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Citation: *J. Chem. Phys.* **137**, 214702 (2012); doi: 10.1063/1.4767389

View online: <http://dx.doi.org/10.1063/1.4767389>

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Structural stability and electronic properties of sp^3 type silicon nanotubes

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(Received 8 June 2012; accepted 16 October 2012; published online 3 December 2012)

A density functional theory study of the structural and electronic properties and relative stability of narrow hydrogen passivated sp^3 silicon nanotubes of different growth orientations is presented. All nanotubes studied and their corresponding wire structures are found to be meta-stable with the wires being more energetically stable. Silicon nanotubes show a dramatic bandgap increase of up to 68% with respect to the corresponding wires. Furthermore, a direct relation between the bandgap of the system and the molar fraction of the passivating hydrogen contents is found. These results suggest that by careful control over their crystallographic growth orientation, dimensions, and chemical composition it should be possible to design and fabricate silicon nanotubes with desired electronic properties. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4767389>]

INTRODUCTION

Silicon nanowires (SiNWs) and nanotubes (SiNTs) have recently appeared as promising candidates for basic components of future nano-devices.¹ Their low dimensionality leads to quantum confinement effects which can be harnessed to control their electronic properties.^{2–7} This opens the way for many possible applications including electronic components such as nanoscale field-effect transistors,^{8,9} high sensitivity chemical and biological detectors,^{10–14} and optoelectronic devices.^{15,16}

In recent years, several methods have been developed for SiNWs fabrication including laser ablation,^{17,18} metal-catalytic vapor-liquid-solid methods,^{19–21} electron beam evaporation,²² oxide-assisted catalyst-free approaches,^{23–25} as well as solution based techniques.²⁶ These methods yield wires with different crystallographic orientations and dimensions scaling down to diameters which are in the single nanometer regime.^{17,19,23,26} The obtained wires often consist of an oxide layer which can be removed and replaced by hydrogen termination.²³ Alternatively, hydrogen passivation can be achieved by using molecular hydrogen as a carrier gas in the chemical vapor deposition process.²¹ Many efforts have been further invested in the synthesis of SiNTs;^{27–30} however, only recently techniques enabling the robust synthesis of crystalline SiNTs have emerged. Ben-Ishai and Patolsky³¹ have reported the formation of robust and hollow single-crystalline silicon nanotubes, with uniform and well-controlled inner diameters, ranging from as small as 1.5 up to 500 nm, and controllable wall thickness and chemical passivation. Quitoriano *et al.*³² have also reported single-crystalline SiNTs growth using vapor-liquid-solid techniques.

Several theoretical studies have investigated the structural and electronic properties of SiNWs as a function of crystallographic growth orientations, radial dimensions, chemical doping, surface passivation, and surface

reconstruction.^{2–5,33–43} To this end, different computational methods have been utilized to treat the electronic structure of the various systems including semi-empirical methods,⁴² density functional based tight binding calculations,^{36,41} density functional theory (DFT) calculations,^{4–7,39,42,43} as well as many-body perturbation theory within the GW approach.³⁹ These studies have indicated that for SiNWs with diameters smaller than 4 nm quantum size effects become dominant. As can be expected, decreasing the diameter of the NW was found to result in an increase of the material bandgap accompanied, in some systems, by a transition from an indirect to a direct gap.^{4,5,44}

Theoretical studies of SiNTs have recently emerged focusing on single-walled sp^2 type silicone analogues of carbon nanotubes (CNTs).^{45–49} The electronic structure of these systems was found to be chirality dependent with transition from metallic to semi-conducting depending on the chiral vector orientation similar to the case of their carbon counterparts.^{45,47} It was further shown that a slightly distorted structure of single-walled SiNTs where the Si–Si bonds have a somewhat enhanced sp^3 character is more stable than the pristine CNT-like structure.^{47,50–52} Controlling the structural and electronic properties of sp^2 SiNTs via different hydrogenation schemes has also been explored.⁵² Beyond the sp^2 model, prismane-like⁵³ SiNTs constructed from stacked and covalently bonded square, pentagonal, and hexagonal silicon rings have been investigated predicting a metallic character.⁵⁴

