2011

Silicon nanowire anode for lithium-ion batteries: fabrication, characterization and solid electrolyte interphase

Wanli Xu
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SILICON NANOWIRE ANODE FOR LITHIUM-ION BATTERIES:
FABRICATION, CHARACTERIZATION
AND SOLID ELECTROLYTE INTERPHASE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Gordon A. and Mary Cain Department of Chemical Engineering

by

Wanli Xu
B.S., Dalian University of Technology
August 2011
DEDICATION

To My Loving Parents,
Grandparents,
And Husband Zhe Nan

谨以此文
献给
我挚爱的父亲母亲
爷爷奶奶
和丈夫南哲
ACKNOWLEDGEMENTS

First of all, my heartfelt gratitude goes out to my supervisor, Professor John C. Flake, for successful completion of my dissertation. I am so honored to join in his research group as the first graduate student, and worked with him to set up the lab and equipment from scratch. His untiring effort, encouragement, guidance and support helped me greatly in my graduate studies as well as successful completion of this dissertation. I will be benefiting from this valuable experience for my lifelong endeavors in academia.

I also want to thank all of my committee members: Professor Gregory L. Griffin, Karsten E. Thomson, Jayne Garno and Richard L. Kurtz for their valuable suggestions and help in my academic research. I appreciate great help from Dr. Dongmei Cao from Material Characterization Center (MCC) and Dr. Vadim Palshin from Center for Advanced Microstructures and Devices (CAMD), and Dr. Ying Xiao from Department of Biology, LSU in material characterization training and expertise.

My sincere thanks go to all the people who have contributed to my graduate studies in Louisiana State University, including Professor James J. Spivey, James E. Henry, and Kerry M. Dooley from Department of Chemical Engineering, and Professor Phillip T. Sprunger from Department of Physics, LSU.

I am greatly appreciative of all the people who took part in my research, including other members from our research group: Sri Sai Vegunta, Joel Nino Bugayong, Purnima Narayanan, Minh Le, Johnpeter Ngunjiri and Maoming Ren; as well as Nitin Kumar, Nachal Devi Subramanian, Andrew Campos, and Mia Dvora from Department of Chemical Engineering; Golden Hwang, Wenyu Song and Xiaofeng Chang from Department of Electrical Engineering; Li Lu, Weiping Qiu, and Ranran Liu from Department of Mechanical Engineering for their generous help throughout these years.
Many great thanks also go to all the supporting staff from Department of Chemical Engineering: Paul Rodriguez, Joe Bell, Darla Dao, Melanie McCandless, and Robert Willis for their generous help.

Last but certainly not least, I cannot imagine going through the past five years in graduate study and complete this dissertation without endless support from my family and friends. I want to thank my loving husband Zhe Nan for his unconditional love, support and caring for me wholeheartedly throughout this special time. Special thanks also go to my dear friends: Di, Limin, Yuan and Lingyan.
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Depletion of fossil fuels and concerns over CO$_2$ emission have driven the development of electric vehicles (EVs) with high-energy efficiencies and low emissions. Lithium-ion rechargeable batteries, compared to lead acid, nickel cadmium, nickel metal hydroxide, and other popular rechargeable batteries, are considered as the most promising candidates for EVs for their high operating voltage and high energy density. Silicon nanowires are considered as lithium-ion battery anodes for their ultra high capacity at 4200 mAh·g$^{-1}$ (10× higher than conventional graphite anode), as well as stress accommodation for reversible lithiation and delithiation. Silicon nanowires were fabricated via metal assisted electroless etching, and conductive nickel monosilicides ohmic contacts were created via simple one-step thermal annealing procedure between nanowires and nickel electrodes for integration. Composite anodes were prepared from electrolessly fabricated silicon nanowires for lithium-ion batteries, and an addition of only 15% silicon nanowires results in a two-fold increase in reversible capacities for 15 cycles. Silicon anodes with hydride, methylated and siloxane surface terminations were prepared and tested in lithium-ion cells; another silicon anode was cycled with 5% trimethoxymethylsilane. Analyses showed methylated and siloxane terminations lead to passivated surfaces, and hydride-terminated nanowires were relatively more reactive with electrolytes. The addition of silane additive results in more OPF$_x$ compounds and Si-O-Si bonds at the silicon surface with significantly higher capacities (3287 mAh·g$^{-1}$). AFM nano-indentation analyses also showed a significant increase in contact stiffness with silane additive, and the increase in contact stiffness may improve the anode’s ability to withstand large volume changes. Although the chemical composition of the SEI is altered with silane additives, performance improvements were mainly associated mechanical effects.
CHAPTER 1 INTRODUCTION

1.1 Context and Motivation

Based on current annual consumption and available fossil fuels, it is estimated the world’s fossil fuel resource will be running out in the next 50 to 60 years (Denker 2003; Roper 2011). Combustion of fossil fuels has also caused massive environmental and ecological problems associated by emitting air pollutions (AP) and green house gases (GHG). Electric vehicles (EVs) adopt electric motors and use clean and efficient electricity as power supply and secondary battery systems for energy storage. EVs are promising alternatives to conventional motor vehicles to solve the above issues by consuming less energy as well as emitting less AP and GHG (Karden et al. 2007). Comparison of technical characteristics for conventional, hybrid, and electric vehicles, including fuel consumption and emission is shown in Table 1.

Table 1 Technical characteristics for conventional, hybrid and electric vehicles

<table>
<thead>
<tr>
<th>Vehicle Type</th>
<th>Fuel</th>
<th>Specific Fuel Consumption (MJ/100 km)</th>
<th>Specific Fuel Price (US$/100 km)</th>
<th>GHG Emission (kg/100 km)</th>
<th>AP Emission (kg/100 km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Gasoline</td>
<td>236.8</td>
<td>2.94</td>
<td>19.9</td>
<td>0.0564</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Gasoline</td>
<td>137.6</td>
<td>1.71</td>
<td>11.6</td>
<td>0.0328</td>
</tr>
<tr>
<td>Electric</td>
<td>Electricity</td>
<td>67.2</td>
<td>0.901</td>
<td>0.343</td>
<td>0.00131</td>
</tr>
</tbody>
</table>

* Data adapted from Electric and Hybrid Vehicle (Pistoia 2010)

According to data released by the US Energy Information Administration (EIA) in 2009, over 98 % energy consumed by transportation is originated from fossil fuels; while consumption of electricity for vehicles is negligible compared to traditional fuels such as gasoline and diesel (EIA 2009). In 2009, President Obama announced the release of $2.4 Billion in federal funding to develop next generation batteries and EVs, with a target to have 1 million EVs on the road by the end of 2015 (White House 2009). Up to 2011, there are only two commercial EVs available on the US market, including Chevrolet VOLT and Nissan LEAF. With the state-of-art lithium-
ion battery technology, Nissan LEAF (curb weight approximately 3366 lb.) can only travel 100 miles at speed of 60 miles per hour after one single charge for eight hours (NISSAN 2011). Current energy densities achieved for EVs batteries are way below energy density of gasoline. For example, existing batteries may provide an effective energy range of approximately 1-5 miles per 100 lb. (specific energy of 0.1-0.7 MJ/kg) versus approximately 300 miles per 100 lb. of gasoline (46 MJ/kg). In addition to the challenge of increasing specific energy, cost and life span are major concerns for batteries of EVs. Therefore, development of high capacity, high-energy density, long cycle life and economic secondary battery systems poses as main challenges for widespread utilization of EVs.

Lithium-ion rechargeable batteries, compared to lead acid, nickel cadmium, nickel metal hydroxide, and other popular rechargeable batteries, are considered as the most promising candidates for EVs for their high operating voltage, high energy, and high power density. Currently, lithium-ion batteries use graphite as anode for reversible lithium intercalation and disintercalation. Graphite poses as a limitation for the development of high capacity lithium-ion batteries with a maximum theoretical specific capacity of only 372 mAh·g⁻¹ for reversible lithium storage. Silicon has come into view in recent years for its highest capability in safely storing lithium of 4200 mAh·g⁻¹ at fully lithiated state (Li₂₂Si₄) among any substances. Silicon is not suitable for direct usage as anode material in lithium-ion battery technology due to volume expansion for over 300 % when fully lithiated. Silicon nanowire structures have shown great potential in achieving high capacities as well as accommodating reversible volume change in recent studies (Chan et al. 2008). Novel silicon anodes with nanowire structure and engineered surface chemistry will be presented in this work.
1.2 This Work

Chapter 1 is an introduction to the motive and context of the study on silicon nanowire anodes of lithium-ion batteries. A brief description on the content of each chapter in this work is also presented.

Chapter 2 covers literature review and background of lithium-ion batteries and silicon nanowires, including: mechanism for lithium storage, battery electrodes and electrolyte, important solid electrolyte interphase on anode surface, silicon nanowire fabrication, integration, and applications such as anodes for lithium-ion batteries.

Chapter 3 demonstrates the fabrication and integration of silicon nanowires to metal substrate via electrical connections. Silicon nanowires can be fabricated via facile electroless etching methods in aqueous solution under controlled conditions; the nanowires can then be detached from parent substrates, transferred and stored in the form of solution or powders. In order to integrate these silicon nanowires, metallic alloy nickel silicide (such as nickel monosilicide: NiSi) between silicon and nickel metal electrodes can be formed via thermal annealing process to create low-resistivity ohmic contacts so as to create electrical connections in microelectronic devices and other promising applications. The detail experimental procedures and data will be presented, and further material characterization via spectroscopic tools will be carried out to prove the formation of NiSi on silicon nanowires.

In Chapter 4, Silicon nanowires will be applied as anode material for lithium-ion batteries for their massive lithium storage capability and 1-D structure for stress relaxation. The nanowires have been applied in the form of both nanowire arrays and composite anodes (nanowires are mixed with graphite and other materials), and tested in lithium-ion half cells. Silicon nanowire arrays and composite anodes concentrations (by mass) including 5 %, 15 % and 45 % silicon
nanowires will be studied, and charge and discharge capacities will be obtained via electrochemical measurements for each anode.

Chapter 5 further discusses the practice to improve silicon nanowire anodes performance via modifying silicon surface chemistry so as to engineer the composition and mechanical property of the Solid Electrolyte Interphase (SEI) on silicon anodes. Several surface functionalizations including hydride-terminated, methylated, and siloxane-terminated surfaces will be applied to silicon nanowire anode, and electrochemical measurements including voltammetry and charge and discharge tests and material characterizations such as FT-IR, XPS, and AFM analyses will be carried out to study the anode capacity retention and SEI compositions. Discussions including SEI formation mechanism with modified silicon surface chemistry, chemical and mechanical properties of the SEI, and effects of modified surface chemistry as well as SEI on anode capacity retention will be presented.

Chapter 6 is the conclusion of this dissertation, including silicon nanowire electroless fabrication, integration via NiSi, silicon nanowire anodes for lithium-ion batteries, as well as the SEI on silicon anodes with modified surface chemistry presented and discussed in previous chapters. Several suggestions and recommendations are proposed for future work, in hopes of developing high capacity, long life silicon anodes for lithium-ion batteries.
CHAPTER 2 LITERATURE REVIEW

2.1 Lithium-Ion Battery

2.1.1 Introduction

Batteries are energy storage systems that convert chemical energy stored in electrodes to electrical energy via electrochemical reduction-oxidation (redox) reactions. A battery consists of two coupling electrodes for energy storage (positive and negative electrodes), and a conductive electrolyte (either solid or liquid) in which the two electrodes are electrically connected. When a battery is connected to a load, the electrochemical potential between the two electrodes drives electrons from the negative electrode to the positive electrode, and induce redox reactions within the electrodes for continuous electron release. There are two types of battery systems: primary and secondary (or rechargeable) batteries. When chemical sources are depleted, primary batteries can not be restored; while secondary batteries have reversible redox reactions and are capable of restoring to their original chemical composition after charge and discharge for over hundreds or thousands of cycles (Sammells 1983).

Since the invention of the first battery by Alessandro Volta in 1800, a variety of battery systems have been developed (Considine 2002). Lithium metal is an attractive energy storage source for its light weight (0.53 g·cm⁻³), high specific capacity (3862 mAh·g⁻¹), and highest operation voltage (-3.04 V versus SHE) (Tarascon et al. 2001). Upon continuous charge and discharge, dendrites form on lithium surfaces and cause short circuit; therefore, metallic lithium is not widely applied as anode material in rechargeable batteries. Carbon has then been found to safely store lithium and allow lithium intercalation and disintercalation reversibly. Since Yoshio Nishi et al. from SONY have developed the first lithium-ion battery adopting carbonaceous electrodes in 1991, lithium-ion battery system has become one of the most popular battery systems for its high capacity, compact size and light weight (Kezuka et al. 2001).
Lithium batteries have both the highest volumetric and gravimetric energy density among known technologies applied, including lead-acid, nickel-cadmium, nickel metal hydroxide and other systems as plotted in Figure 1 (Tarascon et al. 2001). Similar to any other rechargeable battery systems, Lithium-ion battery typically consists of a carbonaceous anode (negative electrode), a lithium metal oxide cathode such as layered LiCoO$_2$ or spinel LiMn$_2$O$_4$ (positive electrode) and a non-aqueous organic electrolyte in between.

A schematic presentation of a lithium-ion cell is shown in Figure 2. Both of the electrodes work as lithium storage matrix for reversible lithium insertion and extraction; while the electrolyte serves as an ionic pathway for lithium ion transport as well as a separator for the two electrodes. The energy storage mechanism for lithium-ion battery can be explained as: upon charging lithium stored in cathode is oxidized to lithium ion and released to electrolyte, while
lithium ion is reduced and intercalates into anode; upon discharging lithium is oxidized and disintercalates from anode, and lithium ion is reduced and inserted into cathode matrix.

![Schematic of lithium-ion battery](image)

Figure 2 Schematic of lithium-ion battery

Equation [2-1] and [2-2] are the corresponding reactions for anode and cathode upon charging, and the reactions are reversed during discharging:

**Anode reaction:**

\[ x\text{Li}^+ + 6\text{C} + xe^- \leftrightarrow \text{Li}_x\text{C}_6 \]  

[2-1]

**Cathode reaction:**

\[ \text{LiMn}_2\text{O}_4 \leftrightarrow xe^- + \text{Li}_{(1-x)}\text{Mn}_2\text{O}_4 + x\text{Li}^+ \]  

[2-2]

The lithium-ion battery total capacity strongly depends on capacities of anode, cathode and other cell components. For example, the relationship between the total cell capacities and the anode capacities for standard 18650 lithium-ion battery can be plotted in Figure 3 when the cathode capacities are constant at 140 and 200 mAh·g\(^{-1}\), respectively. Total capacity increases as anode capacity increases up to 1500 mAh·g\(^{-1}\) as shown in Figure 3; when anode capacity is over 2000 mAh·g\(^{-1}\), increase in total capacity is negligible. It can be estimated that current carbon
anodes with capacity of 372 mAh·g⁻¹ are able to achieve total capacity of 95-120 mAh·g⁻¹ (Kasavujjula et al. 2007). Therefore, target anode capacity of over 1000 mAh·g⁻¹ is desirable to overcome current capacity threshold and increase total cell capacity by two folds to approximately 200 mAh·g⁻¹.

![Figure 3 Estimation of total cell capacities for 18650 lithium-ion batteries with anode capacities when cathode capacities are constant (Reprinted from Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells by Kasavujjula et al., copyright (2007) with permission from Elsevier.)](image)

2.1.2 Silicon Anodes: Advantages and Challenges

Various materials have been studied as anodes for lithium storage in the past several decades. Besides lithium metal, several materials form alloys with lithium or host lithium and can be applied for lithium storage for battery purpose, such as C, Si, Sn, Sb, Al, Mg, Bi, In, Zn, Pb, Ag, Pt, Au, Cd, As, Ga, Ge, etc. Only C, Si, Sn, Sb and Al have been studied extensively in the previous studies (Zhang 2011). Comparison of several anode material including density,
lithiated phase, specific capacity, volume change after lithiation and onset potential for lithium insertion are tabulated as follows in Table 2.

Table 2 Comparison of various anode materials for lithium-ion battery including: density, lithiated phase, specific capacity, volume change and onset potential for lithiation

<table>
<thead>
<tr>
<th>Material</th>
<th>Li</th>
<th>C</th>
<th>Si</th>
<th>Sn</th>
<th>Sb</th>
<th>Al</th>
<th>Mg</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g·cm⁻³)</td>
<td>0.53</td>
<td>2.25</td>
<td>2.33</td>
<td>7.29</td>
<td>6.7</td>
<td>2.7</td>
<td>1.3</td>
<td>9.78</td>
</tr>
<tr>
<td>Lithiated Phase</td>
<td>Li</td>
<td>LiC₆</td>
<td>Li₂₂Si₅</td>
<td>Li₂₂Sn₅</td>
<td>Li₃Sb</td>
<td>LiAl</td>
<td>Li₃Mg</td>
<td>Li₃Bi</td>
</tr>
<tr>
<td>Theoretical specific capacity (mAh·g⁻¹)</td>
<td>3862</td>
<td>372</td>
<td>4200</td>
<td>994</td>
<td>660</td>
<td>993</td>
<td>3350</td>
<td>385</td>
</tr>
<tr>
<td>Volume change (%)</td>
<td>100</td>
<td>12</td>
<td>320</td>
<td>260</td>
<td>200</td>
<td>96</td>
<td>100</td>
<td>215</td>
</tr>
<tr>
<td>Potential vs. Li (V)</td>
<td>0</td>
<td>0.05</td>
<td>0.4</td>
<td>0.6</td>
<td>0.9</td>
<td>0.3</td>
<td>0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Carbon in the form of graphite has been widely used as anode material for its laminated structure to safely store lithium. As shown in Table 2, carbon has the lowest specific capacity of 372 mAh·g⁻¹ and the minimum volume change of 12% after lithiation. Although the low capacity for carbon is a disadvantage in developing lithium-ion battery with ultrahigh capacity, low volume change allowing carbon to maintain its integrity and be cycled for over hundreds or thousands of cycles, as well as low fabrication cost facilitate its wide applications.

Silicon has attracted great attention due to its highest theoretical capacity of approximately 4200 mAh·g⁻¹ for lithium insertion at fully lithiated phase (Li₂₂Si₅ or Li₄.₄Si) among known substances (Okamoto 1990). The reaction of silicon with lithium to its richest phase can be expressed as:

\[
22Li^+ + 5Si + 22e^- \leftrightarrow Li_{22}Si_5
\] [2-3]
Other than highly lithiated Li$_{22}$Si$_5$ phase for maximum lithium storage, crystalline Li$_{15}$Si$_4$ phase appears below 60 mV versus Li/Li$^+$ as investigated via in-situ X-ray diffraction study (Li et al. 2007). Therefore, cut-off potential for anode charging maintained above 70 mV is preferable to avoid the formation of less lithiated crystalline Li$_{15}$Si$_4$ phase.

Successful application of silicon anodes in lithium-ion batteries would allow over 10 times increase in anode specific capacity, which could double or even triple lithium-ion cell capacity with conventional cathode and electrolyte (Dimov et al. 2003). Large volume change for over 300 % for lithium insertion and extraction causes critical issues for silicon anodes, posing severe problems in practical applications:

Silicon structural expansion results in anode pulverization and cracking, as well as delamination of anodes and loss of active material. Surface morphology change can be observed for silicon anodes with cracking and pulverization as shown by SEM analysis. Volume expansion also causes contact loss among silicon and other material within the anodes, as well as contact loss between anodes and current collectors. Increases in internal resistance and decreases in charge and discharge current can be observed when contact loss happens, and are the main reasons that cause large irreversible capacity loss for the first several charge and discharge cycles and capacity fade for prolonged cycles.

Lithium species may be permanently consumed or trapped in silicon anode matrix continuously, causing irreversible capacity fade throughout charge and discharge cycles. For example, during the initial charge cycle, surface silicon oxide may react with lithium to form lithium oxide which cannot be reduced upon discharge. Lithium ion may also react with by-product from electrolyte reduction and form insoluble lithium compound such as lithium fluoride. Lithium can also be trapped in silicon sites, in which it may lose contact with other anode
material during silicon structural expansion and cannot be released during discharge. The trapping of lithium will result in low coulombic efficiency and continuous capacity fading.

The large volume expansion may also result in nearby silicon particles (in the case of silicon particle composite anodes) to merge with each other and agglomerate into bulky silicon structures. Bulky silicon structures see severe cracking and pulverization due to increased internal stress, and results in further capacity loss.

The solid electrolyte interphase (SEI) formed on silicon anodes plays a critical role in anode capacity retention by protecting anode surface, conducting lithium ion, maintaining anode integrity, etc. Unlike graphite anodes, large volume change results in a series of SEI formation, breakage, and reformation processes for silicon anodes. Compared with relatively inert carbon, silicon is reactive to electrolytes and reduction products, which may cause significant capacity loss for silicon. Incomplete coverage of the SEI and the SEI breakage due to anode volume change expose active silicon surface to the electrolyte, which induces further undesired reactions. The solid electrolyte interphase and silicon surface chemistry will be discussed in detail in section 2.1.3.

Tremendous efforts have been devoted to developing silicon anodes for lithium-ion batteries in various forms and via various methods in order to overcome the above issues with silicon. As proposed by Graetz et al., the critical size free from cracking for polycrystalline silicon has been estimated by applying equation for brittle material crack propagation:

\[
\alpha_c = \frac{2 K_{1c}^2}{\pi \sigma^2}
\]  

[2-4]

where \( \alpha_c \) is the critical size for crack propagation [m], \( K_{1c} \) is fracture toughness [MPa/m \(^{1/2}\)], and \( \sigma \) is yield strength [GPa]. The values for \( K_{1c} \) and \( \sigma \) are 0.751 MPa/m \(^{1/2}\) and 1.1 GPa, respectively (Graetz et al. 2003). Based on the calculation, the critical silicon size below 300 nm is suggested
to avoid cracking for silicon. A variety of forms of nano and bulk silicon has been extensively studied and great effort has been made to prepare anode with silicon (Kasavajjula et al. 2007). To date, silicon anodes reported in lithium-ion batteries generally fall into two main categories: composite silicon anodes and pure silicon anodes.

◆ Composite Silicon Anodes

Composite graphite anodes are the most common anodes for current lithium-ion battery technologies, featuring a combination of graphite, carbon black, PVdF, NMP, etc. All anode materials are mixed homogenously to create a paste or slurry, and coated onto current collector (Scrosati 2002).

