



Probing Stress States in Silicon Nanowires During Electrochemical Lithiation Using *In Situ* Synchrotron X-Ray Microdiffraction

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Silicon is considered as a promising anode material for the next-generation lithium-ion battery (LIB) due to its high capacity at nanoscale. However, silicon expands up to 300% during lithiation, which induces high stresses and leads to fractures. To design silicon nanostructures that could minimize fracture, it is important to understand and characterize stress states in the silicon nanostructures during lithiation. Synchrotron X-ray microdiffraction has proven to be effective in revealing insights of mechanical stress and other mechanics considerations in small-scale crystalline structures used in many important technological applications, such as microelectronics, nanotechnology, and energy systems. In the present study, an *in situ* synchrotron X-ray microdiffraction experiment was conducted to elucidate the mechanical stress states during the first electrochemical cycle of lithiation in single-crystalline silicon nanowires (SiNWs) in an LIB test cell. Morphological changes in the SiNWs at different levels of lithiation were also studied using scanning electron microscope (SEM). It was found from SEM observation that lithiation commenced predominantly at the top surface of SiNWs followed by further progression toward the bottom of the SiNWs gradually. The hydrostatic stress of the crystalline core of the SiNWs at different levels of electrochemical lithiation was determined using the *in situ* synchrotron X-ray microdiffraction technique. We found that the crystalline core of the SiNWs became highly compressive (up to -325.5 MPa) once lithiation started. This finding helps unravel insights about mechanical stress states in the SiNWs during the electrochemical lithiation, which could potentially pave the path toward the fracture-free design of silicon nanostructure anode materials in the next-generation LIB.

Keywords: *in situ*, lithium-ion battery, single-crystalline silicon nanowires, lithiation, stress, deformation, synchrotron X-ray microdiffraction

INTRODUCTION

In today's modern world, efficient energy storage systems are very important particularly for portable electronic devices, electric vehicles, solar farms, and grid stations. Among electrical storage systems, the lithium-ion battery (LIB) is the most promising candidate because of its high-energy efficiency (Omar et al., 2012), high-energy density (Lukic et al., 2008; Omar et al., 2012), high normal voltage,

limited self-discharge, and no memory effect (Saw et al., 2016). It has a longer life cycle (Lukic et al., 2008) with a capacity of accepting high charging and discharging rates (Saw et al., 2016). These specifications/factors are important for battery requirement in the present modern era.

Silicon is considered as a promising anode material for next-generation LIBs because of its high theoretical charge capacity ($\sim 4,200 \text{ mAh g}^{-1}$), which is roughly 10 times higher than commercially available graphite anodes ($\sim 372 \text{ mAh g}^{-1}$) (Chan et al., 2008; Li et al., 2017). It has a low discharge potential (Chan et al., 2008) and attractive operating voltage (Chan et al., 2008; Li et al., 2017). Despite these benefits, silicon is not yet commercialized as an anode material in LIBs because of its large expansion up to 300% upon lithiation (Lee et al., 2001). Such large-volume changes in silicon could induce high stresses in the anode resulting in structure pulverization, cracking, delamination, and loss of electronic contact (Beaulieu et al., 2001; Li et al., 2017).

It has been found that nanoscale electrode materials can facilitate strain relaxation, shorten lithium-ion and electron diffusion paths, and increase the surface area for lithium electrode reaction (Bruce et al., 2008; Park et al., 2009). The experimental studies on the size effect have demonstrated that nanomaterials exhibit better capacity retention as compared to their bulk counterparts (Ryu et al., 2011; Lee et al., 2012; Liu et al., 2012a). Many different nanostructures have been developed, such as nanoparticles (Liu et al., 2012a; Zhou et al., 2012; Shelke et al., 2017), nanospheres (Ma et al., 2007, 2017), nanowires (Chan et al., 2008; Kennedy et al., 2016), nanotubes (Shim et al., 2016; Park et al., 2009), and nanocones (Zhang et al., 2010), with an improved cycling life and better performance.

