Int. J. Nanoelectronics and Materials **7** (2014) 77-84

Effect of Al doping on Band Gap of hexagonal cross section SiNWs

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Received 16 July 2013; Revised 20 August 2013; Accepted 14 November 2013

Abstract

In this work band structure of hydrogen-passivated, free-standing silicon nanowires, oriented along [111] direction with hexagonal cross section was studied by using density functional theory using GGA approximation. Effect of doping of aluminum atom on band gap of silicon nanowire is also analyzed. It is found that doping of single Al atom can reduced the band gap of Si nanowire.

Keywords: Castep; nanowires; DFT; GGA.
PACS: 31.15.A-, 81.07.Gf, 71.20.Ps.

1. Introduction

Recently Nanowires have been amongst the most studied nanomaterials due to continuous discoveries and superior physical properties compared to larger bulk materials. The intrinsic properties of silicon nanowire like high surface-to-volume ratio, biocompatibility, one dimensionality as well as the tunable band gap makes it special class of semiconductors. However, they may replace carbon nanotubes in some applications. Some experiments have shown that they can be used to build the next generation computing devices. The first key step to create active electronic elements is doping a nanowire. This has already been done to individual nanowires to create n-type and p-type semiconductors. The next step was to find a way to create a p-n junction. In particular, silicon nanowires (SiNWs) have been studied both theoretically and experimentally and they have attracted much attention due to their applications in various field, like nanosensors [1], solar cells [2], FET [3] and energy conversion devices [4]. To use nanowire for these applications, it is necessary to control the electronic properties of nanowires, which depends on the diameter of nanowire, crystallographic orientation, doping element, doping concentration, cross sectional geometry and optimized structure of the nanowires [5]. Band structure of SiNWs can be modified by changing its cross sectional area, cross sectional geometry, orientation, surface morphology, dangling bond passivation and by doping of impurity atom [6]. Reduced dimensionality systems are characterized by a large surface-to-bulk ratio and offer the possibility of doping through the external adsorption of molecules [7] rather than

incorporation of substitution impurities [8]. Álvaro Miranda [9] has studied molecular doping of NH_3 on silicon nanowires grown along [112], [110], [001] and [111] orientations. Rurali et al [10] have studied the structural properties of Nanowires with diameters below 10nm, where quantum effects become important and the properties diverge significantly from that of bulk silicon. Many unique properties of these systems are at the same time defying challenges and opportunities for technological advances. Structures and energetic of hydrogen passivated SiNWs were reported by using tight binding method [11]. Impurity doped SiNWs have also attracted attention since the dopant atoms provide excess carriers required in device applications, such as diodes and transistors. Fernandez-Serra et al [12] investigated effect of Mn, B and P doping on the electronic structure and band gap of hydrogen passivated SiNW by using DFT. Furthermore, growing research interest has been devoted to the functionalization of SiNW surface with various species to study its chemical and biological sensitivities. Few ab initio calculations now reported for InP nanowires [13] to study its band gap. In our previous study we have studied the area of cross section dependence of H-SiNW on band gap along [111] direction [14, 16] and we found that on increasing the area of cross section of nanowire band gap reduces. Here we want to check whether doping of Al atom could reduce band gap or not. In this article we extend our earlier study in which we have studied the effect of doping on band gap of silicon nanowire of triangular [14] and rectangular cross section [15] along [1 1 1] direction using generalized gradient approximation (GGA) by implementing density functional theory (DFT). Since rectangular, triangular and pentagonal cross sectional nanowire have already been studied hence in this research paper effect of doping on band gap of hexagonal cross sectional silicon nanowire along [1 1 1] direction is analyzed by implementing density functional theory using GGA. In this work [111] configuration is used since it is more stable than [100] configuration.

2. Band Gap of SiNW along [1 1 1] Direction

To simulate the nanowire CASTEP module of material studio is used. In this study, silicon nanowires with hexagonal cross section is built which has 68 atoms in its primitive unit cells and are grown along [1 1 1] direction. The top (upper) view of silicon nanowire along [111] direction is shown in Fig. 1. Yellow spheres stand for silicon atoms and white spheres for hydrogen. Hydrogen passivation is used to eliminate the defect states within the band gap so that the band structure of the chain should briefly feature the characteristics of silicon. For eliminating the inter-layer interaction, a vacuum layer of 4 Å thicknesses is built between two neighboring chains. The lattice constant C_o and all the atomic positions are fully optimized. Upon relaxation, the structure of the ideal bare nanowire gets reconstructed. Furthermore, to allow possible reconstructions involving two unit cells, structure optimization of an ideal nanowire is performed. In the later optimization, the energy per Si atom and the atomic structure did not change from the single cell optimization. Table 1 lists the studied cases with the atomic numbers, area of the cross section and band gap. First-principles plane wave calculations [17] within DFT using ultrasoft pseudopotentials are performed for studying the electronic properties of silicon nanowire [17]. The exchange correlation potential has been approximated by generalized gradient approximation using Perdew Burke Ernzerhof exchange correlation functional [19] both for spin-polarized and spin unpolarized cases. For partial occupancies, Methfessel-Paxton smearing method is used [20]. The adopted smearing width is 0.1 eV for the atomic relaxation and 0.05 for the accurate band structure analysis and density of states calculations, here total energy/atom convergence tolerance is 0.1000E-05 eV. All structures have been treated within a super cell

