Electronic and optical properties of single-walled silicon nanotubes: the sp^3 tight-binding model

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***Abstract*— In this paper, we investigate the curvature effects on the electronic band structure and dielectric function of single-walled silicon nanotubes and carbon nanotubes, based on tight-binding method. The curvature nature of nanotubes causes radius-dependent σ-π-orbital hybridization which leads to optimization of tight-binding model for each radii. First, the effects of orbitals overlap and the structural optimization on the electronic band structure of small radius nanotubes are investigated. Second, the imaginary part of dielectric function of nanotubes, which is related to optical absorption coefficient, is obtained by calculating the interband optical matrix elements using gradient approximation. It is shown that the σ-π-tight-binding model optimization due to the curvature effects, introduces small changes to the optical transition energies obtained by simple π-band tight-binding model. The results show that the curvature effects are more important in small radius tubes.**

Keywords: **silicon nanotube; silicene; carbon nanotube; curvature effect; electronic properties; optical properties; density function theory;**

I. INTRODUCTION

Carbon nanotubes (CNTs) were synthesized in 1991 and in last decade, significant effort have been attracted to their amazing properties. After carbon nanotubes, other types of nanotubes such as BN, GaN and AlN have been studied theoretically and experimentally synthesized [1]. Two dimensional Silicon (Si) hexagonal honeycomb lattice was proposed as silicene, recently. Silicene also has a lattice like graphene sheet, which exhibit a linear dispersion. Si atoms of silicene in honeycomb lattice have sp^2 configuration. When a two dimensional sheet of silicon is rolled up along a chiral vector, Si nanotubes is created.

In this work, we apply Tight-binding (TB) model to study Silicon nanotube's (SiNT) band structure which have been done previously by accurate ab-initio calculation [2]. Also TB model was applied to the similar two dimensional materials like CNTs and graphene, successfully In silicene sheet, sp^2 hybrid orbitals lie on the same plane, make three σ-bonding, , and the remaining out-of-palne p_z-orbitals of silicon atoms,

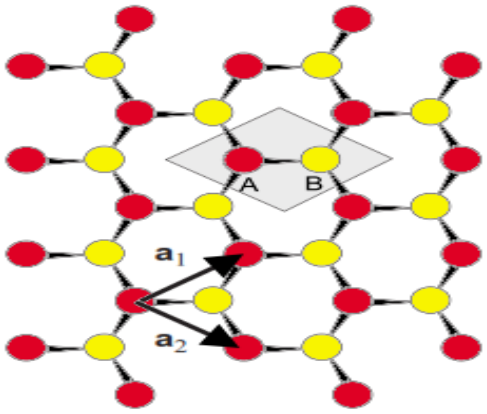

Fig. 1. Lattice of a silicene sheet

Make π-bonding. In case of SiNT, atomic orbital rearranges in sp^3 hybridization and simple π-TB model, based on single orbital per atom, is no longer valid [3]. So more complicated model should be used. Our TB model is based on a mixture of four atomic orbitals: 3s, $3p_x$, $3p_y$ and $3p_z$.

The curvature of SiNT's wall, modifies the angle of hybrid sp^3 orbitals bonds and depends on SiNT's radius [4-5]. Radius-dependent σ-π-orbital hybridization changes the atomic orbitals overlap [6]. The deviation from the sp^2 hybridization alter electronic properties of SiNTs and the curvature effect is more significant in the case of narrow nanotubes compared to the simple π-TB model.

After calculation of electronic band structure of SiNTs, their optical properties have been treated within π-TB and σ-π-TB models [7]. The optical transition can be obtained from optical matrix elements of the linear momentum for interband transitions. The dielectric function of SiNTs is calculated using gradient approximation [8].

Our paper is organized as follows: in Sec. II we describe σ-π Tight-binding model for two dimensional materials like CNT and SiNT, then we employ TB model to obtain optical transition rules and optical properties of SiNTs. In Sec. III, we present results and discussion, and finally in Sec. IV we provide concluding remarks.

