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Reversible crystalline-amorphous phase transformation in Si nanosheets with lithi-/delithiation

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Abstract
Silicon (Si) has a large theoretical capacity of 4200 mAh g⁻¹ and has great potential as a high-performance anode material for Li ion batteries (LIBs). Meanwhile, nanostructures can exploit the potential of Si and, accordingly, many zero-dimensional (0D) and one-dimensional (1D) Si nanostructures have been studied. Herein, we report on two-dimensional (2D) Si nanostructures, Si nanosheets (SiNSs), as anodes for LIBs. These 2D Si nanostructures, with a thickness as low 5 nm and widths of several micrometers, show reversible crystalline–amorphous phase transformations with the lithi-/delithiation by the dimensionality of morphology and large surface area. The reversible crystalline–amorphous phase transformation provides a structural stability of Li⁺ insertions and makes SiNSs promising candidates for reliable high-performance LIBs anode materials.

Supplementary material for this article is available online

Keywords: two-dimensional nanostructures, silicon nanosheets, recrystallization, reversible phase transition, lithium ion batteries

(Some figures may appear in colour only in the online journal)

1. Introduction
Lithium-ion batteries (LIBs) have been successfully used as a means of energy storage in many electronic devices and transportation vehicles. The energy density of LIBs, which is a critical performance characteristic in most applications, is 180 Wh kg⁻¹ [1] and the materials used in cathodes or anodes are usually the determining factors affecting the electrochemical performance. For anodes, carbon, with a theoretical capacity of 372 mAh g⁻¹, is used; however, this is still low for many applications that require a larger capacity such as electric vehicles (EV) [2]. Si has since emerged as a promising anode material with a large theoretical capacity of 4200 mAh g⁻¹.

Meanwhile, nanomaterials have been of great interest for use in high-performance LIB electrodes because they provide novel electrode reaction paths, active chemical reaction due to short distances for Li⁺ insertion, short electron transport path, high contact area with electrolytes, change in electrode potentials, and extensive composition modulations. Importantly, control of the structural changes can be expected from these nanostructured materials because of the possibility of accommodation of stresses associated with the lithi-/delithiations. In light of this, Si nanomaterials have been of interest as anode materials for LIBs. Indeed, zero-dimensional (0D) Si nanostructures, i.e., Si nanoparticles, provide better electrochemical properties owing to their high surface area in addition to less pulverizations [3]. One-dimensional (1D) Si nanostructures, i.e., Si nanowires, also provide short electronic and ionic paths
in combination with stress-tolerant lithiation and thus provide higher capacity and better capacity retention [4, 5].

Two-dimensional (2D) Si nanostructures are also attractive as anode materials for LIBs since they can provide high specific surface area and short electronic and ionic paths, as 0D and 1D Si nanostructures. Accordingly, 2D Si nanostructures, that is Si nanosheets (NSs), have been synthesized in various ways including topochemical reactions [6], molten salt extrafolatation and chemical reduction processes [7], magnesiothermic reduction [8], graphene oxide (GO) nanosheets as sacrificial templates [9] and DC (direct current) arc discharge methods [10], and the electrochemical properties as anode materials have been studied [7–10].

In this study, we synthesized the SiNSs by a chemical vapor deposition (CVD) process by using SiCl₄ as precursor and H₂ as carrier gas, and characterized the properties as anode materials for LIBs. Interestingly, we found reversible crystalline–amorphous phase transformation of SiNSs in the course of lithi- and delithiations, that is, crystalline SiNSs transform to an amorphous phase during lithiations and reversibly transform back to a crystalline phase during deli- thiations. This reversible crystalline–amorphous phase transformation seems to be due to two-dimensionality on the nanometer scale as well as the large surface area of SiNSs. It also reveals that the surface state is critical to the reversible crystalline–amorphous transformations in SiNSs.

2. Materials and methods

2.1. Synthesis of Si nanosheets as electrodes

Si nanosheets were grown directly on the substrate by a CVD process in a high-flux H₂ environment with a flow rate of 3000 sccm. Grafoil was used as the substrate that works as a current collector in the following electrochemical testing. The composition of SiNSs was investigated by an EDS (Energy Dispersive Spectrometer, JEOL-ARM 200F).

