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Identification of an intermediate state during electrochemical lithiation of silicon using in-situ TEM techniques

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In-situ TEM studies of structural changes during lithiation of active materials have recently become an important method for understanding intercalation mechanisms. We have developed an in-situ TEM battery setup which allows us to investigate the lithiation of Si. We observe that the formation of metastable amorphous lithiated Si is preceded by the growth of planar Li precipitates. We propose that the precipitates destabilize the Si lattice and allow the formation of the metastable amorphous phase rather than the stable crystalline phases. Figure 1(a) shows one of the silicon lamellae which was used as a cathode inside the TEM. The lamellae are prepared using common FIB techniques and are attached to TEM lift-out copper grids using electron beam Pt deposition. To prepare a lithium anode an electrochemically thinned tungsten wire is scraped across lithium metal. Figure 1(b) shows a dark field image of one of these wires. It can be seen that a layer of lithium metal remains at the tip of the wire. It takes about 1min to mount the wire into the STM-TEM holder and to transfer the holder into the high vacuum of the TEM. The surface of the lithium metal oxidizes during this time and forms various compounds like Li_3N, Li_2O and LiOH. These insulating compounds exhibit a high diffusivity for Li^+-ions and therefore act as solid state electrolytes. Figure 1(c) shows a sketch of the STM-TEM holder and the respective positions of both electrodes. The tungsten wire is mounted on a movable piezo actuator opposite to the Si-cathode which is attached to a conventional lift-out copper grid. The STM-TEM holder allows application of voltages of -10V to 10V between wire and copper grid. Currents can be measured with an accuracy of 100pA. The in-situ battery experiments were carried out in the following way: At first both electrodes are mechanically connected using the movable piezo actuator. The connection results in bending contours. Then a voltage of -10V is applied and the lamella continuously monitored. Figure 2(a) shows the lamella at the beginning of a battery experiment and Figure 2(b) 30min later. As can be seen in Figure 2(b) a line like defect has appeared which is visible due to the interruption of bending contours. Figure 2(c) shows the development over time of another line like defect. Further analysis of these defects shows that they are planar. This is proven by oscillating contrast in dark field imaging (Figure 3(a)). The planar defects can evolve into channel like amorphous structures during further lithiation (Figure 4(a)). High resolution TEM imaging reveals a sharp interface between the amorphous and the crystalline phase (Figure 4(b)). EELS measurement shows the Li K-edge at 57eV and the Si $L_{2,3}$-edge at 99eV energy loss (Figure 4(c)), indicating an amorphous lithiated Si phase, which is expected during the lithiation of silicon. The fact that this amorphous phase forms at the location of the planar precipitates suggests that the planar precipitates are nucleation sites for the amorphous phase. We envision the following two-step process (Figure 5):

1. Lithium dissolves in the crystal matrix and clusters in planar precipitates, at locations perhaps determined by mechanical stress.

2. The planar Li precipitates break the covalent bonds of the Si lattice, possibly accounting for the formation of metastable amorphous lithiated Si rather than the expected crystalline phases.

A similar process is suggested in the literature [1] and used to explain the unexpected shrinkage of Si-nanopillars. We provide the first direct observation of the proposed Li-based precipitates, which are similar in structure to H-based precipitates in silicon [2].

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2. N. Martsinovich, M.I. Heggie and C.P. Ewels , J. Phys.: Condens. Matter 15 (2003), p. 2815.

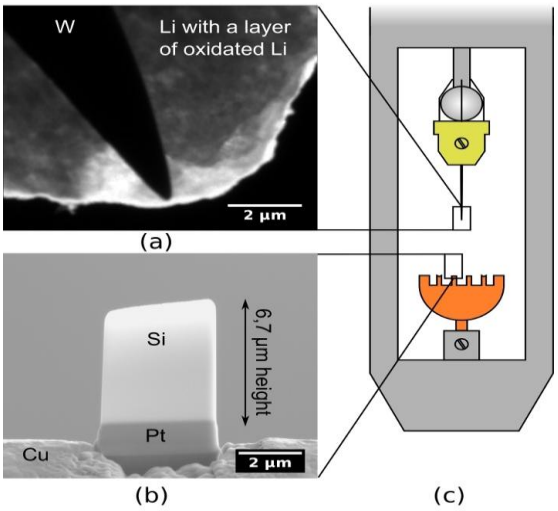

Figure 1. (a) A tungsten tip with lithium is used as anode. The layer of oxidated lithium acts as solid state electrolyte. (b) A Si-lamella used as cathode and is attached to a conventional TEM lift-out copper grid. (c) Sketch of the STM-TEM holder and the respective positions of both electrod