In the present study, inspired by the work of Patolsky *et al.*³¹ and Quitoriano *et al.*,³² we present a first-principles study of the structural stability and electronic properties of hydrogen passivated narrow sp^3 type SiNTs with a wall thickness of a few atomic layers. We find that all SiNTs and SiNWs considered are meta-stable structures with the SiNWs being more stable than the corresponding SiNTs. Furthermore, the formation of an inner cavity results in a significant bandgap increase of the SiNTs often preserving the direct/indirect character of the bandgap. We also identify a direct relation between the hydrogen molar fraction and both the structural

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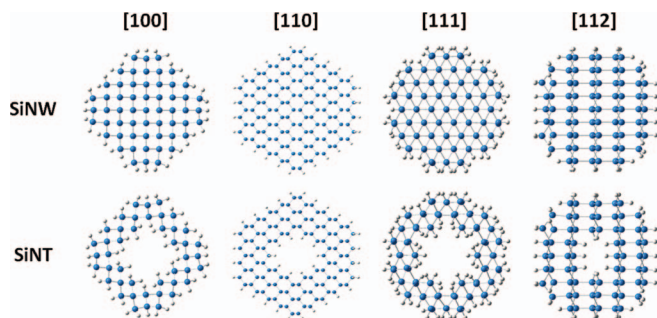


FIG. 1. Schematic representation of the various SiNWs and SiNTs which were carved out of bulk silicon along the [100], [110], [111], and [112] crystallographic orientations.

stability and the bandgap of the different systems suggesting that by careful design of their structural parameters and chemical composition it should be possible to fabricate SiNTs with diverse electronic properties.

METHODS

We consider a set of SiNWs and SiNTs of different crystallographic orientations including the [100], [110], [111], and [112] directions (see Fig. 1). The SiNWs unit cells have been carved out of bulk silicon and passivated to avoid dangling bonds using hydrogen atoms. To obtain the corresponding SiNTs, the inner core of the SiNWs has been further removed and the resulting new dangling bonds have been passivated using more hydrogen atoms.

To study the structural and electronic properties of the different systems considered DFT calculations have been performed using the GAUSSIAN 09 suite of programs.⁵⁵ Three different functional approximations have been used including the local density approximation (LDA),^{56,57} the PBE realization of the generalized gradient approximation,⁵⁸ and the screened exchange hybrid density functional, HSE.^{59–62} The latter functional has been tested for a wide set of materials and was shown to accurately reproduce experimental structural parameters and bandgaps⁶³ including the lattice constants and direct and indirect bandgaps of cubic diamond-like bulk silicon.⁶⁴

Initial geometry optimizations have been performed using the LDA with the 3-21G atomic centered Gaussian basis set. Further geometry relaxation has been performed for each functional approximation separately using the double- ζ polar-

ized 6-31G** basis set.⁶⁵ Convergence tests of the electronic structure calculations with respect to the size of the basis set have been performed for the SiNT [100] system showing convergence of the calculated LDA, PBE, and HSE bandgaps to within 1.4%, 0.21%, and 0.36%, respectively.⁶⁶ The radial dimensions of the different SiNTs and SiNWs are summarized in Table I. Coordinates of the fully relaxed structures can be found in the supplementary material.⁶⁶

RESULTS AND DISCUSSION

We start by analyzing the relative structural stability of the different NWs and NTs shown in Fig. 1. As the SiNWs and SiNTs structures have different chemical compositions the cohesive energy per atom does not provide a suitable measure for the comparison of their relative stabilities. Therefore, we define the Gibbs free energy of formation (δG) for SiNT and SiNW as^{5,36,46,67}

$$\delta G(\chi_{\text{Si}}, \chi_{\text{H}}) = E(\chi_{\text{Si}}, \chi_{\text{H}}) - \chi_{\text{Si}}\mu_{\text{Si}} - \chi_{\text{H}}\mu_{\text{H}}, \quad (1)$$

where $E(\chi_{\text{Si}}, \chi_{\text{H}})$ is the cohesive energy per atom of a SiNW/T of a given composition, χ_i is the molar fraction of atom i ($i = \text{Si}, \text{H}$) in the system with $\sum_i \chi_i = 1$, and μ_i is the chemical potential of element i . Here, we choose μ_{H} as the binding energy per atom of the ground state of the hydrogen molecule and μ_{Si} as the cohesive energy per atom of bulk silicon. This definition allows for a direct energetic stability comparison between SiNWs/NTs with different chemical compositions, where negative values represent stable structures with respect to the constituents. It should be stressed that this treatment gives a qualitative measure of the relative stability while neglecting thermal and substrate effects and zero point energy corrections.³⁶ We note that the temperature dependence of the formation energy of several SiNWs was previously studied showing that while the absolute effect of temperature on the formation energy can be large its effect for SiNWs grown along different crystallographic orientations is similar and thus the stability ordering of different structures up to ~ 800 K does not change.⁵