Silicon nanowires (SiNWs) are among the nanostructures that have been studied and used as an anode material for LIBs (Liu et al., 2011; Yang et al., 2012; Kennedy et al., 2016). In these studies, the SiNWs were produced using the metal-assisted chemical etching (MACE) process resulting in an ordered and densely packed arrays of nanowires with a high aspect ratio and a uniform crystallographic out-of-plane orientation of $\langle 100 \rangle$ (Chang et al., 2009). This process has several advantages such as the ease of fabrications, the potential ease of scalability for the high-volume manufacturing, and low cost (Peng et al., 2007; Chang et al., 2009). Besides the ease of fabrication, SiNWs have also been widely studied because their geometry (together with nanospheres) allows simple (1D or 2D) kinetics modeling leading to the core-shell model proposed by Zhao et al. in nanospheres (Zhao et al., 2012) and Yang et al. in SiNWs (Yang et al., 2014).

Lithium reacts with crystalline SiNWs and forms core-shell structures. The core of SiNWs is found to be crystalline and the shell is amorphous lithiated silicon (Li_xSi) (Liu et al., 2012b). Morphology and volume change in silicon anode materials have been widely studied during/after lithiation utilizing simulation and experiments (Lee et al., 2011; Wu et al., 2012; Zhao et al., 2012). It is suggested that SiNWs have an anisotropic volume expansion with respect to axial orientation (Lee et al., 2011; Liu et al., 2011; Yang et al., 2014). Liu et al. fabricated an electrochemical cell based on SiNWs and observed morphological change in SiNWs during lithiation using *in situ* transmission electron microscope (TEM) (Liu et al., 2012b). Further experimental work is required

to examine the morphological change in SiNWs during real battery operation.

In addition, to design and utilize high-capacity silicon nanostructures anode that could minimize fracture, it is also important to study and characterize stress states during lithiation. The stress states have been recently simulated in silicon nanostructures during lithiation (Liu et al., 2011; Zhao et al., 2012; Yang et al., 2014). Zhao et al. developed an analytical model which undergoes volume expansion and plastic deformation that described stress states in spherical crystalline silicon nanoparticle during lithiation (Zhao et al., 2012). Yang et al. (2014) reported anisotropic electromechanical model for stress generation in SiNWs upon lithiation. The most important stress developed in the lithiated outer shell of SiNWs was found to be hoop stress, which was tensile upon lithiation. However, stress at the core of SiNWs was found to be compressive (Yang et al., 2014). The model was developed by utilizing several key features observed in previous TEM studies (Liu et al., 2011, 2012b; Yang et al., 2012). The lithiation-induced stress in the silicon nanoparticles has been measured using micro-Raman spectroscopy (Zeng et al., 2016). However, up until this point, no experimental study has been reported for the direct quantitative measurements of stress states in SiNWs during electrochemical lithiation (*in situ*) inside a realistic battery cell (i.e., battery cells that are typically used in commercial products).

Synchrotron X-ray microdiffraction (μSXRD) has proven to be effective for revealing insights of mechanical stress and other mechanics considerations in small-scale crystalline structures in many important technological applications, such as microelectronics (Budiman et al., 2006, 2009, 2010, 2012a; Kim et al., 2012a), nanotechnology (Budiman et al., 2012b,c; Kim et al., 2012b), and photovoltaics (Rengarajan et al., 2016; Handara et al., 2017; Tippabhotla et al., 2017a). This is especially true where the knowledge of how the stress evolves during the operation of the device could reveal the effective methodology to design higher-performance, more robust, and reliable nanostructure-based systems. In the present study, this technique is used to investigate the stress states in one form of Si nanostructures, i.e., SiNWs, while they are undergoing electrochemical lithiation inside a realistic battery cell that we designed specifically to allow electrochemical lithiation of SiNWs while allowing high-energy X-ray beams to access them.

For the first time in this experimental work, direct and quantitative stress state measurements were demonstrated in SiNWs during lithiation using *in situ* μSXRD . This proposed methodology and the experimental procedure can also be useful to study *in situ* stress states in other crystalline anode materials which are undergoing a large-volume expansion during electrochemical lithiation.

EXPERIMENTAL SETUP AND PROCEDURE

In this experimental work, the hydrostatic stress of the crystalline SiNWs is determined during lithiation (at different levels of lithiation) using the *in situ* μSXRD experiment. A special battery cell

is designed to allow high-energy X-ray beams to access SiNWs during electrochemical lithiation inside a realistic battery cell. The morphological change in SiNWs is also examined at different levels of lithiation using scanning electron microscope (SEM). In addition, stress states and morphological change are compared. The following subsections describe the materials, the battery test cell, and the methodology of μ SXRD to reveal stress states in SiNWs during lithiation.

