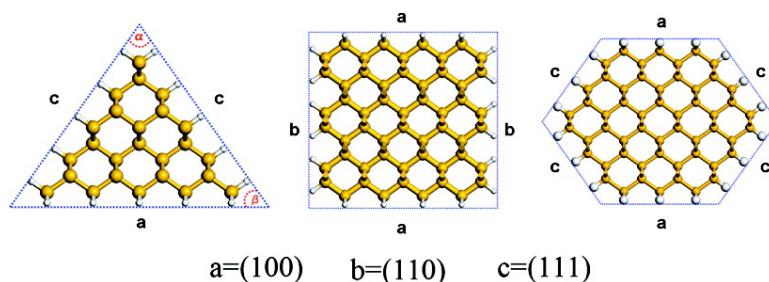


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A Universal Expression of Band Gap for Silicon Nanowires of Different Cross-Section Geometries

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ABSTRACT

We use the first-principles tight binding method to investigate the electronic structure and band gap of [110] oriented hydrogen-passivated silicon nanowires (SiNWs) of different cross-sectional geometries. A quantitative universal band gap expression for [110] SiNWs is obtained, which shows a linear dependence of band gap on the surface area to volume ratio (SVR), and it is independent of the cross-sectional geometry. In contrast to the ambiguity in the definition of the SiNW transverse dimension, using of SVR has the advantage to readily predict band gap for SiNWs with any cross-sectional shapes. Our results demonstrate that the SVR is an ideal “gauge” to describe the band gap of SiNWs.

Silicon nanowires (SiNWs) are one of the promising building blocks for future nanoscale devices due to their ideal interface compatibility with Si-based electronic technology. Their fascinating potential applications such as biosensor,^{1,2} thermoelectric materials,^{3–6} and power devices⁷ have attracted broad interests in recently years. Extensive investigations have been carried out on the synthesis, properties, and applications of SiNWs. Experimental technology has been developed to control the growth of SiNWs not only in various growth orientations but also with various shapes of transverse cross sections including rectangle (square), hexagon (rough circle), and triangle.^{8–12} A large number of theoretical and experimental works have been done to explore the effect of chemical passivation, surface reconstruction, and growth orientations on electronic structures.^{9,13–18} However, compared with the study of these impacts on electronic properties of SiNWs, much less has been done on the impacts of cross-sectional geometries.

The surface area to volume ratio (SVR) increases as the system scales down. It thus plays a more and more important role when the device becomes smaller and smaller. For

example, materials with high SVR react at much faster rates than monolithic materials. It has also been shown that SVR also affects the physical properties of nano materials remarkably.^{18–21} However, the research so far has been qualitative.

In this Letter, we study *quantitatively and systematically* the impact of SVR on electron band structure of [110] oriented, hydrogen passivated SiNWs. The impacts of cross-sectional shapes, including triangular-, rectangular-, and hexagonal-SiNWs are investigated. For simplicity, they are named as tri-SiNWs, rect-SiNWs, and hex-SiNWs, respectively. We find, for the first time, a general expression for band gaps of SiNWs, which shows linear dependence on SVR, and it is independent of cross-sectional shape.

We focus on SiNWs oriented along the [110] direction because small diameter SiNWs have been observed to grow experimentally mostly along this direction and it has been demonstrated that [110] is the optimum orientation that offers the highest ON-current and smallest intrinsic device delay for the same OFF-current for SiNW transistors.^{17,22} Moreover, [110] wires seem to be the most sensitive candidate for the nanowires sensor because the band gaps of [110] SiNWs are the smallest among those of the [100], [112], and [111] wires of the same diameter.¹⁰ Figure 1 shows the schematic pictures of the SiNWs of different cross section, the transverse size, D is between 1.4 and 7.2 nm. Here, D is defined as the largest distance between the terminating hydrogen atoms in the cross section plane. D , the number of atoms per supercell (N), and cross-sectional area (A) of