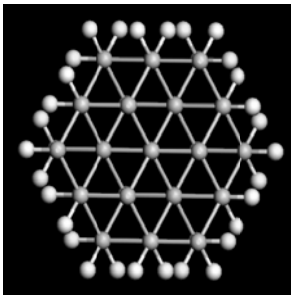
geometry using the periodic boundary conditions. The lattice constants of the tetragonal super cell in the *x-y* plane are taken as *asc*=23.10918, *bsc*=22.661879 Å and *csc*=9.616978 Å along the *z* axis. In the self consistent potential and total energy calculations, the Brillouin zone of SiNW is sampled in the k space within the Monkhorst-Pack scheme [21] by 1x1x40 mesh points as determined by the convergence tests. A plane wave basis set with kinetic energy in the range from 200 to 400 eV has been used depending on the structure of SiNWs. All atomic positions and lattice parameters are optimized by using the BFGS where total energy and atomic forces are minimized. The convergence or energy is chosen as 10^{-4} eV between two ionic steps, and the maximum force allowed on each atom is 0.3000E - 01eV/A. The band structures around the Fermi energy levels is displayed in Fig. 1 (b) for hexagonal cross sectional SiNWs along [111] direction.

30 38 a = 22.000000 62.56512 2.282
b = 22.000000
c = 9.406000
alpha = 90.000000

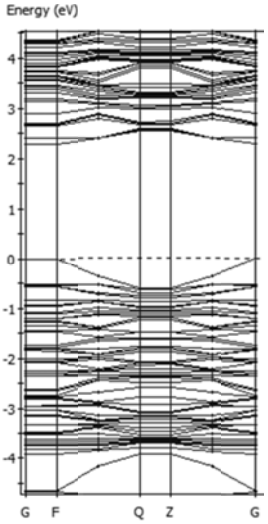
Table 1: Parameter of silicon nanowires grown along [1 1 1] direction with cross sectional area and band gap

H	Si	Al	Lattice parameters (A)	Area of cross section	Band Gap (eV)
29	38	1	a = 22.079875 b = 21.664206 c = 9.516670 alpha = 89.900585 beta = 90.779618 gamma = 90.432221	62.56512	1.528

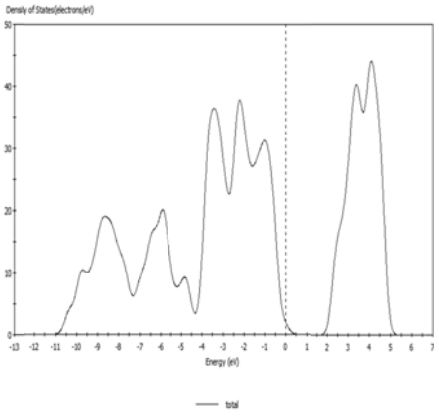
CASTEP Band Structure
Band gap is 2.282eV



1(a)



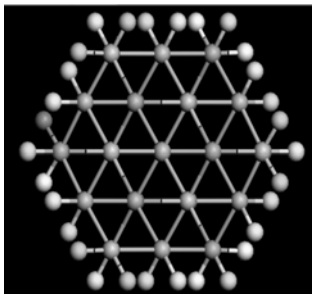
1(b)



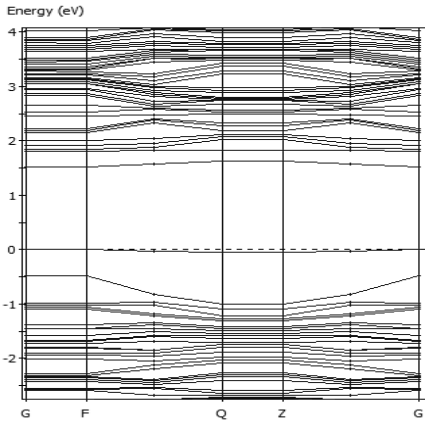
1(c)

Fig. 1: (a) The hexagonal cross sectional nanowire along [111] direction. Yellow sphere represents the silicon atom and white spheres represent hydrogen atoms in Fig. 1 (b) energy band structure of Si nanowire along [111] direction is presented (c) The density of states.

