Determination of Silicon Electrical Properties Using First Principles Approach

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Abstract. Silicon nanowires have attracted attention as basis for reconfigurable electronics. However, as the size decreases, the electronic properties of the nanowires vary as a result of confinement, strain and crystal topology effects. Thus, at the thin diameter regime the band gap of Silicon nanowires can no longer be derived from a simple extrapolation of the isotropic bulk behaviour. This study compares band gap parameters in sub 10nm nanowires obtained from first-principles density-functional band structure calculations with extrapolations using continuum theory in order to rationalize the changes of the overall conductance, resistance and band gap. The device consists of silicon nanowire of size between 1 nm to 6nm. The results indicate an increase of, both the energy gap and the resistance along with reduced conductivity for the thinnest wires and a dependence on the crystal orientation with gaps reaching up to 4.3 eV along <111>, 4.0 eV along <110>, and 3.7 along <100>.

1. Introduction

Small scale structures have brought new electrical properties to the field of science. Compared with macroscopic structures, small scale structures such as nano scale materials and nano devices have been found to possess distinct and unique physical properties because of their small size and their high surface to volume ratio. Such phenomena allow the electrical properties to be manipulated by the design and the controlled fabrication and integration of nanomaterials and nanodevices [1]. The possibilities of manipulation provoked substantial interest in nanoelectromechanical systems (NEMSs) such as mass sensors, atomistic dust detectors, high-frequency electromechanical oscillators and pressure sensors [2]. Several studies have been reported which intensively probe the electrical properties in particular for their use in NEMSs device with good reliability [3]. Both theoretical and experimental studies to predict the electrical properties of such nanowires have been reported, however, a predictive, bulk-based theory of the electrical properties of silicon nanowires is still missing [4]. Silicon has been the prototype electronic material for decades [5]. However, experimentally realized device concepts still base on large scale bulk material properties of the two major distinct classes, i.e. of melt-grown single crystals, and of polycrystalline silicon (poly-silicon). Semiconductor nanowire (NWs), especially from Si, but also from other compounds such as Ge or the III-V semiconductors, have been widely studied over the past 25 years due to their unique growth behaviour and crystal structures [6]. In the recent years, one-dimensional silicon nanowire structures thinner than 100nm have been obtained both via bottom-up and top-down techniques [7]. Previous
Studies have demonstrated that the synthesis of semiconductor NWs with small diameter distributions can be achieved using well-defined nano sized seeds and a vapor-liquid-solid (VLS) growth process. Solution phase synthesis of Si NWs has also been shown using gold nanoparticles as supporting elements. The SiNWs produced in this way show excellent dimension uniformity [8]. They promise tremendous technological potential in nanoscale devices, and first achievements in reconfigurable electronic circuits have been demonstrated [9]. Top-down structured wires and wire arrays have been manufactured for sensing applications and have proven excellent stability in aqueous medium along with a sensitivity down to the nanomolar regime [11]. Other nano structures of silicon have also been exploited such as silicon quantum dots, porous silicon, nano flowers, etc. However, these structures are mainly employed for their ability to exhibit luminescence in the visible range due to strong quantum confinement effects, but show less interesting electronic transport behaviour [12]. From the theoretical side, Si-based devices have for decades been simulated successfully [13] using the well-characterized bulk properties [14]. On the other hand, Si nanostructures, have been intensively studied by electronic structure calculations only recently [15]. In particular, for SiNWs first-principles calculations indicated that the transition between nano-scale and bulk-like transport behavior occurs in the single nanometer regime, and suggest that bulk properties can be employed to extrapolate to unexpectedly thin SiNWs [16]. The present study explores this assumption and focuses on scaling relations to deduce the band gap, resistance and conductivity of SiNWs based on first principles calculation of bulk silicon [17]. The virtue of the present approach is that it avoids an arbitrary choice of termination groups and that it yields an average effect of the dopants [18-21].

2. Computational Details

Density-functional band-structure calculations were performed for pristine and doped silicon bulk supercells with the ABINIT code. A kinetic energy cut-off of 20 Hartree, a 4x4x4 Monkhorst-Pack Brillouin zone integration grid, Troullier-Martins pseudopotentials was used and the Generalized gradient approximation (GGA) used as gradient-correlation functional were employed. The cell calculated using density-functional theory (ABINIT) were (1x1xn (1, 2, 3, 4 5, 6) unit cell size of 23 Bohr according to the method used by [22]. The two elements were considered for the dopant these include Boron and Phosphorus with 24 atoms). The minimum spacing between the dopants in units of is 2.33 Å. The effect of the band gap comes from the nanowire size and the orientation as evident from the band gap figure 1 based on vesta structure Figure 1 was found. It can be observed above, the electronic activated as results of reaction between silicon boron and Silicon Phosphorus. The vacuum layer between the wires amounted to 8 Å. To study the problem, I first consider a cylindrical nanowire with size (1, 2, and 3...6nm). Here size determines how large the resistance with the size reducing. The density and log files from the full quantum-mechanical calculation serve as input to a Matlab code according the following references.

