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Microstructure Study on Initial Lithiation/Delithiation Cycle of Crystalline Silicon Wafer

Jun Liu*, Taeho Yoon, Chunmei Ban, and Mowafak Al-Jassim

National Renewable Energy Laboratory, Golden, Colorado, 80401, U.S.A.
* Corresponding author: jun.liu@nrel.gov

Silicon (Si) is a promising next-generation anode material for lithium-ion batteries due to its large theoretical specific capacities of 3579 mAh g^{-1}. The huge volume expansion of Si during the electrochemical cycling results in cracks and phase transformations between crystalline and amorphous silicon [1]. Although there have been many studies on the change in the mechanical properties and crack behavior during the cycling, it is still not clear how cracks nucleate and propagate at the initial lithiation/delithiation cycle.

A purchased boron-doped p-type Si (100) wafer with electron resistance of 0.001 ~ 0.005 Ω was used in this study. A cleaned Si wafer with size of 6.35 x 6.35 x 1 mm^3 was used as anode. 2032-type coin cell was used for electrochemical tests with Li foil as the counter electrode. The electrolyte was prepared as 1.2 *M* $LiPF_6$ in EC/EMC = 1/1 (v/v) with 10 wt.% FEC. The Si wafer and Li foil were separated by polyolefin and glass fiber separator. 21 µL of electrolyte was used for each cell. For lithiation, 40 µA (100 µA cm^{-2}) current was applied to the working electrode for 6 hours using BioLogic potentiostat. The same current density was applied for delithiation with a cutoff voltage of 1.5 V (*vs.* Li/Li+). The surface morphology and detailed microstructure of the initial lithiated Si wafer were characterized by SEM and TEM.

Fig. 1(a) is the top-view SEM image of the Si wafer after delithiation. Cracks propagate along <110> and <100> directions. Obviously, the width of the cracks along <110> direction is thicker than that of <100> one. The cross-sectional SEM image in Fig. 1(b) indicates that the <110> crack penetrates into the bulk wafer deeper than 5 µm and the crack shows a zigzag shape in the vertical direction, whereas the <100> crack is only at the very surface of Si wafer as indicated in Fig. 1(c).

Fig. 2(a) is the cross-sectional bright field TEM image of a region close to the <110> crack. The plane is viewed from [011] zone axis, as confirmed in Figs. 2(c) and 2(d). Interestingly, the cracking region shows a complicated structure, composing of amorphous and crystalline Si layers alternatively. SAEDs in Figs. 2(b)-2(c) indicate that the top surface of the Si wafer in Spot 1 is amorphous, Spot 2 is crystalline, and Spot 3 composes of both amorphous and crystalline structures because the smallest selected aperture is larger than the thickness of the amorphous layer. This suggests that the formation of the amorphous layer can happen far away from the surface, at least 5 µm deep according to this study. EELS analysis at Region A displays a remained Li at the wafer surface after delithiation (Figs. 2(e) and 2(g)), whereas there is no Li signal in the bulk no matter the Si layer is amorphous or crystalline (Fig. 2(g)). Fig. 2(i) is the cross-sectional bright field TEM image of a region containing the <100> crack. The plane is viewed from [001] zone axis as indicated in Fig. 2(k). The amorphous layer is only observed at the wafer surface and its thickness is ~200 nm. No Li signal is detected by EELS even at the surface. This is because the penetration depth of Li in the <100> crack can be very shallow, and Li is easily extracted from the Si wafer during the delithiation.

We also coat a PAA layer on the Si wafer surface. No cracks appear in the Si wafer after the lithiation/delithiation cycle. A very thin amorphous layer exists on the Si wafer surface and its thickness is only ~15 nm.

In this work, we found that Si wafer has a preferential expansion along <110> directions during the initial lithiation/delithiation cycle, as the evidence of wider <110> cracks. These cracks also propagate much deep, at least 5 μm. The morphology of the amorphous Si layer appearing after the initial cycle shows a dependence on the plane orientation, *i.e.*, multi and deep layers on the {110} plane, whereas a single layer with ~200 nm on the {100} plane. A PAA coating layer on the Si wafer mitigates the cracks and reduces the thickness of the amorphous Si layer.

