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Multi-scale modeling of edge effect on band gap offset in polygonal cross-section Silicon nanowires

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ABSTRACT

The band gap offset is an effect of coordination numbers (CNs) of atom reduction at the edge of transversal cross-section of Silicon nanowires (SiNWs). In this paper, a hierarchical multi-scale technique is developed to model the edge effect on the band gap shift of SiNWs since the geometric effect is dominant in the energy gap due to the appearance of strain in the self-equilibrium state. The multi-scale model is performed based on the molecular dynamics approach and finite element method for the micro- (atomistic) and macro-scale levels, respectively. The Cauchy–Born (CB) hypothesis is used to relate the atomic positions to the continuum field through the deformation gradient. Finally, the applicability of proposed multi-scale model is illustrated in numerical simulations of four SiNWs cross-sections, i.e. the circular, hexagonal, rectangular and triangular, and the results are compared with the fully atomistic model, experimental data and analytical solution.

1. Introduction

Silicon nanowires (SiNWs) have been known as the most important nano-materials for use in next generation battery electrodes, sensors and solar cells [1,2]. The SiNWs have an efficient thermoelectric property that converts heat to electricity in thermoelectric devices [3,4]. Furthermore, they have a wide range of applications including use in transistors [5,6], memory devices [7] and batteries, solar cells and nano-electronic power sources [8–10]. SiNWs have been of great interest in experimental, theoretical and analytical researches [11–13]. One of the most important research areas extensively referred in the literature is its use in the determination of the electrical conductivity of material in solid state physics, known as the band gap, or the energy gap. The band gap is an energy range where no electron states can exist; in which the materials with large band gaps are insulators, those with smaller band gaps are semi-conductors such as SiNWs, and the materials with very small or no band gaps are conductors. The band gap can be related to the strong structure dependency of electronical and optical properties, particularly the diameters and growth orientations. Hence, there is a need to investigate SiNWs with various sizes and cross-section shapes, such as rectangular, triangular, circular, and hexagonal. Furthermore, these types of nanowires have special properties in comparison with spherical ones due to high imperfection of atoms located at the edges and quantum potential depression of nanowires.

Recent research studies in SiNWs have been focused on the relationship between the size and band gap of nanowires. It has been shown that the coordination numbers (CNs) of atom reduction at the edge of polygonal SiNWs, referred to as the 'edge effect', leads to a stronger bond strength at the edges than that of the interior bulk. Nolan et al. [14] investigated the influence of various species for surface termination on the band gap modification of small-diameter (~1 nm) SiNWs. It was shown that the band gap narrows while the wire diameter increases. Yao et al. [15] studied the electronic structure and band gap of SiNWs with different cross-sectional geometries, including the triangular, tetragonal and hexagonal. They presented the dependency of band gap on the dimension of SiNWs. In a later study, Yao et al. [16] investigated the influence of cross-sectional shape and size on electron effective mass and surface lattice constant of SiNWs. Zhu et al. [17] established an analytical model for SnO_2 nano-structures in the self-equilibrium state to obtain a relationship between the band gap offset with the bond length and bond strength in self-equilibrium state. It was shown that the crystal potential and band structure may change due to the compression strain, and that the band gap shift is in relation to the lattice strain and coordination imperfection in the surfaces of nano-structures. A theoretical model was developed by Zhu et al. [18] for semiconductor nano-structures to elucidate the band gap tunability in association with self-equilibrium strain state by taking the size and temperature effect into account, based on the relationship between the bond length and bond energy. They also investigated the edge effect on the band gap shift in polygonal cross-sectional SiNWs [19], and highlighted that the geometry of SiNWs has an important effect on

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the band gap because of self-equilibrium state strain. Ng et al. [20] and Ma et al. [21] obtained the energy gap for small-diameter SiNWs, and presented that the energy gap increases by decreasing the SiNW diameter from 1.1 eV for a SiNW diameter of 7 nm to 3.5 eV for 1.3 nm, which is in agreement with previous theoretical predictions. Zhao et al. [22] studied the structural, electrical and optical properties of SiNWs with diameters up to 4.2 nm, and demonstrated the dependency of gap energy on the size and orientation of SiNWs. Ouyang et al. [23] presented an analytical thermodynamic model to explain the size effect, the interfacial orientation and the interfacial mismatch on the interface energy of multilayered nano-structures. An analytical solution was developed by Ouyang et al. [24] by combining the size, pressure and the nature of the bond involved in the band gap energy for semiconductor nano-crystals. There are also a number of theoretical and experimental investigations reported in literature that demonstrates the influence of self-equilibrium strain on the electronic properties of SiNWs and as a result on the band gap energy of SiNWs [25–34].