Materials and Battery Test Cell

The SiNWs are fabricated on the surface of a p-type $\langle 100 \rangle$ silicon wafer of thickness 500 μm using MACE process at the Laboratory of Materials for Micro and Nano Systems, Massachusetts Institute of Technology (MIT). The p-type $\langle 100 \rangle$ silicon wafers used in the present study have a dopant concentration of $\sim 5\text{--}10 \times 10^{14}/\text{cm}^3$ and with a resistivity of 1–25 $\Omega\text{ cm}$. Details regarding the MACE process are described elsewhere (Peng et al., 2007; Choi et al., 2008; Chang et al., 2009), and the SiNWs thus obtained were roughly 6–8 μm high, standing on a 490- μm silicon substrate as shown in the schematic diagram in **Figure 1A**. A 200-nm thick copper layer was later deposited on the backside of the silicon wafer for electric contact (Tippabhotla et al., 2017a). Further details about the fresh samples are available in Figure S1 in Supplementary Material.

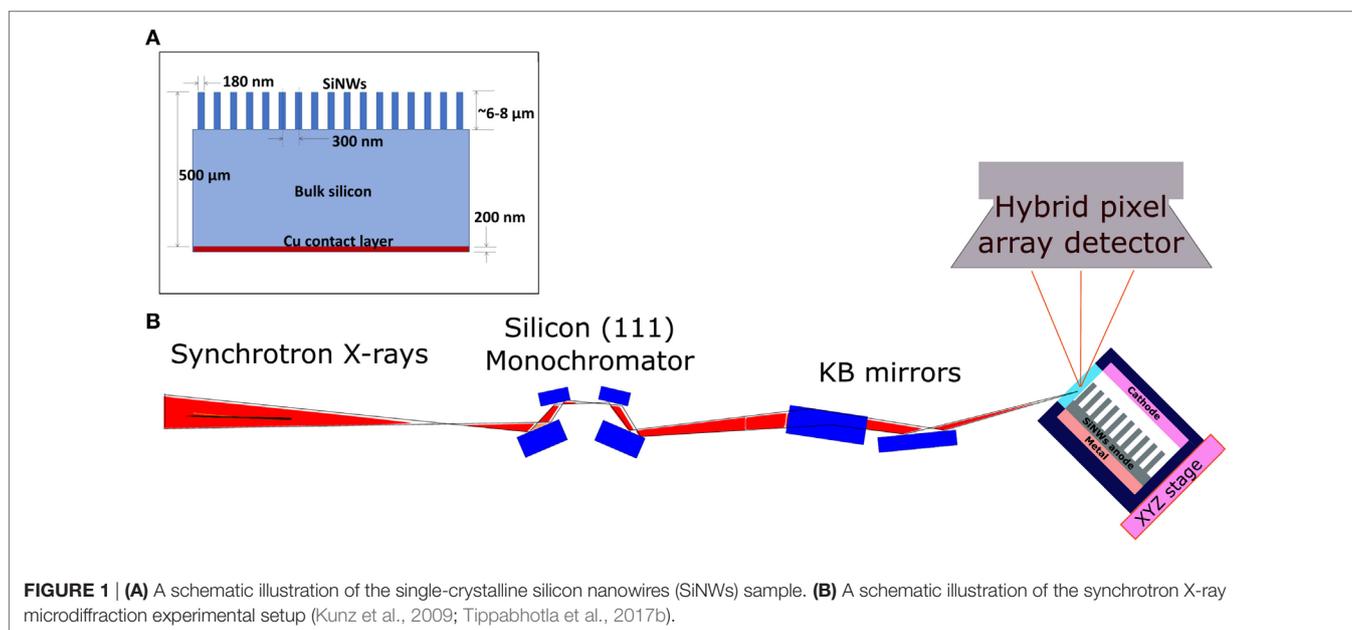
A unique battery test cell was specially designed to enable the *in situ* study using μ SXRD. A schematic of the test cell is shown in **Figure 1B** as part of the overall *in situ* μ SXRD experiment. This unique battery test cell design is needed to allow the X-ray beam to access the SiNWs during the lithiation process inside the battery test cell, thus enabling the *in situ* μ SXRD experiment. The design and fabrication of the battery test cell has been described in detail in our earlier report (Tippabhotla et al., 2017b). The electrochemical cycling of the test cell from open circuit voltage (OCV) of $\sim 3\text{--}0.01\text{ V}$ was done on a single-channel portable Potentiostat/Galvanostat (Bio-Logic Science Instruments).