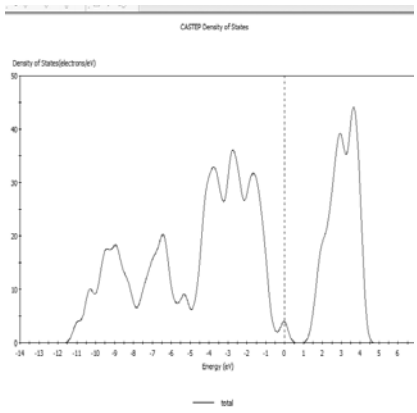
CASTEP Band Structure
Band gap is 1.528eV



2(a)



2(b)



2(c)

Fig. 2: (a) Al replaced a hydrogen atom at the edge. Yellow sphere represents the silicon atom and white spheres represent hydrogen atoms and violet sphere represents the Al atoms (b) energy band structure of Al doped Si nanowire along [111] direction is presented. The energy band structure at the bottom indicates a p-type behavior (c) The density of states.

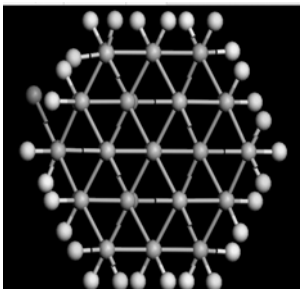


Fig. 3: Optimezed geometry of doped silicon nanowire.

3. Doping Dependence of the Energy Bandgap

Doping causes the bandgap to get reduced. This effect is explained by the fact that the wave functions of the electrons bound to the impurity atoms start to overlap as the density of the impurities increases. This overlap forces the energies to form an energy band rather than a discrete level. This impurity band reduces the energy band of the host material by:

$$\Delta E_g(N) = -\frac{3q^2}{16\,\pi\varepsilon_s}\sqrt{\frac{q^2 N}{\varepsilon_s kT}}$$

where N is the doping density, q is the electronic charge, e_s is the dielectric constant of the semiconductor, k is Boltzmann's constant and T is the temperature in Kelvin.

3.1 Effect of Doping of Al Atoms on Bandgap

Until now we have discussed hydrogen passivated SiNWs. However, impurity and dopant may be absorbed on the silicon nanowire surface in the practical usage. The absorbents could take effect on the electronic structures and thus other related properties. The doping of single B or P atom in [110] SiNWs has been studied in Ref [22], where the authors found that impurity favors the surface position and doping reduces the density of carriers. It means that the doping influences the electrical properties of [110] SiNW remarkably. But it is unknown whether a similar conclusion could be drawn with [111] SiNWs. Therefore in our previous study we have studied the electronic properties of silicon nanowire doped with single Al atom oriented along [111] direction with rectangular and triangular cross section [14-15]. In those studies it is observed that doping of Al atoms reduces the band gap by .7 eV. But still it is unknown whether similar results will obtain for hexagonal cross sectional nanowire. Therefore in this paper effect of doping of Al atom on the surface of hexagonal cross sectional Si nanowire oriented along [111] direction is analyzed at room temperature. On increasing temperature band gap could reduced so the calculations are made at room temperature. A hydrogen atom at the edge of nanowire is replaced with Al atom as shown in Fig. 2 (a) and then doped structure is optimized by using Generalized Gradient Approximations. Optimized structure of Al doped silicon nanowire along [111] direction is shown in Fig. 3, from the optimized structures, we found that the adsorbed structure kept almost the original feature of the SiNW without impurity but at the doped surface there is small distortion. The Si-Al bond length was about 2.5 Å and there was a distortion around the Al atom locally as shown in Fig. 3.Surprisingly, Al doping

causes energy levels to shift closer to the conduction band. The location of impurity states in the band gap occurs in a reverse order as compared to the n-type (N, P, As) and p-type (Al, Ga) dopants in bulk Si crystal. We found that the band gap surprisingly decrease from 2.282 to 1.528 eV by replacing one hydrogen atom by one Al atom at the edge as shown in Fig. 2 (a). It means band gap reduces by .75eV on doping it with single Al atom. Due to the reduced adatom-adatom interaction, dispersion less impurity bands are obtained. Electronic band structures of hydrogen passivated and doped Si nanowire were different from that of the bare wire since a defective state emerged in the middle of the band gap, and some bands appeared at the bottom of the conduction band. The band decomposed charge density analysis indicates that these levels originate from doping elements. H-SiNW semiconductor can be modified as a p type through substitution of Al atom.

4. Conclusion

From above results it is obvious that doping of Al atoms could reduce the band gap of silicon nanowire and at that time silicon nanowire will start behaving as bulk silicon. Some of the parameters that characterize the electronic band structures are listed in TABLE-1. It has been found that the band gap of the SiNWs decreases as the doping concentration increases. It is found that doping of Al atoms does not affect the geometry of silicon nanowire along [1 1 1] direction very much which is clear from Fig. 2 (a) and Fig. 3. The optimized structure of hydrogen passivated silicon nanowire is nearly similar to the optimized structure of silicon nanowire which is doped with Al atoms with little distortion at the doped surface. From this study it is clear that the doping of Al atom does not affect the geometry of nanowire but it could reduce the band gap of silicon nanowire up to great extent.

Acknowledgement:

The authors are thankful to ABV-IIITM, Gwalior for providing the infrastructural support to perform the present computation at Computational Nano science and Technology Lab.

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