Manuscript received June 01, 2016; accepted August 01, 2016
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II. METHODS

A. Nantube structure

The SiNT can viewed as silicene sheet rolled up around a certain vector, which determine nanotube's diameter. The structure of silicene consist of two sub-lattice, A and B, as seen in Fig. 1. In silicene three orbitals, 3s, $3p_x$ and $3p_y$ hybridize in an sp^2configuration and forming σ bonds, whereas the other $3p_z$ orbitals only participate in π bond. The lattice constant length of silicene, a_0 is about 3.82 Å [1, 2]. Notice that the basis vector and Brillouin zone of silicene are similar to that of graphene.

TABLE I
. TIGHT-BINDING PARAMETERS FOR SI SHEET . [1]

parameter	Hopping integral
$(ss\sigma)_1^{AB}$	-2.066
$(sp\sigma)_1^{AB}$	2.1184
$(pp\sigma)_1^{AB}$	3.1866
$(pp\pi)_1^{AB}$	-0.8867

B. Tight-binding model

The TB model has moderate precision and can be combined with the other method to enhance the accuracy. TB model is based on an approximate set of wave functions which are a superposition of isolated atomic orbitals and describes the properties of tightly bound electron in solids.

As a sheet of silicene is rolled up to construct a SiNT, orbitals are hybridized into sp^3 configuration and all orbitals participate in π and σ bonding. So it is necessary to take account all orbitals in our TB model [6]. We consider four orbitals per atom and the Hamiltonian matrix size is four times of Si atoms in the unit cell. The wave functions sub-lattice A/B can be expressed as linear combinations of atomic wave functions as:

$$\left|\psi_{A/B}\,,\alpha,k\right\rangle = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{ik.R_i}\left|R_i,A/B,\alpha\right\rangle \qquad (1)$$

Where = s, p_x, p_y, p_z are atomic orbitals, R_i is a lattice vector of honeycomb lattice, *k* is wavenumber and N is the number of the atomic wave function in the unit cell.

In our TB model we use the first nearest neighbor TB parameters, were taken from previous ab-initio calculations [1]. The TB parameters are given in Table 1.

C. Optical properties

Most of the works on the optical properties of CNTs is based on π-TB model. The selection rules for allowed dipole interband transition discussed by Ajiki [7]. In the same manner, we calculate dielectric function of SiNTs within π-TB model. Then we consider the effect of σ-π-hybridization in our TB model and inclusion of the curvature effect. By assuming that the wave vector of the optical field is negligible compared to the electronic wave vector, the dipole operator $\left\langle\psi^c\left|\frac{E.p}{m_e}\right|\psi^v\right\rangle$ is evaluated within gradient approximation to $\left\langle\psi^c\left|\frac{\partial H}{\partial k}\right|\psi^v\right\rangle$, where ψ^c and ψ^v are conduction and valance wave functions, p is linear momentum operator and m_e is electron mass [8].

III. RESULT AND DISCUSSION

The TB model is used for electronic band structure and dielectric function calculation of some small-radius SiNTs and CNTs. The effect of curvature on band structure and optical transition energies have been investigated based on σ-π-TB calculation. Fig. 2(a) shows the electronic band structure of SiNT (8, 0) based on density function theory (DTF) calculations reported in [1].compared to our π-TB calculations in Fig. 2(b).we find good agreement between them.

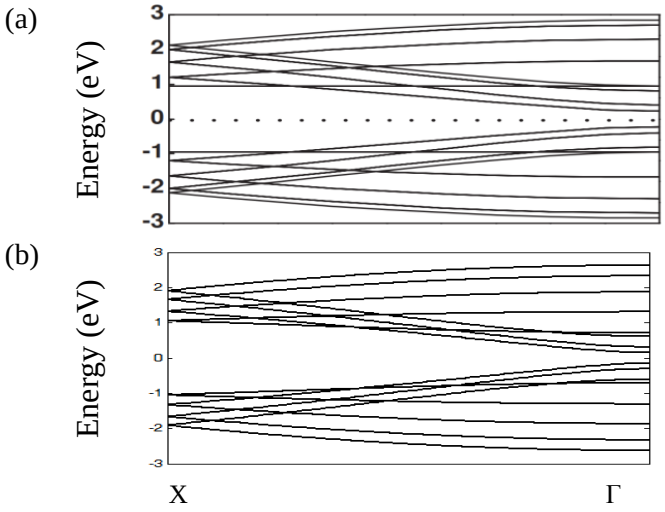

FIG.2. BAND STRUCTURE OF SINT (8, 0) OBTAINED FROM A) DFT CALCULATON IN [1] AND B) OUR TIGHT-BINDING MODEL.