Silicon micro and nano powders have been integrated into composite anodes for lithium-ion batteries in the following procedures:

1. Silicon (micro or nano particles) is mixed with or without other active material (graphite), conductive material (carbon black), binders (PVdF, CMC), solvents (NMP with PVdF, H₂O with CMC) and other additives to form a paste;
2. The paste is applied as a thin layer (~100 µm) to current collector (copper/nickel/aluminum foil) via doctor blade technique;
3. Anodes are dried and cured by thermal heating before assembled into lithium-ion cells.

Graphite and binders provide a flexible and resilient matrix for silicon particles to accommodate large volume change, and carbon black helps to increase internal conductivity for better performance. Silicon particle size, silicon content concentration and ratios of other components need to be carefully tailored to achieve optimal anode performance in both initial capacities and capacity retention for prolonged cycles.
In attempt to overcome issues with silicon anodes, six types of methods have been applied to improve the reversible capacity and cycle life for silicon composite anodes as discussed in following paragraphs.

**Combining silicon with lithium-inactive elements**

Inactive material matrix has been studied for silicon composite anode to solve the issues of volume change. Co, Fe, Ni, Ca, B, and several other materials have been studied; however, the reversible capacities are reduced with the presence of these inactive materials, suggesting the replacement for other materials (Kasavajjula et al. 2007).

**Combining silicon with lithium-active elements**

Besides carbon, silicon particles mixed with lithium active substances, such as Mg, Ag, and Sn., have been studied as composite anodes. These lithium active additives react with lithium to form alloy as well as silicon, serving as hosting matrix and conductive path way for silicon particles (Kasavajjula 2007).

**Mixing silicon particles homogenously via high energy mechanical milling**

High-energy ball milling was introduced into composite anode preparation, particle size can be greatly reduced and homogenously distributed into anode matrix, so as to reduce agglomeration and improve anode capacity retention. Silicon and polypyrrole composite created via high energy ball milling showed stable reversible capacity of approximately 1000 mAh·g⁻¹ with 50% silicon content (Guo et al. 2005). Silicon particles have been mixed with carbon nanotube by mechanical ball milling to establish a “lamellar” matrix. This composite anode material showed a reversible capacity of 584 mAh·g⁻¹ was retained for over 20 cycles (Zhang et al. 2006).
• **Coating silicon with carbon and carbon derivatives**

Carbon coating on silicon surface has been demonstrated as an effective way to improve electrical connections within the anode matrix as well as preserve silicon particle integrity. Recent studies have shown improved capacity retention and cycle life with carbon-coated silicon particles. It has been demonstrated that silicon particles coated with carbon via thermal vapor deposition (TVD) maintained high reversible capacity of 800 mAh·g⁻¹ for over 20 cycles (Yoshio et al. 2002). Composite anode with silicon and graphite embedded in carbon matrix pyrolyzed from petroleum pitch via heat treatment demonstrated approximately 700 mAh·g⁻¹ reversible capacity for over 50 cycles (Lee et al. 2008).

• **Applying various binders**

Binders are essential for composite anodes by forming cross-link and providing inner adhesion among anodes and current collectors. Besides PVdF, a widely applied polymer binder applied in electrodes for batteries, various binders have been studied for silicon composite anodes, such as polyethylene oxide with lithium perchlorate (PEO–LiClO₄), polyethylene glycol with lithium perchlorate (PEG–LiClO₄), Oppanol B200 (BASF), rubber-like ethylene propylene diene monomer (EPDM), styrene butadiene rubber (SBR), and sodium carboxymethylcellulose (CMC) (Chen et al. 2006; Kasavajjula et al. 2007; Lestriez et al. 2007). Capacity retentions for silicon composite anodes were greatly improved with the help of these binders.

• **Applying advanced micro/nanostructure**

Advanced structured silicon has been applied in composite anodes to mitigate capacity loss and improve anode performance. Amorphous silicon coated core-shell carbon nanotube composite anode applies carbon nanotube as backbone to support high capacity silicon layer, and shows high capacity of over 2000 mA·hg⁻¹ for over 50 cycles (Cui et al. 2009). Magasinski et al.
has reported 3D hierarchical structured silicon coated carbon nano-composite anodes for lithium-ion battery with initial discharge capacity of 1950 mAh·g⁻¹ at C/20 with approximate 50 % silicon content (Magasinski et al. 2010).

Hundreds of silicon composite anodes have been reported in the past decade using various silicon concentrations, particle sizes, additives, binders, anode preparation techniques, and charge and discharge cycling conditions. Performance comparison for various silicon composite anodes may not be conclusive if only reversible capacities are addressed. Selective silicon composite anodes reported including anode types, binders, silicon concentrations, reversible capacities and cycling conditions are summarized and are tabulated in Table 3.

As can be obtained from these silicon composite anodes, the maximum anode capacities and reversible capacities are greatly limited despite the fact that composite anode technique is a well-established and widely applied industrial fabrication procedure.

The composite silicon anode capacities are limited by the theoretical specific capacity of silicon and the concentration of silicon applied in the composite, because only a proportion of silicon is contained in the composite matrix. The maximum reported silicon composite anode capacities fall in the range from several hundred to less than 1000 mA·hg⁻¹ with various silicon concentrations from 3.6 % to 70 % as shown in Table 3.

◆ Silicon Only Anodes

Bulk silicon is considered non-applicable as anode for reversible lithium storage as discussed in previous sections. With the development of advanced techniques for nano-scale silicon structure syntheses, silicon only anodes featuring structured silicon without binder or other materials (e.g. graphite or carbon black) to achieve high capacity as well as retain cycle ability have become a major breakthrough in lithium-ion battery technologies in recent years.
Table 3 Selective silicon composite anodes

<table>
<thead>
<tr>
<th>Reference</th>
<th>Anode</th>
<th>Binder</th>
<th>Si (%)</th>
<th>Reversible Capacity (mAh·g⁻¹)</th>
<th>Cycling Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Yoshio et al. 2002)</td>
<td>Si/C</td>
<td>PVdF</td>
<td>~70</td>
<td>800</td>
<td>50 cycles</td>
</tr>
<tr>
<td>(Guo et al. 2005)</td>
<td>Si-DC</td>
<td>PVdF/DMP</td>
<td>10-70</td>
<td>754 (10%)</td>
<td>0.02-1.2V ~C/15 20 cycles</td>
</tr>
<tr>
<td>(Yang et al. 2006)</td>
<td>Si with Ag</td>
<td>PVdF</td>
<td>50</td>
<td>800</td>
<td>30 cycles</td>
</tr>
<tr>
<td>(Zhang et al. 2006)</td>
<td>Si/carbon nanotube</td>
<td>PVdF</td>
<td>Various ratio</td>
<td>584</td>
<td>20 cycles</td>
</tr>
<tr>
<td>(Datta et al. 2006)</td>
<td>Si/C/PAN-C</td>
<td>PVdF/NMP</td>
<td>30</td>
<td>660</td>
<td>0.02-1.2V ~C/4 30 cycles</td>
</tr>
<tr>
<td>(Lestriez et al. 2007)</td>
<td>Si/C</td>
<td>CMC</td>
<td>~1000</td>
<td></td>
<td>0-1 V 15 cycles</td>
</tr>
<tr>
<td>(Zhang et al. 2007)</td>
<td>Si/SiO</td>
<td>PVdF</td>
<td>40</td>
<td>538.9</td>
<td>0-2 V 20 cycles</td>
</tr>
<tr>
<td>(Alias et al. 2007)</td>
<td>Nano Si (5-30 nm) deposited on carbon</td>
<td>PVdF/NMP</td>
<td>3.6</td>
<td>377</td>
<td>C/5 10 cycles</td>
</tr>
<tr>
<td>(Khomenko et al. 2007)</td>
<td>Si deposited on graphite Formula BTTM SLA1025</td>
<td>N/A</td>
<td>7.9</td>
<td>~575</td>
<td>20 cycles</td>
</tr>
<tr>
<td>(Kobayashi et al. 2008)</td>
<td>SiO/C</td>
<td>PVdF</td>
<td>~500</td>
<td></td>
<td>0-2.5 V C/8 100 cycles</td>
</tr>
<tr>
<td>(Kim et al. 2008)</td>
<td>Si/C</td>
<td></td>
<td></td>
<td>800</td>
<td>30 cycles</td>
</tr>
<tr>
<td>(Lee et al. 2008)</td>
<td>Si/C composite (SBR/CMC)</td>
<td>~23.5</td>
<td>~700</td>
<td>0.02-1.5V 50 cycles</td>
<td></td>
</tr>
<tr>
<td>(Bridel et al. 2009)</td>
<td>Si/C</td>
<td>CMC</td>
<td>33</td>
<td>~900</td>
<td>20 cycles</td>
</tr>
<tr>
<td>(Luo et al. 2009)</td>
<td>Si/C various particle size</td>
<td>PVdF/NMP</td>
<td>Various ratio</td>
<td>350</td>
<td>0.005-2V &gt; 30 cycles</td>
</tr>
<tr>
<td>(Eker et al. 2009)</td>
<td>Si/C</td>
<td></td>
<td>10-15</td>
<td>520</td>
<td>0.005-2V C/5 20 cycles</td>
</tr>
<tr>
<td>(Chou et al. 2010)</td>
<td>Si/carbon nanotube paper anode</td>
<td></td>
<td>2.2</td>
<td>163</td>
<td>50 cycles</td>
</tr>
</tbody>
</table>
Amorphous silicon thin films deposited on metal substrate via chemical vapor deposition (CVD) and physical vapor deposition (PVD) have been reported as anodes for lithium-ion batteries (Bourderau et al. 1999; Graetz et al. 2003). Extensive studies have been focused on silicon thin film anodes, including mechanism of lithium insertion (Peng et al. 2010), stress evolution within anodes during charge and discharge cycles (Sethuraman et al. 2010; Sethuraman et al. 2010), surface film formation (Christensen 2010), etc. Although thin film silicon anodes cracking and pulverization have been observed after prolonged cycles, the capacity retention and reversibility of thin film silicon are greatly improved compared to silicon composite anodes. It has been demonstrated that the thinner silicon film is the better it performs in both capacity retention and cycle ability. Recent studies with ultra-thin silicon film studies showed high reversible capacity of approximately 3500 mAh·g⁻¹ over 200 cycles for thin film of 50 nm amorphous silicon; while the thin film of 150 nm was greatly reduced to only 2200 mAh·g⁻¹ for 200 cycles (Ohara et al. 2004). Preparation of silicon thin film anodes via expensive CVD or PVD processes requires toxic silane as silicon source and rigorous conditions, such as high vacuum and high temperature. High fabrication cost and low energy density relative to anode surface area for silicon thin film anodes still pose as big challenges for their practical applications.

Silicon nanowires (SiNWs) have attracted significant attention for applications in lithium-ion battery anodes. The nanowire structures have several advantages over silicon powder and thin films as anode: 1) facile strength relaxation of nanowire allows accommodation of large volume change without fracture; 2) 1-D structure of silicon nanowire provides direct electronic path way allowing sufficient electron transport; 3) direct contact between nanowire and current
collector promotes electrical conduction; 4) large surface area allows sufficient lithium insertion and extraction (Chan et al. 2008).

Figure 4 Schematic of structural change before and after cycling for silicon anodes in the form of film, particles and nanowires (Reprinted by permission from Macmillan Publishers Ltd., High-performance lithium battery anodes using silicon nanowires by Chan et al., [Nature Nanotechnology], copyright 2008)

Silicon nanowire anodes synthesized via Vapor-Liquid-Solid (VLS) grown are capable of accommodating volume changes caused by lithium insertion and extraction with near theoretical capacities (Chan et al. 2008). As shown in Figure 4, the VLS-grown nanowires undergo reversible lithium insertion and extraction without significant pulverization or detachment from the current collector. The VLS-grown silicon nanowire anodes maintain reversible capacity for over 2000 mAh·g⁻¹ after 80 consecutive cycles as reported in later studies (Chan et al. 2009; Chan et al. 2009). The VLS-grown silicon nanowire anodes are also confronted to similar issues
as thin film anodes, such as expensive and complicated preparation procedures, and may not be widely applied in commercial batteries.

Peng et al. has demonstrated self-aligned silicon nanowires fabricated via facile metal assisted etching as anode for lithium-ion battery (Peng et al. 2008). Not only does the fabricated silicon nanowire array enjoys the advantages of low cost, large surface area, and facile etching procedures, but it also has controllable conductivity, which facilitates charge transport and insertion and extraction of lithium ions. The electrolessly-fabricated silicon nanowire anodes show discharge capacity of approximate 0.5 mAh·cm⁻² in the third cycle and cycling stability for 9 consecutive cycles via cyclic voltammetry. The capacity reported is normalized by anode area and not comparable to that of VLS-grown silicon due to the difficulties in estimating the weight of silicon nanowires on substrate (Chan et al. 2008). The silicon nanowire arrays showed great potential as anodes; however, the attachment of nanowires to bulk silicon substrate limited its applications in practical batteries. Bulk silicon substrate reduces electrical conductivity between anodes and current collector significantly, and may pulverize and crack as other bulk silicon anodes after prolonged cycles.

Similar to other carbon coated silicon anodes, silicon nanowire arrays coated with carbon have also been reported (Huang et al. 2009). Helmut and co-workers plated a copper layer at the root of electrolessly etched silicon nanowires as anode. The copper layer behaves as mechanical support as well as electrical conductor. The modified silicon nanowires anode shows cycle ability for over 10 cycles (Helmut et al. 2010). Although these modified anodes show slightly improved performance than electrolessly fabricated silicon nanowires, reversible capacities are not comparable to that of VLS-grown silicon nanowire anodes. Nexeon (UK) has developed novel battery anodes via combining particles containing electrolessly etched silicon nanowire arrays into composite anodes (Nexeon 2010).
Other anodes containing silicon only with advanced structures have also been reported. A virus-enabled silicon anode was fabricated for lithium-ion batteries. Nickel current collector was integrated by electroless deposition on nano-structured virus template on stainless steel substrate; followed by physical vapor deposition of silicon to create the 3-D tobacco mosaic structure. The novel silicon anode showed high initial charging capacity of over 3300 mAh·g⁻¹ with capacity loss of 0.2 % per cycle, and reversible capacity of approximately 1000 mAh·g⁻¹ was maintained after over 300 cycles (Chen et al. 2010).

In summary, anodes containing silicon only with advanced structures have shown the abilities to accommodate massive volume change during lithium insertion and extraction, and significantly improve capacities approaching theoretical maximum in the initial cycles. Moreover, over 50 % capacity fade from initial capacities still persists with these anodes. This phenomenon suggests other effects on anode capacity fade, such as silicon surface reactions with electrolytes might attribute to the significant capacity fade issue.

2.1.3 Solid Electrolyte Interphase

◆ Electrolyte

As discussed in previous sections, the electrolyte in lithium-ion cell acts as an ionic conductor for lithium transport between anode and cathode during cell cycles. Lithium-ion battery generally adopts lithium aprotic compound as lithium ion source, such as lithium hexafluorophosphate (LiPF₆), lithium tetrafluoroborate (LiBF₄), lithium hexafluoroarsenate (LiAsF₆), lithium Bis(Oxalato)Borate (LiBOB), etc. The lithium compound is dissolved in alkyl carbonate solvent or solvent mixtures including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), etc. (Perla B. Balbuena 2004). Several commonly used carbonate solvent structures are presented in Figure 5.
One of the most important solvent selection criteria is the reduction and oxidation potential window. On one hand, it is essential for electrolyte to have oxidation potential greater than cathode charge and discharge potential to prevent detrimental oxidation reactions during cell cycles, as well as to maintain thermal stability and ionic conduction; while on the other, electrolyte should be reduced prior to lithiation to form a passivation film on anode surfaces. Selective alkyl carbonate solvent reduction and oxidation potentials with 1M LiPF$_6$ are listed in Table 4.

Table 4 Oxidation and reduction potentials of selective alkyl carbonate solvent

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Oxidation Potential /V (with 1M/L LiPF$_6$)</th>
<th>Reduction Potential /V (with 1M/L LiPF$_6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC</td>
<td>&gt;6</td>
<td>1.36</td>
</tr>
<tr>
<td>PC</td>
<td>&gt;6</td>
<td>1-1.6</td>
</tr>
<tr>
<td>DMC</td>
<td>&gt;6</td>
<td>1.32</td>
</tr>
<tr>
<td>DEC</td>
<td>&gt;6</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Figure 5 Alkyl carbonate solvent structures
Table 1 (Scrosati 2002). Typical charge and discharge capacities versus electrode potential for both anode and cathode in lithium-ion batteries are shown in Figure 6. The dashed lines represent oxidation and reduction potential for electrolytes.

Figure 6 Anode and cathode normalized capacities versus electrode potentials

Anode surface reactions involve carbonate solvent, lithium salt, contaminants such as water, dissolved oxygen, and carbon dioxide in electrolyte under anodic polarization. Reactions products on graphite anodes have been well identified and mechanisms have been discussed extensively in previous studies (Scrosati 2002).

As shown in Figure 7, Aurbach et al. have proposed possible mechanisms for EC reduction to form passivation film on graphite anodes (Aurbach et al. 1999). EC and other organic solvents are reduced and react with lithium ion under cathodic bias through several steps
to generate a continuous passivating organic film on carbon anodes. Reactions of organic solvents, lithium hexafluorophosphate and their derivatives on carbon anodes are summarized as follows (Scrosati 2002):

Alkyl carbonate reduction reactions:

\[
2\text{EC} + 2e^- + 2\text{Li}^+ \rightarrow \text{CH}_2\equiv\text{CH}_2 + (\text{CH}_2\text{OCO}_2\text{Li})_2
\]

\[
2\text{PC} + 2e^- + 2\text{Li}^+ \rightarrow \text{CH}_3\text{CH}\equiv\text{CH}_2 + \text{CH}_3\text{CH}(\text{OCO}_2\text{Li})\text{CH}_2\text{OCO}_2\text{Li}
\]

\[
\text{DMC} + e^- + \text{Li}^+ \rightarrow \text{CH}_3\text{OCO}_2\text{Li} + \text{CH}_3\cdot \text{or} \text{CH}_3\text{OLi} + \text{CH}_3\text{OCO}\cdot
\]

Figure 7 Various EC reduction patterns on graphite anode surface and relevant products (Reprinted from On the correlation between surface chemistry and performance of graphite negative electrodes for Li ion batteries by Aurbach et al., copyright 1999, with permission from Elsevier)
DEC + e⁻ + Li⁺ \rightarrow CH₃CH₂OCO₂Li + CH₃CH₂OLi

Possible reaction with reduction products and contaminant water:

2ROCO₂Li + H₂O \rightarrow Li₂CO₃ + 2ROH + CO₂

R• + Li \rightarrow RLi

R• + R’• \rightarrow RR’

Possible surface reaction of lithium salt, e.g., LiPF₆ with trace amount of water contaminant:

LiPF₆ \leftrightarrow LiF + PF₅

PF₅ + H₂O \rightarrow POF₃ + 2HF

POF₃ + 2xLi⁺ +2xe⁻ \rightarrow xLiF(s) + LixPOF₃₋ₓ

PF₅ + 2xLi⁺ +2xe⁻ \rightarrow xLiF(s) + LixPF₅₋ₓ

(CH₂OCO₂Li)₂ + H₂O \rightarrow Li₂CO₃ + CO₂ + (CH₂OH)₂

ROCO₂Li(s) + HF \rightarrow LiF(s) + ROCO₂H

Possible CO₂ reduction:

CO₂ + e⁻ + Li⁺ \rightarrow •CO₂Li

•CO₂Li + CO₂ \rightarrow O═ •CO-CO₂Li

O═ •CO-CO₂Li + e⁻ + Li⁺ \rightarrow CO + Li₂CO₃

2LiOH + CO₂ \rightarrow Li₂CO₃ + H₂O

Li₂O + CO₂ \rightarrow Li₂CO₃

ROLi + CO₂ \rightarrow ROCO₂Li

where R represents alkyl functional groups such as CH₃, CH₃CH₂, etc.

◆ Solid Electrolyte Interphase (SEI)

The SEI is defined as a thin layer (30-50 nm) composed of inorganic and organic products deposited on the anode surface during charge and discharge cycles due to electrolyte reduction and other surface reactions.
A stable and continuous SEI layer is considered as a crucial factor as it provides a protective passivation layer and allows ion conduction for lithium insertion and extraction as well as maintains anode integrity. The SEI on graphite anodes has been extensively studied, including its formation mechanism, composition, morphology and other properties in previous works (Perla B. Balbuena 2004). The SEI has been characterized via XPS, FT-IR, Raman Spectrum and spectroscopic analysis tools. Based on these analyses, the SEI is mainly composed of lithium oxides, lithium salts, and other carbonates. A schematic of the SEI on a graphite or lithium metal anodes is shown in Figure 8 as proposed by Peled et al. (Peled et al. 1997). Lithium oxide, lithium fluoride, and lithium carbonates are attached close to anode surface.
within SEI layer, while other organic compounds such as polyolefins and semicarbonates are near electrolyte phase. The SEI is formed in the first few cycles; however, the composition of SEI is dynamic and varies at different anode potentials. The SEI can be formed and dissolved into electrolyte continuously over prolonged cycles (Bryngelsson et al. 2007).

◆ SEI on Silicon Anodes

SEI layer on silicon anodes is significantly different from the film typically formed on graphite negative electrodes for two main reasons:

(1) The silicon surface is more reactive to electrolytes than graphite and will result in a complex SEI composition that includes hydrocarbons, C$_2$H$_5$OCOOLi, LiCO$_3$, Li$_2$O, LiF, and silicon containing products (such as lithium silicates, SiF$_6^{2-}$, etc.) (Chan et al. 2009).

(2) Over 300 % volume change for silicon during lithium insertion and extraction may cause breakage of the SEI and expose reactive silicon surface to electrolytes for further undesired reactions. (Kong et al. 2001; Kasavajjula et al. 2007).

