Charge Confinement in Silicon Nanowires by Surface Functionalization

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ABSTRACT

The electronic structure of the supercell formed from two different segments of silicon nanowire was investigated using the self-consistent-charge density functional tight binding method. The surfaces of both silicon nanowire segments are saturated by different functional groups. We found that the electrons of conduction band maximum and valence band minimum can be confined in a specific segment of the SiNW supercell, resulting in a series of quantum dots in one-dimensional nanostructures. Our study indicates that saturating surface functional group could be an effective way to modulate the electronic structure of SiNWs, which could offer potential applications in novel electronics such as optical nanobar codes and nanoscale LEDs.

Keywords: density functional tight-binding, silicon nanowires, charge confinement, surface functionalization

1 INTRODUCTION

Silicon nanowires (SiNWs) are expected to play an important role in nanotechnology because they possess remarkable electronic, thermal, optical and mechanical properties due to their unique one-diemensional nanostructures. They have been demostrated in advance applications such as biosensors[1], nanotransistors[2], and optoelectronic devices[3]. Recent research reports indicated that small single crystal SiNWs can be fabricated repetitively as well as their orientations and diameters could be controlled very well by using the vapor-liquid-solid (VLS) technique [4,5]. With the diameter down to ~1 nm [6], SiNWs exhibit the direct nature of band gap and strong blueshift of photon emission, which could be used for silicon-based light-emitting diodes and lasers, due to quantum confiement effect [7]. Experimental result indicated that the optical gap of 3.2 and 2.3 eV are displayed by SiNWs with diameters of 1.3 and 2.0 nm [3], respectively. With this effect, one can design supercells by using SiNWs of different diameters. Cahangirov et al. reported an *ab initio* study of the electronic properties of the supercell of SiNWs with different diameters [8]. They concluded that the supercell can form a multiple quantum structure or a series of quantum dots in SiNWs, where specific electronic states are confined in either narrow or wide regions of supercell. On the other hand, small diameter SiNWs with large surface-to-volume ratio were found to be sensitive to surface chemical passivation. This enable us to tune the electronic and optical properties of SiNWs by surface functional group. By means of *ab initio* calculations, Migas et al. addressed that the band gap of the SiNWs whose more 50% surface covered by the fluorine and hydroxyl functional groups decrease effectively [9].

In this study, we have investigated the electronic structures of the SiNW supercell using the self-consistent-charge density functional tight binding (SCC-DFTB). The supercell is constructed from two joined SiNW segments which surfaces are terminated with different surface functional groups. We found that the electrons of conduction band maximum and valence band minimum can be confined in specific segments of the SiNW supercell. Our study indicates that the surface functional group could be an effective way to modulate the electronic structure of SiNWs, which could lead to potential applications in novel electronic and optical devices.

2 METHOD AND MODEL

The self-consistent-charge density-functional tight-binding (SCC-DFTB) method implemented in DFTB+ [10,11] was employed for structural optimization and electronic structure calculation of SiNWs in this study. The DFTB method is derived from density-functional theory (DFT) as a second-order expansion of the DFT total energy functional with respect to the charge-density fluctuations around a given reference density [12]. The basis sets of numerically described s, p, and d atomic orbitals for Si, s and p orbitals for F, and an s orbital for hydrogen were used in all calculations. The same method and the basis set parameters, denoted as pbc-0-3, have been successfully employed to bulk silicon, SiNWs [13] and functionalized silicon dots [14], where it was found to have the high degree of accuracy and reliability compared with other ab-initio calculations and experiments. The periodic boundary condition was applied in all the calculations.

To construct the model of the supercells, we utilized two type of SiNWs unit cell, SiNW-H and SiNW-F as shown in figure 1 and figure 2. The surfaces of SiNW-H and SiNW-F are fully saturated by the hydrogen and fluorine atoms,

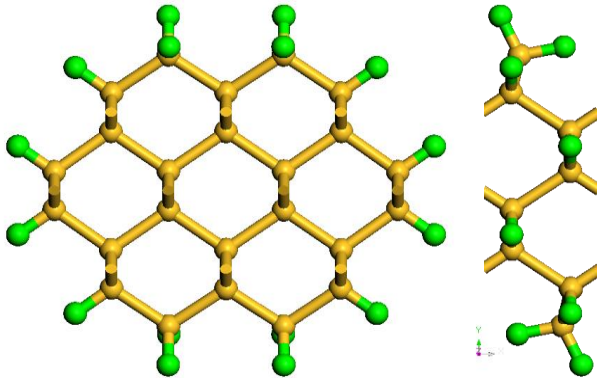

Figure 1: Cross-section and side view of [110] SiNW with surface terminated by hydrogen atoms, denoted as SiNW-H. Yellow and green spheres represent silicon and hydrogen atoms, respectively.