As shown in Fig. 3, the calculated electronic band structure for SiNT (4, 0) within π-TB model without curvature effect, exhibits major differences from that of π-TB and σ-π-TB model with inclusion of the curvature effect. Fig. 3(a) shows the π-bands of SiNT (4, 0) in sp^2 configuration. Fig.3 (b) shows only the π-bands of SiNT (4, 0) in sp^2 configuration and the curvature effect have been considered. Obviously curvature effect alters the band structure of simple sp^2 configuration. Curvature induced σ-band and π-band mixing is presented in Fig. 3(c).

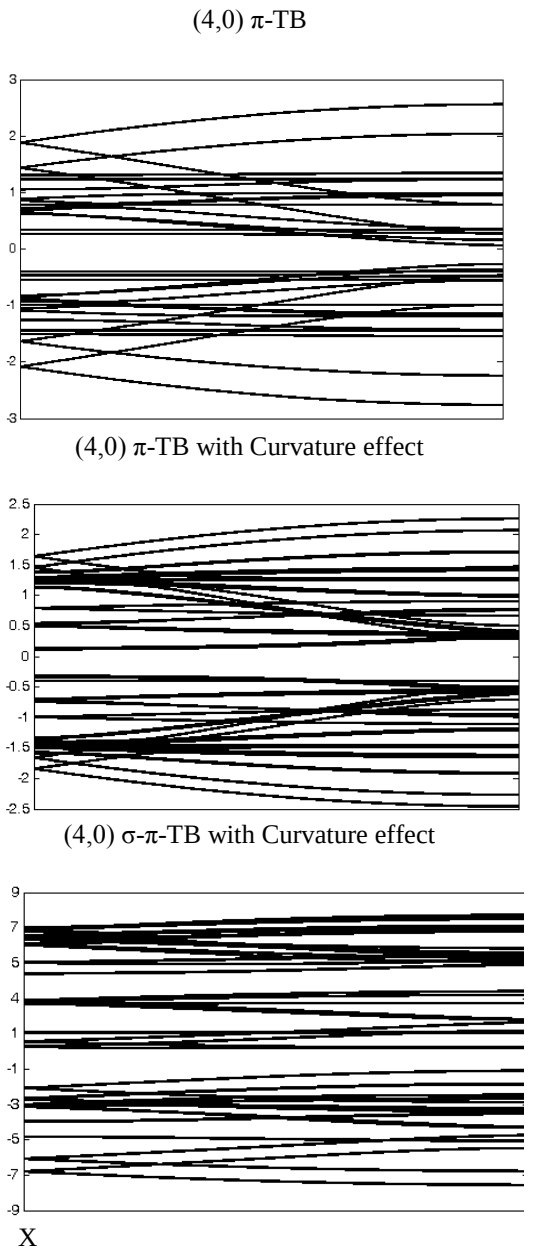

Fig. 3. Band structure of SiNT (4,0) obtained from our TB model.

Curvature-induced rehybridization has stronger effects in thinner SiNTs and CNTs (below 1nm) and decreases for thicker tubes. As shown in Fig. 4(a), SiNT (3,0) seems to be metallic (zero-gap semiconductor) in π-TB model, but the curvature effect, opens the gap. The effect of curvature on the energy gap, plotted versus SiNT radius in Fig. 4(b) and compared with simple π-TB model.