Besides similar electrolyte reduction reactions as summarized for carbon anodes, several specific reactions for silicon anodes were proposed based on the SEI composition reported in previous studies:

\[
\begin{align*}
\text{SiO}_x + 4\text{HF} + 2\text{F}^- + 2h^+ & \rightarrow \text{SiF}_6^{2-} + 2\text{H}^+ + \text{H}_2\text{O} \\
\text{SiO}_x + 2x\text{Li}^+ + 2xe^- & \rightarrow x\text{Li}_2\text{O} + \text{Si} \\
\text{SiO}^- + 2\text{Li} & \rightarrow \text{Li}_2\text{O} + \text{Si} \\
\text{SiO}_x + \text{Li}^+ & \rightarrow \text{LiSO}_x \\
\text{EC} + \text{Li}^+ + \text{Si} + e^- & \rightarrow \text{ROCO}_2\text{Li}/\text{Si} + \text{other carbonates}
\end{align*}
\]

Silicon-specific irreversible reactions may result in the consumption of lithium, silicon etching, or products that block lithium transport, leading to further capacity fade. (Kong et al. 2001; Kasavajjula et al. 2007) An in situ analysis has shown that oxidized silicon species may
strip fluoride from complexes such as PF$_6^-$, which results in formation of silicon fluorides. These reactions may either result in localized silicon etching, or increase production of LiF or other fluorinated species (Flake et al. 1999). *In situ* oxidation of silicon anodes and irreversible reactions with fluorine at the silicon-SEI interface (including the formation of organic phosphorus-fluorine and P-F-containing inorganic species) are also known to affect capacity fade in silicon thin film anodes (Song et al. 2009). It has been reported that silicon is reactive with electrolyte decomposition products, such as HF derived from LiPF$_6$ in the presence of trace amounts of water, and forms complex products within the SEI. Such reactions may exacerbate capacity decrease by consuming active silicon in the anode and lithium ions in the electrolyte through prolonged cell cycles (Choi et al. 2007; Song et al. 2009; Yen et al. 2009). Possible SEI composition on silicon anodes is illustrated in Figure 9 based on literature.

![Figure 9 Schematic of the solid electrolyte interphase (SEI) on silicon anodes](image)

Various approaches have been applied to mitigate the silicon surface reactions. Among these approaches, coating silicon with conductive carbon or other active/inactive materials is
effective in both protecting silicon as well as increasing internal conductivity within anode matrix, and greatly improves capacity retention for silicon composite anodes (Kim et al. 2008; Cui et al. 2009; Huang et al. 2009; Yu et al. 2009; Xiao et al. 2010).

Electrolyte can be modified with additives to stabilize SEI as well as improve anode performance. Choi et al. have demonstrated that 3 % fluoroethylene carbonate (FEC) additive is effective in creating SEI consisting of stable Si-F and Li-F compounds, and increases reversible discharge capacity up to 88.5 % compared to FEC free electrolyte (Choi et al. 2006). More recently, Ryu and Song have proposed that adding alkoxy silanes in the electrolytes with thin film silicon anodes passivates silicon surface and capacities may be greatly improved. (Ryu et al. 2008; Song et al. 2009) Song et al. showed that reactive binding agents may double the silicon thin film anode capacity (up to approximately 50 % of silicon’s theoretical maximum specific capacity) and significantly improves capacity retention. This result was attributed to Si-O-Si bonds which was proven to form within the SEI, and the Si-O-Si bonds were considered to stabilize the SEI layer (Song et al. 2009; Nguyen et al. 2010).

Surface chemistry of anodes affects the SEI formation and anode performance significantly. Aurbach et al. have studied the effects of surface chemistry on graphite anodes of lithium-ion battery and the SEI on graphite anodes (Aurbach et al. 1999). Although silicon surfaces are considered more reactive than graphite, the relationships between surface chemistry and anode performance are not well established. Chen et al. have described hydride-terminated silicon surfaces as “highly reactive” and shown nanowires with native oxides surfaces with over 50 % increase in capacity retention then hydride-terminated anodes, as well as a significantly different SEI composition (Chan et al. 2009). In addition to influencing anode stability, surface chemistry may also affect the transport and adsorption of lithium. Theoretical calculations based on density function theory show the lithium fast transport is limited by a high intrinsic energy
barrier of lithium surface intercalation for silicon thin film anode, and the high energy barrier can be reduced by surface modification via doping with aluminum (Peng et al. 2010). An ab initio study also shows lithium binding energy is the highest on silicon surface; and Si [110] surfaces are relatively favorable for lithium doping (Zhang et al. 2010). A recent simulation study by Chan et al. also shows silicon without any surface termination has significantly lower binding energy with lithium than silicon with hydride surfaces (Maria et al. 2010).

The SEI is of great importance in silicon anode capacity retention, and more efforts are required to further explore the formation mechanism, composition and properties of the SEI, so as to maintain high reversible anode capacities over prolonged cycles.

2.2 Silicon Nanowire: An Overview

Benefiting from its semiconductor properties and nano structures, silicon nanowire structures have garnered great attention for its promising application as basic building block in micro-electronic devices. Silicon nanowire has been reported to be applied in field effect transistors (Cui et al. 2003; Zheng et al. 2004), sensors (Wang et al. 2005; Wanekaya et al. 2006), solar cells (Tian et al. 2007; Peng et al. 2008; Stelzner et al. 2008; Peng et al. 2009), lithium-ion batteries (Chan et al. 2008; Peng et al. 2008; Chan et al. 2010), etc. Extensive research has been carried out in the past decades for silicon nanowire synthesis, assembly and integration, targeting its applications in electronics, energy conversion and storage.

2.2.1 Synthesis

Silicon whisker structure with diameter of approximately 100 nm was first synthesized by Wagner and Ellis in 1964 (Wagner et al. 1964). In 1997, Westwater et al. have proposed to use gold catalyst with silane as silicon source for silicon nanowire vapor-liquid-solid (VLS) growth (Westwater et al. 1997). It is not until Lieber and coworkers that the VLS method has become one of the most adopted silicon nanowire fabrication methods for device applications in recent
years (Cui et al. 2001; Cui et al. 2001; Cui et al. 2003; Agarwal et al. 2006). Besides VLS grown method, silicon nanowire growth methods, including solution-liquid-solid method (Wang et al. 2006), simple physical thermal deposition (Yu et al. 1998), laser ablation method (Morales et al. 1998; Wang et al. 1998), solution grown method (Holmes et al. 2000; Tuan et al. 2005), and etc., have been reported previously.

Other than directly growing silicon nanowires via additive methods, subtractive methods for nanowire structure fabrication have also been reported. Subtractive silicon nanowire fabrication is accomplished by removing silicon from bulk substrates via dry or wet etching processes, and leaving free standing nanowire structures on substrates.

Silicon nanowire with 100-200 nm width has been reported by electron beam lithography (Juhasz et al. 2004). Large arrays of silicon nanowire can also be fabricated via etching in fluoric acid solution with or without templates, including anodic etching, photoelectrochemical etching, laser assisted etching, and electroless etching (Kolasinski 2005). Patterns can be generated via conventional photolithography and silicon rods can be created via cathodic etching in HF solution (van Kats et al. 2004). Silicon nanowire structure can also be formed via etching with the help of aluminum oxide template generated nano-holes as pattern (Shimizu et al. 2007). Polystyrene spheres are also used as templates to define the lateral dimensions of silicon nanowire during etching process (Huang et al. 2007). Silicon nanostructures have also been reported using a combination of interference lithography and catalytic etching (Choi et al. 2008).

Peng and co-workers proposed that silicon nanowire can be fabricated via electroless etching in hydrofluoric acid solutions with silver nitrate (Peng et al. 2002; 2003; Peng et al. 2006). The mechanism of silicon nanowire formation is shown in Figure 10.
When silicon is immersed into aqueous solution with hydrofluoric acid and silver nitrate, silver ion is spontaneously reduced and deposited on silicon surface as nano size cathodic nuclei. The silver nuclei catalyze oxidation of silicon followed by silicon oxide dissolution in hydrofluoric acid. Silicon nano nuclei then sink below silicon surfacing, creating nanowire structures. Silver ion continues to be reduced and forms dendrite structure and accumulated on top of the silicon surface. The dendrite structure is of great importance, which is permeable to hydrofluoric acid for continuous dissolution of silicon to form nanowire structures.

The cathodic reaction for silver reduction and anodic reaction for silicon oxidation are as follows (Peng et al. 2006):

\[
\begin{align*}
\text{Ag}^+ + e^- & \rightarrow \text{Ag} & E_0 = +0.79 \text{ V/SHE} [2-6] \\
\text{Si} + 2 \text{H}_2\text{O} & \rightarrow \text{SiO}_2 + 4 \text{H}^+ + 4 e^- & E_0 = -0.84 \text{ V/SHE} [2-7]
\end{align*}
\]

Silicon oxides are etched by HF and dissolved in aqueous solution:

\[
\text{SiO}_2 + 2 \text{HF}_2^- + 2 \text{HF} \rightarrow \text{SiF}_6^{2-} + 2 \text{H}_2\text{O} \quad [2-8]
\]

Large arrays of silicon nanowire can be fabricated via this metal assisted electroless etching methods. The electroless methods do not require lithography or pre-patterned template
and are particularly interesting for producing larger volumes of nanowires due to the advantages of large scale, low cost creation of silicon nanowire, and relative simple procedures.

### 2.2.2 Assembly and Integration

In order to utilize silicon nanowires as basic building blocks for microelectronic mechanical devices, silicon nanowire are deposited and aligned on substrate following a series of treatments to create electrical contacts with device components.

Silicon nanowires can be randomly deposited on a substrate. After deposition, intensive SEM assisted “find and wire” bottom-up approach is used for integration, by which the specific silicon nanowire is located with SEM and further PVD or other metal deposition followed by thermal annealing is applied to integrate nanowire. Silicon nanowire can also be deposited in ordered pattern via printing deposition (McAlpine et al. 2005) or fluidic alignment with surface-patterning techniques (Huang et al. 2001).

A key challenge associated with integrating silicon nanowires involves creating electrical connections. Low-resistivity ohmic contacts can be created via metal silicidation between metal and silicon. Selective common silicide applied are listed in Table 5 adapted from literature (Gambino et al. 1998).

### Table 5 Properties of selective common metal silicide

<table>
<thead>
<tr>
<th>Silicide</th>
<th>NiSi</th>
<th>NiSi$_2$</th>
<th>TiSi$_2$</th>
<th>PtSi</th>
<th>CoSi$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film resistivity (µΩ•cm)</td>
<td>14-20</td>
<td>35-50</td>
<td>13-20</td>
<td>28-35</td>
<td>14-20</td>
</tr>
<tr>
<td>Si consumed per nm metal (nm)</td>
<td>1.8</td>
<td>3.6</td>
<td>2.3</td>
<td>1.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Formation temperature (°C)</td>
<td>400-600</td>
<td>600-700</td>
<td>600-700</td>
<td>300-600</td>
<td>600-700</td>
</tr>
</tbody>
</table>
Among several common silicides, nickel monosilicide (NiSi) is particularly useful for ohmic contacts due to their relatively low resistivity (~14-20 µΩ·cm), low silicon consumption during silicidation, low temperature (400-600 °C) and simple one step thermal annealing formation process (Gambino et al. 1998). NiSi phase is thermodynamically unstable compared to NiSi₂ phase, and not suitable for applications when temperature is over 600 °C.

Nickel silicides are typically formed in planar COMS (Complementary Metal Oxide Semiconductor) processes using a series of steps including nickel deposition onto single crystal silicon wafers followed by thermal annealing and wet etching to remove excess nickel (Wu et al. 2004). Likewise, silicides may be formed in silicon nanowires by annealing nanowires with nickel reservoirs allowing radial or axial diffusion (Zheng et al. 2004; Weber et al. 2007). Silicidation reactions with single VLS grown nanowire have been demonstrated using SEM intensive “find-and-wire” approach where Physical Vapor Deposition (PVD) nickel is locally deposited onto unoxidized nanowires followed by thermal annealing. An estimated resistivity of (9.5 µΩ cm) of these nanowires after annealing has been obtained, which suggests the low-phase NiSi formation. Silicide contacts have also been reported with VLS-grown Silicon nanowires following deposition, electroless plating nickel, and thermal annealing. Resistance measurements also suggest the low-resistance NiSi phase is formed (Zheng et al. 2004).

In summary, integration of silicon into anodes for lithium-ion batteries to achieve high capacity as well as long cycle life is confronted with great challenges in practical applications. Both the large volume swelling and surface reactions need to be addressed for silicon anodes. Silicon nanowire structures are adopted to accommodate stress induced by large volume change and maintain anode integrity for prolonged cycles. Other than VLS-grown nanowires anodes, electrolessly fabricated silicon nanowires are great alternatives for their facile, low-cost fabrication in relative large quantities. Silicon surface chemistry and its effects on the SEI need
to be addressed to improve anode capacity as well as capacity retention. The SEI is created on
anode surface via a series of surface reactions among silicon, lithium salts and alkyl organic
solvents, and its properties strongly depend on silicon surface termination as well as electrolytes
composition. Based on the literature review, there are great potentials in silicon nanowire anodes
for lithium-ion batteries, and following studies are carried out in fabricating and characterizing
silicon nanowires via electroless etching; integrating nanowires by creating low-resistant NiSi
ohmic contact; preparing composite anodes with silicon nanowires and testing anode in lithium-
ion cell; and modifying silicon surface as well as using additive in electrolyte, characterizing
corresponding SEI chemical composition and mechanical properties as well as anode
performance.
CHAPTER 3 SILICON NANOWIRE FABRICATION AND INTEGRATION VIA NICKEL MONOSILICIDE CONTACTS

3.1 Introduction

Silicon nanowires can be fabricated and applied as lithium-ion battery anodes, as well as basic building blocks for sensor devices, integrated (nanowire-CMOS) devices, or photovoltaic cells or other possible applications as reviewed in previous chapter. Electrical contacts between silicon nanowires and metal substrates are essential to nanowire integration and applications. Metal silicides created via metallurgical reactions between silicon and metal are used as electrical contacts for silicon. Among many metal silicides, nickel monosilicide (NiSi), due to its low resistivity as well as low formation temperature and low consumption of silicon, has been widely applied in industrial processes to create low resistance ohmic electrical contacts between planer silicon and substrates.

In this chapter, we discuss a method for silicon nanowires fabrication via electroless etching procedure and an alternative silicidation process allowing one-step facile silicidation of high numbers of silicon nanowires. Silicon nanowires are created in an electroless-etching process in aqueous solution, separated from a parent wafer, deposited onto pre-existing nickel inter-digitated electrodes (IDEs) and directly annealed via thermal heating to form silicides. This method allows the facile and low-cost creation of low-resistance ohmic contact between silicon nanowire and metallic nickel electrodes or substrates. Nanowires with nickel silicides are characterized by electrical resistance measurements, Transmission Electron Microscopy (TEM), X-ray Photoelectron Spectroscopy (XPS) and X-ray Absorption Near Edge Spectrum (XANES) analysis are reported to demonstrate the formation of a nickel monosilicide (NiSi) phase.

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3.2 Material and Methods

3.2.1 Silicon Nanowire Fabrication via Electroless Etching

P-type (boron doped) and n-type (phosphorus doped) single crystal silicon wafer with (100) surface orientation and resistivity of 1-5 Ω·cm were obtained from Montco Silicon Technologies, CA. Silicon wafers were first cleaved and degreased with acetone. Samples were then cleaned via standard wet cleaning procedures including the following steps: de-ionized (DI) water rinse, HF/H₂O₂/H₂O/surfactant ultrasonic cleansing, 1 % HF rinse, and DI water ultrasonic cleansing to remove native oxide and any other surface contamination. Samples were etched in 5.0 M hydrofluoric acid (HF, Aldrich, USA) solutions containing 0.02 M silver nitrate (AgNO₃, Fluka, UK) at 50 ºC for a variation of time ranging from 5 minutes to 1 hour. Bulk layer of silver dendrite were removed using 1:1 volume ratio nitric acid solution and followed by 1 % HF dip for 10 seconds to expose the fabricated silicon nanowires. (Note: Silicon nanowires used in the following NiSi formation were p-type and fabricated via 30 minutes etch.)

3.2.2 Silicon Nanowire Deposition

The fabricated silicon nanowires were detached from parent substrates via simple mechanical scraping or ultra-sonication and dispersed in transfer solution (e.g. methanol or acetone). These nanowires were then deposited via micropipette on silicon substrate for SEM characterization; Inter-digitated electrodes (IDEs, 3 mm long with 25 comb pairs each, total length 150 mm) with 5 µm platinum digit electrode plated with nickel and 5 µm wide spaces were obtained from ABTECH. Silicon nanowires were also deposited on IDEs via micropipette. IDEs deposited with silicon nanowires were dried in argon atmosphere to evaporate transfer solution.
3.2.3 NiSi Formation via Thermal Annealing

IDEs deposited with silicon nanowires were annealed at 450 °C for 30 minutes in a reducing atmosphere (Ar: H₂ = 4:1 in volume ratio) with fast temperature ramp rate of 10 °C per minute. In addition to silicidation of nanowires on IDEs, freestanding arrays of nanowires were also used to create silicides for characterization purposes. In this alternative method, a thin (~100 nm) blanket layer of nickel was deposited onto arrays of silicon nanowires attached to the parent substrate via physical vapor deposition or thermal evaporation. These samples were annealed in the same reducing environment for the same duration and excessive nickel was then stripped by wet etching at 40 °C in commercial thin film nickel etchant (TFG etchant) obtained from Transene, Inc.

3.2.4 Electrical Resistance Measurement

Figure 11 Probe station with optical microscope and adjustable micropositioner
Electrical resistance measurements for IDEs with or without silicon nanowire deposition and before and after thermal annealing were carried out with Potentiostat PAR 2273 system. IDEs was connected to Potentiostat inlet via Probe station assisted with optical microscope and MPC Pivot coupler DMC 100 series Micropositioner (Cascade Microtech, Inc) as shown in Figure 11.

3.2.5 Material Characterization

◆ Scanning Electron Microscopy (SEM)

Nanowire morphology and IDE structures were characterized by Scanning Electron Microscope (SEM). The scanning electron microscope (SEM) images the sample surface by scanning it with a high-energy beam of electrons. The electrons interact with the sample and produce signals that contain information about the sample's surface topography. SEM can produce very high-resolution images of a sample surface up to nanometer scale depending on individual SEM system specification (Egerton 2005).

Prepared silicon nanowire and IDE samples were attached to SEM sample holder with conductive tape and loaded into SEM chamber to characterization. In this work, a Hitachi S-3600N variable pressure SEM/EDS system was applied. All SEM images were obtained under 15 kV at various amplifications. Silicon nanowire diameters and lengths were measured on screen and converted to true dimensions. A thin layer of gold (~10 Å) was sputtered onto the surface of IDE deposited with silicon nanowires to improve image qualities.

◆ Transmission Electron Microscopy (TEM)

TEM applies a beam of high-energy electrons to transmit through an ultra-thin sample; the electrons interact with sample atoms and then reach to a fluorescence screen or sensor for imaging. TEM is a useful tool in material characterization and nanotechnology, which can provide nanometer scale high-resolution images for crystal lattices and atomic layer structure,
such as crystal orientation and atom position within the specimen. Due to mechanism of TEM imaging technique, samples need to be transparent to incident electrons, and thickness should be in the nanometer scale (Egerton 2005).

Transmission Electron Microscope (TEM) was applied to characterize silicon nanowire with NiSi. The silicon nanowire arrays annealed with nickel were detached from parent substrate in methanol and deposited onto 3840C-FA 200 meshes Lacey Carbon TEM grids (SPI supplies). A JEOL 2010 high-resolution transmission electron microscopy (HRTEM) was used for characterization. Total time for transferring to TEM chamber was limited to 30 minutes in order to avoid excess native oxide formation on silicon nanowires.

◆X-ray Photoelectron Spectroscopy (XPS)

XPS spectra are obtained by irradiating the sample with a beam of X-ray and measuring photoelectrons escaped from the material. Each element produces a characteristic set of XPS peaks at characteristic binding energy values. A typical XPS spectrum is a plot of the number of electrons detected versus the binding energy of the electrons detected, which directly identify each element that exist in or on the surface of the material being analyzed. XPS is a quantitative spectroscopic analysis tool, providing useful information in determining chemical state of specific species, and quantifying the material composition. XPS analysis has been widely applied to study silicon surfaces and SEI chemical composition (Peled et al. 2001; Bryngelsson et al. 2007; Jung et al. 2007; Chan et al. 2009).

XPS characterization for NiSi on silicon nanowires was carried out via a Krato AXIS-165 XPS/Auger surface analysis system. XPS spectra were obtained with Al Kα X-ray source at passing energy of 40 eV. As for depth profiling, Ar⁺ ion gun was used to sputter the sample surfaces and XPS spectra was obtained at sputtering time at 5, 15, 25, 40 minutes. (Note: Due to
the condition of the XPS system, the sputtering depth corresponding to sputtering time was not identified).

**X-ray Absorption Near Edge Structure (XANES)**

X-ray Absorption Near Edge Spectroscopy (XANES) or known as Near Edge X-ray Absorption Fine Structure (NEXAFS) is a X-ray absorption spectroscopy to characterize excitation state of an element in the specimen (Bianconi 1980). Similar to XPS analysis, XANES not only measures the photoelectron emitted by X-ray radiation, but also collects all initial photoelectrons, Auger electrons, and directly emitted electrons to sum all final state electrons, and measures the total final states. XANES has been reported to study metal silicides (such as nickel silicides) formation on planer silicon substrates (Naftel et al. 1997; Naftel et al. 1998).

XANES analysis for Si-K edge and Ni-K edge was conducted using the Double Crystal Monochromator (DCM) X-ray beam line of synchrotron source from Center for Advanced Microstructure and Devices (CAMD) of Louisiana State University. The lowest energy at which data have been successfully collected is the Cu LIII edge at 932.5 eV and the highest is the Mo K edge at 20,000 eV.

**3.3 Results and Discussion**

**3.3.1 Silicon Nanowire Fabrication**

Silicon nanowires were fabricated via electroless etching of single crystal silicon wafer in aqueous solution as proposed. The nanowires retain the doping and orientation (<100> along the major axis) from the parent substrate. The fabricated silicon nanowires on parent silicon wafer appear in Figure 12 as charcoal black due to the large surface area for light absorption.

The fabricated nanowires were then detached from parent substrate via mechanical scraping or ultra-sonication and stored in transfer solution (e.g. methanol or ethanol). As can be
seen in Figure 13, the initially clear solution gradually acquires brownish tinge as silicon nanowires are dissolved into methanol after 2 minutes sonication.

Figure 12 Optical image of silicon nanowire on parent wafer as fabricated

Figure 13 Optical images of silicon nanowire on parent wafer sample sonicated in methanol for (A) 0 minutes, (B) 1 minute and (C) 2 minutes
SEM images of fabricated silicon nanowire via electroless etching have also been obtained. Figure 14 shows a 15-degree titled top-down view SEM image of silicon nanowires fabricated on p-type (100) silicon substrate after 30 minutes etching at 50 ºC. Bundles of silicon nanowire can be clearly observed with residual silver dendrite on top of the nanowire arrays.