Synchrotron X-Ray Microdiffraction Experiment and Stress States in SiNWs

The μ SXRD technique allows focused X-ray beam at a submicron resolution which is crucial to enable us to study stress states in SiNWs during electrochemical lithiation. The current experimental work was conducted using the μ SXRD setup at beamline 12.3.2 of Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA, USA (Kunz et al., 2009). The μ SXRD at this beamline provides 1- μm spatial resolution and a high-crystal orientation resolution of 0.01° (MacDowell et al., 2001; Chen et al., 2016). The μ SXRD technique at this beamline has been widely used to study microstructural changes and stress states in many technologically important devices and structures, such as the through-silicon via (TSV) in the microelectronics, as well as Cu/Nb nanopillars for nanotechnologies in energy applications (Budiman et al., 2006, 2012a, 2015).

Figure 1B shows the schematic diagram of the μ SXRD setup. The beamline end station (BL 12.3.2) produced a high-energy (5–24 keV) polychromatic X-ray beam of 1 μm diameter. A four-crystal monochromator in the setup is used to select a single wavelength from the polychromatic beam, if required. Kirkpatrick-Baez mirrors are used as focusing optics (Kunz et al., 2009). The battery test cell was assembled on the sample stage as shown in the schematic in **Figure 1B**. The sample stage can move in XYZ directions where Y is along SiNWs and Z is across the SiNWs as shown and X is perpendicular to the viewing plane. The sample stage was approximately adjusted to the focus of the X-ray beam on to the SiNWs electrode using a laser triangulation system available in the beamline setup.

The SiNWs sample produced multiple diffraction signals upon interaction with the polychromatic X-ray beam. The diffracted signal was captured by a 2D X-ray hybrid pixel array (DECTRIS Pilatus 1 M) detector. Initial μ SXRD scans were performed along the SiNWs (Y-direction) covering the entire thickness of the SiNWs electrode, i.e., a line scan covering SiNWs on the top and



bulk Si substrate on the bottom. The resulting intensity variation of the diffracted signal along Y-direction was studied to locate the SiNWs. This is because the bulk Si generates a high-intensity diffraction signal, and the SiNWs at the same time generate a weak diffraction signal, at least 10 times lower in intensity than that of bulk Si.

Once the location of SiNWs was identified, they were scanned by both monochromatic and polychromatic X-rays before and after assembly of the battery cell. Furthermore, an *in situ* μ SXRD scanning of the SiNWs was conducted during the electrochemical cycling of the test cell from OCV of ~ 3 – 0.01 V. Based on analysis of the initial polychromatic μ SXRD scan from the SiNWs, the diffraction peaks from the crystal planes (7, 5, 1) and (6, 4, 2) with approximate energies of 14.08 and 14.62 keV, respectively, were identified for further analysis using energy scan. The first monochromatic scan was performed within the energy range of 14.02–14.14 keV with a step size of 0.002 keV for the (7, 5, 1) crystal plane. Similarly, the second monochromatic scan was performed from 14.56 to 14.7 keV with a step size of 0.002 keV for the (6, 4, 2) crystal plane. The diffraction data were analyzed using the XMAS software (Radchenko et al., 2016). From the monochromatic data analysis, we obtained the d -spacing of the diffraction planes, at different levels of lithiation (d_{Lith}). The strain (ϵ) in the crystalline part of the lithiated SiNWs was calculated using Eq. 1 given below (Tamura, 2014). The d_{Unst} is the d -spacing of the respective (h,k,l) planes in the theoretically unstrained state, which in this experiment has been confirmed to be the same as that of the silicon substrate in the sample. Since the focused monochromatic X-ray beam is an ellipsoid of a few microns in size, it covers many SiNWs in this experiment, and

hence the strain calculated by Eq. 1 would be an average strain over several SiNWs