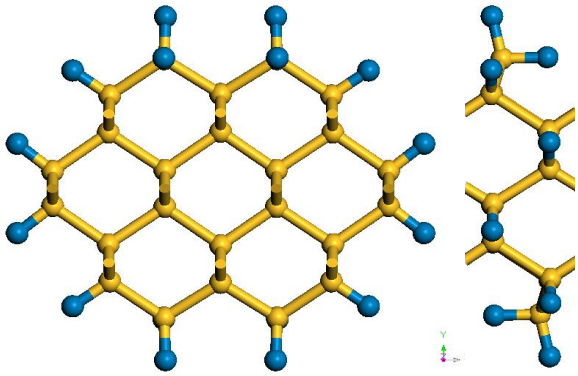

Figure 2: Cross-section and side view of [110] SiNW with surface terminated by fluorine atoms, denoted as SiNW-F. Yellow and blue spheres represent silicon and fluorine atoms, respectively.

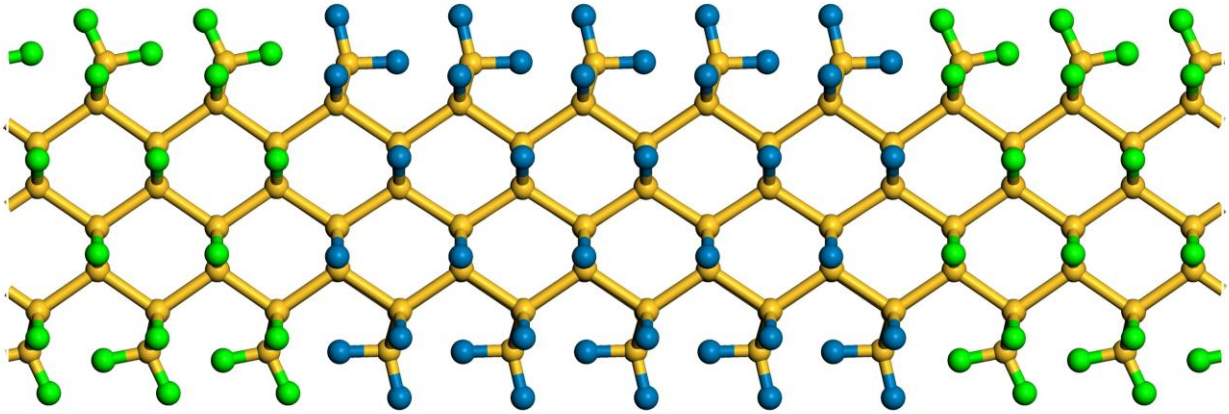

Figure 3: The supercell consist of 5 unit cell of SiNW-H and 5 unit cell of SiNW-F.

respectively. The orientation of both SiNW unit cells is [110] direction of bulk silicon crystal, which is found mostly during VLS growth. Each diameter of SiNWs is 1.2nm. The optimized structures of SiNW-H and SiNW-F are shown in figure 1 and figure 2. Our calculated lattice length of 3.87Å for SiNW-H unit cell is in good agreement with the experimental value (3.8Å) [6]. Figure 3 shows the optimized structure of SiNW supercell consisted of two segments, which are 5 unit cell of SiNW-H and 5 unit cell of SiNW-F. The segment of 5 unit cell of SiNW-F was placed in the center because the symmetry condition was applied.