Silicon nanowire can be easily deposited on any substrate. Solution containing silicon nanowires can be deposited on substrate with micropipette, and excessive solvent can be evaporated. Piles of detached electrolessly-fabricated silicon nanowires on silicon substrate were observed by SEM as shown in Figure 15.

Powder forms of nanowires can also be prepared via centrifuging and drying of the nanowire solution for other applications, such as composite anodes for lithium-ion batteries. The weight of nanowire powders can be measured by precision scale and the average yield of nanowire powders after 30 minutes etch is approximately 1.24 mg·cm⁻² as determined by measuring the weight of parent wafer before and after nanowire detachment.
Figure 15 SEM image of detached silicon nanowires on substrate

Figure 16 Synthesized silicon nanowire diameters distribution
The diameters of one hundred silicon nanowires have been measured via SEM characterization, and the diameter distribution is ranging from 50 nm to over 500 nm as presented in Figure 16. The average silicon nanowire diameter is 253 nm with standard deviation $\sigma$ for 91 nm. The electroless etching technique is based on the random deposition of silver nano nuclei, and does not have strict control over nanowire diameters compared to other catalytic nanowire growth methods or etching methods with templates.

![Image of Cross-section SEM images of fabricated silicon nanowires on p-type silicon wafers after (A) 5 minutes, (B) 10 minutes, (C) 30 minutes and (D) 60 minutes](image)

Figure 17 Cross-section SEM images of fabricated silicon nanowires on p-type silicon wafers after (A) 5 minutes, (B) 10 minutes, (C) 30 minutes and (D) 60 minutes

Silicon nanowires created in the electroless-etching process typically have diameters ranging from 50 to 500 nm and are 10 to 50 $\mu$m in length depending on etching time. A 30 minutes electroless etch used to fabricate nanowires for this study resulted in randomly
distributed nanowires arrays with lengths in the range of 18-20 µm. Sonication can break nanowire structures and detach nanowires from parent substrates, SEM analysis revealed that separated nanowires are approximately 8-12 µm in length after 2 minutes sonication in acetone or methanol. Some nanowires failed to separate in the sonication procedure resulting in nanowire bundles (< 10 % estimated by SEM analysis).

Figure 18 Cross-section SEM images of fabricated silicon nanowires on n-type silicon wafers after (A) 5 minutes, (B) 10 minutes, (C) 30 minutes and (D) 60 minutes

To further elucidate the silicon nanowire fabrication via different doping and etching time, both p-type and n-type silicon with (100) surface orientation and 1-5 Ω · cm resistivity were etched in aqueous solution containing hydrofluoric acid and silver nitrate from 5 minutes to over 1 hour. The cross-section SEM images of p-type silicon wafer after 5 minutes, 10 minutes, 30
minutes and 1 hour are presented in Figure 17. The cross-section SEM images of n-type silicon wafer after 5 minutes, 10 minutes, 30 minutes and 1 hour are also presented in Figure 18.

As can be seen from SEM images, the nanowires created on both p-type and n-type silicon substrates show similar structures after electroless etch, and the lengths of silicon nanowire are dependent on etch time.

![Figure 19](image_url)

Figure 19 Electrolessly fabricated silicon nanowire lengths versus etching time for both p-type and n-type silicon

The nanowire lengths for both p-type and n-type versus etching time were obtained from SEM analysis and plotted in Figure 19. The rate for nanowire growth is slightly faster for n-type silicon in the first 10 minutes and gradually slows down and reaches to over 20 µm after 60 minutes etch; while that of p-type silicon is approximately linear. Generally, silicon nanowire
structure of 20 µm in length can be obtained after 30 minutes electroless etch at 50 ºC. This observation is also in agreement with the fact that electroless etching processes are chemical reactions. The n-type and p-type silicon differ in electrical properties but have similar chemical properties (Lehmann et al. 1990).

3.3.2 Nickel Silicide Formation on Silicon Nanowires

In order to form nickel silicide between silicon nanowires and nickel electrodes, comb-like IDEs in series IME 0525.3 was obtained from ABTECH and applied for silicon nanowire deposition and nickel silicides formation in this work. Figure 20 is a simplified schematic for IDEs. There are 25 pairs of digit electrodes on one IDEs, each digit electrode is 5 µm wide and with 5 µm in between, the effective length for the digit is 3mm. Electrode pads of IDEs are located and connected to tungsten tips of micropositioners on probe station assisted by optical microscope, and the micropositioners are connected to Potentiostat for electrical measurements.

Figure 20 Schematic of the inter-digitated electrode
Figure 21 A is SEM image of a partial area the IDEs. The digit electrodes are approximately 5 µm wide with 5 µm spacing in between. Silicon nanowires were deposited on IDEs as described previously by dripping nanowire solution with micropipette. Solvent was removed using a low-pressure nitrogen stream followed by annealing at 450 °C in reducing atmosphere. A thin layer of gold was sputtered on to IDEs prior to SEM analysis to achieve better image quality. As shown in Figure 21 B, multiple silicon nanowires are deposited on top of a partial area of IDEs.

![Figure 21 SEM images of IDEs (A) without silicon nanowire and (B) with silicon nanowires deposition](image)

Figure 22 shows the close-up (× 17 k times) view of one single silicon nanowire across a pair of digit electrodes after deposition and thermal annealing, where two ends of the silicon nanowire are in direct contact with the electrodes. A schematic of cross section view for silicon nanowire across digit electrodes is illustrated in Figure 23, and nickel silicides may be formed starting at the two ends of silicon nanowires in contact with nickel electrodes.
Figure 22 Close-up SEM image of one silicon nanowire across two electrodes.

Figure 23 Schematic of cross-section view for silicon nanowire deposited on nickel electrodes with nickel silicidation formation
Statistic analysis by counting silicon nanowires deposited on a partial area (10 % of the IDE comb area) from SEM images shows the total number of silicon nanowires bridged across IDEs surface (1.5 mm²) was 1800 (±372 1σ), and average length of silicon nanowire across the electrodes is 5.38 µm.

◆ Electrical Measurements

Electrical measurements were carried out on IDEs before and after silicon nanowires deposition as well as before and after thermal annealing. Prior to silicon nanowires deposition onto IDE electrodes, (two-probe) resistance measurements indicate an open circuit (>1·10⁹ Ω). After Silicon nanowires deposition, the resistance of IDEs decreased significantly to approximately 4·10⁶ Ω, which suggest conductive nanowires or ionic contamination from the transfer solution. Following Silicon nanowires deposition, electrodes with Silicon nanowires were annealed in reducing atmosphere resulting in a resistance decrease of more than three orders of magnitude (2·10³ - 6·10³ Ω). The high range in resistance is indicative of the random number of Silicon nanowires bridging electrode pairs from transfer solution deposition in each experiment. Resistance values remained unchanged after IDEs were repeatedly cleaned with de-ionized water and dried suggesting stable connections between electrodes and Silicon nanowires. As shown in Figure 24, linear current-voltage behavior is observed for three IDE samples with annealed nanowires over a potential range of ±10 mV. Application of higher voltages (±1 V) also showed linear behavior; however, abrupt failures were observed under higher current densities (j<sub>max</sub> > 1.4 · 10⁷ mA·cm⁻²).

The resistivity of individual nanowire was estimated based on the number of nanowires bridging electrode pairs and their average diameter. Based on the number and average measured length and average diameter of silicon nanowires deposited on IDEs, a nanowire resistivity of 2.36 Ω·cm can be estimated. This value is approximately equal to the parent wafer resistivity (1-
$5 \, \Omega \cdot \text{cm}$) and suggests ohmic connections are localized to nanowire regions near nickel-silicon interface.

Figure 24 I-V behavior of IDE with silicon nanowires after thermal annealing

**Material Characterization**

Nickel silicides have been characterized on planar silicon substrates using XPS and XANES analyses, respectively. Verification of a nickel silicide phase in nanowires is particularly challenging due to the limiting spatial resolution of conventional analytical tools. In this case, silicide characterizations were performed using arrays of electrolessly-etched silicon nanowires attached to parent wafer. A thin film of metallic nickel (~100 nm) was sputtered onto freshly etched silicon nanowire films and annealed by the same procedure described in the IDE study. Following anneal, excessive nickel was striped in a wet etch, following characterizations such as TEM, XPS and XANES analyses.
Silicon nanowires with NiSi were separated and transferred onto lacey carbon coated gold grids for TEM analysis. As shown in Figure 25, TEM images of one single silicon nanowires show sharp contrast differences and an amorphous phase near nanowire tip. Bright region with a periodic structure inside the nanowire is single crystal silicon and the bright amorphous region along the wall of nanowire is oxide formed after annealing. The dark amorphous region is indicative of an amorphous nickel silicide phase.

Figure 25 TEM images of silicon nanowire with NiSi formation

XPS analysis, including depth profiling using argon ion gun sputtering, was used to determine compositional details of nickel silicides formed on silicon nanowire after thermal
annealing. XPS spectra were analyzed and identified by referencing reported data (Gambino et al. 1998). As shown in the O (1s) spectra in Figure 26, the characteristic peak of oxygen at 533 eV decreased, indicating the gradual elimination of surface oxides by ion sputtering. The characteristic peak of O (1s) for nickel oxide at 529.9 eV is not present which indicated the oxide is solely associated with silicon.

![XPS spectra for NiSi on silicon nanowire with argon sputtering from 5 to 40 minutes](image)

**Figure 26 O (1s) XPS spectra for NiSi on silicon nanowire with argon sputtering from 5 to 40 minutes**

As seen in the silicon (2p) spectra shown in Figure 27, the peak for silicon oxides at 103.7 eV decreased as sputter time increased in accordance with oxide removal by ion sputtering. A slight shifting of Si (2p) peak at 99.6 eV to higher energy level 99.8 eV can be observed after 15 minutes of sputter time indicating silicidation. The 99.8 eV peak returned to 99.6 eV after 25 minutes sputter time where the XPS detection was dominated by the bulk silicon signal.

The nickel (2p) $^{3/2}$ peak (Figure 28) at 852.3 eV shifts from lower energy level to higher energy (854 eV) as sputtering time increases, suggesting the low resistance NiSi phase consistent with a previous study using planar silicon.
Figure 27 Si $(2p)$ XPS spectra for NiSi on silicon nanowire with argon sputtering from 5 to 40 minutes

Figure 28 Ni $(2p)$ XPS spectra for NiSi on silicon nanowire with argon sputtering from 5 to 40 minutes
Concentration depth profiles of nickel silicides formed on silicon nanowires were also obtained quantifying XPS data for each element. Figure 29 shows concentrations variations of Ni, Si and O on silicon nanowire arrays versus sputtering time. As can be seen in Figure 29, prior to sputtering, the sample contains high level of oxygen at 70 % for oxides contaminant on the sample surface, while both silicon and nickel concentrations are lower than 20 %. Therefore, the sample surface is originally dominated with silicon and nickel oxides. As argon sputter continues, the oxygen level is gradually reduced and Ni and Si concentrations are increased. The oxides cannot be eliminated completely due to the complex structure of silicon nanowire arrays. Note due to limitation of XPS instrument used in this work, argon ion sputtering is not calibrated with sputter depth, hence, XPS data provided here are related to sputtering time instead of sputtering depth.

Figure 29 Concentration of Ni, Si, and O versus sputtering time via XPS characterization
Figure 30 XANES Si K-edge spectra of unreacted silicon wafer and silicon nanowires

Figure 31 XANES Ni K-edge spectra of nickel monosilicide formed on planar silicon (reported by Naftel et al.) and silicon nanowires compared with metallic nickel foil
Composition of the NiSi phase in nanowires was further verified using Ni and Si $K$-edge XANES analysis in total electron yield (TEY) mode. As noted in previous work with planar NiSi films, NiSi has significantly different Si $K$-edge spectra with bulk silicon or other nickel silicide phases (Naftel et al. 1997; Naftel et al. 1998; Naftel et al. 1999).

In our case, the Si $K$-edge XANES results showed only slight spectral differences for silicided nanowires relative to unreacted silicon (as shown in Figure 30). This is considered to be due to the comparable X-ray probe depth and silicide thickness in nanowires. Silicon appears to dominate the TEY signal and the thin silicide phase near the tips of nanowires does not yield strong Si $K$-edge signal.

The XANES Ni $K$-edge spectra of silicided silicon nanowires are shown along with nickel foil and results from a previous XANES NiSi study with planar substrates as shown in Figure 31. Spectra of silicon nanowire after nickel silicidation show the presence of un-oxidized nickel phase significantly different from metallic nickel including: the reduced amplitude of the pre-edge peak (~8335 eV), a new shoulder appearing at around 8344 eV, broadening of the white line due to a peak appearing at 8363 eV, and a disappearance of the large resonance around 8383 eV. The nickel phase remains even after stripping excessive nickel by wet etching. These observations are consistent with XANES work on planar NiSi films by Naftel et al. (Naftel et al. 1998), which suggests NiSi formation on silicon nanowire arrays. The NiSi phase formed on silicon nanowire arrays indicates that silicidation nanowires under identical conditions yields the low-resistance NiSi phase in areas where nanowires are annealed in direct contact to nickel electrodes.

In summary, nickel monosilicides are created between silicon nanowires and nickel electrodes as well as with deposited nickel thin films via thermal annealing. Low resistivity NiSi may be adopted to prepare silicon nanowire anodes for lithium-ion batteries. Electrical
conductivity is one of the most important parameters for battery anodes to allow efficient electron transfer during charge and discharge cycles. As for VLS-grown silicon nanowires, the nanowire structures are directly attached to stainless steel or other metal substrates, and have sufficient electrical contacts in between. As for silicon only anodes using electrolessly-fabricated nanowires, NiSi may be applied as electrical contacts between silicon nanowires and current collectors for its low resistivity, low silicon consumption as well as facile formation procedures. Composite anodes, differed from anodes containing silicon only, adopt graphite, carbon black and elastic polymer binders as conductive matrix; therefore, NiSi is not necessarily applied in silicon nanowire composite anodes.

3.4 Conclusions

Silicon nanowires are fabricated via electroless etching, separated, transferred, deposited and integrated with nickel electrodes in a facile process that does not require any vacuum, SEM, or additional metal depositions steps. Silicon nanowires created via 30 minutes electroless etching after are approximate 20 µm in length and average 253 nm in diameter regardless of doping type. In contrast with VLS-grown nanowires, no catalysts and rigorous conditions are required and high volumes of nanowires can be created in this electroless process. Experimental results show nanowires retain the resistivity of their parent wafer and verify the formation of a nickel monosilicide phase in regions where nanowires contact with nickel electrodes during annealing. These results demonstrate a novel (vacuum-free) method to integrate large numbers of silicon nanowires with pre-existing electrodes and the potential to create dense nanowire anodes for lithium-ion battery via nickel monosilicides electrical contacts. The method may also be applied for highly integrated electrical devices such as silicon nanowire photovoltaic cells, nanowire transistor arrays, optical receivers, and chemical or biological sensors.
CHAPTER 4 SILICON NANOWIRE COMPOSITE ANODES FOR LITHIUM-ION BATTERIES†

4.1 Introduction

Silicon nanowires are excellent candidates for lithium-ion battery anodes benefiting from its high theoretical specific capacity (4200 mAh·g⁻¹), 1-D diffusion, stress accommodation without cracking or agglomeration during cycling, and length scales allow multiple contact points with active and inactive materials within the anode matrix.

Novel composite anodes are prepared from electrolessly fabricated silicon nanowires. Silicon nanowires are mixed with conventional graphite, conductive carbon black, and binders to create composite anodes for lithium-ion batteries. Target anode composition of silicon to graphite at 15:85 (mass ratio) is selected to maximize cell capacity with the least amount of silicon considering conventional cathode capacities (e.g. LiCoO₂ or Li₂MnO₄). Electrochemical performance of the silicon nanowire composite anodes is measured via chronopotentiometry in the potential range from 0.01 V to 1.5 V versus Li/Li⁺ at scan rate of approximate C/10 for 15 cycles, and data are compared with graphite composite anodes prepared via similar procedures. Morphologies of silicon nanowire composite anodes before and after charge and discharge cycles are also characterized by SEM.

4.2 Material and Methods

4.2.1 Silicon Nanowire Anode Preparation

Silicon nanowire arrays were fabricated via electroless etching of p-type boron-doped (100) silicon wafers, 100 mm in diameter, with resistivity in the range of 1-5 Ω·cm (Montco, Spring City, PA) as described in the Chapter 3. The hydride-terminated Silicon nanowires were

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separated from the parent wafer by sonication for 1 minute in ethanol. Nanowires were centrifuged at 5000 rpm for 10 minutes, separated from the transfer solvent and combined with graphite (synthetic, diameter <20 µm, Aldrich) to create a mixture of active materials containing silicon nanowire to graphite at 15:85 (mass ratio).

![Figure 32](image)

**Figure 32** Total cell specific capacity versus anode specific capacity for 18650 lithium-ion battery with constant cathode capacity at 200 mAh·g⁻¹ and differential total capacity versus anode capacity (data adapted and processed from Kasavajjula et al. 2007)

The mass ratio of 15:85 for silicon nanowires and graphite was selected based on the relationship between the total cell specific capacity and the anode specific capacity as discussed in Chapter 2 for a typical 18650 lithium-ion battery with constant cathode capacity. As shown Figure 32, data adapted from 18650 lithium-ion battery with cathode capacity at 200 mAh·g⁻¹ is plotted as blue dots (Kasavajjula et al., 2007); while the first derivative was taken and shown as red dots, and fitted with red line. The first derivative of total capacity versus anode capacity
suggests that the rate of total capacity increases as anode capacity increases from 250 mAh·g⁻¹, reaches to a maximum at 750 mAh·g⁻¹, and approaches to zero when anode capacity is over 2500 mAh·g⁻¹. When the anode capacity is over 1000 mAh·g⁻¹, the increase in total capacity is negligible if cathode capacity is constant. To achieve maximum increase in total cell capacity with least silicon nanowire content, a target anode capacity of approximate 1000 mAh·g⁻¹ is selected in this work. Base on the theoretical specific capacities of both silicon and graphite, a mass ratio of 15:85 for silicon to graphite will result in specific composite capacity of 943 mAh·g⁻¹, therefore, the ratio is selected targeting maximum total cell capacity increase with least silicon nanowires applied.

Active materials containing silicon nanowires and graphite were combined with carbon black (30-50 nm, Mitsubishi Chemicals, Japan) and polyvinylidene fluoride (PVdF, Aldrich) in n-methyl-2-pyrrolidone (NMP, Aldrich) and ball milled for 24 hours followed by deposition onto nickel foil (1mm thick, 99.99 % pure, ESPI Metals, Ashland, OR) using doctor blade technique. Anodes were thermally treated at 120 °C for 12 hours in argon to yield a dry anode composition of 60 % active material, 20 % carbon black and 20 % PVdF. Conventional graphite composite anodes without Silicon nanowires were prepared using same procedures as described for comparison. Graphite composite anodes consisted of 60 % graphite as active material, 20 % carbon black and 20 % PVdF. Average active material per anode area was approximate 1.25 mg·cm⁻².

4.2.2 Anode Characterization

◆ Lithium-ion Half Cell Set-up

An electrochemical cell (such as lithium-ion cell) is set up to study the chemical and physical phenomenon, especially redox reaction mechanisms of the system. A typical redox reaction can be described as:
where $O$ is the oxidation species, $R$ is the reduction species, and $n$ represents the number of
electrons transferred during the reaction.

The typical cell setup for electrochemical measurements contains a working electrode,
reference electrode and a counter electrode. The working electrode is the study subject. The
reference electrode is an electrode maintaining constant potential throughout experiments, such
as standard hydrogen electrode (SHE), saturated calomel electrode (SCE: 0.242 V versus SHE),
silver-silver chloride electrode (0.197 V versus SHE) and etc. The counter electrode is non-
polarized and the surface area should be significantly greater than working electrode to eliminate
the limitation by counter electrode during experiment. Electrochemical cell is connected to the
potentiostat, a device applying polarization potential or current to the working electrode, and
recording corresponding variation in current or potential.

The relationship between the electrochemical potential ($E_{cell}^0$) and the redox reaction
Gibbs free energy ($\Delta G$) can be described as follows:

$$-\Delta G = nFE_{cell}^0$$  \[4-2\]

If $E_{cell}^0 > 0$, $\Delta G < 0$, the reaction is spontaneous

If $E_{cell}^0 < 0$, $\Delta G > 0$, the reaction is non-spontaneous

The more negative $E_{cell}^0$ is, more energy it requires to allow the red-ox reaction to happen.
Take lithium reduction on graphite anode in a lithium-ion battery for example, the reduction
potential is approximately 0.05 V versus Li/Li$^+$ (equivalent to $E$=-2.995 V versus SHE), and six
moles of graphite can accommodate one mole of lithium for full insertion. The Gibbs free energy
for lithium reduction and intercalation with graphite is estimated to be 48.16 kJ·mol$^{-1}$. In other
words, when graphite anodes are fully charged, 48.16 kJ·mol⁻¹ is converted from electrical energy into chemical energy and stored in graphite anodes.

It is also necessary to clarify the electrochemical convention used in this work to avoid confusion. International convention and American convention are the two types of electrical polarity conventions existed for electrochemical analyses. International convention defines cathodic current as negative, but it is opposite for American convention. In this work, if not specified, all the electrochemical data and plots observe international convention. Note the term “charge” for lithium-ion battery anodes (as well as in this work) refers to the cathodic or reductive reaction \( \text{Li}^+ + e^- \rightarrow \text{Li} \), where an electron is obtained; while in other field of electrochemistry, the term “charge” generally means anodic or oxidation reaction that electrons are given away.

Figure 33 Schematic of lithium-ion half cell

Lithium-ion half cell was set up as a typical three-electrode cell with excess electrolyte, a lithium foil counter electrode and lithium rod reference electrode (99.99 %, Aldrich) as shown in Figure 33. The electrolyte included 1M lithium hexafluorophosphate (LiPF₆, Thermo Fisher
Scientific, Waltham, MA) in ethylene carbonate and dimethyl carbonate (EC/DMC, anhydrous, Aldrich) solution in a 1:1 volumetric ratio mixed in dry box. A 20 µm microporous trilayer membrane (CELGARD 2320, Celgard, LLC) was used to separate electrodes.

Several types lithium-ion half cells were tested in this work, including beaker cell (Figure 33), reactor cell (Figure 34) and Swagelok cell (Figure 35). Beaker cell is the simplest cell set-up, where working anodes, lithium reference and counter electrodes were immersed in electrolyte in a glass beaker, and followed by electrochemical measurements. Facile assembly is the main advantage for beaker cell.