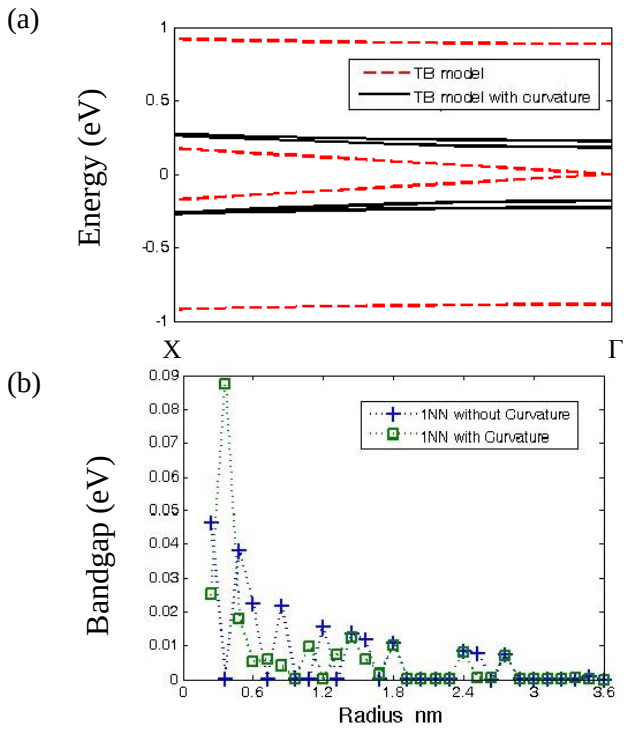

Fig. 4. Comparison of Energy gap with and without curvature effect. (a) SiNT (3, 0). (b) as a function of tube radius.

For better comparison, the deviation of band gap energy of π-TB model from σ-π-TB model, plotted in Fig. 5 as a function of SiNTs radius.

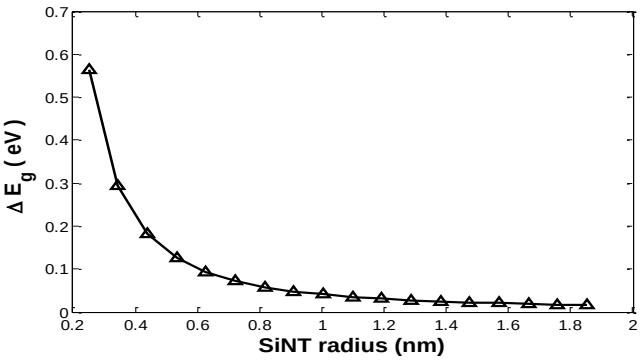

Fig. 5. Deviation of energy gap of the simple TB model as compared to band structure calculated with σ-π-TB model as a function of nanotube radius for SiNTs.

In the presence of electromagnetic illumination on nanotube, the electrons are excited from occupied valance bands into the empty conduction bands. The optical absorption spectra is derived from the imaginary part of dielectric function and plotted for some different radius. The dielectric function calculated within π-TB model and σ-π-TB model, and the effect of curvature on the dielectric function are investigated. The results are shown in Fig. 6. As seen in Fig. 6 (a), the dielectric function of SiNT (4,0) shows two peaks, the lowest peak located below 1*eV* energy and the other peak at about 1.8 *eV*. The results show that the curvature strongly

affects the lower peak. In the case of SiNT (4, 0), inclusion of the curvature effect, causes a red shift in absorption spectra, but in general case, there is no rule.

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Fig. 6 (b) shows the dielectric function of three SiNTs, (3,0), (4,0) and (5,0) within σ-π-TB model and inclusion of the curvature effect. In the case of SiNT (3, 0), which thought to zero gap semiconductor, curvature effect opens the gap and blue shift occurs in the dielectric function. The presence of two close peaks in the curves can be explained with the curvature-induced σ-π-rehybridization.