2.2. Characterization of Si nanosheets

The morphologies of Si nanosheets were observed by field effect scanning electron microscopy (FESEM, Hitachi 3000). The structure of the Si nanosheets was determined by using transmission electron microscopy (TEM, Titan 80–300TM, JEOL-ARM 200F) and x-ray diffraction (Synchrotron x-ray, PAL). For ex situ TEM analysis of lithi-/de- lithiated Si nanosheets, the cycling cells were disassembled and sampling was carried out in an argon filled box (<1 ppm oxygen and water) using a vacuum holder. For in situ XRD analysis, half cells were fabricated (figure S3(b), available online at stacks.iop.org/NANO/28/255401/mmedia) and mounted on sample stages in XRD chamber, and connected to the potentiostat (Reference 600TM, Gamry Instruments). The in situ cell was aligned with the beam path and the XRD analysis was performed during lithiation/de-lithiation processes. The composition of SiNSs was investigated by an EDS (Energy Dispersive Spectrometer, JEOL-ARM 200F).

2.3. Electrochemical testing

The coin-type half cell was fabricated to analyze the electrochemical properties. Si nanosheets grown on the grafoil were assembled as the positive electrode and Li metal as a reference electrode. The electrolyte was 1 M LiPF₆ salt in a 1:1:1 mixture of ethylene carbonate (EC)/diethyl carbonate (DC)/dimethyl carbonate (DMC). The cells were subjected to galvanostatic cycling using the Maccor system (Series 4000) between 0.005 to 1.5 V at C/10 ~ 20 rate.

3. Results and discussion

The SiNSs were grown on substrates by using chemical vapor deposition (CVD) [11, 12]. Grafoil was used as the current collecting substrate in the half cells. Our preliminary study indicated that the Grafoil was not involved in the insertion of the Li ion in the cell cycling and just functions as a current collector (online supplementary figure S1). Figures 1(a), (b), show scanning electron microscopy (SEM) images of SiNSs grown on a Grafoil substrate. The SiNSs grow like a wad of cotton wool with a diameter of about 30 μm. Upon closer observation, a great number of small SiNSs were observed (figure 1(b)). The thickness of the individual SiNSs was characterized via transmission electron microscopy (TEM) and atomic force microscopy (AFM) to be as small as 1–100 nm depending on the processing time [12]. In this study, SiNSs with an average thickness of 5 ± 2 nm were grown by considering our previous studies [12] and used for the cell test. As shown in figures 1(c) and d, the TEM images demonstrate that individual SiNSs possess a single-crystalline nature. The lattice spacings of the (112) and (110) planes correspond to those of Si. A selected area electron diffraction (SAED) pattern indicates that the stacking axis is in the [111] direction (inset in figure 1(d)). The SiNSs were also characterized by x-ray diffraction (XRD): all peaks were indexed to a Si diamond structure (online supplementary figure S2).

The lithi-/delithiation of SiNSs is carried out by fabrication of half cells using SiNSs as the working electrode and Li metal as counter electrodes (figure S3(a)). Figure 2(a) shows the cycle versus capacity of SiNSs electrodes measured with a constant current/constant voltage (CC/CV) charging mode over the range of 0.005 V to 1.5 V at C/10 rate (10 h per half cycle). The first discharge (lithiation) capacity was 4225 mA g⁻¹, which is comparable to the theoretical capacity and then decreased to 2950 mA g⁻¹. The capacity then further gradually decreased, but remained over 450 mA g⁻¹ until the 270th cycle. The irreversible capacity loss is common in many Si and SiNSs electrodes and presumably arises from the electrolyte decomposition and formation of the solid electrolyte interphase (SEI) layer, electrical disconnection due to the volume change, and the ‘trapping’ of the Li atoms in the
electrically connected Si electrodes [13]. The secession from Grafoil current collectors without binders in our preliminary half-cell system configuration should also attribute to the capacity loss. After the initial cycles, the Coulombic efficiency increased and remained relatively high, which corresponds to 98% capacity retention, and was stable throughout cycles.

