

# Inclusion of Electromagnetic Stress to explain Lithiated Silicon Nanowires

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**Abstract:** This study considers the electromagnetic stresses and simulates the lithium insertion into a silicon nanowire. The resulting model uses a multi-physics approach to explain the two detrimental effects that could result during the lithiated silicon process: (1) The partial lithiation effects that are observed in some silicon nanowires under negligible volume expansion; (2) The excessive volume expansion that is observed after full lithium insertion with a resulting Cassini oval shaped silicon nanowire. Magnetic and electric fields are included in this computational model in order to introduce additional tensile and compressive stresses and as a result alters the band structure of the silicon nanowire as it transition from crystalline silicon (c-Si) structure to an amorphous lithiated silicon (a-LiSi) heterogeneous material.

### 1. The Continuum Model

The computational model that will be presented is based on the elastic-diffusion model of a silicon spherical nanoparticle that was presented in Golmon et-al. [1]. This model described the lithiation process from an electrochemical point of view. Lithium ions diffused through the crystalline silicon (c-Si) lattice, breaking silicon-silicon bonds and reforming lithium-silicon bonds, creating tensile stress throughout the nanoparticle while simultaneously Li-Si alloy material concentration builds up a compressive stress uniformly within the nanoparticle shell. Although the elastic-diffusion model does explain the volume expansion, it fails to explain for the slowing of the interfacial reaction front which is the interface between the c-Si and a-LiSi alloy that causes partial lithiation within the Si nanowire as was reported by Liu et-al. [2]. Therefore, an extension of this model is performed on a cylindrical silicon nanowire with the addition of electromagnetic theory. In the computational model or simulation that was performed, a series of partial differential equations (PDE) and trail functional (TF) were utilized to determine the effects of four solutions that comprised the varies stresses within our silicon nanowire model. The solutions of PDE with the use of TF are: 1) Elastic Displacement  $\mathbf{u}$ , 2) Concentration  $\bar{c}$ , 3) Magnetic Field  $\mathbf{B}$ , and 4) Electric Field  $\mathbf{E}$  which culminates in radial stress equation

$$\sigma_r = \bar{E} \left[ \frac{\nu}{2} \left( \frac{\mathbf{u}}{R_c} \right) - \frac{\Omega}{6} \bar{c} (1 + \nu) + \frac{a\mathbf{B}}{\rho P} (1 - 2\nu) \right] \quad (1)$$

$$\text{where } \mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2)$$

where  $\bar{E}$  is the modulus of elasticity, ( $\nu$ ) is the Poisson constant, ( $a$ ) is the lattice constant and  $R_c$  is the radius of curvature.

### 2. The Quantum Mechanical Model

Unlike continuum mechanics to describe the lithiation process in terms of varies stresses where a computer generated model was created from a large group of differential equations, the quantum mechanics approach that will be presented will use a heuristic method in examining the lithiated silicon process. Prior to the beginning of the lithiation process, there is no electron flow through the silicon nanowire. We will start the description of our model from the quantum mechanical perspective by developing the band structure of our pre-lithiated silicon nanowire. Silicon, which is a semiconductor material, is made up of band structures composed of valence and conduction bands which are separated by indirect band gap energy  $E_g$ . Silicon is a diamond cubic crystalline structure made up of tetrahedral molecules with its hybridized  $sp^3$  orbitals within their valence shells filled with covalent bonding electrons from neighboring silicon atoms. Because the valence orbitals are completely filled, electron are not able to move freely within the crystal until a voltage is applied to the band structure. For silicon material, electrons within the valence band needs a minimum band gap energy of 1.1 electron volts in order to transition by way of trans-versing the band gap from the valence band to conduction band to create current flow. The Schrödinger equation is used to calculate the band structure by solving this eigenvalue equation in order to derive the band energies and wavefunctions of the individual electrons. For our model, we will use the Time-Dependent Schrödinger equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi \quad (3)$$