Special reactor resembling commercial coin cell (two electrodes cell without reference electrode) was designed and fabricated with the help of mechanical shop from Department of Chemical Engineering, LSU. The schematic of designed cell is shown in Figure 34. The cell is composed of a TEFLON cell shell and two protruding brass rods. Prepared Anode and lithium counter electrode was placed at the two sides of TEFLON cell filled with electrolyte, and brass fittings were screwed to form back contact with the two electrodes. TEFLON O-rings were applied to seal the reactor.

Figure 34 Schematic of designed lithium-ion cell
Figure 35 Optical image of assembled Swageloc lithium-ion cell

Similar to reactor cell, Swagelok cell assembled from commercial Swagelok fittings were applied in this work. Swagelok SS-810-SET and perfluoroalkoxy (PFA) union Swagelok PFA-820-6 were obtained from Capital Welders, LA, and other parts were obtained from MacMaster.com and mechanical shop from Department of Chemical Engineering, LSU. The completed Swagelok cell is shown in Figure 35.

◆ Electrochemical Measurements

Chronocoulometry is applied to determine the chemical species reacted in a specified time range. The current or potential of the working electrode is held constant, and the corresponding potential or current on that electrode over time is recorded to generate chronocoulommogram. There are two types of chronocoulometry, namely, chronopotentiometry and chronoamperometry, where chronopotentiometry measures working electrode potential when the applied current is constant, and chronoamperometry measures current through working electrode when the applied potential is constant.
In this work, chronopotentiometry was applied to measure anode capacities as well as characterize silicon nanowire composite anodes electrochemically. Take charge cycle of silicon anodes for example, the applied cathodic current of silicon nanowire anode is held constant as shown in Figure 36.

The working electrode potential is recorded as time elapsed as shown in Figure 37. The potential is gradually dropping to more cathodic since lithium is gradually reduced when cathodic current is applied. The variation in potential can be described via Nernst equation:

\[ E = E^{0'} + \frac{RT}{nF} \ln \frac{c_O^*}{c_R^*} \]  \[4-3\]

where \( c_O^* \) and \( c_R^* \) are bulk concentrations of O and R species, respectively, and \( E^{0'} \) is the formal potential for the redox couple. In this case, the concentration of O species Li\(^+\) on anode surface decreases as it is reduced to lithium, so as the anode potential.

In electrochemical reactions, Faraday’s law of electrolysis can be summarized in Equation [4-4] that the mass of a substance reacted at an electrode during redox process should be directly proportional to quantity of electricity or charge transferred at that electrode (Scholz 2009).

\[ m = \frac{Q \times M}{F \times z} \]  \[4-4\]

Where

\( m \): mass of the substance, g

\( Q \): charge transferred, C

\( M \): molar mass of the substance, g·mol\(^{-1}\)

\( F \): Faraday’s constant

\( z \): electrons transferred per ion
Figure 36 Current versus time ($i$-$t$) when current $i$ applied at $t_0$ in chronopotentiometry

Figure 37 Resulting potential versus time ($E$-$t$) when current $i$ applied at $t_0$ in chronopotentiometry
Figure 38 Potential versus capacity ($E$-$q$) plot converted from potential versus time ($E$-$t$) by Faraday's Law

Figure 39 Differential charge (or capacity) versus potential ($dq/dE$-$E$) derived from potential versus time ($E$-$q$)
and the charge transferred can be obtained by the electric current (I) integrated over time (τ):

\[ Q = \int_{0}^{\tau} I \, d\tau \]  

[4-5]

The total charge going through the working electrode can be obtained from integration of electrical current over time, and the consumption and generation of the chemical species on the working electrode can be obtained by applying Faraday’s law (Scholz 2009). The potential versus total charge (or anode capacity) through the working electrode can be plotted as shown in Figure 38. In battery studies, anode capacities are normalized to anode weight and converted to \([\text{mA} \cdot \text{hg}^{-1}]\) rather then \([\text{C} \cdot \text{g}^{-1}]\).

The potential versus capacity plot is essential in anode studies, which can also be derived into \(dq/dE\) (differential charge or capacity) versus potential plot by taking the first derivative of anode charge capacity versus anode potential as shown in Figure 39. \(dq/dE\) corresponds to the rate of charge versus potential, and provides significant information in characteristic reduction or lithiation potentials for anodes. In Figure 39, negative \(dq/dE\) represents increase in charge rate, and approaches maximum when potential \(E\) is approaching zero.

During discharge, similar chronopotentiometry is applied, only the applied current is reversed to be anodic.

Silicon nanowire anodes charge and discharge experiments were performed in argon filled dry box system (OMNI-LAB dry box system, Vacuum Atmospheres Company, Hawthorne, CA) with less than 1 ppm \(\text{H}_2\text{O}\) or \(\text{O}_2\). Electrochemical measurements were carried out via PARSTAT 2273 Potentiostat system (Princeton Applied Research). Charge and discharge cycles were performed at 0.1 mA·cm\(^{-2}\) (normalized by anode effective area) in the potential range from 0.01 V to 1.5 V versus Li/Li\(^+\) for silicon nanowire composite anodes. The current density was selected based on the average active material per anode area, estimated anode capacity and a
prorated charge and discharge rate at approximate C/10. The term C over a number (e.g. C/10 in this work) refers to charge and discharge rate in battery characterizations, where C means the electrode’s full capacity, and the number corresponds to how many hours it takes to be fully charged or discharges; therefore, C/10 in this work means each charge or discharge cycle will take 10 hours, and a full charge and discharge cycle will last 20 hours. For charge cycle, constant cathodic current of 0.1 mA·cm\(^{-2}\) was applied to anode until potential reached 0.01 V; for discharge cycle, the constant current is reversed to be anodic, and cut off until anode potential reached 1.5 V. As for silicon nanowires on parent substrate, current density of 25 µA·cm\(^{-2}\) was applied. Charge and discharge chronopotentiometry was programmed via potentiostat POWER STEP software console and auto executed with a time interval for 5 minutes between each cycle.

![Figure 40 OMNI-LAB dry box system](image)

All anode preparation and lithium-ion cell assembling and testing were carried out in the dry box system (shown in Figure 40).
SEM Characterization

Silicon nanowire anodes before and after charge and discharge battery tests were sealed in argon-filled containers and then transferred to Hitachi S-3600 SEM for characterization. Silicon nanowire anodes after charge and discharge tests were rinsed with DMC to remove electrolyte residuals prior to SEM analysis. Transfer time from dry box to SEM chamber was limited to 30 minutes or less in order to prevent silicon oxidation when exposed to atmosphere.

4.3 Results and Discussion

4.3.1 Silicon Nanowire Array Anodes

Figure 41 SEM images of (A) top-view of SiNWs as fabricated by electroless etching, (B) top-view of SiNWs after 10 cycles at 25 μA·cm⁻² charging and discharging rate, (C) tilted view of SiNWs as fabricated by electroless etching, and (D) tilted view of SiNWs after 10 cycles at 25 μA·cm⁻² charging and discharging current density.
Silicon nanowire arrays on parent wafer were tested in lithium-ion half cell. Figure 41 shows SEM images of silicon nanowires before (Figure 41 A and C) and after (Figure 41 B and D) charge and discharge cycles. A visible organic layer (SEI layer) covering silicon nanowires arrays are observed after charge and discharge cycles. Near-by nanowires are merged into bulky bundles after cycling compared to nanowire as fabricated in the SEM images.

Charge and discharge capacities for silicon nanowire array anodes on parent substrates are shown in Figure 42. Silicon nanowire array anodes show high charge capacity at approximate 4000 mAh·g⁻¹ with greatly decreased discharge capacity of 750 mAh·g⁻¹ in the first cycle. Significant capacity fade is observed after the first cycle, and no noticeable capacities are observed after the initial cycles.

![Figure 42 Silicon nanowire anode specific capacities versus cycle number](image-url)

Figure 42 Silicon nanowire anode specific capacities versus cycle number
Peng et al. have shown cycle ability for silicon nanowire arrays on parent substrates as anodes for several cycles, however, no applicable specific capacity data have been obtained due to difficulties in normalize capacity by mass (Peng et al. 2008). In our case, specific capacities of silicon nanowire arrays are normalized by weight obtained by silicon nanowire yield per substrate area described in Chapter 3. As observed from Figure 42, silicon nanowire arrays failed to be charged and discharged in lithium-ion half cell after the initial cycle. This may be caused by large volume expansion for silicon nanowires and bulk silicon substrates, and detachment of nanowires from parent substrate as well as agglomerations.

4.3.2 Silicon Nanowire Composite Anodes

◆ Composite Anodes Containing 15 % Silicon Nanowires

The morphology of silicon nanowire composite anodes as prepared can be characterized via SEM analysis. Figure 43 shows SEM image of a composite anode surface created with 15 % silicon nanowires and graphite as prepared. Nanowires with diameters of approximate 250 nm and 10 µm in length are visible at the anode surface and randomly distributed in anode matrix at this concentration.

Figure 44 shows SEM image of the composite anode after 15 charge and discharge cycles showing the formation of an organic (SEI) layer including intact nanowires at the surface. Nanowires after charged/discharged from 0.01 V to 1.5 V versus Li/Li⁺ with larger diameters (~1 µm) and similar lengths as observed prior to charging without significant structural damage. This behavior suggests single crystal silicon nanowire is converted into amorphous structure after the first charge and discharge cycles by lithium insertion and extraction.
Figure 43 SEM image of silicon nanowire composite anode surface before charge/discharge

Figure 44 SEM image of silicon nanowire composite anode surface after charge/discharge
Composite anodes were cycled from 0.01 V to 1.5 V (versus Li/Li⁺) for 15 consecutive cycles via chronopotentiometry as described. Charge and discharge specific capacities versus anode potentials profiles for the silicon nanowire composite anode are presented in Figure 45 for the first, the second, and the fifth cycles. Charge and discharge capacities decrease significantly over the first 5 cycles. A potential plateau is observed below 0.2 V for charge cycles, which corresponds to lithiation for both silicon and graphite. In discharge cycles, potential plateau under 0.2 V is delithiation of graphite, and another plateau at 0.5 V shown in the first discharge cycle is in agreement with characteristic delithiation potential for silicon as reported (Chan et al. 2008). The 0.5 V plateau also decreases as anode cycles while the 0.2 V plateau remains constant as anode cycles, which indicates capacity fade is due silicon capacities loss.

Figure 45 Charge/discharge specific capacities for silicon nanowire composite anode (15 %) for the 1st, 2nd, and 5th cycle.
The corresponding differential charge versus potential curves derived from capacities versus potentials profiles for the first, second and fifth cycles for the composite anode are shown in Figure 46. The differential capacity versus potential curves for the composite anode shows characteristics of both silicon nanowires and graphite when compared with differential charge behavior of the graphite anodes and previously reported silicon nanowire anodes.

Figure 46 Differential capacities versus potential of silicon nanowire composite anode (15 %) for the 1\textsuperscript{st}, 2\textsuperscript{nd}, and 5\textsuperscript{th} cycle

In the initial charge curve a small peak is observed at 0.85 V (versus Li/Li\textsuperscript{+}) corresponding to initial SEI layer formation on anode surface. Several peaks are seen in the charging curves below 0.1 V (versus Li/Li\textsuperscript{+}) showing lithiation of graphite and silicon. Differential discharge curves show peaks associated with graphite disintercalation at potentials less than 0.3 V (versus Li/Li\textsuperscript{+}) similar to the behavior of the graphite anode. A characteristic silicon delithiation peak at
approximately 0.5 V (versus Li/Li⁺) is consistent with the lithiation and delithiation of crystalline silicon reported. As shown in the second and fifth charge and discharge cycles for silicon composite anode, multiple discharge peaks suggest the combined extraction of lithium amorphotized silicon and disintercalated from graphite. Graphite discharge behavior does not significantly change with cycling; however, as seen in the discharge curves and differential discharge curve, the silicon delithiation peak (~0.4-0.5 V versus Li/Li⁺) decreases with cycle number, suggesting silicon capacities fade as anode cycles.

Figure 47 Charge/discharge capacities and coulombic efficiencies of composite anode with 15 % silicon nanowires versus cycle number

Silicon nanowire composite anodes charge and discharge specific capacities versus cycle number can be obtained from charge and discharge current and time by applying Faraday’s law via electrical measurements. As shown in Figure 47, the initial charge capacity is 811 mAh·g⁻¹.
and represents 95% of predicted capacity of the composite anode. The initial composite anode capacity is approximately 2.7 times greater than equivalent graphite anode prepared via same method, and the reversible capacity of over 500 mAh·g⁻¹ is approximately 1.7 times greater than that of graphite anode. Coulombic efficiency is the ratio of discharge capacity over charge capacity in the same cycle, and describes the reversibility of anode reactions. Coulombic efficiencies for composite anode with 15 % silicon nanowire increase from less then 76.45 % for the first cycle to near 96.48 % for the 15th cycle. Finally, a stable reversible capacity of 512 mA·h·g⁻¹ is achieved after 10 cycles with a fade of approximately 36.87 % of the total anode capacity.

The results demonstrate composite anode materials with capacities 2.7 times greater than graphite anodes without the addition of 15 % silicon nanowires. Nanowires benefit from 1D radial diffusion, multiple contact points with the electrolyte and current collector, and agglomeration resistance on cycling. The charge and discharge behavior is similar to other composite anode studies with silicon showing graphite charging in the potential range below 0.1 V (versus Li/Li⁺) and discharging below 0.2 V (versus Li/Li⁺) and characteristic silicon charging peaks at below 0.2 V (versus Li/Li⁺) and discharging peak approximately at 0.5 V (versus Li/Li⁺). Differential charge and discharge curves showing the broadening of the discharge peak at 0.2 V after the first cycle are indicative of a crystal to amorphous transition.

Silicon composite anodes can be prepared with various silicon concentration and techniques. Normalizing silicon capacity of composite anodes is necessary to compare different anodes performance in order to compare anode capacity and capacity retention over prolonged cell cycles. Dimov et al. describes capacity of the composite electrode ($C_{total}$) as the sum of the capacities of each component. $C_{Si}$ and $C_g$ represent the capacity of silicon and graphite
respectively, while $Si\%$ and $g\%$ are the percentage of silicon and graphite in the anode (Dimov et al. 2003).

$$C_{Total} = C_{Si} \times Si\% + C_{g} \times g\%$$  \[4-6\]

Assuming the loss in capacity is solely attributed to a reduction in silicon capacity (consistent with the differential discharge behavior observed here), we can indirectly compare results without composition dependency. The percentage of capacity loss associated with silicon ($Si \text{ Capacity Loss } \%$) may be estimated using the measured capacity ($C_{Si}$) and theoretical capacity ($C_{The}$) of silicon.

$$Si \text{ capacity loss } \% = 1 - \frac{C_{Si}}{C_{The}}$$  \[4-7\]

Over 60% silicon capacity loss has been observed after 15 cycles for silicon nanowire composite anodes based on this calculation. Similar calculations have been done with other silicon anodes from selective works with applicable data after the first 15 charge and discharge cycles, and normalized silicon capacity and capacity loss are listed in Table 6 for comparison. As for some silicon composite anodes only containing silicon as active material and pure silicon anodes, the silicon capacity loss can be directly derived from reported data. Silicon capacity losses in composite anodes are ranging from 12% to over 80% within the first 15 cycles depending on charge and discharge parameters, particle sizes and anode preparation procedures.

A significant capacity loss mechanism associated with silicon composite anodes is attributed to particle agglomeration in cycling (Kasavajjula et al. 2007). Aside from a few bundles (<10%) of nanowires observed prior to anode fabrication, agglomeration was not observed in SEM analysis of composite anodes after cycling in this work. Nanowires in the
composite anode appeared to swell in diameter (2-3 fold) similar to VLS grown nanowires, which increased in diameter from approximately 89 nm to 141 nm on charging. These composite

Table 6 Selective silicon anodes: reversible capacities and silicon specific capacity loss after 15 cycles (adapted from reported data)

<table>
<thead>
<tr>
<th>Reference</th>
<th>Si</th>
<th>C</th>
<th>Total capacity mAh·g⁻¹</th>
<th>Si capacity mAh·g⁻¹</th>
<th>Capacity loss %</th>
<th>NOTE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beattie 2008</td>
<td>0.33</td>
<td></td>
<td>1200</td>
<td>3636.36</td>
<td>13.42</td>
<td></td>
</tr>
<tr>
<td>Dimov 2003</td>
<td>0.4</td>
<td>0.6</td>
<td>800</td>
<td>1445.00</td>
<td>65.60</td>
<td>10 % Ag additive; nickel foam current collector</td>
</tr>
<tr>
<td>Dimov 2004</td>
<td>0.3</td>
<td></td>
<td>900</td>
<td>3000.00</td>
<td>28.57</td>
<td></td>
</tr>
<tr>
<td>Dimov 2005</td>
<td>0.27</td>
<td>0.63</td>
<td>600</td>
<td>1358.89</td>
<td>67.65</td>
<td>CMC/SBR</td>
</tr>
<tr>
<td>Dimov 2007</td>
<td>0.437</td>
<td>0.437</td>
<td>480</td>
<td>727.14</td>
<td>82.69</td>
<td>carbon coated SiO</td>
</tr>
<tr>
<td>Ding 2009</td>
<td>0.4</td>
<td></td>
<td>738</td>
<td>1845.00</td>
<td>56.07</td>
<td></td>
</tr>
<tr>
<td>Holzapfel 2006</td>
<td>0.2</td>
<td></td>
<td>500</td>
<td>2500.00</td>
<td>40.48</td>
<td>calcium additive</td>
</tr>
<tr>
<td>Kim 2008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>29.76</td>
<td>various C/Si ratio</td>
</tr>
<tr>
<td>Kumta 2004</td>
<td>0.287</td>
<td>43</td>
<td>700</td>
<td>2435.38</td>
<td>42.01</td>
<td>spheroid amorphous carbon coating</td>
</tr>
<tr>
<td>Liu 2004</td>
<td>0.3</td>
<td></td>
<td>900</td>
<td>3000.00</td>
<td>28.57</td>
<td>SiO/Li/C composite</td>
</tr>
<tr>
<td>Luo 2009</td>
<td>0.07</td>
<td>0.87</td>
<td>450</td>
<td>1830.00</td>
<td>56.43</td>
<td>thermal evaporation deposition</td>
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<tr>
<td>Ng 2006</td>
<td>0.44</td>
<td></td>
<td>1600</td>
<td>3636.36</td>
<td>13.42</td>
<td>unspecified percentage of Si; various value</td>
</tr>
<tr>
<td>Seong 2009</td>
<td>0.9</td>
<td></td>
<td>900</td>
<td>1000.00</td>
<td>76.19</td>
<td>plasma assisted thermal evaporation C₆₀ coated</td>
</tr>
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<td>Wen 2003</td>
<td>0.28</td>
<td>0.42</td>
<td>700</td>
<td>1945.00</td>
<td>53.69</td>
<td>mesoporous Si-c core shell nanowire</td>
</tr>
<tr>
<td>Wolf 2009</td>
<td>0.19</td>
<td></td>
<td>700</td>
<td>3684.21</td>
<td>12.28</td>
<td>non-cycle data provided for laser ablation SiNW</td>
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<tr>
<td>Lestriez 2007</td>
<td>0.33</td>
<td></td>
<td>900</td>
<td>2727.27</td>
<td>35.06</td>
<td>CMC</td>
</tr>
<tr>
<td>Cui 2009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45.24</td>
<td>core shell SiNW</td>
</tr>
<tr>
<td>Ryu 2009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>40.48</td>
<td>thin film silicon with silane additive</td>
</tr>
<tr>
<td>Chan 2008</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>22.62</td>
<td>VLS SiNW</td>
</tr>
<tr>
<td>Chan 2009</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34.52</td>
<td>VLS SiNW</td>
</tr>
</tbody>
</table>
results suggest nanowires do not suffer from pulverization or agglomeration and undergo reversible volume changes similar to VLS-grown nanowires. Since the nanowires were fabricated from relatively low resistivity (1-5 $\Omega \cdot \text{cm}$) single crystal wafers, electrical conductivity is relatively higher than comparable laser-ablated silicon particles used in other composite anode studies.

Also, the electrolessly-etched nanowires benefit from hydride termination as opposed to the native oxides present in typical microparticles and nanoparticle studies. Hydride-termination may improve the relative quantity of silicon available for lithium alloying and improve interfacial behavior in comparison with conventional untreated silicon particles with native oxides. These effects (no agglomeration, excellent conductivity, and hydride termination) may all attribute to the improved capacity retention relative to conventional (particle-based) silicon composite anodes.

Other loss mechanisms such as mechanical and electrical contact loss or surface reactions specific to silicon may be responsible for a large fraction of capacity loss observed here. Several recent works show modifications to the silicon-electrolyte, silicon-SEI, or silicon-graphite interface greatly reduce the capacity fade. In fact, composite anodes including silicon particles coated with carbon via pyrolysis and other thermal deposition methods show significantly lower capacity fade in some cases after 15 cycles depending on the method of carbon deposition and uniformity. In addition to improving particle conductivity and preventing agglomeration, the thin uniform amorphous carbon coatings are thought to improve reversible volume changes and allow a more uniform distribution of lithium within the silicon particle. The reduced capacity loss observed in these reports suggests carbon coatings improve the electrical and physical contact between particles and the electrolyte, SEI layer, and other active and inactive anode materials. In addition to effects from surface coatings, maintaining physical and electrical
Contact with silicon surfaces may be a strong function of the electrolyte. Recent works with non-PVdF binders also show lower levels of capacity loss. In particular, carboxymethyl cellulose (CMC) binders are believed improve the silicon interface through esterification reactions between hydroxyl groups on Si surface and carboxyl in CMC (Lestriez et al. 2007). This may allow the electrolyte or SEI layer to expand and retract with the particle during swelling and shrinking to form more closely packed anodes and improved cell performance.