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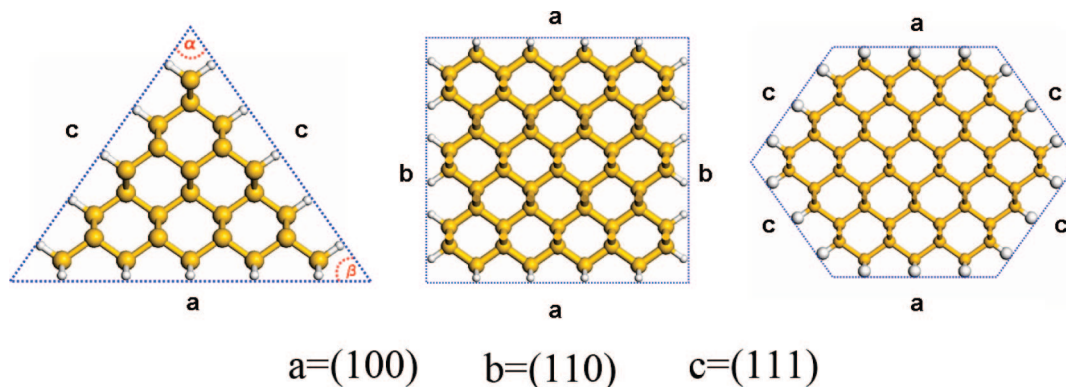


Figure 1. Schematic diagrams of the SiNWs used in our calculations. From left to right, they are the tri-, rect-, and hex-SiNWs. In tri-SiNW, the angle α is 70.6° and β is 54.7° , where this structure is in accordance with the nanowires studied in the experimental work in ref 23. The blue dotted lines represent the virtual cages used to construct the SiNWs. Si and H atoms are represented in yellow and white, respectively.

Table 1. Transverse Dimension D (in nm), Cross Section Area A (in nm^2), and the Number of Atoms N in the Supercell in Our Calculations^a

tri-SiNW			rect-SiNW			hex-SiNW		
N	D (nm)	A (nm^2)	N	D (nm)	A (nm^2)	N	D (nm)	A (nm^2)
90	1.79	0.83	96	1.66	1.09	80	1.40	1.05
154	2.56	1.88	164	2.28	2.29	156	2.17	2.50
234	3.32	3.34	288	3.22	4.69	256	2.94	4.58
330	4.09	5.21	396	3.85	6.93	380	3.71	7.29
442	4.86	7.51	520	4.50	9.59	528	4.48	10.63
570	5.63	10.22	724	5.43	14.08	700	5.24	14.58
714	6.40	13.35	888	6.08	17.78	896	6.01	19.17
874	7.16	16.89						

^a The dimension D is defined as the largest distance between the terminating hydrogen atoms in the cross section plane.

the SiNWs are summarized in Table 1. The transverse size, D , of SiNWs can be controlled experimentally from 1.3 to 7 nm⁹ so the SiNWs we explore here are within the range of the experimental observation.

The tri-, rect-, and hex-SiNWs are the realistic crystalline structures of SiNWs, which have been studied widely.^{17–27} For each NW, the atomic structure is initially constructed from diamond structured bulk silicon. The structure of the silicon core of the NWs is constructed by selecting all the Si atoms that fall within a virtual cage placed in bulk silicon while silicon atoms falling outside this virtual cage are removed and the surface dangling bonds were terminated with hydrogen atoms placed at a standard bond length of 1.48 Å that eliminate artificial dangling bonds. This Si–H bond length corresponds to that in SiH₄ molecule. Because of the small dimensions, the surface reconstruction will affect the band structure.¹⁷ Here, we concentrate on the dependence of band structure on the size and transverse cross sectional shapes. Therefore, no surface reconstruction is considered in this study. This H-termination model without surface reconstruction is widely used to study the size effect on electronic structure of SiNWs.^{15,16} The dimensions and cross-sectional shapes of the NWs are varied by changing the virtual cages. The initial geometries are then relaxed to their closest minimum total energy. A supercell approach is adopted where each wire is periodically repeated along the growth direction [110]. The size of the supercells in the transverse plane is so large as to avoid interaction between

