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EFFECT OF THE LENGTH OF SILICON NANO-DOT/WIRE ON BAND GAP

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***Abstract* — We will report on the role of the length of silicon nanowire (SNW) in determining the band gap of a structure. We find that the band gap decreases with SNW length for the same diameter and approaches the band gap for an ideal infinitely long SNW. The H/T atomic ratio can be used to express the *S/V* ratio, which is approximately linearly related to band gap value.**

Index Terms - Silicon nanowire, Theoretical, Length, band gap.

I. INTRODUCTION

Silicon nanowires (SNWs) are one of the most promising materials for the future of electronic and optoelectronic applications.[1,2] Their broad spectrum of applications has attracted a large group of researchers. Extensive investigations have been made on their synthesis, properties, characterization, and applications.[3,4] Modification of SNWs by surface passivation techniques have been subjected to many experimental studies to increase the efficiency of energy conversion and to decrease surface recombination.[5-7] Theoretical studies of the chemical band gap tuning in SNW have also been performed.[8,9] A recent reported work demonstrates that a highly ordered array of SNW (400 nm diameter) increases the path length of incident light by a factor of 73, where the enhanced absorption dominates over surface recombination even without surface passivation.[10] Modern experimental techniques enable us to greatly control the diameter, length, orientation, crystalline shape, and density of the formed SNWs.[11-13] As a general trend, the band gap has been found to decrease as the diameter increases, until the bulk band gap has been achieved.[2] The sub-band structure and quasiparticle band gap energy of SNWs have been calculated using tight-binding models.[14] In general, the SNWs length depends on incubation time[15,16] and growth rate.[17] The relation between surface to volume ratio with band gaps for different diameter SNWs has also been investigated.[18] However, what is missing in most of these studies is an understanding of the effect of the length of the SNWs on their electronic properties. Theoretical studies usually apply a periodic boundary condition (PBC), which makes the length infinite, and therefore excludes that parameter. In this study we theoretically investigate the variation of the band gap of the SNW with SNW length, using hybrid density functional theory methods.

II. COMPUTATIONAL DETAILS

The calculations in our work were performed using Gaussian 09[19] using 3-21G as a basis set and b3lyp as a hybrid density functional theory. This work focuses on a [110] axially aligned SNW, since it has shown outstanding mechanical and electronic properties[1,20]. A SNW is constructed by building a cylindrical nanostructure of 7 Å radius and height of about 4 Å using base plane 110. A refinement to the strucuture was done by eliminating the Si atoms that are bonded to only one other Si atom. The final touch to the constructed structure is done by capping the broken Si bonds with H atoms.

Geometry optimization was done without applying neither symmetry restriction nor special restriction to H atom movement. Actually, when we tried to apply symmetry, it sometimes resulted in a structure that was not fully optimized, especially in a considerably long SNW.

The computations were done using the TEXAS supercomputing facility; on what is called a "Stampede" supercomputer that utilizes massively parallel computing. It is equipped with 6400 computing nodes. The majority of the 6400 nodes are configured with two Xeon E5-2680 processors and one Intel Xeon Phi SE10P Co-processor (on a PCIe card). These computing nodes are configured with 32GB of "host" memory with an additional 8GB of memory on the Xeon Phi coprocessor card. The aggregate peak