Computational modeling has been widely used in numerical simulation of nano-materials [35,36]. One of the most popular computational techniques used to simulate the material behavior at nano-scale is the molecular dynamics (MD) method that takes into account the inter-atomic potential [37–40]. However, this method is costly and time consuming because of its order of time scale (femtosecond) and length scale (angstrom). In order to overcome this problem, multi-scale methods have been proposed by involving a combination of the micro- and macro-scale levels [41–43]. There are different multi-scale techniques proposed by researchers, including the quasi-continuum [44,45], bridging domain [46] and bridging scale [47] methods, in which their constitutive law is based on the Cauchy–Born (CB) hypothesis [48]. The Cauchy–Born hypothesis provides a hierarchical approach in molecular dynamics of crystal elasticity that performs a relationship between the continuum and atomic deformations, and has been extensively used as the constitutive law of continuum regions in multi-scale models. Zhang et al. [49] evaluated the strain energy density on the continuum level using the CB rule, in which the atomistic model was combined with the continuum model to predict the Young modulus of single-wall carbon nanotubes. The bridging length scales method was developed by Broughton et al. [50] that describes a seamless coupling of continuum to quantum mechanics, involving an algorithm implemented on a parallel computer system, for handshaking between the finite element method and molecular dynamics, in which the total energy of the system was constructed based on the Hamiltonian method. The technique was applied to simulate the crack propagation in silicon. A coarse-grained molecular dynamics (CGMD) method was proposed by Rudd and Broughton [51] based on a statistical coarse graining prescription to construct a scale-dependent constitutive equation, which was suitable for the atomistic level. Rudd and Broughton [52] presented a combined molecular dynamics – finite element model for the multi-scale simulation of temperature dependent behavior of MEMS. It was shown that the multi-scale technique can significantly improve the numerical simulation of MEMS in sub-micron length scales. The material size dependency was investigated based on an augmented continuum theory by Miller and Shenoy [53] and Shenoy [54] for nano-homogenous materials and by Sharma et al. [55] for nano-inhomogenous materials. Dingreville et al. [56] developed a model to incorporate the surface free energy into the continuum theory, and investigated the size dependency of elastic behavior of nanowires, thin films and nano-particles. A modified CB rule was proposed by Jiang et al. [57] to combine the inter-atomic potential with the continuum theory in order to investigate the effect of nanotube radius in the single wall carbon nanotubes. A surface Cauchy–Born (SCB) model was proposed by Park et al. [58] by decomposing the potential energy of the system into the bulk and surface components. The SCB model was incorporated into the nonlinear finite element model by Park and Klein [59,60] to simulate silicon nano-structures and metallic nanowires. A boundary Cauchy–Born (BCB) technique was developed by Qomi et al. [61] for multi-scale modeling of metallic nano-structures, which was capable of capturing the edge and corner effects as well as the surface effect. The BCB model was implemented in the temperature-dependent multi-scale method by Khoei and Ghahremani [62] to illustrate the role of temperature on the surface effects of nano-structures. A modified BCB multi-scale technique was recently developed by Khoei and Aramoon [63] to model the surface effects of nano-structure using the radial quadrature algorithm.

The main goal of this research is to develop a multi-scale approach to investigate the edge effect on the band gap shift of SiNWs with different cross-sections. To this end, a hierarchical multi-scale model is developed based on the Cauchy–Born hypothesis for the diamond structure SiNWs to capture the edge and corner effects. The BCB multi-scale method is performed using the radial quadrature technique, which is a local regression at the vicinity around its surface quadrature in a least-square scene that makes it capable of approximating data at the edges and corners without any limitation upon the arrangement of atomic structure. The nonlinear FEM is applied to model the surface effect at macro-scale level. The deformation gradient is obtained at each quadrature point in macro-scale domain and transferred to nearby representative atom to obtain the first Piola–Kirchhoff stress and tangential stiffness tensors from the CB hypothesis at the atomistic level. Finally, the band gap shift is evaluated using the BCB multi-scale method for four cross-section SiNWs, and the results are compared with the fully atomistic model, experimental data and analytical solution. The paper is organized as follows; in Section 2, the band gap offset formulation is introduced based on the coordination number (CN) and bond contraction coefficient. In Section 3, modeling of atomistic medium is presented using the molecular dynamics (MD) technique based on the many-body Tersoff potential. In order to model the real behavior of SiNWs, the stress and elasticity tensors are calculated in Section 4 using the Tersoff potential based on the concept of CB hypothesis. In Section 5, the Lagrangian finite element formulation is described for the equivalent continua. In Section 6, the concept of multi-scale model and its computational algorithm are demonstrated on the basis of radial quadrature algorithm. In Section 7, numerical results are presented for four SiNWs with different cross-sections, and the results are compared with fully atomistic model. Finally, some concluding remarks are given in Section 8.

2. The band gap offset formulation

Because of different bond interaction energy at the surface of SiNWs in comparison with the interior of the bulk, the bond strength differs at the surfaces and edges. Consequently, the bond length of atoms shrinks spontaneously, resulting in a total energy depression in the self-equilibrium state [18,26]; and as a result the induced lattice strain emerges. This lattice strain can be determined using the total strain energy based on the following relation as [19]

$$\varepsilon = \frac{d^*}{d_0} - 1 \tag{1}$$

where d^* is the average bond length and d_0 is the bulk bond length. On the basis of above definition, the strain of surface atoms is larger than that of the central region for polygonal nanowires. In this study, four SiNWs cross-sections, including the tetragonal, hexagonal, trigonal and circular cross-sections are investigated to