VLS-grown silicon nanowires anodes show ability to accommodate volume change for lithium insertion and free from mechanical failures resulting severe capacity loss, however, up to 45% silicon capacity loss still persists with these anodes. Reactions specific to the silicon-electrolyte or silicon-SEI interface may result in capacity loss through either lithium loss or silicon loss mechanisms. The SEI layer on silicon is composed of both organic and inorganic reduction products including hydrocarbons, C$_2$H$_5$OCOOLi, LiCO$_3$, Li$_2$O, LiF, and silicon containing products, such as: Li$_2$SiO$_3$, Li$_2$SiO$_4$, SiF$_6^{2-}$, resulting in the consumption of lithium or loss of silicon from cycle to cycle and further capacity fade. Intermediates such as silicon-fluorides may exacerbate the loss of active lithium. For example, oxidized silicon species may strip fluoride from complexes such as BF$_4^-$ (or PF$_6^-$) resulting in the formation of silicon fluorides. These reactions may result in localized silicon etching or may increased production of LiF or other fluorinated species (Choi et al. 2007). In fact, the use of lithium salts without fluorides such as lithium bis(oxalato) borate (LiBOB)-based electrolyte significantly improved the discharge capacity retention of silicon thin-film electrodes. It is proposed that LiBOB-originated SEI layer effectively diminishes the preferable reactions of HF and the Si-Si site and thereby limits the formation of global cracks of anode (Choi et al. 2007). Song et al. also suggests silicon oxidation and irreversible reactions at the silicon-SEI interface including the formation of organic phosphorus-fluorine and P-F-containing inorganic species are critical to
capacity fade. Their experimental results show fade is reduced by more than 5-fold when amorphous Si surfaces are treated with methyl silane (Si-O-Si-CH₃); however, the mechanism responsible for the improved capacity retention in that study is not clear. In any case, the reactivity of untreated silicon appears to be as a function of surface chemistry, binder, and lithium source; Carbon coating, surface functionalization, or the use of less reactive electrolyte species may improve the physical and chemical interphase and improve capacity retention. Therefore, continuing work is needed to understand loss mechanisms and methods to mitigate their effects.

◆ Composite Anodes Containing 5 % and 45 % Silicon Nanowires

In order to further analyze fade mechanisms for silicon nanowire composite anodes for lithium-ion batteries, another two composite anodes containing 5 % and 45 % silicon nanowires were also prepared via same method, and charged and discharged for 10 cycles in lithium-ion half cell under identical conditions. Figure 48 and Figure 49 show the charge and discharge capacities versus cycle number for composite anodes containing 5 % and 45 % silicon nanowire as well as coulombic efficiencies of each cycle. For composite anode containing 5 % silicon nanowire, the maximum theoretical capacity is 563 mAh·g⁻¹, and initial discharge capacity of only 226 mAh·g⁻¹ is obtained; reversible capacity of 160 mAh·g⁻¹ is observed after 10 consecutive cycles. Coulombic efficiency gradually increases to nearly 97 % as cell cycles to 10th cycle, and suggests improved cycleability after initial cycles. Composite anode containing 45 % silicon nanowire poses a maximum capacity of 2095 mAh·g⁻¹, the initial discharge capacity is only 525 mAh·g⁻¹, and reversible capacity of less than 100 mAh·g⁻¹ is maintained after 10 cycles. Coulombic efficiency for composite anode containing 45 % silicon is significantly less than that of 5 % and 15 % composite anodes; only 87.27 % efficiency is
obtained after 10 cycles, indicating poor cycle ability for composite anode containing 45 % silicon nanowires.

Figure 48 Charge/discharge capacities and coulombic efficiencies versus cycle number for composite anode with 5 % silicon nanowire

Figure 49 Charge/discharge capacities and coulombic efficiencies versus cycle number for composite anode with 45 % silicon nanowires
Silicon specific capacity and capacity loss for nanowire composite anodes containing 5% to 45% silicon after 10 cycles can be obtained and listed in Table 7.

Table 7 Silicon nanowire composite anode reversible capacities, silicon specific capacities and silicon capacity loss for silicon nanowire concentrations of 5%, 15% and 45% after 10 charge and discharge cycles

<table>
<thead>
<tr>
<th>Silicon nanowire composite anodes</th>
<th>Theoretical capacity mAh·g⁻¹</th>
<th>Anode reversible capacity mAh·g⁻¹</th>
<th>Silicon specific capacity mAh·g⁻¹</th>
<th>Silicon capacity loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% SiNW</td>
<td>563</td>
<td>160</td>
<td>N/A</td>
<td>100</td>
</tr>
<tr>
<td><strong>15% SiNW</strong></td>
<td><strong>943</strong></td>
<td><strong>512</strong></td>
<td><strong>1660</strong></td>
<td><strong>60.5</strong></td>
</tr>
<tr>
<td>45% SiNW</td>
<td>2095</td>
<td>67</td>
<td>N/A</td>
<td>&gt;100</td>
</tr>
</tbody>
</table>

The composite anode with 15% silicon nanowire considered in this work shows a silicon capacity loss of approximately 60.5% after the first 10 cycles, while that of 5% and 45% silicon nanowire composite anodes see over 100% capacity loss for silicon based on the same calculations. Silicon capacity in 5% composite anode fades completely after 10 cycles, while anodes still maintain reversible capacity comparable to graphite anode. Low concentration of silicon nanowires in composite anode was supposed to perform better than high silicon concentration for less internal stresses caused by nanowire volumetric changes; however, with only 5% silicon nanowire, the silicon capacity faded completely after 10 cycles. The complete silicon capacity fade may be attributed to the issues with silicon anodes, such as irreversible silicon surface reactions with electrolyte. As for composite anode containing 45% silicon nanowire, not only silicon capacity is compromised, the anode total capacity is significantly less than graphite. Detrimental effects derived from volume expansion of large amount of silicon nanowires in anode matrix may attribute to the significant capacity loss.
In summary, composite anodes containing 15 % silicon nanowire (by mass) applied in this work has shown great advantages in achieving both high total capacity as well as maintain cycleability when compared with composite anodes containing low (5 %) and high (45 %) concentration of nanowires.

4.4 Conclusions

Silicon nanowire composite anode containing 15 % Si and 85 % graphite as active material is demonstrated with initial capacity 2.7 times greater than graphite with a reversible anode capacity of 512 mAh·g⁻¹ after 10 charge and discharge cycles. SEM analysis of silicon nanowire anode shows the silicon nanowire structure grows in diameter and remains intact after charge and discharge cycles, suggesting the anode structure can sustain large volume change during cell cycling. Silicon nanowire composite anodes with 5 % and 45 % nanowire contents with graphite as active material were also prepared and tested in lithium-ion battery and 5 % and 45 % silicon composite anodes show reversible capacities of 160 and 67 mAh·g⁻¹ after only 10 cycles, respectively. Low-level silicon content anode maintains good reversibility but low anode capacity; while high-level silicon content sees severe capacity fade, which may be attributed to volumetric changes of high numbers of silicon nanowires within the anode matrix. The electrolessly-etched silicon nanowires are considered promising candidates for use in composite anodes due to their unique geometry, natural hydride termination, controllable doping, and a facile (vacuum-free) fabrication process.
CHAPTER 5 SURFACE CHEMISTRY AND SOLID ELECTROLYTE INTERPHASE OF SILICON NANOWIRE ANODES

5.1 Introduction

Composite anodes with an addition of only 15% silicon nanowires (by mass) have shown two-fold increase in reversible capacity compared with graphite composite anodes prepared via same procedures. SEM characterizations have shown nanowire structures within the anode matrix maintain mechanical integrity after continuous charge and discharge cycles, and the anodes are free from cracking and agglomerations. Significant specific capacity loss for over 60% for silicon, however, is still observed for these composite anodes after only 15 charge and discharge cycles.

One key factor determining anode performance may be the solid electrolyte interphase (SEI) formed on silicon anode surfaces, and silicon surface chemistry may affect the SEI formation and its chemical and mechanical properties. To further analyze the SEI formation mechanism and its effects on anode capacity retention, we examine the role of silicon surface chemistry and consider the potential for engineered solid electrolyte interfaces that are suited to mitigate deleterious side reactions while allowing reversible lithium insertion and extraction over prolonged cycles. In this chapter, silicon nanowires with hydride-terminated, methylated, and siloxane-terminated surfaces are prepared through chemical or electrochemical or thermal grafting the electrolessly-fabricated nanowires. Both silicon nanowire arrays as anodes and composite anodes prepared by the same methods applied in Chapter 4 are tested in lithium-ion half cell for electrochemical characterization. The SEI formed on these anodes surfaces are characterized by FT-IR, XPS, and AFM to study properties including chemical composition and mechanical stiffness.

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5.2 Materials and Methods

5.2.1 Anodes Preparation

Silicon samples (approximately 2×2 cm²) were cleaved from p-type silicon wafers, and native oxides were removed using Buffered Oxide Etchant (BOE). Dried samples were immersed in silver nitrate and hydrofluoric acid solutions for electroless etching to fabricate silicon nanowires as described in previous work (Peng et al. 2002; 2003). Residual silver was stripped in nitric acid solution (1:1 volume ratio). The samples were then dipped in BOE again and rinsed with de-ionized water to renew the hydride termination before transferring to the argon atmosphere OMNI-LAB dry box (< 1 ppm water and oxygen, Vacuum Atmosphere, Hawthorne, CA).

Anodic electrografting of methyl groups was performed using silicon nanowire sample as working electrodes in methyl magnesium chloride solution (3 M in THF) with a platinum counter and a silver pseudo-reference under quiescent conditions. The electrografting was carried out via Princeton PAR 2273 Potentiostat system at potential 0.1 V (versus Ag/AgCl) for 120 s as been reported by Vegunta et al. (Ngunjiri et al. 2009; Vegunta et al. 2009). Electrografted sample was thoroughly rinsed with isopropyl alcohol to remove adsorbates followed by drying. Chemical treatment of silicon nanowire was performed by immersion of the hydride silicon nanowire sample in 5 \% trimethoxymethylsilane in THF solution at ambient temperature for 24 hours in the dry box system.

Prepared silicon nanowire can be detached via sonication in transfer solution or simply scraping from the sample substrate. The silicon nanowires were then weighed and well mixed with graphite, carbon black and Polyvinylidene Fluoride (PVdF) in N-Methylpyrrolidone (NMP) to form a paste containing 15 % silicon and 85 % graphite as active material. The paste was
applied to a copper foil via doctor blade method, and the samples were dried at 120 °C for 24 hours to remove excessive solvent in argon atmosphere.

5.2.2 Electrochemical Measurements

Potential sweep method is a potential-dynamic electrochemical measurement technique. Working electrode potential is ramped linearly at a specific rate within a setup potential range as shown in Figure 50. The current at the working electrode is plotted versus the applied voltage to give the voltammogram trace, or linear sweep voltammetry (LSV) (Bard et al. 2001).

![Figure 50 Linear potential sweep (E-t) starting at $t_0$](image)

For a simple one-step one-electron redox reaction on an electrode, the reaction mechanism is governed by basic electrochemical relationship between electrical current and potential. Upon the premise that the electrode kinetic is not limited by mass transport, the general form of Butler-Volmer equation considering both cathodic and anodic reactions happen on the same electrode can be expressed as:
\[ I = A \cdot i_0 \cdot \left\{ \exp \left[ \frac{(1-\alpha)nF}{RT}(E - E_{eq}) \right] - \exp \left[ -\frac{\alpha nF}{RT}(E - E_{eq}) \right] \right\} \] \hspace{1cm} [5-1]

Where

\( I \): electrode current, A

\( i_0 \): exchange current density, A/m²

\( E \): electrode potential, V

\( E_{eq} \): equilibrium potential, V

\( A \): electrode active surface area, m²

\( T \): absolute temperature, K

\( n \): number of electrons involved in the electrode reaction

\( F \): Faraday constant

\( R \): universal gas constant

\( \alpha \): dimensionless symmetry factor

Current-overpotential equation can be derived from Butler-Volmer equation and Nernst equation (equation [4-2]) by adopting bulk concentrations of O and R:

\[ i = i_0 \left[ \frac{c_o(0,t)}{c_o} e^{-\alpha f \eta} - \frac{c_R(0,t)}{c_R^*} e^{(1-\alpha) f \eta} \right] \] \hspace{1cm} [5-2]

where \( f \) equals to \( F/RT \), and \( \eta \) is overpotential \( E - E^{0'} \).

Figure 51 shows a typical LSV current response to potential. When the potential start to ramp anodically from time \( t_0 \), only non-faradic currents flow at the very beginning due to ionic conduction without redox reactions. When the electrode potential reaches to formal potential, the R species starts to be oxidized to O species and the current begins to rise. As potential ramps more anodic and passes the formal potential, the redox reaction continues to happen, so as the current increases. Current will increase to a maximum point and then decline as the surface species gradually depletes as potential continues to ramp.
Figure 51 Resulting $i$-$E$ curve from linear potential sweep

Figure 52 Differential current versus potential ($di/dE$-$E$) curve from linear potential sweep
To manifest the change in current response, the first derivative \( \frac{di}{dE} \) of the current response can be obtained from the \( i-E \) curve to show the current change rate versus potential. Figure 52 shows the first derivative of \( i-E \) curve in Figure 51. As shown in Figure 52, the current starts to increase and reach to maximum, and then gradually decline as depletion effect sets in.

Besides simple linear sweep, potential sweep methods also include cyclic voltammetry (CV), where the potential is ramped to a set point and then reversed for several cycles within one experiment. Each cyclic voltammetry cycle is composed of two linear potential sweeps with reversed bias (Bard et al. 2001). Figure 53 is a sample potential time behavior in one cyclic voltammetry cycle, the applied potential starts to ramp at time \( t_0 \), reverses at time \( t' \). Current-potential response is plotted in Figure 54.

![Figure 53 Cyclic voltammetry: (E-t) starting at \( t_0 \) and potential is reversed at \( t' \)](image)

When potential is ramped anodically from \( t_0 \) to \( t' \), R species are oxidized to O species and the current-potential response is identical to linear potential sweep. Starting at time \( t' \), the
potential is reversed to move cathodically, O species will begin to be reduced to R species. Anodic current will gradually decrease to zero, and start to increase cathodically as reduction reaction continues to happen. Finally, the cathodic current will reach to a maximum point and then decline as the surface species gradually depletes.

![Figure 54 Resulting i-E curve from cyclic voltammetry](image)

Potential sweep techniques, especially the cyclic voltammetry, offer both the kinetic and thermodynamic details of an electrochemical system (Bard et al. 2001). CV is of great importance in analyzing anodes in lithium-ion batteries, including reversibility of the system, electrolyte reduction, lithiation and delithiation onset potentials, etc.

The prepared samples were assembled as anodes in typical three electrodes lithium-ion half cell, with lithium foil as reference and counter electrodes. The electrolyte is 1M LiPF₆ in 1:1 (volume ratio) EC/DMC. Cyclic voltammetry of each anode was performed at a scan rate of 0.05
mV·s⁻¹ in the potential range from 0.01 to 1.5 V versus lithium. Data were normalized by anode surface area for silicon nanowire array anodes.

Lithium-ion half cell charge and discharge measurements for composite anodes were taken at approximately C/10 in potential range 0.01 to 1.5 V versus lithium as described in Chapter 4. Current and capacity data were normalized by active material weight. All electrical measurements were carried out in dry box system via potentiostat PAR 2273 system.

### 5.2.3 SEI Characterization

Silicon nanowire anodes were rinsed with DMC and dried in argon prior to surface characterization. The anodes were then transferred to analytical tools in sealed polyethylene containers filled with argon. SEM images were obtained using a Hitachi S-3600N variable pressure SEM system. *Ex-situ* X-ray Photoelectron Spectroscopy (XPS) data were collected from Perkin-Elmer PHI 5100 system using Al Kα X-ray source with passing energy of 20 eV. Samples were sputtered with argon inside the XPS chamber to remove surface contaminants.

**Fourier Transform Infrared Spectroscopy (FT-IR)**

Fourier Transform Infrared Spectroscopy (FT-IR) is well documented technique to obtain specimen chemical composition by identifying bond structures of certain organic species (Stuart 2004). FT-IR analysis is of great importance on studying SEI on anodes’ surface of lithium-ion batteries. The FT-IR spectra of SEI on graphite anodes surface have been extensively studied, and characteristic peaks and surface composition has been well established (Perla B. Balbuena 2004). FT-IR has also been applied to study SEI on silicon thin film anodes (Song et al. 2009).

*Ex-situ* Fourier Transform Infrared (FT-IR) spectroscopy in Attenuated Total Reflectance (ATR) mode was performed using a Nicolet 6700 FT-IR spectrometer system. All FT-IR spectra were taken at resolution of 2 cm⁻¹ for 128 scans using Mercury-Cadmium-Telluride (MCT)
detector. Spectroscopic data were recorded and analyzed via OMNI software console installed with the FT-IR system.

**Atomic Force Microscopy (AFM)**

AFM analysis is a scanning probe microscopy with high resolution on the order for fractions of nanometer. AFM generally employs a cantilever with tip travelling through a specimen surface, due to the topology change and surface conditions, the cantilever deflects when tip contacts or approaches the specimen surface, the deflection is magnified and recorded to provide useful information on the topology of a specimen surface.

![Figure 55 Picture of AFM system with custom-made noise cancelling shell](image)

Currently, AFM has been extended to imaging, measuring, and manipulating the specimen surface with developed techniques. AFM analyses have been reported to study the
morphology of SEI layer on graphite and other anodes for lithium-ion batteries (Alliata et al. 2000; Inaba et al. 2004; Leroy et al. 2005; Lucas et al. 2009). AFM nano-indentation methods were used to determine the relative mechanical stiffness of the SEI layer on nanowire anodes. Silicon nanowire arrays on parent wafer were charged and discharged as anodes in lithium-ion half cell for 10 cycles to generate the SEI film thick enough for AFM analyses. The nanowire anodes with the SEI layers were slowly contacted with a nonconductive silicon nitride tip using an Agilent 5400 STM/AFM operated in contact mode (shown in Figure 55). The tip approached the surface and was retracted at a constant tip-speed of 100 nm·s⁻¹. Deflection was measured as a function of Z-distance from -1000 to +1000 nm using Picoscan software console.

All SEM, FT-IR, XPS and AFM analyses were carried out immediately after samples were moved out of the dry box system, and all spectra of the samples were obtained under fully discharged condition.

5.3 Results and Discussion

5.3.1 Silicon Nanowire Array Anodes

Silicon nanowires were fabricated by electroless etching of single crystal silicon wafers in aqueous solution containing hydrofluoric acid and silver nitrate as described in previous studies (Peng et al. 2002; Xu et al. 2010).

Figure 56 shows silicon nanowires created in this process are approximately 30 µm in length and range from 50 to 500 nm in diameter (average diameter of 253 ± 91 nm 1σ) after 30 minutes of electroless etching. Nitric acid was used to strip silver dendrites followed by a BOE treatment to remove oxides and provide a hydride-terminated surface. All electrochemical measurements were carried out with nanowires attached to the bulk silicon substrate or detached from substrate and combined with graphite (in case of composite anodes). Ohmic loses across
the bulk silicon substrate (500 µm thick) were negligible due to the relatively low resistivity (1-5 Ω cm) of the parent wafer.

Figure 56 SEM image of silicon nanowire arrays on parent substrate as fabricated

5.3.2 SEI Modification of Silicon Nanowire Anodes with Surface Functionalizations

The nanowires are initially crystalline and retain the (100) orientation of the parent wafer with sidewalls including a large fraction with (110) surface orientation. The three back bonds of surface silicon atoms are shared with other silicon atoms and the surface bonds are functionalized as shown in Figure 57.

Silicon nanowire arrays with three types of surface terminations were prepared for use as electrodes: hydride-terminated (denoted as: Si-H), methyl (denoted as: Si-CH₃), and siloxane (denoted as: Si-O-Si-R; due to the polymerization of trimethoxymethylsilane on silicon surface, representative surface bond R is applied to all possible bonds such as –CH₃, -OCH₃, or -OSi).
Another silicon anode, initially hydride terminated was cycled with 5% trimethoxymethylsilane (structure as shown in Figure 58) as an additive in the EC/DMC electrolyte (denoted as: Silane Additive) in a similar manner as described by Song et al. for thin film anodes (Song et al. 2009).

Figure 57 Possible bonds on silicon (110) surface via functionalization

Figure 58 Structure of trimethoxymethylsilane
5.3.3 Electrochemical Measurements of Silicon Nanowire Anodes

Cyclic voltammograms for the first cycle (from 1.5 to 0.01 V versus Li/Li⁺) are shown in Figure 59.

![Cyclic-voltammogram (0.05 mV·s⁻¹) of various silicon nanowire anodes](image.png)

Figure 59 Cyclic-voltammogram (0.05 mV·s⁻¹) of various silicon nanowire anodes

The nanowire anode which was initially hydride-terminated (Si-H) shows charge peaks at approximately 0.4-0.6 V versus Li/Li⁺, corresponding to electrolyte reduction. The charging current increases sharply at potentials more cathodic than 0.2 V, which corresponds with lithiation. When trimethoxymethylsilane is added to the electrolyte with the hydride-terminated silicon nanowire anodes, current densities increase significantly and reach a maximum of approximately 0.17 mA·cm⁻² near 0.1 V versus Li/Li⁺ consistent with lithiation. Both the methyl-terminated (Si-CH₃) and siloxane-terminated (Si-O-Si-R) anodes show low current densities (less than 0.04 mA·cm⁻²) at all potentials without significant lithiation currents. All four
anodes show relatively low discharge currents, which may be due to nanowire agglomeration (observed after the reactions) and possible mechanical failures between nanowires and substrates.

Figure 60 Onset potentials for anodes tested derived from voltammograms.

Lithiation onset potentials may be estimated from Figure 60 showing the derivative of current density versus potential (based on the voltammograms shown in Figure 59). Lower onset potential for lithium insertion is believed to be associated with higher energy barriers for lithium adsorption and transport through silicon surfaces (Maria et al. 2010; Peng et al. 2010; Zhang et al. 2010). It is reported that lithiation potential for silicon nanowire with surface oxide appears approximately below 200 mV versus Li/Li⁺, which can be explained by favorable SiOₓ surface intercalation with lithium other than intrinsic single crystal silicon (Chan et al. 2009). The lithiation potential for the hydride-terminated silicon anode occurs at potentials near 130 mV versus Li/Li⁺, which is the most anodic among all four anodes considered here. When silane
additives were added, Si-O-Si crosslinking occurs and the lithiation onset potential shifts cathodically to approximately 102 mV, suggesting a higher barrier for adsorption. The onset potential for the directly methylated silicon anode occurs near 46 mV, suggesting lithium insertion into silicon may be hindered due to the passivating nature of the methyl group (Vegunta et al. 2009). The siloxane-terminated silicon anode shows no obvious onset potential for lithiation similar to methylated surface.

5.3.4 SEI Characterization

◆ FT-IR Analysis

Identification of IR spectra is difficult due to the complex composite of SEI layer on silicon anodes. IR analysis is not able to detect soluble and intermediate species due to the DMC wash and ex-situ technique. FT-IR spectra in attenuated total reflection (ATR) mode of silicon nanowire anodes surface after the first charge and discharge cycle were obtained, and careful assignments of IR peaks were carried out by comparing previous reported results on IR analysis of SEI on both silicon anodes and graphite anodes (Scrosati 2002; Perla B. Balbuena 2004; Song et al. 2009).