3 RESULT AND DISCUSSION

The band structures of the SiNW-H and SiNW-F unit cell are shown in figure 4. Both of the SiNW segments display the direct nature of band gap at Γ-point. The gap values of SiNW-H and SiNW-F are 2.75 and 1.63 eV, respectively. Compared to the band gap of bulk silicon, 1.1 eV, the band gap of SiNWs is larger due to the quantum confinement effect. From figure 4, the influence of the surface functional group of SiNW-F on the band structure could be seen. We found surface functional group such as fluorine atoms can reduce the band gap of SiNWs significantly because the conduction bands close to the bottom of the conduction band go down at Γ-point and the valence bands close to the top of the valence band shift up at Γ-point.

Since the band gaps of SiNW-H and SiNW-F are different, the band lineup occurs when the two segments connect to each other. Figure 5 and 6 show the isosurfaces of the charge density of the lowest conduction band state and the highest valence band state in the SiNW supercell, respectively. We found that the electrons of valence band maximum and conduction band minimum are confined in the SiNW-F segment. This phenomena is due to the narrow band gap of the SiNW-F segment. When supercell is formed, the electrons in the conduction band are localized in the lowest band of the conduction band and the holes in the valence band are confined in the highest band of the valence band. In our case, SiNW-F is the segment where electrons and holes are confined (localized). It can be seen as a series of quantum well structures or quantum dots in one-dimensional nanostructures.

4 CONCULSION

In this paper, we studied a [110] SiNW supercell formed from two type of segments which surfaces were terminated

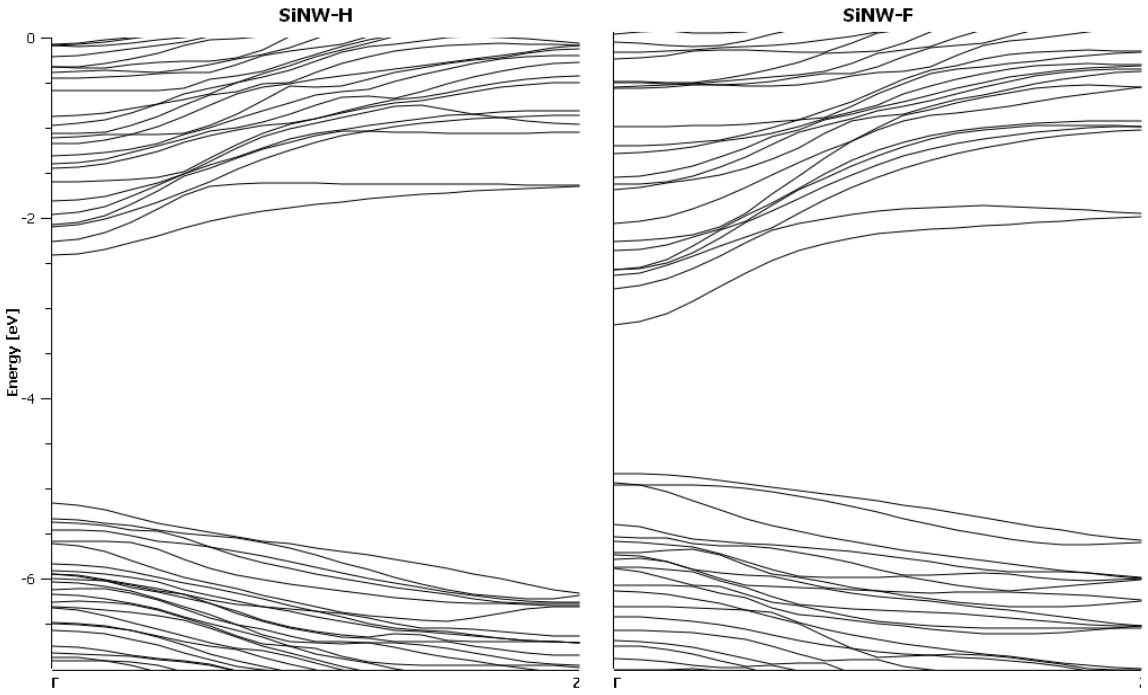

Figure 4: Band structures of SiNW-H and SiNW-F unit cell.