The Hamiltonian is defined as

$$H = H_0 + H_p \quad (4)$$

The total Hamiltonian ( $H$ ) is composed of an initial or unperturbed Hamiltonian  $H_0$  that represents the state of the silicon nanowire before the start of lithiation and a perturbed Hamiltonian  $H_p$  that define the additional energy the nanowire will be subjected to by electromagnetic field. The unperturbed Hamiltonian  $H_0$  is defined as:

$$H_0 = \frac{\hbar^2}{2m} \nabla^2 + V(r) + \frac{\hbar}{4m^2 c^2} \frac{1}{\mathbf{R}} \cdot \nabla V \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \quad (5)$$

where  $\hat{\mathbf{S}}$  and  $\hat{\mathbf{L}}$  are defined as the spin and angular momentum operators respectively. The spin operator  $\hat{\mathbf{S}}$  are the Pauli matrices that are commonly used in quantum mechanics. The mass ( $m$ ) is defined as the rest mass of the electron,  $\hbar$  is the Planck's constant,  $c$  the velocity of light and  $\mathbf{R}$  is the position operator. The potential  $V(r)$  is a sum of several terms that are the interactions of the constitutive particles of this nanowire model namely silicon, lithium and electrons. The overall electric potential is defined as:

$$V(r) = V_{e-e} + V_{e-Si} + V_{e-Li} + V_{Si-Si} + V_{Si-Li} + V_{Li-Li} \quad (6)$$

The unperturbed Hamiltonian  $H_0$  is used in the  $\mathbf{k} \cdot \mathbf{p}$  theory which is a mathematical method used to calculate the band structure in semiconductor materials such as silicon. In equation 5, the first term is the kinetic energy term (the  $\mathbf{k} \cdot \mathbf{p}$  method formulates this term as being positive instead of negative as is the case in most Hamiltonians in Schrödinger equation), the second term as was mention is  $V(r)$  and the third term is the spin-orbital interaction term responsible for the energy that is generated from the interaction between the particles spin and orbital angular momentum. Figure 1 illustrates the conduction band structure due to  $H_0$  prior to the application of the electromagnetic fields at the moment lithium insertion begins. The band structure is crystalline silicon (c-Si) with an indirect band gap energy which are represented by the dispersion relation equations that are the result of the solution of the Schrödinger equation using the unperturbed Hamiltonian  $H_0$ .

Minimum conduction band

$$E_c = E_{k0} + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{E_{Si} m^2} \sum_n |\langle u_c | \mathbf{k} \cdot \mathbf{p} | u_v \rangle|^2 \quad (7)$$

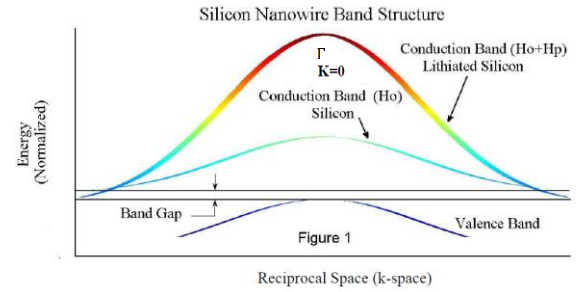
and the maximum valence band

$$E_v = -\frac{\hbar^2 k^2}{2m} \quad (8)$$

where  $E_{k0} = E_{k0}(0, t)$  is an energy coefficient,  $\mathbf{k}$  is the wavevector,  $\hat{\mathbf{p}}$  the momentum operator,  $u_c$  and  $u_v$  are gaussian functions for the conduction and valence bands respectively, and  $E_{Si}$  is the band gap energy of silicon. This as was stated previously is a constant at 1.1 eV. From equations 7 the effective mass  $m_{eff}$  can be derived as

$$\frac{1}{m_{eff}} = \frac{1}{m} + \frac{2}{E_g m^2} \sum_n |\langle u_c | \mathbf{k} \cdot \mathbf{p} | u_v \rangle|^2 \quad (9)$$

and  $E_g$  is in general the band gap energy.



The perturbed Hamiltonian  $H_p$  is the energy added to the silicon nanowire the moment lithiation process begins.  $H_p$  is defined as:

$$H_p = -\frac{e}{2 m_{eff} c} \mathbf{B} \cdot \hat{\mathbf{L}} + \frac{e^2}{8 m_{eff} c} [\mathbf{B}^2 \mathbf{r}^2 - (\mathbf{B} \cdot \mathbf{r})^2] + \frac{e^2 \mathbf{E}^2}{2 m_{eff} \omega^2} \quad (10)$$

where ( $e$ ) is the electron charge and ( $\omega$ ) is the angular frequency of the electric field. In our computational continuum model, the applied electric field  $\mathbf{E}$  and magnetic field  $\mathbf{B}$  magnitudes are of a small scale to a degree that the electric field  $\mathbf{E}$  is just above the threshold to allow electrons from the silicon to transition from valence band to the conduction band. The magnitude of the applied magnetic field  $\mathbf{B}$  is several orders below the electric field  $\mathbf{E}$ . When the lithiation process begins, this initiates a process of transforming from crystalline silicon (c-Si) to an