As shown in Figure 61, FT-IR spectra of silicon nanowire anodes surfaces charged to 0.5 V and 0.01 V are compared to FT-IR spectrum of electrolyte used in lithium-ion battery (1M LiPF$_6$ with 1:1 EC/DMC). A platinum foil charged to 0.01 V versus Li/Li$^+$ in the same electrolyte containing 1M LiPF$_6$ with 1:1 EC/DMC was applied as a control sample.

Silicon nanowire anodes charged to different cut-off potential shows distinctive FT-IR spectra. FT-IR spectra of silicon nanowire anode charged to 0.01 V versus lithium shows several new peaks than those of electrolyte, platinum charged to 0.01V and anode charged to 0.5V. A strong peak at approximately 854 to 841 cm$^{-1}$ can be assigned as Li-F (850 cm$^{-1}$), P-F stretching (850-800 cm$^{-1}$) for P-F species derived from LiPF$_6$. A peak at 1635 cm$^{-1}$ suggests the carbonyl
group R-OCO₂⁻M⁺, where M represents Li/Si alloy and R is an alkyl group. Absorbance peaks at 1482, 1418 and 1071 cm⁻¹ are attributed to CH₃CH₂⁻ and C=O, C-O of carbonates. Likewise, peaks at 1304 and 1211 cm⁻¹ are attributed to C-H bending from carbonates. The enhancement at approximately 1300 to 1500 cm⁻¹ overlapped with other peaks and can be assigned to organofluorine compound by cross-referencing with the XPS data. While that of silicon nanowire anode charged to 0.5 V shows similar spectra with original electrolyte, suggesting negligible electrolyte decomposition and no lithiation when cathodic potential is above 0.5 V versus Li/Li⁺.

Figure 61 FT-IR spectra of SEI on silicon anodes charged to 0.01 and 0.5 V, Pt foil charged to 0.01 V, and electrolyte (1M LiPF₆ in EC/DMC)

FT-IR spectra of the SEI after charge and discharge cycles are presented in Figure 62: hydride-terminated silicon nanowire anode (Figure 62 top), methylated silicon nanowire anode
(Figure 62 middle) and hydride-terminated silicon anode cycled with 5% trimethoxymethylsilane (Figure 62 bottom).

Hydride-terminated silicon anode spectra show a strong peak at approximately 854 to 841 cm\(^{-1}\), which can be assigned as Li-F (850 cm\(^{-1}\)), P-F stretching (850-800 cm\(^{-1}\)) for P-F species derived from LiPF\(_6\). A peak at 1635 cm\(^{-1}\) suggests the carbonyl group R-OCO\(_2\)M\(^{n+}\), where M represents Li/Si alloy and R is an alkyl group. Absorbance peaks at 1482, 1418 and 1071 cm\(^{-1}\) are attributed to CH\(_3\)CH\(_2\)\(^{-}\) and C=O, C-O of carbonates. Likewise, peaks at 1304 and 1211 cm\(^{-1}\) are attributed to C-H bending from carbonates. The enhancement at approximately 1300 to 1500 cm\(^{-1}\)
cm$^{-1}$ overlapped with other peaks and can be assigned to organofluorine compound by cross-referencing with the XPS data.

The FT-IR spectra from methylated silicon anodes showed fewer peaks arising from the first cycle. A diminished characteristic peak at 832 cm$^{-1}$ is attributed to residual LiPF$_6$. Peaks at 1380, 1149, 1064, 960 and 760 cm$^{-1}$ can be assigned to characteristic peaks for carbonates. There is no measurable peak near 1633 cm$^{-1}$ for R-OCO$_2$M$^{n+}$ groups. These results suggest the methyl monolayer on silicon surface impedes the reduction of electrolyte.

As can be seen from FT-IR spectra for hydride terminated silicon nanowire anode cycled with silane additive, similar FT-IR spectrum is obtained as reported on silicon thin film (Song et al. 2009). Strong peaks are present at approximately 822 cm$^{-1}$ and 772 cm$^{-1}$, which can be assigned as P-F stretching (850-800 cm$^{-1}$) and P-O-C (830-740 cm$^{-1}$) from O=PF-OR compounds, as well as C-O bending (846-740 cm$^{-1}$) for Li$_2$CO$_3$ formed in SEI. The absorption peak at 1621 cm$^{-1}$ suggests the carbonyl group R-OCO$_2$M$^n$. Also, peaks at 1499, 1414, 1311 and 1173 cm$^{-1}$ are attributed to CH$_3$CH$_2$-, C=O, C-H and C-O of carbonate. Other absorbance peaks at approximately 1130-1000 cm$^{-1}$ can be assigned to (1173 cm$^{-1}$ in spectra) Si-O-Si asymmetric stretching, and the peak at 1110-1050 cm$^{-1}$ (1070 cm$^{-1}$ in spectra) can be assigned to Si-O-C stretching. The enhancement from approximately 1300 to 1500 cm$^{-1}$ may be assigned to C-F for organofluorine compound by cross-referencing the XPS data.

As previously reported by Song et al., silicon thin film anodes surface is passivated by stable silane-derived organic layer by forming Si-O-Si crosslink and shows greatly improved anode performance. The silane derived the SEI is mainly composed of carbonate, alkyl carbonate Si/Li functionalities, organic phosphorous fluorine compounds (O=PF-OR) and P-F containing species, and complete coverage with phosphorous fluorine compounds indicates stable SEI (Song et al. 2009).
Interestingly, siloxane-terminated silicon anode shows identical IR as well as XPS spectra to silicon anode cycled with silane additive, this phenomenon can be explained by the possible reactions between silicon surface siloxane groups with electrolyte under polarization, or incompletely coverage of siloxane on silicon surface.

Clearly, both hydride-terminated anode and silicon anode cycled with silane additive showed similar SEI composition of carbonate, alkyl carbonate Si/Li functionalities, organofluorine compounds and P-F containing species, whereas Si-O-Si and organic phosphorous fluorine are present for silicon anode cycled with silane additive, which attribute to stable SEI. Methylated surface appears to passivate silicon surface from lithium insertion and shows no lithiation or negligible reduction products from electrolyte.

While the methylated surface appears unreactive, the hydride-terminated anode shows active SEI formation including lithium or silicon alkyl carbonates, lithium salts and P-F containing species. The formation of PF containing products may originate from LiPF₆ decomposition to LiF and PF₅. PF₅ is strong Lewis acid and reacts with trace water to form O=PF₃ and HF.

\[
\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{O=PF}_3 + \text{HF}
\]

The HF and O=PF₃ may then react with lithium to from LiF and P-F species. When hydride-terminated silicon anodes are cycled with silane additives, the only significant differences between the hydride-terminated spectra and the same anodes with silane additives are the generation of Si-O-Si bonds and new organic phosphorous fluorine compounds. This Si-O-Si bond is likely formed through hydrolysis and condensation with the presence of water and Li⁺, and the overall reaction can be expressed as:

\[
\text{RSiOCH}_3 + \text{R'SiOCH}_3 \xrightarrow{\text{H}_2\text{O,Li}^+} \text{RSiOSiR'} + \text{CH}_3\text{OH}
\]
When silane additives are used, more methoxy groups are introduced and reactions with OPF₃ may lead to organic phosphorous fluorine compound as observed by FT-IR analyses.

◆ XPS Analysis

XPS C (1s), O (1s), F (1s) and Si (2p) spectra of SEI on silicon nanowire anodes after the first charge and discharge cycle are shown in Figure 63. Peaks are assigned using standards or previous silicon and graphite anode XPS studies (Bryngelsson et al. 2007; Chan et al. 2009; Yen et al. 2009).

The C (1s) spectra of silicon anodes with methylated-termination in Figure 63 show a broad peak from 286.2 indicating the presence of C-O, C=O in carbonate and/or Si-C of Si-CH₃ surface. The O (1s) peak at 534.2 eV can be attributed to hydrocarbons. The strong peak at approximately 688.2 eV for F (1s) suggests LiPF₆ residues. As with the FTIR analysis, the XPS
data indicate the surface of methylated silicon anodes is relatively unreactive and primarily includes electrolyte residuals in addition to the grafted layer.

The C (1s) spectra of hydride-terminated silicon anodes (Figure 63 bottom spectra) shows a shoulder from 286 to 288 eV suggesting the presence of C-O, C=O in carbonates, while a peak at 291 eV corresponds to organofluorine compounds. The O (1s) peak at 532.8 eV can be attributed to O in carbonates. A strong peak at 686.4 eV for F (1s) suggests C-F bonds from fluorocarbons and LiF, which are consistent with C (1s) spectrum.

![Figure 64 XPS spectra of silicon nanowire and SEI on silicon nanowire anodes cycled with silane additives](image)

When 5 % trimethoxymethylsilane is added to electrolyte with hydride-terminated nanowires, the C (1s), O (1s) and F (1s) spectra of the SEI (Figure 63 middle spectra) were similar to the hydride-terminated silicon anodes without any silane additives suggesting similar composition for C, O and F species. As showing in Figure 64, the SEI is enriched with Si species.
Bare (uncycled) silicon nanowire Si (2p) spectra typically show two peaks at 99.2 eV and 103.6 eV corresponding to Si and native oxides; while that of silicon anodes cycled with silane additives show these peaks are shifted to 99.3 eV and 104.3 eV indicating Si-O-Si and Si-O-C bonds are formed when silanes are added to the electrolyte.

Figure 65 Composition of the SEI on hydride terminated (Si-H), methylated (Si-CH₃) silicon surfaces and silicon anode cycled with silane additive (Silane Additive)

SEI compositions on hydride-terminated, methylated and hydride-terminated silicon nanowire anodes were also quantified by XPS analyses. As shown in Figure 65, the SEI of hydride-terminated silicon anodes cycled in silane additive shows similar composition in C, F, Li, O, and P species, except for higher concentration in silicon than without silane additive, which indicates the SEI is enriched with silicon due to the formation of Si-O-Si from silane additive; while the SEI of methylated contains high concentrations in C, F, and O species with low level of lithium, which is similar to electrolyte used in this work.

Significant quantities of fluorocarbons are observed in the SEI on silicon anodes both with and without silane additives in this work as well as reported in previous studies (Chan et al.)
Fluorocarbons are unique to silicon anodes (not typically observed at graphite anodes) and indicate reactions associated with both silicon and electrolyte. Yen et al. have proposed that fluorocarbon compounds are generated from the reactions between the SiF$_6^{2-}$ and hydrocarbons (Yen et al. 2009); however, it seems unlikely that SiF$_6^{2-}$ species are capable of transferring fluorine to hydrocarbons ($\Delta G_f = -525.7$ kcal/mol obtained from CRC Handbook of Chemistry and Physics) (Lide 1990). A more likely scenario may indicate silicon in fluorocarbon formation. It is possible alkyl carbonate radicals may react with fluorophosphates to generate fluorocarbon compounds rather than bonding with silicon surfaces as is possible with graphite.

Although the anode performance may be strongly affected with silane additives (as described on the next section), FT-IR spectra and XPS spectra from pretreated siloxane-terminated anodes (rather than adding silanes to the electrolyte) is similar to the silicon anode cycled with silane additives. This suggests excess silane additives in the electrolyte may not alter the surface chemistry of the SEI.

**AFM Analysis**

SPM and AFM analyses have been reported to study the morphology of SEI layer on graphite and other negative electrodes for lithium-ion batteries (Alliata et al. 2000; Inaba et al. 2004; Leroy et al. 2005; Lucas et al. 2009); however, the mechanical aspects of SEI has not yet been studied by AFM. Since AFM can be extended to study the elastic modulus of polymeric materials via nano-scale indentation technique (Vanlandingham et al. 1997; VanLandingham et al. 2001), AFM nano-indentation for the first time is reported to study the mechanical properties of the SEI on silicon nanowire anodes.

Figure 66 shows the AFM tip deflection vs. Z-distance profile for the SEI layers formed on hydride terminated silicon nanowire anode and silicon anode cycled with silane additive. From Figure 66 a, the dashed line indicates the AFM tip approaches the SEI surface from +1000
to -1000 nm in Z-direction. Constant deflection (V) is observed from 1000 to -550 nm corresponding to no external load. At -550 nm, a drop in deflection is noticed due to additional Vanderwaal’s forces attracting the tip towards the surface. The linear region beyond -550 nm corresponds to the steady increase in force as the tip is indented into the SEI layer. The solid line represents the retention section from -1000 to 1000 nm where initially the applied force is alleviated during the linear region. The tip stays attached to the sample due to adhesion energy until an increase in deflection is observed at -250 nm where the tip comes off the surface.

Figure 66 Deflection versus Z-distance profile for the SEI layers on (a) hydride-terminated silicon anode, and (b) silicon anode cycled with silane additive

The atomic force spectra provide valuable information regarding the SEI contact stiffness in the linear region of the approach spectra(Vanlandingham et al. 1997; Wyart et al. 2008). In order to quantify the effect, the deflection versus Z-distance (nm) data were converted to external load (P, [N]) versus depth as per equation,
where $k$ is the spring constant of the cantilever, $\alpha$ is the deflection sensitivity (nm·V$^{-1}$) measured from the slope of the approach curve linear region when the tip is pressed against a hard surface (silicon in this case) and $V_t$ is the difference between deflection voltage at a given $Z$-distance and that corresponding to zero external load. As the spectra were obtained using the same tip, the values of $k$ (0.57 N·m$^{-1}$) and $\alpha$ (22.5 nm·V$^{-1}$) as estimated to be constant.

![Figure 67 External load versus Z-depth profiles for SEI layers on hydride-terminated silicon anode and silicon anode cycled with silane additive](image)

Contact stiffness ($S$, [N·m$^{-1}$]) of SEI on silicon composite anodes is derived from equation,

$$S = \frac{\partial P}{\partial h} = 2aE_r$$  \[5-4\]

where $P$ is load and $h$ [nm] is displacement of the AFM tip, $a$ [nm] is the contact radius of tip-
sample contact, and the reduced modulus, $E_r$, accounts for deformation of both the indenter and the sample (VanLandingham et al. 2001).

Figure 67 is the converted external load versus depth profiles for approach spectra of SEI both for hydride-terminated anode and anode cycled with silane additive. The slope of the linear region yields surface contact stiffness of the SEI layers. Specific to silicon nitride tip, contact stiffness of the SEI with silane (0.9568 N·m$^{-1}$) is 125 % greater than that of the SEI without silane (0.429 N·m$^{-1}$). This indicates silane additive provides a plasticizing effect to an otherwise disintegrated the SEI layer with weak intermolecular forces. The higher contact stiffness suggests silicon crosslinking within the SEI, which may be associated with improved adhesion within the anode matrix. Silane additive imparts mechanical stability during cycling by forming a Si-O-Si network within the SEI.

5.3.5 Charge and Discharge for Silicon Nanowire Composite Anodes with Modified Silicon Surfaces

While silicon nanowire anodes offer a homogeneous substrate for analytical purposes, their use as reversible anodes in this form is severely limited due to agglomeration upon cycling. For this reason, we evaluated the capacity and cycle performance of functionalized silicon anodes using composite anodes. Silicon nanowire composite anodes (containing 15 % silicon nanowire and 85 % graphite as active material) including hydride-terminated, methylated, siloxane terminated were also prepared and cycled in lithium-ion half cells. Another hydride-terminated silicon nanowire composite was cycled in lithium-ion half cell with trimethoxymethylsilane additive.

As can be observed from SEM images, silicon nanowires are randomly distributed among graphite flakes in the composite anode as prepared (Figure 68 A); while after 15 successive
charge and discharge cycles, the anode surface is covered with an observable organic layer (SEI layer) as shown in Figure 68 B.

Figure 68 SEM images of silicon nanowire composite anodes (A) before and (B) after 15 charge/discharge cycles

Composite anodes charge and discharge specific capacities versus cycle number with cycle coulombic efficiencies for 15 cycles are plotted in the following graphs in Figure 69 (methylated silicon nanowires), Figure 70 (siloxane terminated silicon nanowires) and Figure 71 (hydride-terminated silicon nanowires cycled with 5% trimethoxymethylsilane).

Initial charge capacity of methylated silicon nanowire composite is 577 mAh·g⁻¹ and reversible capacity of 312 mAh·g⁻¹. Siloxane terminated silicon nanowire composite anode has slightly high initial charge capacity at 694 mA·hg⁻¹ and similar reversible capacity of 310 mAh·g⁻¹.

Composite anode cycled in silane additive shows significantly higher capacity among all the anodes with initial charge capacity of 869 mAh·g⁻¹ and a reversible capacity of 607 mAh·g⁻¹ after 15 cycles.
Figure 69 Charge/discharge specific capacities and coulombic efficiencies of methyl-terminated silicon nanowire composite anodes versus cycle number

Figure 70 Charge/discharge specific capacities and coulombic efficiencies of siloxane-terminated silicon nanowire composite anodes versus cycle number
Figure 71 Charge/discharge specific capacities and coulombic efficiencies of silicon nanowire composite anodes cycled in 5% trimethoxymethylsilane versus cycle number.

Figure 72 Silicon specific discharge capacities versus cycle number of various silicon nanowire composite anodes (from top to bottom): anodes cycled with 5% trimethoxymethylsilane, hydride-terminated, siloxane-terminated and methylated anodes.
As discussed in Chapter 4, anode capacities are normalized by silicon weight to show the capacity retention specific to silicon. The discharge specific capacities versus cycle number for composite anodes are calculated and plotted in Figure 72. The initial discharge capacity for hydride-terminated silicon composite anode is 2433 mAh·g⁻¹. Reversible capacity of approximately 1364 mAh·g⁻¹ after 15 cycles with a capacity fade of approximately 5.7 % per cycle is observed. While the Methylated composite anode shows significantly decreased initial specific discharge capacity of 538 mAh·g⁻¹ and a reversible capacity of approximately 383 mAh·g⁻¹ is obtained after 15 successive cell cycles; The siloxane-terminated composite anode shows high initial discharge capacity at 1087 mAh·g⁻¹, and reversible capacity at 368 mAh·g⁻¹. The reversible capacities for methylated and siloxane-terminated composite anodes are significantly lower than that of hydride-terminated anode, suggesting silicon capacities are compromised by surface functionalization. Hydride-terminated composite anode cycled in silane additives demonstrates high initial discharge capacity at 3287 mAh·g⁻¹ while the reversible capacity is greatly increased by over 75 % to 2348 mAh·g⁻¹ after 15 cell cycles. This increase in capacity retention is in agreement with the previous studies in silicon thin film electrode involving silane additive, which may be attributed to the Si-O-Si linkage within the SEI layer forming a reinforcing matrix (Song et al. 2009).

5.3.6 Summary

Hydride-terminated silicon nanowire surfaces are reactive to electrolyte reduction and lithium insertion and extraction. The hydride-terminated silicon composite anode can obtain a reversible capacity of over 500 mAh·g⁻¹ after 15 cell cycles. SEI is mainly composed of carbonate, LiF, PFx and organofluorine compounds.

Methylated silicon nanowire composite anodes have only 300 mAh·g⁻¹ reversible capacities after 15 cycles. SEI is mainly composed of residue of electrolyte; minimum reduction
product has been observed. The methyl monolayer on the silicon surface impeded the electrolyte reduction and lithium insertion during cell cycles, so as compromise the silicon capacity within composite anode. As has been discussed in recent theoretical calculation studies on silicon anode, the silicon surface active site plays an important role in the transport of lithium into the anode on atomic level (Peng et al. 2010). The methyl functional group bonded on silicon surface may increase barrier energy so as to block ion transport into the silicon within the anode charge potential window. Further studies are required to validate the presumption.

Although siloxane-terminated composite anode showed capacity of only 300 mAh·g⁻¹, the SEI composition is similar to silicon anodes cycled silane additive. The siloxane layer on silicon surface may also prevent silicon to react during cell cycles. The failure to allow lithium insertion nanowire anodes may be due to the blocked entrance site for lithium ion by siloxane on the silicon surface.

Composite anodes cycled in trimethoxymethylsilane additive show over 600 mAh·g⁻¹ reversible capacity after 15 cycles, which is over 20 % increase in total capacity and 75 % increase in silicon capacity than hydride-terminates silicon anode. The SEI contains carbonate, LiF, organofluorine compound, OPFx, Si-O-Si, and Si-O-C from the electrolyte and silane additive reactions obtained from FT-IR and XPS analyses. The linkage formed by Si-O-Si bonding within SEI by silane additive resulted in two folds increase in contact stiffness than hydride-terminated silicon anode SEI characterized by AFM, suggesting strong intermolecular force within the SEI for silane additive sample. A schematic of SEI on silicon anode cycled with silane additive is shown in Figure 73 by referencing published results and this data obtained from this work, where red elbow lines represent Si-O-Si linkages within the SEI. Stronger SEI may improve the mechanical adhesion within SEI and silicon anodes, so as to prevent contact loss and anode disintegration.
5.4 Conclusions

Silicon nanowire anodes with hydride, methylated, and siloxane terminated surfaces were prepared, and their SEI layers were characterized by cyclic voltammetry, FT-IR, XPS and AFM analyses. Vibrational and binding energies show methylated silicon nanowires are unreactive while hydride-terminated silicon nanowire show SEI layers include carbonates, lithium salts, P-F species and fluorocarbon compounds. Lithiation potentials appear to be a strong function of surface chemistry, for example, hydride-terminated silicon anode on-set potential is 104 mV, while that of methylated anode is 46 mV versus Li/Li⁺. Pre-treating nanowires with silanes and adding silanes to the electrolyte show similar SEI compositions, including Si-O-Si groups and OPFx species, however, the improved capacity retention with silane added to the electrolytes is remarkable. Charge and discharge capacities of composite anodes show reversible silicon specific capacity is increased by approximately 75 % for hydride-terminated silicon nanowire
composite anode cycled with silane additive (2348 mAh·g⁻¹) compared with hydride-terminated anode (1364 mAh·g⁻¹) after 15 cycles. AFM nano-indentation analyses show contact stiffness for silicon anodes cycled with silane additives is 125 % greater than without silane additives. Although the chemical composition of the SEI contains more Si-O-Si and OPFₓ compounds with silane additives, the results suggest the primary benefit of silane additives is associated with mechanical (adhesion) improvements that increase silicon’s ability to undergo the large volume cycling associated with lithiation and delithiation cycling.
CHAPTER 6 CONCLUSIONS

6.1 Conclusions

Silicon has the highest theoretical specific capacity for lithium storage (4200 mAh·g⁻¹, over 10× higher than conventional graphite at 372 mAh·g⁻¹), and is considered as a promising anode material to achieve high energy density required by rechargeable battery systems for EVs. There are two main challenges that impede applications of silicon as anode for lithium-ion batteries: large volumetric change for silicon lithiation and delithiation (over 300% volume change) and the solid electrolyte interphase on silicon anodes. VLS-grown Nanowire structure has shown great potential in maintaining high capacity while accommodating repetitive volumetric change for lithium insertion and extraction. In this work, silicon nanowires were fabricated, integrated into composite anodes, aiming at creation of high capacity, long life anodes for lithium-ion batteries.

