The nanostructure/polymer composite allows increased interface area, which allows higher probability of separating the photo-generated excitons or electron–hole pairs for electric current output. For examples, the I–V characteristic curve of Polyvinyl pyrrolidone (PVP) capped cadmium selenide (CdSe) nanoparticles embedded in polyvinyl alcohol (PVA) matrix [2], PbSe QD/PVA nanocomposite films [3], polyaniline (PANI) nanoparticles coated by nanolayer of bismuth oxide (Bi_2O_3) [4], and Poly (vinyl acetate) (PVAc) loaded Bi_2O_3 nanorods [5] all show photovoltaic cell like behavior with decent conversion efficiency. In this paper, we explore the absorption spectra of semiconductor nanowires made of group IV elements (Si and Ge), III–V compounds (InAs, GaSb, and GaAs), and II–VI compounds (CdTe, and ZnSe) for photon energies ranging from infrared to UV. Small band-gap semiconductors (such as InAs) naturally provide strong absorption in the infrared. On the other hand, nanowires made of large-gap semiconductors with suitable doping can also provide strong absorption in the infrared via the intra-band (or inter-subband) absorption process. The intra-band absorption process has been widely explored in quantum-well infrared photodetectors (QWIPs)

---

* Corresponding author at: Research Center for Applied Sciences, Academia Sinica, 11529, Taiwan. Tel.: +886 2 2787 3129; fax: +886 2 2787 3122.
E-mail address: yiachang@gate.sinica.edu.tw (Y.C. Chang).
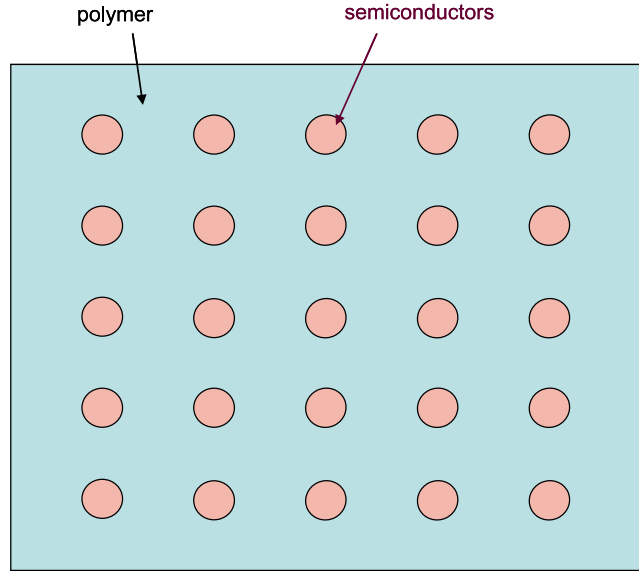
polymer   semiconductors

Fig. 1. Schematic illustration of a periodic array of cylindrical nanowire structures embedded in polymer matrix.

[6–8] and quantum-dot infrared photodetectors (QDIPs) [9–11]. However, extensive studies of intraband absorption properties of quantum wires are still lacking. Thus, the current study can fill in the gap.

2. Theoretical formulations

We adopt an eight-band effective bond orbital model (EBOM) which is suitable for calculating the electronic states within 1.5 eV above the conduction band minimum and 1 eV below the valence-band maximum. The optical excitation spectra of zincblende semiconductor nanowires (NWs), including group IV elements (Si and Ge), III–V compounds (InAs, GaSb, and GaAs) and II–VI compounds (CdTe and ZnSe) will be studied. We choose a super-cell structure with a square lattice to simulate these NWs embedded in a polymer as illustrated in Fig. 1. Since the main function of the polymer matrix is to support the NWs and extract carriers, we have neglected the change in electronic properties of NW at the interface due to binding to polymer molecules. For calculating the subband structures of NW superlattices as shown in Fig. 1, we adopt an eight-band EBOM model. Since the electronic states of interest are expected to be well confined inside the nanowire, we use a confining potential (with a large band off-sets ΔE_c and ΔE_v for the conduction and valence bands, respectively) while keeping other EBOM parameters the same as in the NW region. The electronic states of the NW superlattice are expanded in terms of bulk basis states $|\alpha; \mathbf{G}, k_z\rangle$ of the host material (taken to be the same as the semiconductor nanowire) associated with wave vector $\mathbf{G}$ in the x–y plane, where $\mathbf{G}$ denotes a reciprocal lattice vector of the NW superlattice. k_z is the wave-vector along the wire axis, which is a good quantum number. (We assume the NW to be infinitely long) The superlattice subband structures are obtained by diagonalizing the EBOM Hamiltonian within the basis set $\{|\alpha; \mathbf{G}, k_z\rangle\}$. To reduce the computation effort, we take linear combinations of the basis functions to form a set of symmetrized basis functions, which transform according to the irreducible representations of the underlying point group. Thus, the symmetry properties of the model system are fully exploited. This can improve the computation efficiency significantly.