Figure 2 compares the calculated δG values for the different SiNWs and SiNTs studied. For all functional approximations considered all systems present moderate positive values suggesting that the different structures are meta-stable (see inset). This observation is consistent with the results of Aradi *et al.*³⁶ and Vo *et al.*⁵ using a similar method to evaluate the relative stability of other silicon nanowires. The PBE results

TABLE I. Average radial dimensions of the SiNWs and SiNTs structures optimized using the LDA, PBE, and HSE exchange-correlation functional approximations and the 6-31G** basis set.

Growth orientation	Diameter (nm)								
	SiNW			Outer SiNT			Inner SiNT		
	LDA	PBE	HSE	LDA	PBE	HSE	LDA	PBE	HSE
[100]	1.50	1.50	1.51	1.50	1.54	1.53	0.90	0.94	0.93
[110]	2.64	2.67	2.65	2.63	2.66	2.65	1.37	1.39	1.38
[111]	1.54	1.56	1.55	1.55	1.57	1.56	1.34	1.38	1.37
[112]	1.55	1.56	1.56	1.57	1.59	1.58	1.15	1.16	1.16

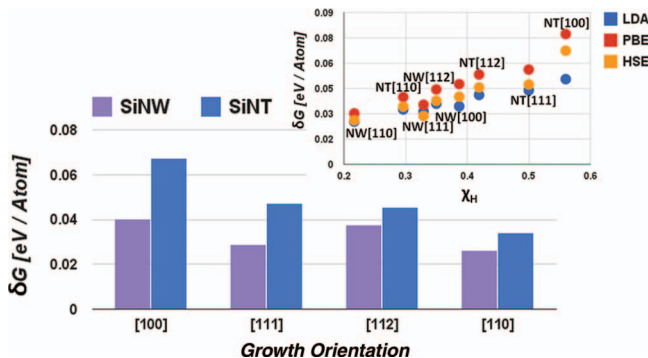


FIG. 2. δG as calculated using Eq. (1) for the different SiNWs and SiNTs considered at the HSE/6-31G** level of theory. A comparative view of these results and similar results obtained using the LDA and PBE functional approximations can be found in the supplementary material.⁶⁶ Inset: δG as a function of the hydrogen molar fraction calculated using the LDA, PBE, and HSE exchange correlation functional approximations and the 6-31G** atomic centered Gaussian basis set.

tend to predict slightly higher δG values than the LDA and HSE functionals. We note that, for the [110] and [112] NWs our calculated δG values are considerably smaller than the values calculated by Aradi *et al.*³⁶ for narrower systems indicating that the stability of the wires should increase with increasing diameter. Nevertheless, this comparison is limited by the fact that the values reported by Aradi *et al.* are normalized to the number of silicon atoms, whereas we normalize our results to the total number of atoms. When comparing the NWs to the NTs we find that for a given growth orientation and radius the SiNWs are more stable than the corresponding SiNTs. We attribute this behavior to the increased surface area of the NTs enhancing surface effects that reduce the stability of the system. In order to support this claim, we plot in the inset of Fig. 2 the δG values of the different systems as a function of the molar fraction of the hydrogen content, χ_H . As the surface is passivated with hydrogen atoms this parameter serves as a measure for the surface to volume ratio. It is clearly evident that as the hydrogen molar fraction reduces and the systems approach bulk silicon (both in terms of chemical composition and in terms of surface effects) δG decreases thus indicating an increased stability.