the SiNW and its images in neighboring cells (>15 Å from surface to surface). Previous calculations by first principles have been performed to study the electronic structure of SiNWs with diameters less than 3.4 nm.^{17,18,21} However, the diameters of the wires considered in these studies were too small to study systematically the size effects on band gap. To investigate the electronic properties of SiNWs with diameter up to 7 nm, the density functional derived tight-binding method (DFTB)^{28,29} is used. The DFTB is based on the expansion of the Kohn–Sham density functional in the local density approximation (LDA) to second order over the density fluctuations around a suitable electron density. In contrast to the tight-binding (TB) method, the one- and two-center matrix elements of the associated Hamiltonian are calculated in an explicit minimal valence basis. The repulsive energy part is approximated by universal pair potentials, which are fitted using the data of self-consistent-field LDA calculations. The DFTB has a minimal number of input parameters and retain the efficiency of TB approaches. In contrast to the conventional density functional theory (DFT) methods, the DFTB has higher computational efficiency, which means that the DFTB allows the simulation of bigger systems than conventional DFT at a reasonable computational time and achieve similar accuracy. This DFTB scheme has been used to calculate structure and band gap of SiNWs^{18,21} and fullerene³⁰ successfully. In this work, the structural relaxation is performed using a conjugate gradient method. The atomic force tolerance of 3×10^{-4} eV/Å is applied. Self-consistent charge tolerance is 10^{-5} au. In assessing the accuracy of the computational method, we perform calculations for the Si–Si bond length and band gap on bulk silicon. The calculated Si–Si bond length and band gap for bulk silicon are 2.30 Å and 1.29 eV, respectively, which are close to the experimental values (2.35 Å and 1.17 eV).³¹ In contrast to the underestimated band gaps (up to 0.6 eV) predicted by commonly used DFT methods,¹⁶ the band gap calculated by DFTB is very close to the experimental value of 1.17 eV. And as all the Si atoms in SiNWs remain in a closed shell configuration with four nearest neighbors similar to the bulk

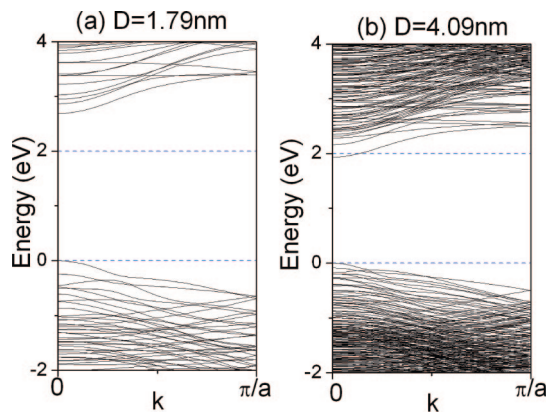


Figure 2. Energy band structure for tri-SiNWs with transverse dimension of (a) $D = 1.79$ nm and (b) $D = 4.09$ nm. The valence band maximum has been shifted to zero. The blue dotted lines are drawn to guide the eyes.

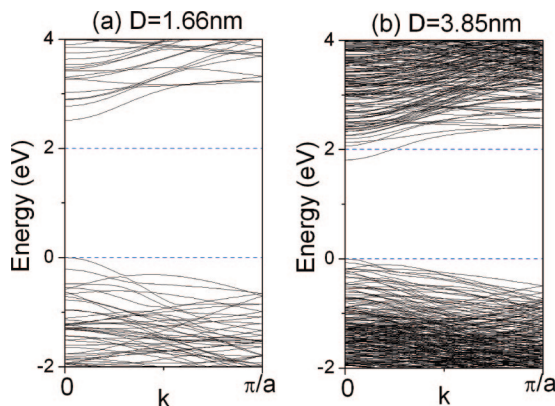


Figure 3. Energy band structure for rect-SiNWs with transverse dimension of (a) $D = 1.66$ nm and (b) $D = 3.85$ nm. The valence band maximum has been shifted to zero. The blue dotted lines are drawn to guide the eyes.

structure, we anticipate that the DFTB calculations will predict the stable nanowire structures to a similar level of accuracy to that of the bulk structure.

