THEORETICAL STUDY OF THE EFFECT OF THE LENGTH OF SILICON NANOWIRES ON THE BAND GAP

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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 the synthesis, properties characterization and applications.[3,4] Modification of SNW by surface passivation technique has 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 been performed.[8,9] A recent reported work demonstrates that a highly ordered array of SNW of (400 nm as diameter) increase the path length of incident light by a factor of 73, where the enhanced absorption dominate 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 increase, until the bulk band gap has been achieved.[2] The subband structure and quasiparticle band gap energy of SNWs have been calculated using tight-binding models.[14] In general, the SNWs length depends on the incubation time[15,16] and growth rate.[17] The relation between surface to volume ratio with band gap for different diameter SNW has also been investigated.[18] However what is missing in most of these studies is a lack of understanding of the effect of the length of the SNWs on their electronic properties. Theoretical studies have usually applied periodic boundary condition (PBC), which makes the length infinite, and therefore simply 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.

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]. The number of unit used in this abstract is defined as the number of repeating units, shown in Fig. 1, terminated in both terminals by 10 H atoms. During geometry optimization neither symmetry restriction nor any special restriction to H atom movement were implemented.

Results and Discussion

Energetic parameters. The optimized geometry of the repeating unit of SNW using PBC is shown in Fig. 1. It has a band gap of 3.2 eV, which is comparable to 3.5 eV obtained experimentally[20]. The energy of the HOMO and LUMO are summarized in Table 1. The band gap is taken as the difference between energies of LUMO and HOMO, which decreases dramatically from 5.4 eV for 1 unit to 4.5 for 3 units. The rate of decrease falls off but continues till it reaches 3.2 eV for more than 18 units, and beyond till 20 unit cells (which was the maximum based on computation and time limitation). The band gap for SNW composed of 20 units is almost 60% lower than that for 1 unit.

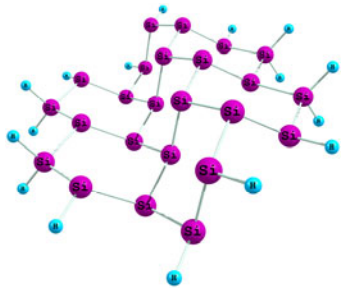

Figure 1. The optimized geometry of the repeating units in SNW.

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

Number of atoms		No. Of Units	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
Si	H				
24	36	1	-6.655	-1.175	5.480
48	52	2	-6.382	-1.564	4.818
72	68	3	-6.330	-1.783	4.546
96	84	4	-6.192	-2.030	4.163
120	100	5	-6.099	-2.204	3.894
144	116	6	-6.040	-2.330	3.711
168	132	7	-6.004	-2.422	3.582
192	148	8	-5.982	-2.492	3.490
216	164	9	-5.968	-2.546	3.422
240	180	10	-5.960	-2.586	3.373
264	196	11	-5.954	-2.616	3.337
288	212	12	-5.949	-2.638	3.311
312	228	13	-5.945	-2.654	3.291
336	244	14	-5.942	-2.665	3.277
360	260	15	-5.938	-2.424	3.514
384	276	16	-5.935	-2.677	3.257
408	292	17	-5.931	-2.681	3.250
432	308	18	-5.927	-2.682	3.245
456	324	19	-5.924	-2.683	3.241
480	340	20	-5.921	-2.684	3.238
24	16	∞	-5.851	-2.645	3.205

Atomic ratio. The number of Si, H and T (total) atoms were drawn against HOMO-LUMO energy difference in Fig. 2. Linear trend lines were obtained for H/T, H/Si and Si/T pairs and the highest regression coefficient 0.96 were obtained in case of H/T ratio. Since the number of H atoms is related to the surface and total number of atoms is related to the volume this simply implies that to a good approximation the band gap is related to the surface to volume (*S/V*) ratio. For a cylinder of radius *r* and length *l* the surface area *S* to volume *V* 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 above equation 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 *1/l* terms 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*), therefore level off. This simple *S/V* model qualitatively agrees with our finding. . The band gap is

usually inversely proportion to reactivity. This may seem to indicate that shorter SNW 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 are not always directly proportional to *S/V* ratio, but may sometimes be inversely proportional depending on the chemical composition of the nanowire itself.[22]

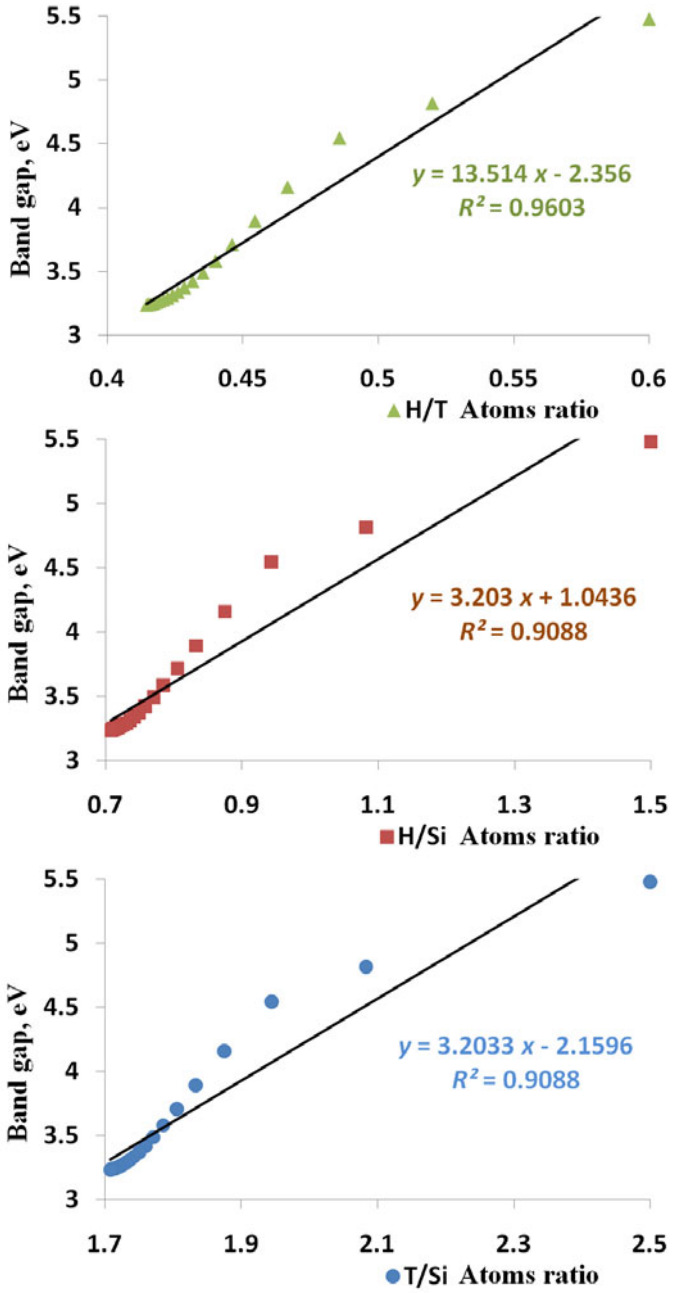

Figure 2. The band gap against all possible Atomic ratios along with a linear regression trend line.

Conclusion

The length of a SNW plays as important role as the diameter for band gaps. The band gap decreases with SNW length for the same diameter. For SNW with length >18 units show almost similar band gap regardless of the length. The H/T atomic ratio can be used to express the *S/V* ratio, which is approximately linearly related to band gap value.

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