Apart from the surface to volume ratio and the overall chemical composition, other factors such as surface reconstruction and type of passivation as well as steric considerations may influence the relative stability of the different structures. The stability analysis presented in Fig. 2 suggests that among all NWs and NTs studied the [110] growth orientation is the most stable followed by the [111] structures. This is in contrast to the findings of Vo *et al.*⁵ suggesting that for temperatures lower than 822 K the [111] NW is the most stable structure followed by the [110] and the [100] directions. These differences may result from two factors: (i) The calculations of Vo *et al.* included the zero point energy. As the differences between the δG values that we obtained for the [111] and [110] NWs are very small (0.006 eV/atom for the LDA functional used in the study of Vo *et al.*) zero point energy may change the calculated stability order; (ii) as the current study focuses on the differences between the NWs and NTs, different system diameters were chosen for structures of

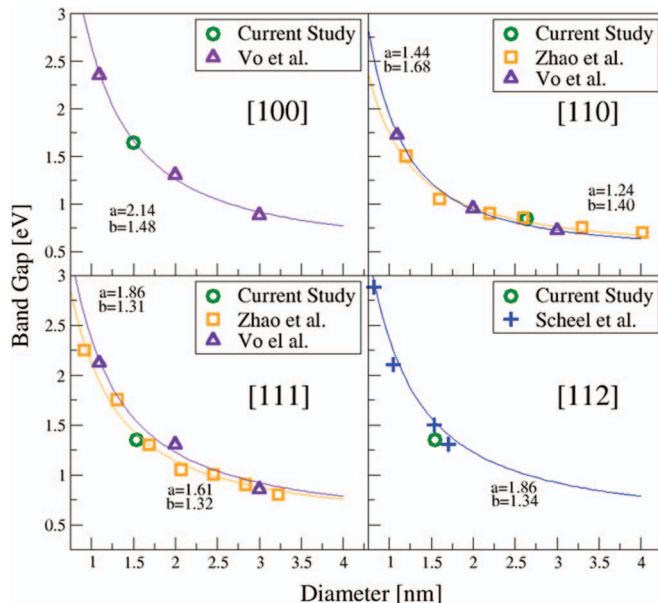


FIG. 3. Comparison between LDA bandgaps obtained for SiNWs of different growth orientations in the present study and reference values. Full lines are added as guide to the eye using a fitting to the following formula $E_{\text{gap}}(D) = E_{\text{gap/bulk}} + aD^{-b}$, where $E_{\text{gap/bulk}}$ is the bulk silicon bandgap calculated at the same level of theory, D is the diameter of the SiNW, and a and b are fitting parameters. The obtained optimal fitting parameters are presented next to their corresponding fitting curve.

different growth orientations. Therefore, the effect of system diameter on the relative stability is not taken into account and thus the direct comparison between the relative stabilities of the different NWs and NTs studied herein is limited to the studied structures alone and is not of general nature.

We now turn to discuss the electronic structure of the different systems considered. First, in order to check the validity of our NWs and NTs atomistic models we compare the calculated bandgaps to previously reported results.^{3-7,36,40} Figure 3 presents NW's bandgaps obtained using the LDA functional here and in previous studies as a function of system diameter and crystallographic growth direction. As can be seen, our calculated bandgaps compare well to previously reported results. Similar agreement was obtained for the GGA and HSE calculated bandgaps⁶⁶ indicating the reliability of our calculations. Furthermore, our HSE results for the bandgap of the [110] SiNW of diameter 2.65 nm (1.57 eV) and the [112] SiNW of diameter 1.56 nm (2.11 eV) compare well with the experimental measurements of Ma *et al.* for a [110] SiNW of diameter of 3 nm (1.5 eV) and a [112] SiNW of diameter of 2 nm (2.28 eV), respectively.²³

Having established the validity of our atomistic models and computational methodology we now focus on the effect of the inner cavity on the electronic properties of SiNTs. Figure 4 compares the bandgaps of the different SiNWs considered to those of the corresponding SiNTs. As can be clearly seen, for all growth orientations studied a dramatic increase of the bandgap is evident when going from the NW to the NT configuration regardless of the functional approximations utilized. Specifically, for the HSE functional, which is expected to produce the most reliable bandgap values, an increase of 17%, 26%, 61%, and 68% was obtained for the [110], [112],