After the optimized structures for these SiNWs are obtained, we figure out the band structures for the SiNWs. In Figures 2–4, the electron band structures of NWs with different cross sections are compared. The band structures are shown along the growth direction of the wires. The band structures corresponding to the three cross-sectional shapes reveal that for [110] SiNWs, all the band gaps are direct. Here we only show the band structures of SiNWs with transverse dimensions of about 1 nm and 3 nm, as the band structures of larger SiNWs are similar. The band structures are generally consistent to those calculated by first-principles methods.^{16,17} It is well-known that bulk silicon has an indirect band gap, with the valence-band-maximum (VBM) located at the Γ point and the conduction-band-minimum (CBM) located approximately 85% from Γ to X. With the dimensions of silicon reduced from the bulk to nano scale, quantum confinement effect increases the energy of CBM and decreases the energy edge of the VBM and increases the band gap of the system. This quantum confinement effect is obvious in Figures 2–4. However, the magnitude of the

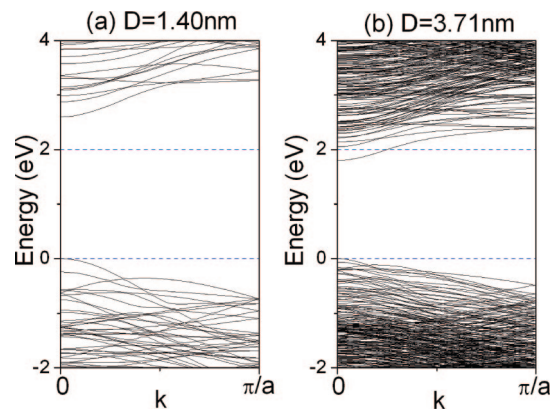


Figure 4. Energy band structure for hex-SiNWs with transverse dimension of (a) $D = 1.40$ nm and (b) $D = 3.71$ nm. The valence band maximum has been shifted to zero. The blue dotted lines are drawn to guide the eyes.

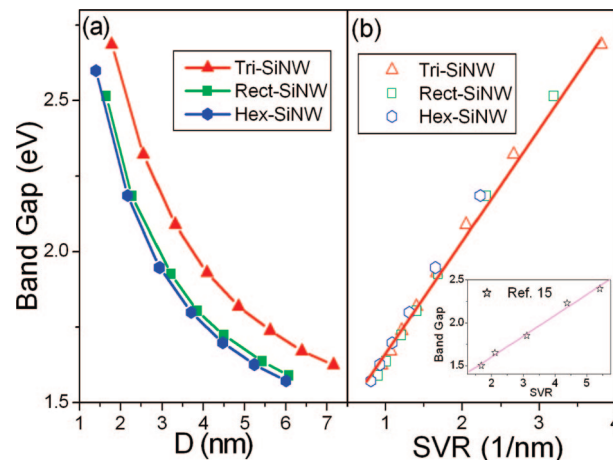


Figure 5. (a) Band gap versus the transverse dimension D . (b) Band gap versus SVR. The red solid line is the best-fit one with slope 0.37 ± 0.01 eV nm. Inset of (b) is the band gap versus SVR relation based on the results from ref 15 for hex-SiNWs.

energy increase/decrease induced by quantum confinement is different for each point in the band structure. It is predicted that the CBM energy increases more near the X point than near Γ . Therefore, for nanowires with sufficiently small dimensions, this difference in energy shifts at different points in the Brillouin zone is large enough to move the CBM at the X point above the CBM at the Γ point.¹⁷ Then a transition from an indirect to direct gap material occurs. Our results show that in [110] SiNWs, the indirect to direct transition does not depend on the special cross-sectional shapes and the band gaps of [110] SiNWs remain direct even for SiNWs with dimensions up to 7 nm.