3. Results and discussion

The reduction of the wire diameter changes the bonding in the surface-near region, hence also the electronic states are modified. Once the number of bulk-like atoms becomes less than the number of surface-near ones, the electronic states of the whole wire will be affected. In that size regime also the direction of the SiNW, which determines the type of surface, becomes of great impact on the conduction properties. This will determine the other parameter such as nanowires band gap that affects the conductance and the resistivity of silicon nanowires. This indicate that nano wire has potential to influence the current, conductivity and resistance through the size and dimensionality. The super cell contain only one wire, the number atoms determine size. This figure show the 6nm wire because it contain highest no of atoms. Boron =6 electrons for 2 atoms and phosphorus 10 electrons for 2 atoms every super cell two atoms of boron and 2 atoms of phosphorus. This shows that 12 atoms as dopants and 100 silicon atoms total 124 atoms. The figure 2 show the decrease in band gap as the wire size increase, this because as the wire size increase, the electron mobility increase and interesting to note that <111> show highest band gap. For all three orientations the band gap increases with decreasing
the diameter of the specimen decreases especially for the (111) direction, which has the value 4.3 eV, followed by the direction (110) 4 eV, while for (001) is 3.7eV. Moreover, these band gap results can be observed exponential functions as shown in equation below decreasing with size increasing, this emphasized the band gap dependency on size. Also from this figures, it can be seen that there is an initial large change in the band gap with the diameter of the nanowire between 1nm and 3nm, following which the band gap changes remain low as the nanowire size decrease except for the <111> which gradual decrease in band gap. This is a typical behaviour of nano wire system in which the electronic properties largely depend of size where formation of electronic confinement of carrier at the nanowire below 10nm, which lead to high band gap, restricting charge carrier mobility. This result has wonderfully agreed with the results of the various theoretical work which presented by the scientist communities working in this field especially (Michael et al, 2007) [18] in where their model give a similar prediction as my own as shown in Figure 1.

\[
E_{\text{gap}} = E_{\text{gap, bulk}} + C \left( \frac{1}{d} \right)^{\alpha}
\]  

Figure 1. The silicon nanowire band gap with respect to diameter: experimental and theoretical.

Here this equation for dependency of band gap and the size, where d is the diameter of the wire and \(E_g\) the equation typical behaviour of nanowire band gap, \(1/d\) show inversely proportionality, which as the size increase the band gap decrease, for atomic interaction exponent \(\alpha\) is equal to 2 as the fitted curve and C is fitting coefficient. It is interesting to note that when the wire diameter increases, the band gap decreases. Furthermore, it can be observed that for different size as it increase, it show that band energy decease, this implies that the Si-NWs when interact exhibit strong interaction between atom to atom to create collision, this create phonon Figure 1. Generally from the literature, for the Si-NWs, the interaction of atoms results in increase electron group velocity, which increase collision and collection effect in the elastic deformation which decreases the lattice atomic interaction which in turn decrease the band gap. The energy gap exhibited as a results from interaction of Si atoms at edge of SiNWs. Equation (1) large value of the energy gap is related to the quantum restriction (quantum confinement) of charge carriers. The nanowire behaviour of band gap can be explained by the increase in the resistance in the band structures of silicon nanowires. Due to the collision of atoms , the effective bond length in the band gap is shorten and this decrease the band gap in silicon nanowirer
The band with more smaller size shows energy shift due to the quantum restriction. These features of the band gap of quantum silicon nanowires can be a basis for many application in semiconductor industry especially integrated circuit. Further, the Figure 1 shows the comparison between the theoretical and experimental results. The red, black and blue curves show the theoretical and the pink dotted curve show the experimental results. The four curves good similarities, all show the band gap reduction as the nanowire increased that proved the silicon nanowire electrical behaviour is dominated by the quantum confinement at the 10nm and below this because the band gap directly related to the atomic restriction and the atomic restriction is function of quantum confinement.

![Figure 1](image1.png)

**Fig. 2.** The resistance of nanowire at lower regime.

The Figure 2 shows the response of the nanowire resistance with size becoming smaller, it shown the response of the nanowire when its size reduced, this typical behaviour of the nanowire as it becomes smaller, it can be assumed that the semiconductor nanowires behave like typical pure conductor at the nano regime because it resistance decrease with size increase which confirm the law of resistivity which stated that the resistance if wire directly proportional it length and inversely proportional to is diameter. Moreover, the dependent resistivity on nanowires for various wire widths is significant, the density of states provides useful information about electron transition from valence to conduction band and at the same time, predicts the possession of electronic orbital over an interval of energy in electronic band structure. The DOS of a material can be easily changed due to presence of dopant and this causes either improvement or deteriorate of device performance. Proving a semiconductor nature character is displayed by band structure. These positions of the peaks are nearly the same as corresponding experimental ones, from x-ray spectroscopy as well as simulation result, showing the validity of our simulation model. It is clearly seen that semi-metallic and metallic character explained in band structure calculation at ZnS alloy were generated by dopant element as presented in Figures 3b and 4. Different electronic properties were noticed in spin up (metallic) and spin down (semiconductor) in ZnS alloy compounds. This allows materials to be used for many applications due to its modification in electronic properties. According to (Tomioka et al, 2012) this factor may be the quantum confinement in the nanowire due to the interaction of atoms the as the wire becomes smaller.

\[
\rho(\theta) = \exp\left[-\frac{4\pi h}{\lambda_e}\cos^2\theta\right]
\]  

(2)

Where \(\theta\) is the angle of incidence relative to the surface normal, \(h\) is the root mean square surface roughness, and \(\lambda_e\) is the Fermi wavelength energy of an electron. Shengrong et al, 2014 [20]
incorporated $\rho(\theta)$ into a model for how the resistivity of small nanowire depends on surface charges or roughness.