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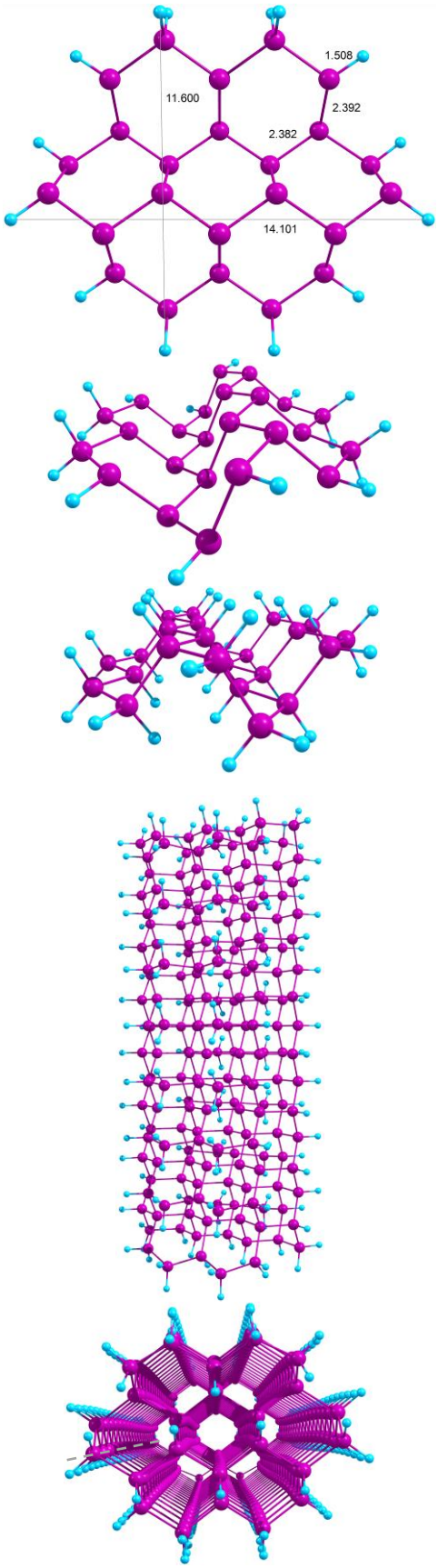

Fig. 1 The optimized geometry of the repeating units (a) top and (b) side view, side views of (c) one unit, (d) two units, (e) eight units in SNW and (f) top view of 20 units.

performance of the Xeon E5 processors is 2+PF, while the Xeon Ph processors deliver an additional aggregate peak performance of 7+PF.

III. Results and Discussion

A. ***Structural parameters*** The optimized structures of some SNWs are illustrated in Fig. 1. The construction of SNWs is done by repeating the PBC optimized structure shown in Fig 1 and Fig 1b. The length of a repeating unit of PBC-SNW is about 3.94 Å. The number of units used in this article is defined as the number of repeating units, terminated at both ends by 10 H atoms. The Si-Si bond length is around 2.380 Å and 2.392 Å in PBC. The Si-Si bond length in two units of SNW ranges from 2.375 Å to 2.385 Å. The Si-Si bond length for eight units of SNW ranges from 2.376 Å to 2.394 Å. This might indicate a minor change in bond length as a result of some atomic stress in the structure, which acts as a factor to slightly shorten the bond lengths. The optimized geometry of the used SNW has a chair-form hexagonal geometry that can be seen in the middle of Fig 1a and 1b. This structure results in the SNW not being a perfect circle, but an oval with external diameter ranging from 11.6 to 14.1 Å. The diameter of the SNW can be taken as the average of these radii, which in our study is about 12.8 Å. This diameter is kept constant during all of the calculations while changing the length. Careful inspection of the bond lengths may show that the stress of the geometry is decreasing as the length parameter increases. This stress may be related to weak interactions between H atoms in adjacent layer forming Hydrogen bonds. Fig 1f and 1e clearly show that hydrogen atoms are stacked above each other, it is worth mentioning that if we start the optimization with Hydrogen atoms aligned horizontally (to be as far as possible from each other) it will end up with the same reported optimized structure. The longer the SNW, the more easily the Hydrogen atoms can rearrange themselves along the SNW. A small distortion is also observed in the stacked unit which means that the repeating units in SNW are not exactly above each other but there is a little displacement as shown in Fig 1f. The dashed dark grey line in the figure is made to facilitate the observation of this minor deviation from the perfect linearity alignment. This deviation between adjacent layers forms a distorted S-shape with an angle of about 179.64º. The real SNW (which is quite longer than the ones used in these calculations) might lead to the prediction of minor deviations in the form of a zig-zag like structure with an angle of less than 0.4º, as obtained in these calculations.

B. ***Energetic parameters***

The calculated band gap of the optimized PBC structure is 3.2 eV, which is comparable to 3.5 eV measured experimentally[20]. The energy differences between the HOMO and LUMO are summarized in Table 1. The length reported in Table 1 is measured from central H atom of one cylinder side to a similar H atom on the other side. The band gap decreases dramatically from 5.4 eV for 1 unit to 4.5 eV for 3 units. The rate of decrease falls off but still continues

Table 1. The Bandgap of SiNW as a Function of Length.