2.1. EBOM and its relation to $\mathbf{k} \cdot \mathbf{p}$ model

The effective bond orbital model (EBOM) is an atomistic model based on bond orbitals of the underlying crystal with symmetry types $|s\rangle, |x\rangle, |y\rangle, |z\rangle$ [12,13]. Their roles are similar to the periodic part of the Bloch states associated with the conduction band minimum and valence band maximum for zincblende semiconductors. The tight-binding like EBOM Hamiltonian within the four bond orbital basis states is given by [13]

$$
H_{bo}^{4\times4} =
\begin{bmatrix}
E_c + E_{ss}T(\mathbf{k}) & 4E_{sx}(S_{xy}(\mathbf{k}) + S_{xz}(\mathbf{k})) & 4E_{sx}(S_{yx}(\mathbf{k}) + S_{yz}(\mathbf{k})) & 4E_{sx}(S_{zx}(\mathbf{k}) + S_{zy}(\mathbf{k})) \\
4E_{sx}(S_{yx}(\mathbf{k}) + S_{yz}(\mathbf{k})) & \begin{aligned}E_v' + 4E_{zz}C_{yz}(\mathbf{k}) + \\ 4E_{xx}(C_{xy}(\mathbf{k}) + C_{xz}(\mathbf{k}))\end{aligned} & -4E_{xy}\sin\bar{k}_x \sin\bar{k}_y & -4E_{xy}\sin\bar{k}_x \sin\bar{k}_z \\
4E_{sx}(S_{zx}(\mathbf{k}) + S_{zy}(\mathbf{k})) & -4E_{xy}\sin\bar{k}_y \sin\bar{k}_x & \begin{aligned}E_v' + 4E_{zz}C_{xz}(\mathbf{k}) + \\ 4E_{xx}(C_{xy}(\mathbf{k}) + C_{yz}(\mathbf{k}))\end{aligned} & -4E_{xy}\sin\bar{k}_y \sin\bar{k}_z \\
4E_{sx}(S_{zx}(\mathbf{k}) + S_{zy}(\mathbf{k})) & -4E_{xy}\sin\bar{k}_z \sin\bar{k}_x & -4E_{xy}\sin\bar{k}_z \sin\bar{k}_y & \begin{aligned}E_v' + 4E_{zz}C_{xy}(\mathbf{k}) + \\ 4E_{xx}(C_{xz}(\mathbf{k}) + C_{yz}(\mathbf{k}))\end{aligned}
\end{bmatrix},
\tag{1}
$$

where E_c and E_v' denote the band edge positions for conduction and valence bands at zone center in the absence of the spin–orbit interaction. $T(\mathbf{k}) = 4(C_{xy}(\mathbf{k}) + C_{xz}(\mathbf{k}) + C_{yz}(\mathbf{k}))$, $C_{\alpha\beta}(\mathbf{k}) = \cos\bar{k}_\alpha \cos\bar{k}_\beta - 1$, and $S_{\alpha\beta}(\mathbf{k}) = \sin\bar{k}_\alpha \cos\bar{k}_\beta$, where $\bar{k}_\alpha = k_\alpha a/2$ (for $\alpha, \beta = x, y, z$) and a is the lattice constant. $E_{ss}, E_{sx}, E_{xx}, E_{zz}$, and E_{xy} are the nearest-neighbor tight-binding interaction parameters for a face-center cubic lattice as defined in Ref. [13]. Here, we have purposely multiplied the bond orbital $\langle s|$ by a phase factor i such that $H_{bo}^{4\times4}$ becomes a real matrix, which would simplify the computation. For small values of $\mathbf{k}$, there is one-to-one correspondence between band parameters obtained in EBOM and $\mathbf{k} \cdot \mathbf{p}$ model [13]. The relation essentially describes the transformation from real-space picture to reciprocal-space picture for near zone-center states. Thus, EBOM can describe the near zone-center states as accurately as the $\mathbf{k} \cdot \mathbf{p}$ model.