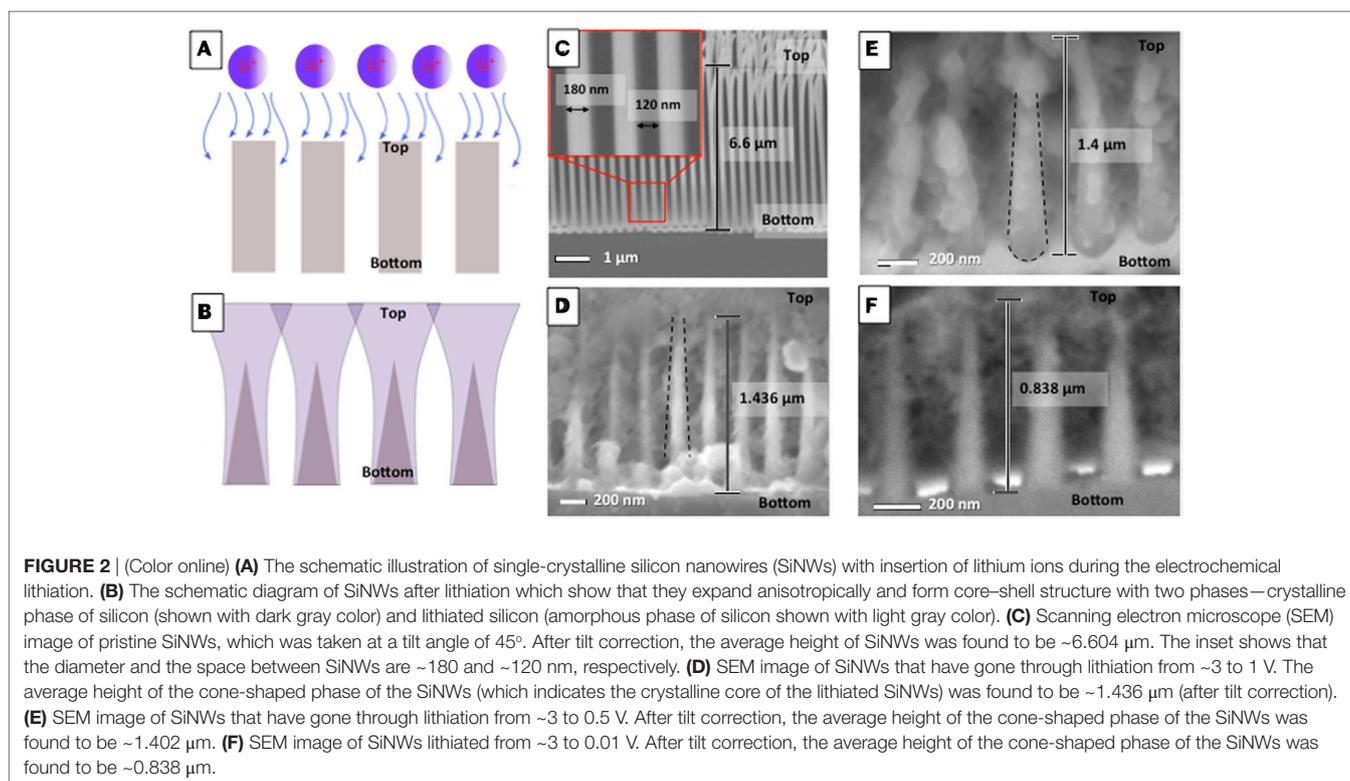
$$\epsilon = \frac{d_{\text{Lith}} - d_{\text{Unst}}}{d_{\text{Unst}}} \quad (1)$$

Morphological Evolution of SiNWs During Electrochemical Lithiation

In addition to the μ SXRD experiment, which provides stress states during the electrochemical lithiation of the SiNWs, a morphological investigation of the electrochemically lithiated SiNWs was also performed using SEM. It assessed morphological changes at different levels of lithiation, i.e., identical SiNW samples were cycled from the initial OCV (~ 3 V) to different final voltages (1, 0.5, and 0.01 V) using the same battery test cell used for μ SXRD, and the resulting lithiated SiNWs were observed under the SEM. Before performing SEM, the lithiated SiNW samples were washed and soaked in 1:1 EC/DMC (ethylene carbonate/dimethyl carbonates) solvent and acetonitrile to remove the electrolyte salt (LiPF_6) deposits to improve clarity of the SEM images. The results of this investigation show core-shell structure as commonly reported (Zhao et al., 2012; Yang et al., 2014) and help correlate with the μ SXRD results.