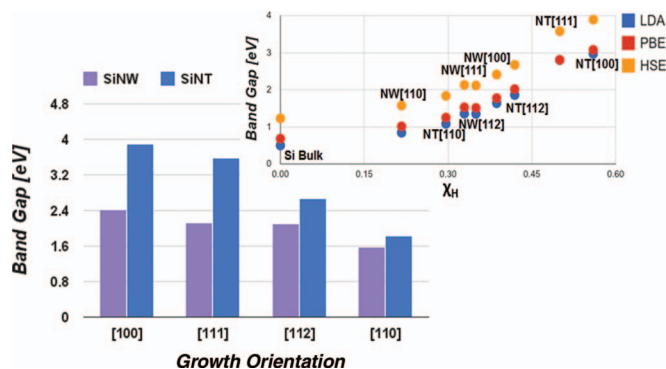


FIG. 4. Bandgaps of SiNWs of different growth orientations and their corresponding SiNTs obtained at the HSE/6-31G** level of theory. A comparative view of these results and similar results obtained using the LDA and PBE functional approximations can be found in the supplementary material.⁶⁶ Inset: Bandgap as a function of the hydrogen molar fraction calculated using the LDA, PBE, and HSE exchange correlation functional approximations and the 6-31G** atomic centered Gaussian basis set.

[100], and [111] crystallographic orientation, respectively. To better understand the surface and chemical composition effects on the electronic structure of SiNWs and SiNTs we plot (see inset of Fig. 4) the bandgaps of the different systems considered as a function of the hydrogen molar fraction. This parameter encompasses a complex combination of several chemical and physical factors dictating the overall electronic structure which include surface reconstruction, surface states, chemical composition, surface to volume ratio, and system dimensions. Interestingly, despite this intricate balance of different contributions a direct relation between the bandgap and the hydrogen content is clearly observed. At the limit of zero hydrogen content the HSE bulk silicon bandgap of 1.22 eV is recovered. As the hydrogen content is increased the bandgap increases monotonously up to a value of ~ 4 eV. These results suggest that by careful control over their crystallographic growth orientation, dimensions, and chemical composition it should be possible to fabricate SiNTs with predesigned desired electronic properties.

In order to obtain a more complete picture of these effects the full band-structure of the different systems has been calculated. In Fig. 5 a comparative view of the band-structures and density of states of the different NWs and their corresponding NTs is presented. As can be seen, the electronic bands of the NTs are generally less dispersive than the corresponding NWs bands and the bandgap widening results from a simultaneous energetic increase of the conduction band minimum (CBM) and decrease of the valence band maximum (VBM). These effects may be attributed to quantum confinement leading to orbital localization in the NTs systems. To verify this we plot in Fig. 6 the VBM and CBM orbitals of the [110] SiNW and SiNT. It is clearly evident that for the SiNW systems both orbitals span the whole core region, whereas the SiNT orbitals are localized at the remaining shell. Interestingly, despite the appearance of the SiNT cavity the orbitals preserve their general character obtained for the corresponding SiNW both in terms of symmetry (notice the axial symmetry of the CBM orbitals in both systems, for example) and in terms of nodal structure (the CBM orbitals form continu-

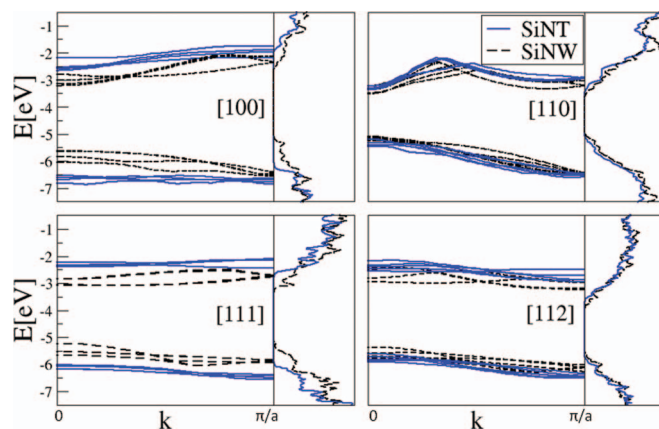


FIG. 5. Band structures and density of states of SiNWs (dashed black lines) with growth orientations of [100], [110], [111], and [112] and their corresponding SiNTs (full blue lines) as calculated at the HSE/6-31G** level of theory. For clarity, only ten bands around the Fermi energy are presented.