![Graph](image_url)

Figure 3. The formation energy as function of the position (a) P doped (b) B doped.

To study dopants in the nanowires, the formation energy is very important. The formation energy $E_{\text{formation}}$ of the impurity which include B and P is generally defined as the energy needed to insert an atom B and/or P into the nanowire which represented by the equation below:

$$E_{\text{formation}} = E(\text{doped SiNW}) - E(\text{SiNW}) + (n + m)\mu_{\text{Si}} - n\mu_{\text{B}} - m\mu_{\text{P}}$$  \hspace{1cm} (3)

Where the notations are $n$ and $m$ are the number dopants B and P, $\mu_{\text{Si}}$ is the chemical potential of Si and $\mu_{\text{B/P}}$ the chemical potential of an atom of the impurity which are Boron B and phosphorous P.

It is clear that the position labelled 2 in Figure 3 is the preferential position for the dopant in both B and P doped. These parameters can be evaluated from dielectric constant as present in Equation (3). The refractive index can be used to determine the tendency of a material to allow passage of electromagnetic radiation while the extinction coefficient is expressed the material behaviour in terms of attenuation of electromagnetic radiation at a particular wavelength. The same trends of variation observed for semiconductor and metallic nature of the system in dielectric function are repeated for refractive index. Therefore, large value of refractive index can be attributed to free movement of electron in metallic nature compounds. Higher values of refractive index in metallic nature can make them promising candidates for photovoltaic or optoelectronic applications. Also, static refractive index can be related to low absorption energy and it was noticed as well that as absorption increased the equivalent refractive index decreased in that order the formation energy for P doping is smaller than for B doping. It is also clearly seen the formation energy for orientation $\langle 111 \rangle$ both dopants are highest compared formation energy for the $\langle 001 \rangle$ and $\langle 110 \rangle$. The interaction between the dopants, which enlarges the formation energy in $\langle 111 \rangle$ orientation as confirmed by Peelaers [22].

The papers show the conductivity of the wire with three different orientation and $\langle 111 \rangle$ give the low conductivity this confirmed the both band gap results where the $\langle 111 \rangle$ show higher band gap. The figure 4 show the conductivity increase drastically as the nanowire electronic width is increase from 1nm to 6nm is due to quantum effect as a results of the quantum confined which imposed and transition atomic dynamic within the silicon nanowire which affects the ionization energy of donors inside the nanowire. Similar observation was made in the study of Mikael [18].
Figure 4. The figure shows the impact of width on nanowire conductivity.

Quantum confinement due to different nanowire surrounding by vacuum and is depend on the wire diameter. The nanowire sizes of 1 to 6nm are very thin, they have a large surface to volume ratio, and therefore, the dangling bond bonds are equal to Si atoms at the surface, which also called the surface charge. Materials will not absorb light when energy band gap is greater than photon energy. So, for the light to be absorbed, the energy band gap must be less than energy of the light. Absorption coefficient is calculated from the dielectric as reveal in Equation (4). In figure 8b, the calculated absorption coefficients are presented for the study compounds. We observed first peak of absorption for all alloy compounds at visible light, with higher peak on metallic nature compound compared to semiconductor. The conductivity there is controlled by the surface effect which allow high conductivity since surface charge dominated the electrical properties of the nanowire at size below 10nm. The resistivity of the wire as it becomes smaller several effect come into play such surface charge and surface roughness, the roughness could be explained by the presented equation by Shengrong. The results is well agreed with (Shengrong et al, 2014) [20] according this study, Simulation results using the nanowire show significant differences compared with bulk, for nanowires with a diameter between 1nm and 6nm, conductivity is high this is attributed to the atomic interaction which create phonon group velocity reduction and the phonon lifetime reduction due to strong phonon-phonon scattering derived from nanowire interaction.

4. Conclusion

The study successfully, demonstrated the behaviour of the nanowire conductance, resistance and band gap with size, the results show that the energy gap, resistance and conductor are all higher at the lower nanosize, the value of band gaps were 4.3 eV, 4 eV and 3.7 eV for (111), (110) and (100) respectively with the nano size of the 1 to 6nm, the nanowire is shown super conductance at lower regime and gradually decrease as the size increase, this is due to the surface of the device. Thus, the effect of the aforementioned parameters was successfully established. As the Nanowire reduces, the mechanism of inducing partial charge through interaction equally revealed.

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