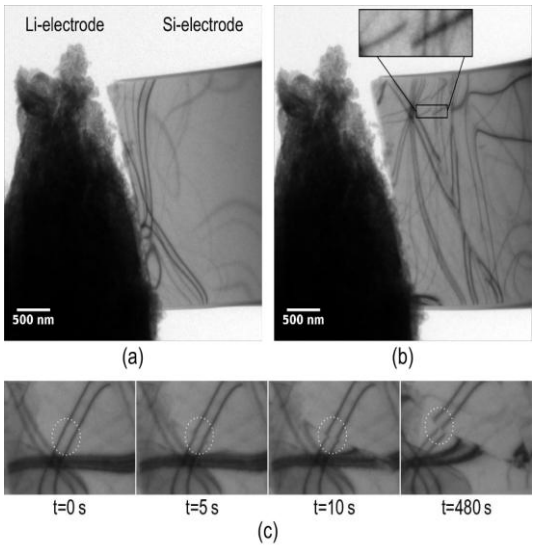

Figure 2. (a) The lamella at the beginning of an in-situ battery experiment. (b) A line like defect has appeared 30min later, visible due to the interruption of bending contours. (c) development over time of another line like defect.

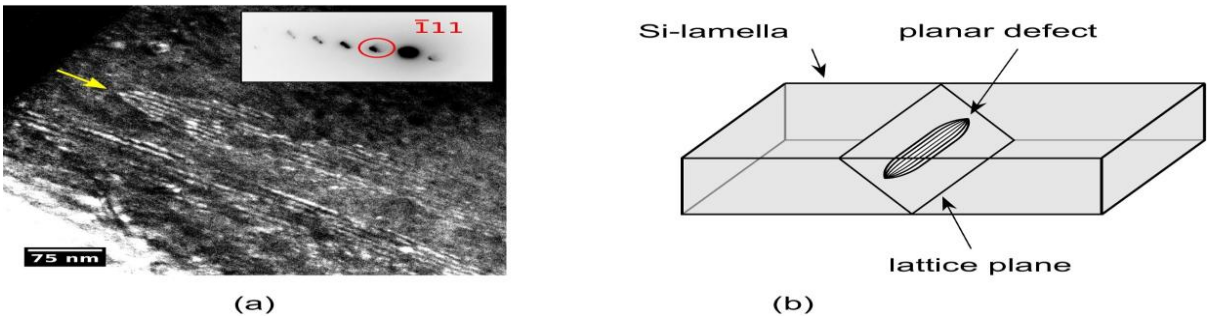

Figure 3. (a) Oscillating contrast reveals that the defects are planar. (b) Sketch to visualize the defect geometry.

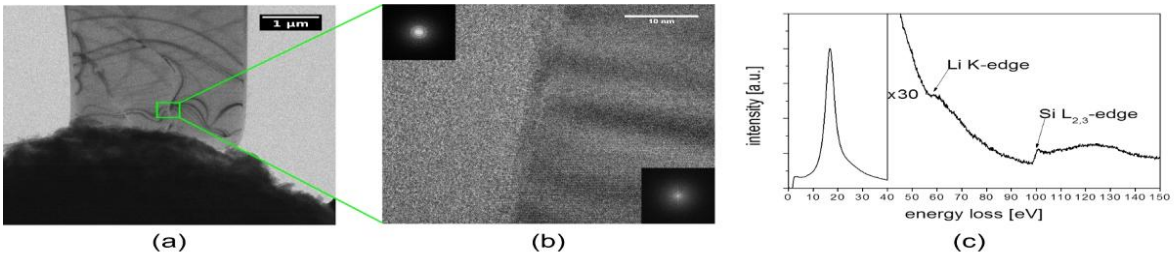

Figure 4. (a) The planar defects can evolve into channel like amorphous structures during further lithiation. (b) High resolution TEM imaging reveals a sharp interface between the amorphous and the crystalline phase. (c) EELS measurement shows the Li K-edge at 57eV and the Si $L_{2,3}$-edge at 99eV energy loss, indicating an amorphous lithiated Si phase, which is expected during the lithiation of silicon.

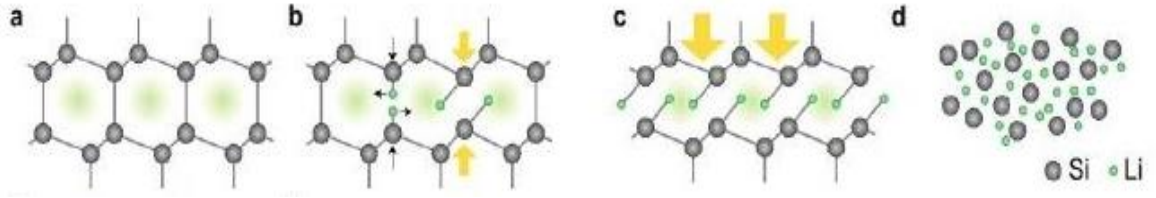

Figure 5. The amorphization of silicon begins with the formation of planar lithium precipitates. These break the covalent bonds of the Si lattice, possibly accounting for the formation of metastable amorphous lithiated Si rather than the expected crystalline phases. Model first proposed in [1].