Supplementary Information for

## Artificial lithium fluoride surface coating on silicon negative electrodes for the inhibition of electrolyte decomposition in lithium-ion batteries: visualization of solid electrolyte interphase by insitu AFM

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## 1. Characterization of the as-deposited Si thin film



Figure S1. Raman spectrum of the as-deposited Si thin film.

2. Surface morphology of the as-received mirror-polished Cu substrate and the as-deposited Si thin films



**Figure S2.** AFM images of the as-received mirror-polished Cu substrate. The scan areas and the height ranges are: (a)  $30 \times 30 \ \mu m^2$  and  $\pm 10 \ nm$ , and (b)  $10 \times 10 \ \mu m^2$  and  $\pm 3 \ nm$ , respectively.



**Figure S3.** AFM images of as-deposited Si thin films (a, b) without and (c, d) with 4-nmthick LiF. The scan areas are: (a, c)  $5 \times 5 \ \mu m^2$  and (b, d)  $500 \times 500 \ nm^2$ .



## 3. Cyclabilities of Si thin-film electrodes coated with LiF layers

**Figure S4.** (a) Discharge capacities and (b) Coulombic efficiencies of Si thin-film electrodes with LiF layers of different thickness ( $t_{LiF} = 0, 2, 4, 8, and 16 nm$ ) in 1 M LiPF<sub>6</sub>/EC+DEC electrolyte, as functions of cycle number.

## 4. Surface analyses of Si thin-film electrodes after cycling



**Figure S5.** Root-mean-square surface roughness of Si thin-film electrodes (a,b) without and (c) with 4-nm-thick LiF after two cycles in 1 M LiTFSI/EC+DEC electrolytes (a,c) without and (b) with 10-wt.% FEC. Analyzed areas of A and B are 10 × 10  $\mu$ m<sup>2</sup> and 3 × 3  $\mu$ m<sup>2</sup>, respectively.