amorphous lithiated silicon (a-LiSi) material. Lithium in its natural metallic crystalline form has electrons in its conduction band and therefore an energy band gap of zero. As lithium atoms diffuses into the silicon structure, the silicon band gap transition to a band gap that is representative of lithiated silicon. As lithium becomes the predominated material within the structure, the newly formed a-LiSi material band gap approaches zero. This transforms the effective mass of the electron from that of c-Si prior to lithiation to a value that of a-LiSi which also approaches zero. As a result, the conduction band energy at the gamma point  $\Gamma$  at  $k=0$  of lithiated silicon (a-LiSi) increases while at the same time the slope on the curve increases as illustrated in figure 1.

### 3. Continuum Model vs Quantum Model

The perturb Hamiltonian in equation 10 is analogous to the third term of the radial stress equation in equation (1).

$$\sigma_{em} = \bar{E} \left[ \frac{aB}{\rho \epsilon_0 \chi E} (1 - 2\nu) \right] \quad (11)$$

$$H_p = -\frac{e}{2 m_{eff} c} \mathbf{B} \cdot \hat{\mathbf{L}} + \frac{e^2}{8 m_{eff} c} [\mathbf{B}^2 r^2 - (\mathbf{B} \cdot \mathbf{r})^2] + \frac{e^2 E^2}{2 m_{eff} \omega^2} \quad (12)$$

In equation 11 the resistivity parameter  $\rho$  approaches zero as lithium atoms diffuses into the c-Si nanowire which is analogous to the effective mass approaching zero as the band gap narrows due to lithium diffusion.

#### Continuum Model:

Resistivity  $\rho \longrightarrow 0$  (approaches zero)

#### Quantum Model:

Band Gap Energy  $E_g \longrightarrow 0$

Effective Mass  $m_{eff} \longrightarrow 0$

The partially lithiated silicon nanowire from the viewpoint of the continuum model, as the resistivity  $\rho$  decreases due to lithium insertion, a compressive electromagnetic stress is generated. The current is minute and constant at 1 nA which results in the magnetic  $\mathbf{B}$  and electric  $\mathbf{E}$  fields close to zero [2]. In addition  $\mathbf{E}$  and  $\mathbf{B} < \rho$ . As the resistivity approaches zero due to lithium diffusion, the resulting electromagnetic stress is small in comparison to a much larger stress

observed when the silicon nanowire is fully lithiated and excessive volume expansion is the outcome. Although the resistivity for the lithiated silicon is approaching zero, the electron flow or current density is extremely small which results in an electromagnetic stress in the order of  $10^2$  smaller in magnitude when the nanowire is fully lithiated with a volume 300% larger in size then the undeformed nanowire (figure 2). Similarly, from the quantum mechanics point of view, as the band gap between the conduction and valence bands become narrower due to lithium diffusion, this decreases the effective mass, however as with the continuum model, the magnetic field and electric field are extremely small and  $\mathbf{E}$  and  $\mathbf{B} < m_{eff}$ . Therefore the perturbed Hamiltonian  $H_p$  approaches zero.

In the case of the fully lithiated silicon nanowire, when analyzing the lithiation process from a continuum perspective, an applied constant voltage of 2-V causes an increase in the current density as the resistivity  $\rho$  decreases from the result of lithium diffusion [3]. This results in  $\rho < \mathbf{E}$  and  $\mathbf{B}$ . The resulting electron flow that is several orders of magnitudes larger than that of the partially lithiated nanowire, results in an increase in the electromagnetic stress which is the cause of the excessive volume expansion of the nanowire. From the quantum mechanics perspective, the magnetic  $\mathbf{B}$  and electric  $\mathbf{E}$  fields grows in magnitude due to an increase in electron flow from lithium diffusing into the silicon nanowire. As a result the band gap decreases and the perturbed Hamiltonian increases from the fact that  $m_{eff} < \mathbf{E}$  and  $\mathbf{B}$ . The lithiated silicon conduction band structure shift upwards along the energy axis as noted in figure 1. This results in greater momentum and kinetic energy for the individual electrons as they transition from the valence band of the lithiated silicon molecules to the conduction band.