Figure 2(b) shows the voltage profile for SiNSs over the range of 0.005 to 1.5 V at C/10 rate. During the first discharge, a sloping plateau is seen between 0.5 and 0.08 V, and the profile shows a change in slope near the end of the first discharge as the full capacity is reached. During the first charge (delithiation), the potential increases to about 0.3 V in a short time. Next, there is a single flat plateau, indicating a
two-phase region, followed by an upwardly sloping region suggestive of a single-phase region. The second discharge and charge profile is similar to the first discharge and charge profile; the same sloping plateaus were observed, and the profile was maintained during the subsequent cycles.

The differential capacity curves measured between 0.005 and 1.5 V were shown in figure 2(c). At first discharge, the peak appearing at ∼580 mV is possibly due to the formation of a SEI layer during the first lithiation. Further discharge occurred at 70 mV indicating that the crystalline Si (c-Si) reacted with Li to form an amorphous lithium silicide, a-Li2Si. The lithiation in this study was performed at a lower voltage compared to bulk or nanowires (at 125 mV) [14–17]. Upon charge at the first cycle, current peaks appeared at about 250 mV and 480 mV. The discharge peak above 70 mV could be attributed to the crystalline Li15Si4 phase. The peak below 70 mV could correspond to the Li22Si4 phase. In the subsequent charge–discharge cycles, discharge peaks were observed at 225 and 70 mV and charge peaks were observed at 290 and 500 mV.

The structural change in SiNSs' anodes during lithiation/delithiation were investigated by using in situ XRD. The in situ XRD data were collected simultaneously with the cycling data using the in situ cell shown in figure S3(b). Figure 3 shows the in situ XRD patterns collected for the cell cycled at C/20 rate with increasing the scan number from top to bottom for each figure during the first charge and discharge from 0.005 to 2 V. In figure 3, the peaks at about 42, 44.5, and 54° are from the Grafoil. Figure 3(a) shows that the intensities of the (111), (220), and (311) peaks of crystalline Si decrease during the lithiation and the peaks completely disappear from the XRD patterns at 0.005 V. This pattern agrees with those reported in previous studies [18]: the crystalline Si phase transforms to the amorphous phase via lithiation. In the scans in figure 3(a), the appearance of a new peak indicates the Li2Si phase to Li15Si4 (332), corresponding to the slope change in the voltage profile at about 60 mV.

Figure 3(b) shows the in situ XRD patterns collecting during the delithiation. It is noted that the crystalline peaks appear with delithiation in addition to the Li2Si phase. During the first delithiation, the intensity of the Li15Si4 peak decreased linearly. Instead, new peaks at around 32, 36, 52, 56, and 62° are observed that start at 200 mV. It is matched with that shown in the TEM study that also showed crystallization starting at about 200 mV (figure 4(c)). The XRD patterns are indicative of the cubic structures of Si-III, space group Ia3 [19, 20]. We examined the in situ XRD at the 2nd cycle to verify whether the recrystallization occurs along the cycle and found that the recrystallization also appears during the 2nd delithiation (online supplementary figure S4).

The structural change of SiNSs anodes during lithiation/delithiation were further investigated by using HR-TEM. Figure 4 shows the representative TEM images and diffraction pattern of SiNSs with lithiation/delithiation at the tenth cycle. Si anodes typically irreversibly transform to being amorphous at the first cycle and the lithiation proceeds with this amorphous phase as the cycling continues [21]. In our TEM study, it is noted that SiNSs possess crystallinity at the initial stage of Li+ insertion at the tenth cycle and become amorphous at the lithiation (figures 4(b)–(d)). The amorphous SiNSs then transform to crystalline structures during the course of delithiation, as shown in the HR-TEM images and diffraction patterns in figures 4(e)–(g), which clearly show that the delithiated SiNSs at the tenth cycle were crystalline. We performed a thorough investigation and found that the delithiated SiNSs at the cycles have crystallinity with the exception of the amorphous area of SEI, indicated in the white arrow area (online supplementary figure S5). These SEI
layers were produced at about \(\sim 10\) nm thickness and contributed to the large irreversible capacity and resistance layer. We also characterized the composition of amorphous SiNSs by TEM-EDS (online supplementary figure S6). It shows that the SiNSs has an element Si composition with carbon and oxygen elements from the electrolytes, phosphor and fluorine from the LiPF\(_6\) salt. This indicates that the impurities, or any other compositional inhomogeneity, are not involved in the recrystallization of SiNSs.