Having discussed the direct nature of the band gap, we now turn to the magnitude of the band gaps. The dependence of band gap on SiNW dimension D is shown in Figure 5a. It is obvious that the smaller the dimension of the wire the larger the band gap due to quantum confinement. As D decreases from 7 to 1 nm, the band gap increases from 1.5 to 2.7 eV. In addition to the size dependence, the most interesting feature we should like to point out is that the energy gap also shows significantly different change with respect to the cross-sectional shape. The band gaps of rect-

and hex-SiNWs are rather close while distinctly smaller than that for the tri-SiNWs. The band gaps of [110] SiNWs with different cross-sectional patterns were investigated by Ng et al.¹⁵ In their calculations, additional hexagonal rings were added onto the surfaces of the fundamental cross section in different ways with the same cross section area. As the cross-sectional shapes considered in their study are quadrangle, hexagon, and those close to hexagon, they concluded that [110] SiNWs exhibiting different patterns at the cross section do not show significant difference in the band gaps. This is verified by our band gap results of rect- and hex-SiNWs. However, as the large geometric discrepancy between tri-SiNW and the other two SiNWs, the band gap variance is remarkable. The large band gap in tri-SiNW is consistent with the idea that the sharp corner structure produces a large band gap.²⁵ Moreover, it is obvious that the band gap of tri-SiNW has stronger size dependence than the band gap of rect-SiNW and hex-SiNW do. For instance, in Figure 5a, the band gap of tri-SiNW decreases 0.86 eV when the dimension increases from 2 to 6 nm. However, in the same range the band gap of rect-SiNW only decreases 0.73 eV and that of hex-SiNW decreases 0.72 eV. The transverse shape effect on the fundamental band gap decreases as the wire dimension is increased and is expected to disappear for very large wires when the band gap approaches that of the bulk material.

The significant cross-sectional shape effects on band gap and size dependence can be understood from the concept of SVR. Because of the quantum confinement effect, the band gap increases as the material dimension is reduced, thus leading to an increase of SVR. In other words, SVR has the impact of enlarging band gap. At the same transverse dimension, tri-SiNW has larger SVR than those of the rect-SiNW and hex-SiNW. As a result, its larger SVR induces the largest band gap among those of the rect- and hex-SiNWs and the strongest size dependence. Our results show the interaction of the SVR with the quantum confinement effect.

We have used the concept of SVR to explain qualitatively the dependence of band gap on dimension and cross-sectional shapes. In the following, we investigate the dependence of band gap on SVR quantitatively. The band gaps versus SVR of the SiNWs are shown in Figure 5b. It is interesting to find that the band gaps of these three SiNWs follow a general relation with SVR. In other words, consistent SVR dependence of band gap is found for SiNWs with any cross-sectional shape. The SVR effect on band gap can be described by a universal expression as

$$E_G = E_0 + aS \quad (1)$$

where E_0 corresponds to the band gap of bulk silicon, a is an adjustable parameter, and S is the value of SVR in unit of nm^{-1} . From our calculated band gaps, the best fitting gives rise to $a = 0.37 \pm 0.01$ eV nm and $E_0 = 1.28 \pm 0.02$ eV. E_0 here is the best fit value of the band gap of bulk silicon, which is very close to the direct DFTB calculated band gap (1.29 eV) of bulk silicon.

This universal band gap expression is applicable to [110] SiNWs with any cross-sectional shape and area. It is the first formula that relates quantitatively the band gap to SVR of

SiNWs. The band gap of SiNWs are usually difficult to measure, but their transverse cross-sectional shape and dimension are easy to know, so it is of significance to predict the band gap values of SiNWs by using the above expression. It is noted that the linear SVR relation with band gap does not depend on the specific calculation methods. In Figure 5b, we also show the band gap versus SVR relation based on the results from ref 15 for hex-SiNWs, calculated with DFT BPW91 functionals and with the Los Alamos effective-core-potential plus double- ζ valence basis set for Si atoms and 6-31G* for H atoms.¹⁵ A good linear SVR dependence also appears from their results (in ref 15, they showed the band gap vs diameter relation). However, the fitting value for a is 0.24 ± 0.01 eV nm and E_0 is 1.11 ± 0.05 eV. The results are smaller than those presented in this paper. The origin of this discrepancy is due to different computational methods used, and it is well-known that there are large differences between band gaps calculated with different DFT functionals.³² Although the values of the best-fitting parameters are not consistent, the linear SVR dependence of the band gap is obvious. This shows the impact of SVR on band gap is an intrinsic phenomenon in nano materials.