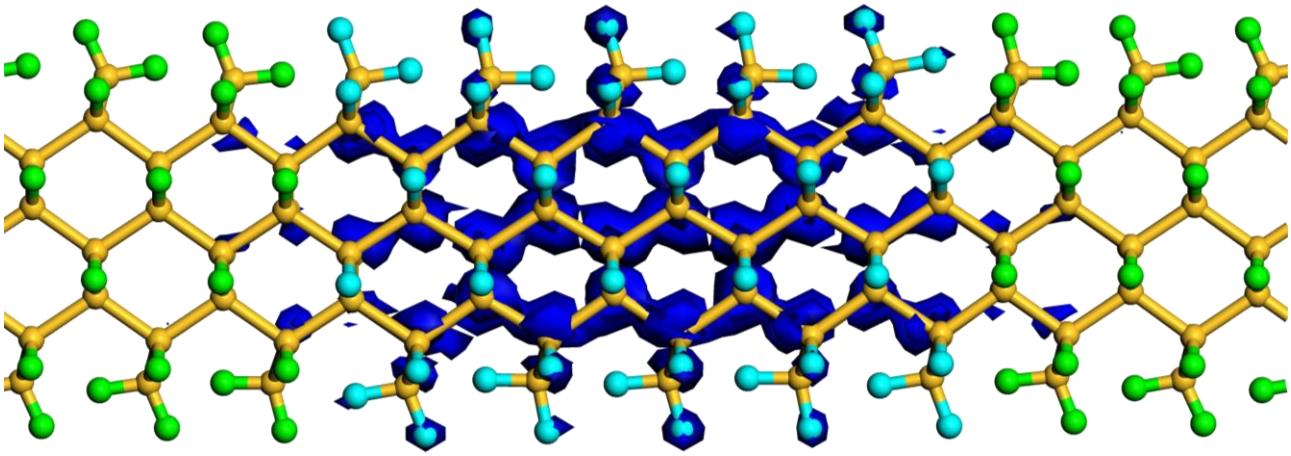

Figure 5: the isosurface charge density of lowest conduction band.

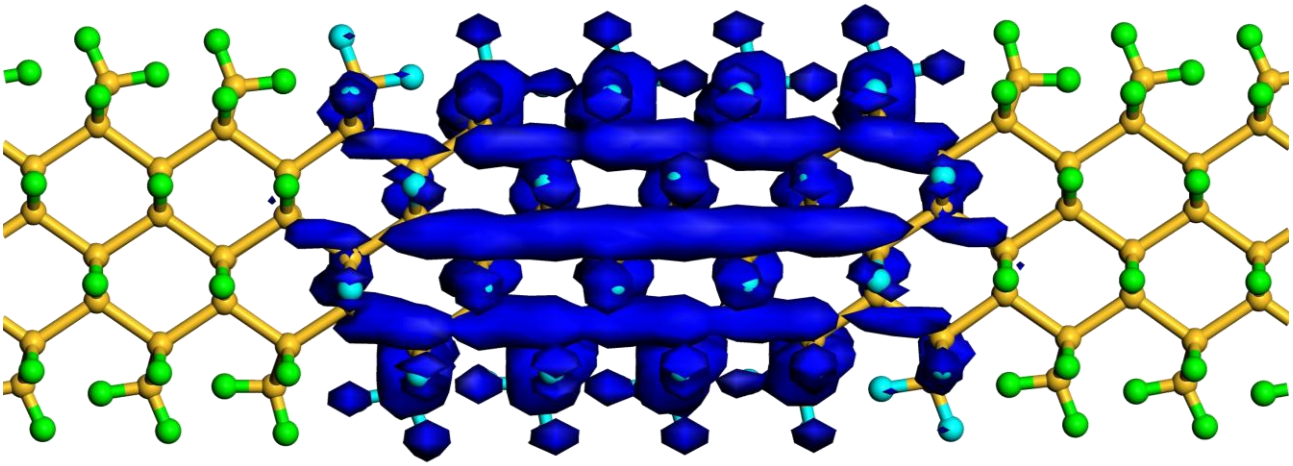

Figure 6: the isosurface charge density of highest valence band.

with different functional group by using SCC-DFTB method. The supercell are found to form quantum dots in the one-dimensional SiNWs because the specific states such as conduction band minimum and valence band maximum are confined in a particular segment. Our findings demonstrate that saturating surface functional group provides an effective way to manipulate the band structure of supercell as well as the position of electrons and holes in the SiNWs.

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