We fabricated silicon nanowires via facile electroless etching in hydrofluoric acid with silver nitrate aqueous solution. Both p-type and n-type silicon nanowires were created through the same procedure, and the electroless etching was nonselective in terms of doping type. After 30 minutes electroless etch at 50 °C, the silicon nanowires were approximately 20 µm in length and diameter distribution was 253 nm with standard deviation 1 σ of 91 nm regardless of substrate doping type. Electrolessly fabricated silicon nanowires were deposited randomly on IDEs following thermal annealing under reducing atmosphere to form NiSi ohmic contacts. The resistance of IDEs with NiSi formation between silicon nanowires and electrodes was three orders of magnitudes lower than that of IDEs without NiSi formation. The NiSi phase on silicon nanowires was also confirmed by XPS and XANES analyses.

We demonstrated silicon nanowires as composite anode material for lithium-ion batteries by mixing nanowires with graphite, carbon black and binders. When silicon nanowire arrays on
parent substrate were directly applied as anode, near theoretical capacities in the first charge cycle with severe fade in following cycles were observed. Composite anode with only 15 % silicon nanowire showed a two-fold capacity increase than conventional graphite composite anodes prepared via the same methods. Silicon nanowire composite anodes showed high initial capacity of 811 mAh·g⁻¹ and a reversible specific capacity of 512 mAh·g⁻¹ with capacity fade of less than 1.4 % per cycled for 10 cycles. Over 60 % silicon capacity loss was still observed for composite anodes, despite the fact that nanowire structures were free from cracking and agglomeration caused by volumetric change.

We also conducted surface functionalizations on electrolessly fabricated silicon nanowires, targeting SEI modification to improve anode capacity retention. Silicon nanowires functionalized with hydride, methylated and siloxane surface terminations were prepared and tested both in the form of nanowire arrays and as composite anodes in lithium-ion half cell. Vibrational and binding energies showed methylated silicon nanowires were unreactive while hydride-terminated silicon nanowire showed SEI layers include carbonates, lithium salts, P-F species and fluorocarbon compounds. Lithiation potentials appeared to be a strong function of surface chemistry. Pre-treating nanowires with silanes and adding silanes to the electrolyte showed similar SEI compositions, however, the improved capacity retention with silane added to the electrolytes was remarkable. Reversible silicon specific capacity was increased by approximately 75 % for hydride-terminated silicon nanowire composite anode cycled with silane additive than that without additives after 15 cycles. AFM nano-indentation analyses showed contact stiffness for silicon anodes cycled with silane additives is 125 % greater than without silane additives. Although the SEI contains more Si-O-Si and OPFₓ compounds with silane additives, the results suggested the primary benefit of silane additives was associated with
mechanical (adhesion) improvements that increase silicon’s ability to undergo the large volume change associated with cycling.

6.2 Suggestions and Recommendations

The potential scope for silicon nanowire anodes is great in doubling or even tripling capacities for current rechargeable lithium-ion batteries considering conventional cathodes and electrolytes; however, there are far more work to be done in the future to explore both the chemical and mechanical aspects of silicon anodes to develop lithium rechargeable batteries with high capacity and long cycle life. Based on the outcome of this study, the following issues should be addressed in the future:

First of all, mechanical integrity for composite anodes has significant impact on capacity retentions for prolonged cycles. Several approaches can be applied to improve mechanical integrity or adhesion within the anode matrix as well as between anodes and current collectors:

1. Preparation techniques: Capacity retention and cycle ability for silicon nanowire composite anodes can be greatly improved by applied advanced anode preparation tools and techniques. Advanced doctor blade system, for example, can create composite anodes as ultra thin film (< 100 µm) uniformly on current collectors.

2. Binders: Advanced binders can be applied in the composite anode matrix. Conventional PVdF binder was used in this work for silicon nanowire composite anodes. For example, CMC binders can be considered to replace PVdF to improve adhesion among anode components to create a more resilient matrix, and maintain anode integrity by accommodating reversible volume change after prolonged cycles.

3. Electrolytes: Coupling agent additive other than alkoxy silane used in this work can be introduced into electrolyte to create a mechanically strong SEI to cover the anode surfaces as well as maintain anode integrity. Trimethoxymethylsilane has resulted in over
75 % increase in silicon nanowire composite anodes capacities for the formation of cross-link Si-O-Si in the SEI layer. Therefore, other coupling agent or film forming agent, which may also create cross-link in the SEI, can be applied in electrolytes to improve capacity retention.

In addition, low resistance nickel silicides created by thermal annealing between silicon nanowire and metallic nickel may be applied in novel silicon nanowire anodes in future studies. Electrical conduction among anode matrix as well as between anodes and current collectors is of great importance for prolonged cycles. Formation of NiSi between silicon nanowires and nickel current collector might be helpful in developing binder-free silicon only anodes with improved conductivity compared to nanowire composite anodes.

Finally, silicon nanowires may be replaced with silicon nanoparticles in composite anodes for lithium-ion batteries. Silicon nanowire arrays on parent wafer are not able to undergo reversible lithium insertion and extraction and are not proper anodes for lithium-ion battery applications. Silicon nanowire arrays on parent substrates are adopted in this work only to study the effects of surface functionalization on anode performance by cyclicvoltammetry and material characterizations. Silicon nanowire arrays on parent substrate can be easily connected to an external bias, and are preferable for electrochemical grafting and other surface functionalizations compared to loose silicon micro or nanoparticles. Silicon nanowires are applied a starting point for silicon anodes for lithium rechargeable battery systems, and for future scale-up industrial battery fabrications, silicon fine particles may be applied to replace relatively expensive silicon nanowires.
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### APPENDIX 1 ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Spectroscopy</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated Total Reflectance</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>IDE</td>
<td>Inter-digitated Electrode</td>
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<td>LIB</td>
<td>Lithium-Ion Battery</td>
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<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Fine Structure</td>
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<td>NiSi</td>
<td>Nickel Monosilicide</td>
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<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
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<td>SCE</td>
<td>Standard Calomel Electrode</td>
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<td>SEI</td>
<td>Solid Electrolyte Interphase</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
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<td>SiNW</td>
<td>Silicon Nanowire</td>
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<td>TEM</td>
<td>Transmission Electron Microscopy</td>
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<tr>
<td>TEY</td>
<td>Total Electron Yield</td>
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<td>VLS</td>
<td>Vapor Liquid Solid</td>
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<td>XANES</td>
<td>X-ray Near Edge Structure</td>
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<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
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APPENDIX 2 EQUIPMENT AND FACILITIES

Electrochemistry Equipment

Potentiostat PARSTAT 2273 (Princeton Applied Research) is the main tool for electrochemical analyses applied in this work, including all linear voltammetry, cyclic voltammetry, and charge and discharge tests. The potentiostat is located in W216 ChE BLDG, LSU.

**Power Amplifier**

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**System Performance**

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<tr>
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<td>Minimum Potential Step</td>
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<td>Minimum Current Range</td>
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**Current Measurement**

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<td></td>
<td>20 nA to 1 µA Range: &lt;0.5%</td>
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<td></td>
<td>2 nA &lt;0.75%</td>
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(Note: Specifications are obtained from [http://www.princetonappliedresearch.com/Our-Products/Potentiostats/PARSTAT-2273.aspx](http://www.princetonappliedresearch.com/Our-Products/Potentiostats/PARSTAT-2273.aspx))

**Material Characterization Equipment**

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<td>FT-IR</td>
<td>Nicolet 6700 FT-IR spectrometer</td>
<td>W335 Chemical Engineering building, LSU</td>
</tr>
<tr>
<td>SEM</td>
<td>Hitachi S-3600 SEM/EDS system</td>
<td>1210 Patrick F. Taylor Hall, LSU (MCC)</td>
</tr>
<tr>
<td>TEM</td>
<td>JEOL 2010 HRTEM</td>
<td>1210 Patrick F. Taylor Hall, LSU (MCC)</td>
</tr>
<tr>
<td>XANES</td>
<td>DMC X-ray synchrotron beam line</td>
<td>CAMD, LSU</td>
</tr>
<tr>
<td>XPS</td>
<td>Kratos AXIS-165 XPS/Auger surface analysis system</td>
<td>1210 Patrick Taylor Hall, LSU (MCC)</td>
</tr>
<tr>
<td>XPS</td>
<td>Perkin-Elmer PHI 5100 system</td>
<td>University of Florida-Major Analysis Instrument Center</td>
</tr>
<tr>
<td></td>
<td></td>
<td>107 MAEC (Bldg. 183), Gainesville, FL 32611</td>
</tr>
</tbody>
</table>

**Facilities**

Center for Advanced Microstructures and Devices (CAMD) is a synchrotron radiation research center at Louisiana State University in Baton Rouge. The heart of the facility is a 1.5
GeV electron storage ring that was built exclusively to provide synchrotron radiation. The centerpiece of the CAMD facility is a normal-conducting electron storage ring optimized for the production of soft X-rays. All XANES analyses were carried out with CAMD facilities.

The LSU Material Characterization Center (MCC) is a university-wide user facility for the microstructural, structural and chemical characterization of materials. This center is hosted by the Mechanical Engineering Department and is available to researchers from LSU, other institution and industry. The MCC currently consists of several state-of-the art pieces of equipment including a JEOL 2010 high-resolution transmission electron microscope (HRTEM) and EDAX EDS system, a Kratos AXIS-165 XPS/Auger surface analysis system and a Hitachi S-3600N variable pressure SEM/EDS system, a FEI Quanta 3D FEG dual beam SEM/FIB system, a Rigaku MiniFlex X-ray Diffractometer, and TEM specimen preparation facility.
APPENDIX 3 LETTERS OF PERMISSION

Chapter 3, 4 and 5 are partially reproduced from following published journal papers. Wanli Xu is the first author and main contributor of these publications. Reproduced with permission from ECS---The Electrochemical Society.

Wanli Xu, Sri S. Vegunta, and John C. Flake, Modified Solid Electrolyte Interphase of Silicon Nanowire Anodes for Lithium-Ion batteries, *ECS Transaction* 33 (23), 55-61 (2011)


LETTER REQUESTING PERMISSION FOR COPYRIGHT

March 23, 2011

Wanli Xu

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Tel: 225-281-2394

Dear Mr/Ms:

I am preparing a dissertation entitled “Silicon Nanowire Anodes for Lithium-Ion Batteries: Fabrication, Integration and Characterization” to be finished in June 2011.

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The following journal papers will be used in the abovementioned dissertation including figures, tables and other contents.

Wanli Xu, Sri S. Vegunta, and John C. Flake, Modified Solid Electrolyte Interphase of Silicon Nanowire Anodes for Lithium-Ion batteries, ECS Transaction 33 (2011) issue 23, page 55


Yours Sincerely,

Wanli Xu

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March 30, 2011
Date

Ann F. Goedkoop, Director of Publications
Composite Silicon Nanowire Anodes for Secondary Lithium-Ion Cells

Wanli Xu,1 and John C. Flaka

1Electrochemical Society Member
2Electrochemical Society Active Member
3E-mail: jfs@illinois.edu

A composite anode with active materials including 15% (w/w) silicon nanowires and graphite is demonstrated for use in secondary lithium-ion cells. The electrochemical behavior of the composite anode including volumetric and charge/discharge capacities over the first 15 cycles is shown and compared with an equivalent graphite anode. Electrochemically induced nanowires with a diameter of 50-200 nm exhibit initial capacities (approximately 941 mAh g⁻¹) near theoretical predictions and a reversible capacity of 512 mAh g⁻¹ after 15 cycles with a capacity fade of approximately 1.5% per cycle. Capacity loss mechanisms are identified and compared with other silicon-containing anodes.

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Manuscript submitted August 26, 2005; revised manuscript received September 28, 2005. Published November 10, 2005.

Experimental

Silicon nanowire arrays were fabricated via electroless etching of boron-doped (100) silicon wafers, 100 mm in diameter, with a resistivity in the range of 1-5 Ω cm (Motorola, Springfield, MA). Small substrates (~2 cm²) were cleaved from wafers and cleaned followed by electroless etching in 5.0 M HF (Aldrich, St. Louis, MO) with 0.02 M silver nitrate (AgNO₃, Fluka) at 50°C for 30 min. Scanning electron microscopy (SEM) analysis showed arrays of freestanding silicon nanowires, approximately 20 µm in length and 100-200 nm in diameter. Metallic silver was removed after etching followed by HF cleaning, deionized water rinsing, and air drying. The hydride-terminated nanowires were separated from the parent wafer by etching for 1 min in ethanol. Nanowires were centrifuged at 3000 rpm for 10 min and then separated from the transfer solvent and combined with graphite (synthetic, diameter <20 µm, Aldrich) to create a 15:85 (w/w) composite of active materials. Active components were combined with carbon black (50 µm, Mitsubishi Chemicals, Japan) and polyvinylidene fluoride (PVDF; Aldrich) in N-methyl-2-pyrrolidone (Aldrich and bulkmilled for 24 h followed by deposition onto nickel foil (1 mm thick, 99.9% pure, ESPI Metals, Ashland, OR) using a doctor blade technique. Anodes were then stacked and dried at 120°C for 12 h in argon to yield an anode composition of 60% active materials, 20% carbon black, and 20% PVDF. A conventional graphite anode (without silicon nanowires) was prepared using the same materials and procedure as described above for comparison.

Electrochemical experiments were performed in a typical three-electrode cell with excess electrolyte, a lithium foil counter, and a lithium wire reference electrode (99.99%, Aldrich). The electrolyte included 1 M lithium hexafluorophosphate (LiPF₆, Thermco Fischer Scientific, Waltham, MA) in ethylene carbonate and dimethyl carbonate (Aldrich) solution at a 1:1 volumetric ratio. Electrochemical experiments were performed in an argon-filled glove box system at 22°C (~1 ppm H₂O or O₂) using a Princeton Applied Research PARSTAT 2272 potentiostat. Charge and discharge cycles were per-
Electrochemical methods do not require lithography and are particularly interesting for producing large volumes of nanowires due to the advantages of large scale, low fabrication cost, and the relative simplicity of processing.

A key challenge associated with integrating nanowires into devices involves establishing electrical connections between semiconducting nanowires and metal electrodes. Nickel silicides are particularly useful for ohmic contacts because of their relatively low resistivity (~10-30 µΩ cm), high thermal stability, and low silicon consumption during silicidation. Nickel silicides are typically formed in planar [complementary metal-oxide-semiconductor (CMOS)] processes in a sequence of steps including nickel deposition onto single-crystal silicon wafers followed by thermal annealing, and wet etching to remove excess nickel. Silicide may be formed in Si NWs by annealing nanowires with nickel reservoirs allowing radial or axial diffusion. Silicidation reactions with single (111)-grown nanowires have been demonstrated using scanning electron microscopy (SEM) intensive "find-and-wire" approaches, where physical vapor deposition (PVD) nickel is locally deposited onto crystallized nanowires followed by thermal annealing. Resistance measurements of these nanowires after annealing result in an estimated resistivity of 9.5 µΩ cm, suggesting that the low phase NIS is formed. Likewise, silicide contacts have also been reported with VLS-grown Si NWs following deposition, electronless nickel deposition, and thermal annealing. These approaches typically involve catalyst-assisted vacuum growth of nanowires and nickel deposition onto nanowire surfaces using either localized PVD or electronless plating. Electrical measurements suggest that the low-resistance NIS phase is formed, however, the nature of nanowires and the incorporation of the catalyst complicate the analysis.

This work presents an alternative process allowing facile silicidation of high numbers of Si NWs and does not require vacuum processing or any metal-deposition steps after nanowire deposition. In this process, NWs are created via electrochemical etching of single-crystal wafers, separated from the parent substrate, deposited onto nickel interdigitated electrodes (IDEs), and annealed to form silicides. This simple method enables facile and low-cost nanowire sensors, integrated nanowire-CMOS devices, or thin nanowire films for use as photodetectors, photonic devices. Silicided nanowires are characterized by electrical measurements, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS, and X-ray absorption near-edge structure (XANES) analysis to determine the formation of a nickel silicide (Ni5Si3). Here, the work shows that a nickel-silicide-based nanowire sensor may be used to create ohmic contacts between high volumes of nanowires and pre-existing electrodes.

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Manuscript submitted January 20, 2009; revised manuscript received March 25, 2009; published May 4, 2009.
Modified Solid Electrolyte Interphase of Silicon Nanowire Anodes for Lithium-Ion Batteries

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The solid electrolyte interphase (SEI) plays a significant role in maintaining reversible capacities by protecting silicon-based lithium insertion anodes from deleterious chemical reactions with electrolyte and mechanical failures. In this work, silicon nanowires were functionalized with s organic species and used as anode to study the effects of surface functionalization. The results from cyclic voltammetry, charge/discharge and SEI characterizations (XPS, FTIR, and AFM) show capacity is a strong function of surface chemistry.

Introduction

Silicon is a promising anode material in place of graphite for lithium-ion batteries; however, the issues associated with large volume change (over 300%) may limit practical capacity and cyclability(1). Silicon nanowires anodes have been considered to mitigate mechanical failures; however, capacity losses remain relatively greater than graphite anodes(2, 3). The thin Solid Electrolyte Interphase (SEI) layer that is formed at the anodes during cell charge/discharge is considered a key factor in capacity retention for anode of lithium-ion batteries(4). The SEI layer formed on graphite anodes has been extensively studied to reveal the surface reaction mechanism and its effects in anode performance(5-8). A stable and continuous SEI layer may protect the anode from irreversible reactions with electrolyte, and keep anode intact while allowing ion conduction for lithium insertion/extraction during charge/discharge cycles(9). Unlike graphite, it has been reported in previous studies that silicon is reactive to electrolyte such as LiPF₆, and forms complex product within the SEI. This may exacerbate capacity losses by consuming active silicon in the anode and lithium ion in the electrolyte through prolonged cell cycles(10-12). Silicon nanowire anodes have significantly larger surface to volume ratios than thin films electrode and providing relatively more active sites for surface reactions(13). Furthermore, a stable silicon-SEI may also be beneficial in maintaining anode integrity by allowing silicon volume change without delamination or agglomeration. Recently, it has been reported that binding agents such as an organosilanes in the electrolyte improve thin film anode capacity retention for over 200 cycles; however, the underlying mechanism for improve performance is not well known(10, 14).

In this work, we consider the effects on surface chemistry at the silicon anode surface using electroslessly fabricated silicon nanowire arrays and composite anodes. Nanowire arrays on silicon substrate were fabricated and functionalized via electrografting and

* ECS student member
** ECS member
Integration and Application of Electrochemically-Etched Silicon Nanowires

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Department of Chemical Engineering
Louisiana State University, Baton Rouge, LA 70803, USA

Silicon nanowires (SiNW) are fabricated through electroless etching of single crystal silicon. The nanowires are separated from substrate, deposited onto electrodes and annealed. Nanowire silicidation methods and analysis of silicides including electrical characterization, SEM, TEM and sputter XPS, and XANES are considered.

Introduction

In recent years, silicon nanowires (SiNW) have attracted attention for applications in high-performance transistors, biosensors with femtomolar detection limits or ultra-high capacity Li battery anodes (1-3). Various fabrication methods of SiNWs have been reported, including Vapor-Liquid-Solid growth (4), solution synthesis (5), thermal-evaporation oxide assisted growth (6), and lithography patterning and etching (7). In addition to these additive methods, electrochemical etching methods to form large-area of SiNWs arrays have also been reported by Qui et al (8-10). These etching methods and mechanisms are similar to those used porous silicon formation (Lehman et al.), which enjoy the advantages of large scale, low cost and simplicity (11).

Electrical contacts between semiconductors and metals have always played a significant role in microelectronics devices. Metal contacts to silicon may form either rectifying or ohmic contacts (i.e. linear current-voltage characteristics), which can be used to make contacts to doped regions (12). In typical CMOS integrations, Ni or Co-silicides are used to provide electrical contact to source, drain, and gate electrodes prior to tungsten contact deposition. Silicides can be formed by either a solid-state reaction between a metal and Si, or by co-depositing the metal and Si. The solid-state reaction method is used in a salicide process (self-aligned salicide process), whereas the co-deposition method is commonly used in a polycide process (13).

Various metal silicides have been studied for potential improvement in CMOS microelectronics, including Ti, W, Mo, Co, Pt, and Ni. Among metal silicide materials, there has been great interest in nickel silicide (NiSi) to form low-resistance electrical contacts. The resistivity of NiSi (1:1 phase) is comparatively low (~14 μΩ·cm) with other phases of Ni silicides and other silicides. The other main advantage of NiSi is that less Si in consumed compared with other silicides, hence reducing the risk of “spiking” under shallow junctions (14).

NiSi can be formed by decomposition of silane on nickel surfaces or in a series of procedures including deposition of nickel on single crystal silicon wafer or nanowires followed by thermal annealing treatment and removal of excessive metal by wet etching (15, 16). In the same sense, the NiSi phase can also be formed with silicon nanowires by
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Figure 1 Comparison of battery technologies including volumetric densities and gravimetric energy densities
Figure 3 Estimation of total cell capacities for 18650 lithium-ion batteries versus anode capacities when cathode capacities are constant.
Figure 4 Schematic of silicon anodes morphology change before and after charge and discharge cycles, including silicon particles, thin films and nanowires
Figure 7 Various EC reduction patterns on graphite anode surface and relevant products
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March 30, 2011

Wanli Xu
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April 4, 2011

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Ann F. Goedkoop, Director of Publications
VITA

Wanli Xu was born in a loving family of Xu in Yichang, Hubei Province, People’s Republic of China on May 25, 1983. She went to high school in Yichang No.1 High School in 1998, and then went to Dalian University of Technology in 2001 and graduated with a degree in Bachelor of Science in Chemical Engineering with a minor in English. She came to the Department of Chemical Engineering, Louisiana State University at Baton Rouge, to pursue a degree in Doctor of Philosophy in chemical engineering in 2006 supervised by Professor John C. Flake. She met her husband, Zhe Nan, and happily married on July 16, 2010.