Length, Å	ΔE = ELUMO-EHOMO (eV)
4.37	5.480
8.25	4.818
12.13	4.546
16.04	4.163
19.96	3.894
24.04	3.711
27.95	3.582
31.79	3.490
35.87	3.422
39.68	3.373
43.62	3.337
47.54	3.311
51.48	3.291
55.75	3.277
59.63	3.266
63.31	3.257
67.61	3.250
71.19	3.245
75.50	3.241
79.39	3.238
∞	3.205

until it reaches 3.2 eV. The reported data clearly shows that for more than 18 units and until 20 units (which was the maximum based on computation and time limitations) the band gap is almost constant and equal to the value reported for an optimized PBC. This may lead to the conclusion that the SNW can be considered as a wire after 18 units which have approximately a length of more than 71Å. While a small number of repeating units can be reported as Silicon's quantum dots. In another words, the ratio between the length and diameter should be larger than 5.5 to observe the SNW's character rather than getting the properties of quantum dot or Silicon nano-structures ones. The band gap for a SNW composed of 20 units is almost 60% lower than that for 1 unit.

It is worth mentioning that the lengths of SNWs of 2 units is shorter than double of the length of 1 unit. Therefore, the SNW gets compressed in length. This may also be evidence of the existence of Hydrogen bonds between the adjacent layers of SNW.

It is obvious to make the band gap less than the $E_{HOMO;}$ while E_{LUMO} must get closer to each other. The careful inspection of E_{HOMO} and E_{LUMO} values shows that E_{HOMO} changes almost double of E_{LUMO} which is not the normal symmetrical decrease observed using quantum confinement for a poly-conjugated system or the Hückel theory for aromatic systems.

C. *Atomic ratio*

The number of Si, H and T (total) atoms were studied against HOMO-LUMO energy differences and linear trend lines were obtained for the H/T, H/Si and Si/T pairs. The highest regression coefficient of 0.96 was obtained in the case of the H/T ratio. Since the number of H atoms is related to the surface and the total number of atoms is related to the volume, this simply implies that for a good approximation: the band gap is related to the surface area to volume (*S/V*) ratio. For a cylinder of radius *r* and length *l,* the surface area to volume ratio can be calculated simply as,

$$\frac{S}{V} = \frac{2\pi rl + 2\pi r^2}{\pi r^2 l} = 2\left(\frac{1}{r} + \frac{1}{l}\right)$$

The equation above shows that at a constant diameter *2r*, as the length of the SNW increases, the *S/V* ratio decreases drastically in the beginning and then with an insignificant slope for large *l*. Furthermore, as the length *l* goes to infinity the *1/l* term goes to zero. Therefore, very long lengths have no apparent effect on the ratio and band gap values for long wires ($l \to \infty$) with the same diameter (*S/V* becomes approximately equal to *2/r*).

This simple *S/V* model qualitatively agrees with our finding That the band gap is usually inversely proportion to reactivity. This may seem to indicate that shorter SNWs with large *S/V* ratio are expected to be less reactive. Reactivity, however, depends on the media reactivity with surface atoms rather than just band gap value. A recent study reported an increased sensitivity for smaller diameter SNW <150 nm (that have larger *S/V* ratio) against change in pH value.[21] In general, the band gap is not always directly proportional to the *S/V* ratio, but may sometimes be inversely proportional depending on the chemical composition of the nanowire itself.[22]

IV Conclusion

The length of a SNW plays as important a role as the diameter for band gaps. The band gap decreases with SNW length for the same diameter. SNWs with length >18 units, show similar band gaps regardless of their length. The H/T atomic ratio can be used to express the S/V ratio, which is approximately linearly related to band gap value. The transition between SNW and silicon quantum dots is observed when the ratio of the length to diameter of the SNW is larger than 6 times. As the length parameter of SNW increases, the E_{HOMO} is much more affected than the E_{LUMO}. There exists a Hydrogen bonding between adjacent layers of SNW that shorten the bond lengths between Si atoms.

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