RESULTS AND DISCUSSION

The morphology of the lithiated SiNWs at different levels of lithiation demonstrates that the lithiation of the SiNWs is not uniform. As shown in the schematic in **Figure 2A**, the top surface and upper side walls of the SiNWs would get lithiated



much more compared to the lower (i.e., bottom) side walls of the SiNWs. This was first illustrated in the model reported by Yang et al. (2014). Due to the lithium-ion insertion, the upper end of the SiNW expands more compared to the bottom, leaving a conical crystalline core surrounded by amorphous Li_xSi as shown in the schematic in **Figure 2B** (Yang et al., 2014). The actual SEM images shown in **Figures 2C–F** are in line with these schematics and confirm simulation results of morphological study (Yang et al., 2014).

The pristine SiNWs are uniform with a diameter of 180 nm and a spacing of 120 nm from each other, and a height of $\sim 6.5 \mu\text{m}$. Their SEM images are shown in **Figure 2C**. As the lithiation starts, they turn into conical structures with a sharp tip and a wide base. **Figures 2D–F** show SEM images of lithiated SiNWs at different levels of lithiation. The SiNWs cycled from 3 to 1 V are shown in **Figure 2D**. The conical, crystalline part of the SiNWs of height $\sim 1.5 \mu\text{m}$ was observed. However, as the lithiated silicon forms Li_xSi , all SiNWs fused together due to expansion greater than the spacing between the SiNWs. **Figures 2E,F** show SEM images of the samples lithiated from $\sim 3 \text{ V}$ that have gone through further lithiation to 0.5 and 0.01 V, respectively. The conical, crystalline core is still visible but further reduced in heights to ~ 1.4 and $\sim 0.8 \mu\text{m}$, respectively, indicating further lithiation which progresses along the longitudinal axis of the SiNWs (from top to bottom of the SiNWs). These results are in general agreement with the widely reported core-shell lithiation model (Zhao et al., 2012; Yang et al., 2014). Further details about the lithiated samples are available in Figures S2 and S3 in Supplementary Material.

To better understand the stress states, SiNWs were initially scanned by polychromatic μSXR D (white beam), then scanned by monochromatic energy before and after the assembly of the battery cell. Before the assembly of the battery cell, SiNWs were scanned by a white beam and the diffraction peak was identified

from the crystal plane (5, 3, 1) with an approximate energy of $\sim 9.716 \text{ keV}$. For further analysis, an energy scan was performed from 9.69 to 9.724 keV with a step size and an exposure time of 0.002 keV and 3 s, respectively. From energy scan analysis, the peak with the highest intensity was found at an energy of $\sim 9.706 \text{ keV}$ as shown in Debye–Scherer pattern in **Figure 3A** with theoretical silicon rings position (i.e., the unstrained silicon). The (h,k,l) indices of the unstrained, theoretical rings are provided above each theoretical ring in **Figure 3A**. The inset shows a magnified image of the diffracted peak. The actual diffracted peak was observed below the theoretical silicon ring, which means, for the experimental setup in the present study, $d_{\text{Lith}} > d_{\text{Unst}}$. Hydrostatic strain (ϵ) was calculated using Eq. 1. The hydrostatic stress (σ) could be determined using the bulk modulus of silicon of 97.6 GPa. The hydrostatic stress was determined to be tensile $\sim 72.85 \text{ MPa}$ in (5, 3, 1) crystal plane before the assembly of battery cell, as it is shown in **Figure 3C**.

Similarly, the hydrostatic stresses in the crystalline, cone-shaped part of the SiNWs were determined after the assembly of battery cell and during lithiation, as shown in **Figure 3C**. SiNWs were scanned by polychromatic μSXR D, and two diffracted peaks from the crystal planes (6, 4, 2) and (7, 5, 1) with approximate energies of 14.62 and 14.08 keV, respectively, were identified for further analysis using energy scan. The first energy scan was performed with energy from 14.56 to 14.7 keV and a step size and an exposure time of 0.002 keV and 3 s, respectively, at different levels of lithiation. Similarly, the second monochromatic scan was performed with energy from 14.02 to 14.14 keV with a step size and an exposure time of 0.002 keV and 3 s, respectively, at different levels of lithiation. **Figure 3B** shows an example of diffracted peak from the energy scan performed on SiNWs after they have gone through lithiation from ~ 3 to $\sim 0.65 \text{ V}$. From the energy analysis, the