The linear SVR dependence of band gap reveals the importance of surface in study of electronic structure of nano materials. It was found that in small SiNWs, the electron band edges have wave function amplitude concentrated in the exterior of the wire. In contrast to that in bulk material, the true electron wave functions are hollow in the wire center in SiNW.³³ Therefore, the transverse dimension is not a good “gauge” to describe the electron band gap and SVR is a better one as it relates directly to the exterior surface and the obtained linear SVR dependence of the band gap is of practical importance as it allows us to avoid the using of nanowire diameter to discuss the quantum confinement effect on band gap. It must be stressed that the definition of the nanowire’s transverse dimension is ambiguous. Indeed, in the literature, different transverse dimensions are reported for wires with the same number of atoms in the super cell.³⁴ This is due to the fact that different definitions of the wire’s transverse dimension exist and the irregular cross-sectional shape of most wires. The difference between these definitions becomes crucial if we consider small SiNW in the transverse dimension in range of 1–10 nm. In contrast to the ambiguity in the definition of the SiNW transverse dimension, the SVR clearly describes the electron band gap of SiNW. It has the advantage to estimate band gap for SiNWs with any cross-sectional shapes.

In the study of SiNWs, the cylindrical shape approximation is commonly used. It is well-known that the band gap of SiNW increases as the diameter is decreased: $E_G = E_0 + C/d^n$, where d is the cylinder diameter¹⁶ and n is found to be between 1 and 2. A value of 2 for n is expected by using a cylindrical confinement potential and in an effective-mass particle-in-a-box approach,³³ with the infinite barrier height. However, in SiNWs, with transverse dimension less than 10 nm, the electron effective mass is not a constant, which makes the effective mass approximation invalid.^{35,36} More detailed analysis of the quantum confinement effect in the

framework of first principles and semiempirical methods shows that a smaller parameter n between 1 and 1.4 are obtained.^{16,34,36–38} However, the diameters of the wires considered in these studies were too small (less than 3.4 nm) to study the size effects on band gap in a large size range and the few data (typically less than 5 band gap values) obtained from first principles calculations also limits the accuracy of the fitting equation. In this work, based on a set of data with 22 band gap values, a highly linear dependence of band gap on SVR for SiNWs with transverse dimension up to 7 nm is obtained. This highly linear dependence benefits to the determination of n value accurately. In a SiNW with cylindrical shape, the SVR is $\sim 1/d$. As such, the highly linear SVR behavior of the band gap observed for the SiNWs implies an inverse dependence $E_G \sim 1/d$ on the SiNW diameter and determines the value of n is equal to 1. This is very close to the value of 1.1 predicted by DFT-LDA calculations corrected with GW approximation.³⁴

In conclusion, with DFTB calculations, we have systematically studied the electronic structures of [110] oriented SiNWs. [110] SiNWs remain direct band gap with transverse dimension up to 7 nm. The band gap of SiNW increases as the transverse dimension is decreased. With the same transverse dimension, the tri-SiNW has the largest band gap among those of rect- and hex-SiNWs. Most interestingly, a linear dependence of band gap on SVR is found for the first time, which is independent of the specific cross-sectional shape. In other words, a universal band gap expression is demonstrated for [110] SiNWs with any cross-sectional shapes. The using of SVR is of practical importance as it allows us to avoid the ambiguous definition of the nanowire's diameter. Intrinsically, the linear SVR dependence is related to the inverse relation between the band gap and the transverse dimension in small SiNWs. Our results show that, in addition to the important factor for the reactivity in chemical reactions, SVR is also a key role on electronic band structure of nano materials.

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