The reversible crystalline–amorphous phase transformation to crystalline from the amorphous phase (i.e., reversible recrystallization) of the Si electrodes during lithi-/delithiation has not been reported thus far. Some discrete Si nanocrystals in the amorphous phase have been found after delithiation in a few studies \([22, 23]\); however, global- and reversible recrystallization has not been observed. It seems that the unique structure of SiNSs with a high surface area and very thin sheets consisting of a few Si layers could make the global and reversible crystalline–amorphous phase transformation possible. It is known that crystallization at the surface is kinetically favorable because it can be accelerated by faster atomic transport on a free surface \([24]\). Additionally, the energy barrier for nucleation in nanomaterials should be smaller because a large fraction of the Si atoms are in high-energy states at the highly metastable surfaces \([25]\). Due to its highly disordered nature, the amorphous Si has many defects, which could act as preferred nucleation sites for the phase transformation during the cycles. Such a phase transformation can cause transition on the surfaces from an amorphous to crystalline phase and thus release the stress or strain; in turn, the total free energy of that system decreases \([26]\). Such stress relaxation should be critical for nanomaterials such as the SiNSs studied here that have a very large surface area. The phase transformation can also remove the defects such as vacancies that are formed during delithiations, which further contributes to the decrease in the free energy of the materials.

It is interesting to consider why this phase transformation has not been observed in previous Si nanomaterial anodes such as nanoparticles and nanowires, although they too have large surface areas. The reasons may be due to the nanostructure morphology. SiNSs are free-standing 2D nanostructures with flat surfaces, i.e., without surface curvatures. Meanwhile, 0D or 1D structures such as nanoparticles or nanowires have curved surfaces with very small surface curvatures and stress is developed due to surface energy that is inversely proportional to the radius of curvature, \(\Delta P \approx 2\gamma / r\) \([27]\).

\(\Delta P \approx 2\gamma / r\)

where \(\gamma\) is surface energy and \(r\) is radius curvature \([27]\). Such stress would be significant on a nanometer scale on a gigapascal range and would act as an energy barrier for the phase transformation. Furthermore, the curved surfaces of the nanoparticles and nanowires confine the compressive stresses in the peripheral direction and tensile stresses in the core during lithiation and vice versa during delithiation. The stresses under self-confinement could also act as energy barriers and complicate the nanoparticles’ and nanowires’ phase transformation.

The inner stress/strain state of SiNSs was estimated by calculation of the lattice strain using the Synchrotron x-ray diffraction data. It shows that the lattice strains in pristine and recrystallized SiNSs (i.e., fully delithiated SiNSs after the first cycle) is 1.61% and 0.94%, respectively. Meanwhile the strain in the pristine Si nanowire is reported as \(\sim 4\)% \([28]\).
This indicates that the SiNSs with a flat surface are under a lower stress/strain state compared to the other Si nanostructures with curved surfaces (i.e., Si nanoparticles or nanowires).

The results of this study indicate that the surface is one of the critical parameters on the phase transformation upon delithiation. To verify the role of the surface and to explore the possibility of phase transformation control, we investigated the behavior of surface-modified SiNSs, i.e., carbon (C)-coated SiNSs. C was coated on the SiNSs at a certain growth temperature after the growth of SiNSs. Our characterization indicates that C was coated on the surface in the form of amorphous carbon and was coated with Si-C bonds (online supplementary figure S7). The half-cell with C-SiNSs was fabricated with the same process and lithiated, and the structures were characterized by TEM. Online supplementary figure S8 also shows the TEM image and diffraction pattern of C-SiNSs after the tenth delithiation, suggesting the formation of amorphous structures in contrast to the crystalline structure of SiNSs under the same conditions (figure 4(g)). This indicates that the phase transformation critically depends on the surface state and can be controlled by surface modification.