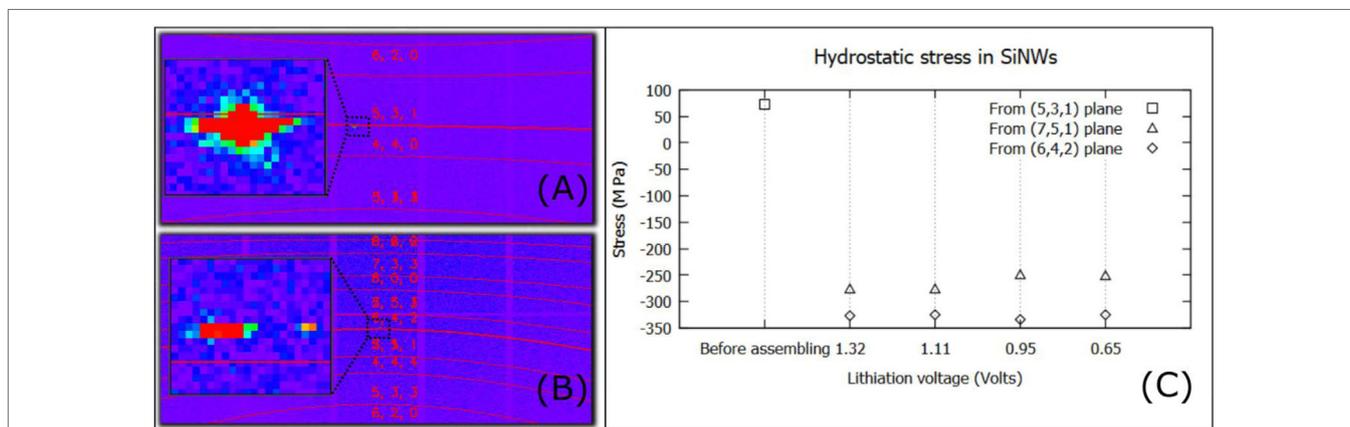


FIGURE 3 | (Color online) **(A)** Before assembling into the battery cell, the single-crystalline silicon nanowires (SiNWs) were scanned by monochromatic beam to obtain Debye–Scherer pattern with theoretical silicon ring positions. The inset shows a zoomed image of diffracted peak from silicon crystal plane of (5, 3, 1) at the energy of 14.08 keV. **(B)** Debye–Scherer pattern is obtained from diffraction of SiNWs, after they have gone through lithiation from ~ 3 to 0.65 V. The inset shows a magnified image of diffracted peak from plane (6, 4, 2) at the energy of 14.62 keV. **(C)** Hydrostatic stress in SiNWs before the assembly of battery cell was determined from a peak, diffracted from (5, 3, 1) crystal plane as shown in **(A)**. After assembling of battery cell, SiNWs were scanned with two different energy ranges at different levels of lithiation. Two peaks were identified from each energy range corresponding to (7, 5, 1) and (6, 4, 2) crystal planes of the crystalline part of the lithiated SiNWs. The hydrostatic stress measurement using this technique has an experimental uncertainty of about $\pm 5 \text{ MPa}$ (strain resolution was limited by pixel resolution in the hybrid pixel array detector in the synchrotron X-ray microdiffraction setup). Further a representative cycling (discharge) curve was presented in Figure S4 in Supplementary Material with a marking of the salient result data points presented in this manuscript.

peak with the highest intensity was diffracted from (6, 4, 2) crystal plane at an energy of 14.67 keV, shown in **Figure 3B**. The inset shows a magnified image of the reflection. It shows that the actual diffracted peak from this experiment was above the theoretically calculated silicon ring, which means $d_{\text{Lith}} < d_{\text{Unst}}$. Hence, from our stress calculation, we found compressive stress of ~ 325.5 MPa in (6, 4, 2) crystal plane as shown in **Figure 3B**. This seems to be more or less the stress state of the crystalline parts of the SiNWs after lithiation as shown in **Figure 3C**, obtained from both the (6, 4, 2) and (7, 5, 1) crystal planes. These stress data indicate a generally compressive stress in the crystalline cores of SiNWs after lithiation. This trend is in qualitative agreement with the core-shell model during lithiation reported in the literature (Liu et al., 2012b; Zhao et al., 2012; Yang et al., 2014).