References:
[1] MN Obrovac, L. Christensen, Electrochemical and Solid State Letters **7** (2004), p. A93.

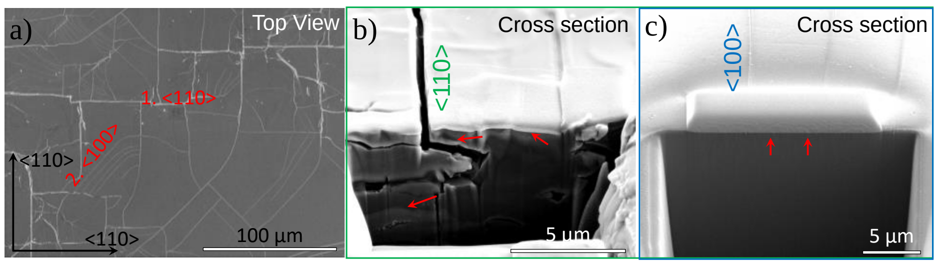

Figure 1. (a) top-view SEM image of the Si wafer after delithiation. Cross-sectional SEM image of (b) <110> crack and (c) <100> crack.

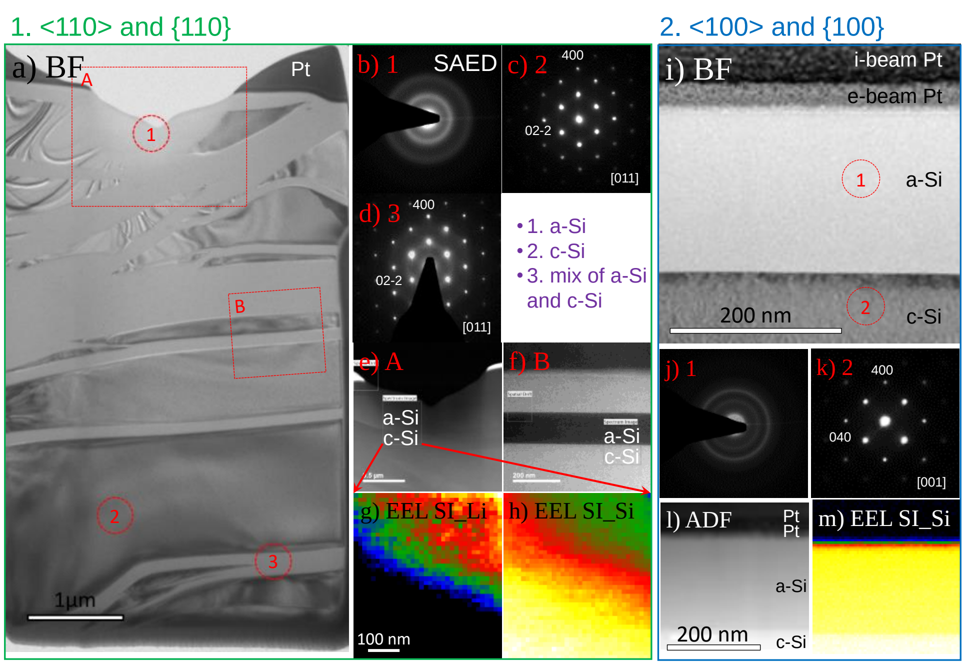

Figure 2. (a) cross-sectional BTTEM image of a region close to the <110> crack. SAEDs of (b) Spot 1, (c) Spot 2, and (d) Spot 3 in (a). ADF images of (e) Region A and (f) Region B in (a). EEL spectrum images of (g) Li and (h) Si from selected box in (e). (i) cross-sectional BFTEM image of a region containing the <100> crack. SAEDs of (j) Spot 1and (k) Spot 2 in (i). (l) ADF image and (m) corresponding EEL spectrum image of Si.

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