ous surfaces in both systems, whereas the VBM orbitals are more fluctuating in sign). A similar behavior was observed for systems constructed along the other growth orientations considered.⁶⁶

Finally, we note that according to our HSE calculations the [100], [110], and [111] NWs are direct bandgap semiconductors while the [112] NW has an indirect gap. Interestingly, all but the [111] NTs have the same type of bandgap as the corresponding NWs. The [111] NT changes from a direct to an indirect gap. This further suggests that not only the value of the bandgap but also its character may be controlled by careful tailoring of the detailed chemical composition and overall structure of the system.

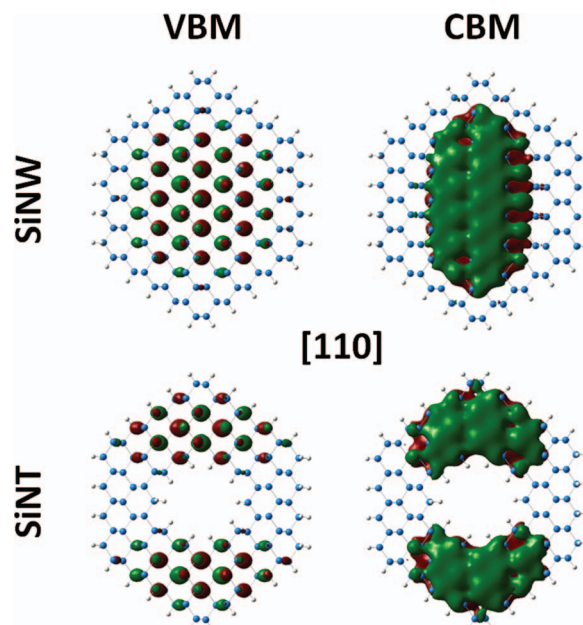


FIG. 6. VBM (left panels) and CBM (right panels) orbitals of the [110] SiNW (upper panels) and SiNT (lower panels). Obtained at the HSE/6-31G** level of theory.

SUMMARY

In this paper, we presented a theoretical study of the structural and electronic properties of hydrogen passivated narrow sp^3 type SiNTs bearing a wall thickness of a few atomic layers. Four SiNT models with growth orientations along the [100], [110], [111], and [112] bulk silicon crystallographic directions were considered. Their energetic stability and electronic properties were compared to the corresponding SiNWs. All SiNTs and SiNWs considered were found to be meta-stable structures. Furthermore, for all growth orientations studied the SiNTs were found to be less stable than the corresponding SiNWs. When comparing the bandgaps of SiNWs and SiNTs of the same growth orientation, the formation of an inner cavity in the wires was found to be accompanied by a significant bandgap increase in the resulting nanotubes. The overall increase in bandgap was found to be 17%, 26%, 61%, and 68% for the [110], [112], [100], and [111] crystallographic orientations, respectively. We have found a direct relation between the hydrogen molar fraction and both the structural stabilities and the bandgaps of the different systems. Generally speaking, as the hydrogen contents decrease the structural stability increases and the bandgap decreases indicating that the SiNWs and SiNTs approach the bulk limit. The [100], [110], and [111] NWs were found to be direct bandgap semiconductors, while the [112] NW bandgap is of indirect character. Interestingly, all but the [111] NT keep the bandgap type of the corresponding NWs. Our results suggest that by careful control over their crystallographic growth orientation, dimensions, and chemical composition it should be possible to fabricate SiNTs with predesigned desired electronic properties.

ACKNOWLEDGMENTS

The authors would like to thank Professor Fernando Patolsky for helpful discussions. This work was supported by the Israel Science Foundation under Grant No. 1313/08, the Center for Nanoscience and Nanotechnology at Tel Aviv University, and the Lise Meitner-Minerva Center for Computational Quantum Chemistry.

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relaxed structures; a comparison between the relative stability results obtained using the three functional approximations considered; GGA and HSE calculations results; a comparison between the bandgap values obtained using the three functional approximations considered; and a graphical representation of the VBM and CBM orbitals of the other SiNWs and SiNTs considered in the present study.

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