### 4. Electron Scattering

Up until now our discussion on the quantum mechanical model has focus solely on the Hamiltonian. We now state the other part of the Schrödinger equation, the wavefunction  $\Psi$ . Each individual electron wavefunction will be defined prior to collision with an atom as

$$\Psi(\mathbf{r}, \theta, \phi, t) = \sum_{\mathbf{k}} c_{\mathbf{k}} \left[ \mathbf{u}_{inc}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} + \mathbf{u}_{sc}(\theta, \phi) \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{r} \right] e^{-\frac{iE_{\mathbf{k}}t}{\hbar}} \quad (13)$$

The wavefunction consist of two terms, the first term is known as the incident wavefunction and the second term is called the scattering wavefunction. When an electron is traveling in the conduction band the first term of the wavefunction describes the electron from a point before impact with the oncoming atom (incident wavefunction) and the second term of the wavefunction describes the electron after impact with the colliding atom (scattering wavefunction). The second term of the wavefunction dissipates with the inverse of the radial distance  $r^{-1}$  which begins from the point of the scattering electron with the atom. The current density is calculated with the use of the wavefunction

$$\mathbf{J} = -\frac{i\hbar}{2m_r} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) \quad (14)$$

where  $m_r$  is defined as the reduced mass between the electron and the colliding atom. The current densities of the incident and scattering parts of the wavefunction are determined separately. If the scattering current density is solved by their individual spherical components -  $\mathbf{J}_r, \mathbf{J}_\theta, \mathbf{J}_\phi$  - it is discovered that the radial current density component  $\mathbf{J}_r$  disperses at a rate of  $r^{-2}$  while both of the angular current density components,  $\mathbf{J}_\theta, \mathbf{J}_\phi$ , dissipates at a rate of  $r^{-3}$

Incident current density:

$$\mathbf{J}_{inc} = \frac{k\hbar}{m_r} |u_{inc}(\theta, \phi)|^2 \quad (15)$$

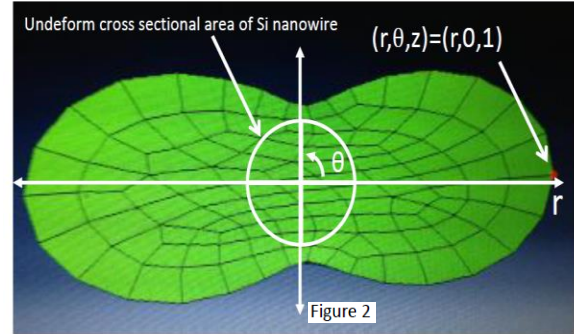
Scattering current density:

$$\mathbf{J}_r = \frac{k\hbar}{r^2 m_r} |u_{sc}(\theta, \phi)|^2 \quad (16)$$

$$\mathbf{J}_\theta = \mathbf{J}_\phi = \frac{k\hbar}{r^3 m_r} |u_{sc}(\theta, \phi)|^2 \quad (17)$$

Since the current density leads to the determination of other observables or measureable quantities i.e. angular momentum, energy, stress etc. – than these observables that are described in the wavefunction should also disperse in a similar way. As displayed in figure 2, the anisotropic cross sectional shape of the silicon nanowire (Cassini oval shape) is the result of excessive volume expansion in the radial direction while the expansion in the other two orthogonal directions is of a lesser extent. The scattering of electrons off of lithium and silicon atoms has the resulting electromagnetic stress that is larger and disperse at a slower rate in the

radial direction as opposed to the zenith angle  $\theta$  and azimuth angle  $\phi$  directions which dissipates at a much faster rate and therefore the electromagnetic stress is weaker in these orthogonal directions.



## 5. Summary

This report presented the possible explanation of two adverse effects that researchers has encountered separately, partially lithiated and excessive volume expansion in silicon nanowires. This paper offers three root causes to these effects that operates in conjunction with each other: 1) The change in band gap energy as c-Si transform to a-LiSi, 2) The current density differences within the nanowire and 3) The collisions of electrons with lithium and silicon atoms. Future research is needed in the way of molecular dynamics and/or density function theory in order to confirm these assertions.

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## References

- [1] Stephanie Golmon, et.al, Stress generation in silicon particles during lithium insertion, Applied Physics Letters 97 033111, 2010
- [2] Xiao Hua Liu, et.al, Self-Limiting Lithiation in Silicon Nanowires, ACS NANO 7 (2) p1495–1503 2013
- [3] Xiao Hua Liu et.al, Anisotropic Swelling and Fracture of Silicon Nanowires during Lithiation, Nano Letter 11 p3312-3318 2011