It should be noted that the effect of carbon coating on the phase-transformation might be related to the surface state of SiNSs. The SiNSs have a high surface area and thus the crystallization at the surface is kinetically favorable by the faster atomic transport on a free surface [24]. The energy barrier for nucleation of the crystalline phase should also be smaller because a large fraction of the Si atoms are in high-energy states at the highly metastable surfaces of SiNSs [25]. However, carbon coating of SiNSs develops Si-C bonds on the surface that stabilize the highly metastable SiNSs’ surfaces as well as retards the atomic transport of Si for the nucleation, and resulted in an amorphous structure after delithiation.

It should be noted that the reversible structural reformation, i.e., reforming and rearrangement of atoms, is feasible during lithi-/delithiation. Such a structural reformation and phase transformation can accommodate the stresses applied to the SiNSs, and prevent cracking and fracture and, in turn, pulverizing with cycling. This can make SiNSs structurally more stable during cycling than other Si anode materials. Indeed, lithiated and delithiated SiNSs showed no cracks or fractures during cycling in our TEM observations in many delithiated SiNSs (online supplementary figure S8). Such cracks and fractures are clearly seen in Si nanowires, thin films, and nanoparticles with sizes of several hundreds of nanometers [29, 30]. It should also be noticed that there is a possibility to control the the structural changes by surface modifications. This will provide a new level of flexibility for designing SiNSs anode materials for LIBs in terms of the state of the phase that is crystalline and/or amorphous.

Meanwhile, our SiNSs electrodes showed a fairly rate-dependent property due to being without a conducting agent and thus should have improved conductivity. The structural stability from the reversible phase transition is a trade-off between the commonly used surface treatment, such as C-coating. The improvement in conductivity should be studied in different approaches in terms of real battery systems. The reversible recrystallization could also provide a novel and stable reversible lithi-/delithiation reaction in Si anode materials. For example, the transformation of crystalline SiNSs to an amorphous phase starts at around 0.1 V of discharge potential in this study. Therefore, a new lithi-/delithiation reaction under a crystalline Si phase can be designed by operation of the cells with a higher discharge potential than 0.1 V. Figure 5(a) shows the cycle versus capacity of the SiNSs electrodes measured with a poly-single crystalline phase transition region over the range of 0.1 V to 1.5 V. It shows that the capacity is about 700 mAg\(^{-1}\). It is, however, noted that it shows a quite stable capacity retention and monotonic capacity with Coulombic efficiency of \(\sim 99\%\). In figure 5(b) the sloping plateau is between 0.2 and 0.3, indicating a phase transition region during cycling.

Figure 5. (a) Specific capacity versus cycle number and Coulombic efficiency of the SiNSs electrode on a poly-crystalline phase transition mode. (b) Voltage profile of the SiNSs electrode on a poly-single crystalline phase transition region.
This indicates that a more stable lithi-/delithiation under the crystalline state of Si could provide excellent capacity retention and make it possible to design stable Si anodes for LIBs. Together with the advantages of SiNSs, including high surface area for Li insertion, this reversible recrystallization would make SiNSs a novel building block for preparing high-performance LIB anode materials. It is noteworthy that additional modifications such as cell configuration, doping and surface coating of SiNSs should also improve the electrochemical properties of SiNSs.

4. Conclusions

In conclusion, we characterized 2D Si nanostructures, SiNSs, as anode materials for LIBs. The SiNSs in this study, synthesized by CVD process using SiCl$_4$ and H$_2$, were highly pure with a thickness of approx 5 nm. The SiNSs first showed reversible crystalline-amorphous phase transformation during lithiation/delithiation in 0D, 1D and 2D Si nanomaterials. Our results suggest that the dimensionality of morphology and large surface area with the surface state may be important parameters related to phase transformation of materials on the nanometer scale. It also suggests that the reversible recrystallization could provide a new way to improve the electrochemical properties of SiNSs as anode materials for LIBs.

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