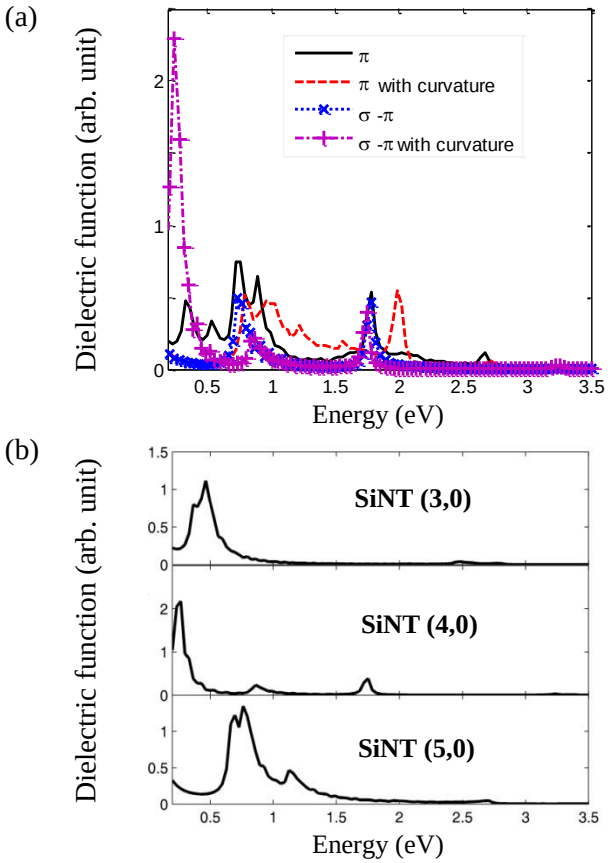

Fig. 6. The dielectric function of SiTNs within TB model. (a) dielectric function of SiNT (4,0) in π-TB, σ-π-TB model with and without curvature effect. (b) the dielectric function of (3,0), (4,0) and (5,0).

Finally, we have used our TB model to study the (n, 0) SiNTs and CNTs, and their band gaps are given in table 2 and table 3 for SiNTs and CNTs, respectively. The results obtained by Durgun et al [9] for SiNTs and by Cao et al [10] for CNTs are also given for comparison. In table 2 and table 3, TB_1, TB_2 and TB_3 are π-TB without curvature effects, π-TB with curvature effects and σ-π hybridized TB model, respectively. The band gap of (9, 0) and (12, 0) SiNT seems to be zero, based on simple π-TB. Inclusion of the curvature effects with our sp^3 TB model, shows that (9, 0) and (12, 0) SiNT have a gap opening, at about 210 meV and 130 meV (see table 2), which is consistent with the result given in [9] performed based on density function theory (DFT) calculation. In table 3, the band gap of three (7, 0), (8, 0) and (9,0) CNTs are shown and compared to the results given in [10] on the basis of sp^3 TB model (TB_4) and DFT calculation. The band gap calculation based on our TB_3 model, are a little larger than those obtained with the DFT.

IV. Conclusion

In this paper, the effect of structural curvature on the electronic band structure and optical properties of small radius SiNTs, band structure and energy gap of SiNTs are studied within π-TB model and σ-π hybridized TB model. It is shown that the calculated electronic band structure and the dielectric function of small radius SiNTs exhibit large differences with the simple π-TB model. In small radius SiNTs, the small atomic rearrangement has a major influence on the electronic structure of SiNTs, due to the curvature-assisted hybridization of π-type and σ-type orbitals. As the radius of SiNTs increase beyond 1nm, the bond angle of π-type and σ-type orbitals increase. So the interaction of orbitals decrease very fast and the sp^3 configuration of orbitals is more like sp^2 configuration. The derived dielectric function of small radius SiNTs differ from sp^2 configuration π-TB model due to the curvature effect. The difference optimized and non-optimized TB model, decrease with the increase of SiNT radius and can be ignored for large nanotube radius.

TABLE II
THE BANDGAP OF THE (N,0) SINTS.

	Our sp^3 TB model Energy gap (eV)			The DFT Energy gap (eV) [9].
Tubes	TB_1	TB_2	TB_3	DFT
(9,0)	0	0.55	0.21	0.05
(12,0)	0	0.45	0.13	0.096
(14,0)	0.43	0.49	0.28	0.165

TABLE III
THE BANDGAP OF THE (N,0) CNTS.

	Our sp^3 TB model Energy gap (eV)			The sp^3 TB model Energy gap (eV) [10].	The DFT Energy gap (eV) [10].
Tubes	TB_1	TB_2	TB_3	TB4	DFT
(7,0)	1.37	0.096	0.998	1.0463	0.09
(8,0)	1.29	1.34	1.23	1.1866	0.62
(9,0)	0	0.156	0.083	0.0754	0.17

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