However, the stress magnitude here appears to be constant after different levels of lithiation in the experiment, while the models proposed higher and higher compressive stresses in the crystalline core of the SiNWs, reaching to high compressive stress of a few GPa (Liu et al., 2012b; Zhao et al., 2012; Yang et al., 2014). It is to be noted that in the present experiment, due to the limitation inherent of the beamline instrumentation capability at the current stage, the X-ray-focused beam (of a few microns) will shine a few SiNWs altogether, and thus the diffraction results would be an average of the few SiNWs. In addition, the core-shell models (Liu et al., 2012b; Zhao et al., 2012; Yang et al., 2014) have also indicated a stress profile with the highest compressive stresses occurring only in the inner part of the crystalline core (i.e., the inner-most few nanometers) and smaller stresses as the diameter approaches the boundary between the core and the shell parts of the SiNWs. This could lead to further averaging effects in the compressive stress state as observed in the current experiment, at least to the level of lithiation shown in **Figure 3C**. The SiNWs were estimated to be about 50% lithiated (with the lithiation voltage of 0.65 V) as shown in **Figure 3C**, based on the experimental setup of the present study.

These results seem to be comparable with previously reported stress states in silicon nanoparticles during lithiation using micro-Raman spectroscopy (Zeng et al., 2016). However, it must be noted that a micro-Raman spectroscopy technique would only examine the outer surface of the crystalline part of the silicon nanoparticles, and thus the level of stress would be as expected in the outer walls of the crystalline core of the nanoparticles, i.e., a few hundreds of MPa. This technique would not provide the complete stress distribution in the nanostructures, but could prove useful in elucidating the qualitative trend of the stress evolution during lithiation. Our present study further confirms the overall qualitative trend of the stress states of the crystalline core of the SiNWs after lithiation and could provide furthermore complete information about the stress state of different parts of the SiNWs (for instance, smaller beam could lead to finer stress information, or the white-beam data could provide deviatoric components of the stress and thus provide richer information about the stress states in the individual SiNWs). In combination, these stress studies could help further improve the understanding of the complete stress states in the SiNWs during the electrochemical

lithiation and could thus lead to the design of fracture-free silicon nanostructures for next-generation LIBs.

Further, these experiments also show that the aspect ratio and spacing of the SiNWs in the electrode will have effect on the lithiation of the SiNWs. **Figure 2** shows the illustrations as well as actual SEM images of the effects of the expanded Li₃Si beyond the spacing between the SiNWs as the electrode in the LIB. Based on these observations, short and wide SiNWs may be better compared to long and thin SiNWs, for a fixed spacing between SiNWs. However, if SiNWs are too wide, then they may pulverize (Kennedy et al., 2016).

CONCLUSION

In situ synchrotron scanning X-ray microdiffraction experiment was conducted to study stress states during lithiation of crystalline SiNWs in an LIB test cell. Morphological changes in the SiNWs at different levels of lithiation were also studied using SEM and compared with stress states. It was found from SEM images that lithiation predominantly began at the top of the SiNWs and progressed gradually down toward the base of the SiNWs.

The crystalline cores of the SiNWs were found to be in compressive stress (up to ~ 325.5 MPa) during electrochemical lithiation using *in situ* μ SXRD. The findings of this research study help to further improve the understanding of the stress states in the SiNWs during the electrochemical lithiation and could further lead to the design of fracture-free silicon nanostructures for next-generation LIBs.

AUTHOR CONTRIBUTIONS

Experimental work (fabrication of the samples, design and development of the battery test cell, synchrotron X-ray microdiffraction, and SEM imaging studies) was conducted by IA, ST, IR, and AA. NT and CS are synchrotron X-ray microdiffraction experts at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory, Berkeley, United States of America (USA)). AB is an expert in mechanics of nanomaterials for advanced energy technologies and the principal investigator of the study. All authors contributed equally in data analysis and discussions.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at <https://www.frontiersin.org/articles/10.3389/fenrg.2018.00019/full#supplementary-material>.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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