

Supplemental Material

Lithium segregation induced structure and strength change at amorphous-Si/Cu interface

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The surface energy of a slab of material can be defined as the energy difference per unit surface area between the slab and the equivalent amount of each constituent in the bulk of the infinite solid [39]. This leads to

$$\sigma_{12} = \frac{1}{2A} (E_{12}^{tot} - \sum N_i \mu_i) + PV - TS \quad (1)$$

where σ_{12} is the surface energy, E_{12}^{tot} is the total energy of the slab, $2A$ accounts for the two surfaces of the slab area, N_i and μ_i denote the number of atoms and the chemical potential of species i . At 0 K and typical pressures, the PV and TS terms may be neglected. The surface energy for non-stoichiometric LiSi_2 ($x=0.5$) slabs depends on the environment as defined by the chemical potentials. This can be seen by rewriting Equation 1 in the form

$$\sigma_{12} = \frac{1}{2A} \left(E_{12}^{tot} - n_{\text{Li}} \cdot e - \underbrace{(N_{\text{Li}}^{tot} - N_{\text{Li}}^{bulk})}_{\Delta N_{\text{Li}}} \cdot (\mu_{\text{Li}}^{\text{LiSi}_2} - \mu_{\text{Li}}^*) \right) \quad (2)$$

where n_{Li} is the number of Li atoms per formula unit of LiSi_2 , e is the energy per unit of LiSi_2 , N_{Li}^{tot} is the total number of Li atoms in the slab, N_{Li}^{bulk} is the number of Li atoms in the bulk, $\mu_{\text{Li}}^{\text{LiSi}_2}$ and μ_{Li}^* are the chemical potential of Li in LiSi_2 and metallic Li, respectively. To study the surface energy profile for (100), (110) and (111) surfaces of crystalline c- LiSi_2 we designed surface models with different surface terminations.

We studied σ_{12} based on the various surface Li terminations of the (100), (110) and (111) LiSi_2 slab models. The surface energy, σ_{12} , depends linearly on $\mu_{\text{Li}}^{\text{LiSi}_2} - \mu_{\text{Li}}^*$ (highlighted region in Fig.1) as defined in Equation 2. When the slab stoichiometry is the same as the bulk, $\Delta N_{\text{Li}} = 0$, hence the surface energy of the slab is independent of $\mu_{\text{Li}}^{\text{LiSi}_2} - \mu_{\text{Li}}^*$. This behavior is represented for all surfaces by a flat line in Fig.S1. If the slab stoichiometry differs from the bulk, $\Delta N_{\text{Li}} \neq 0$, the surface energy varies with $\mu_{\text{Li}}^{\text{LiSi}_2} - \mu_{\text{Li}}^*$ (Fig. 1). Hence, we can define the most thermodynamically stable slab as the slab with the lowest surface energy, i.e. $\text{Li/Si} = 0.54$. Note that $\text{Li/Si} = 0.54$, namely 8 % compared to the bulk, is responsible for decrease in the surface energy per are in all slabs. This tendency of slight Li enrichment on the surfaces when the Li content is sufficiently low ($x=0.5$), is consistent with previous theoretical studies suggesting surface Li enrichment close to the onset of lithiation [35,40].

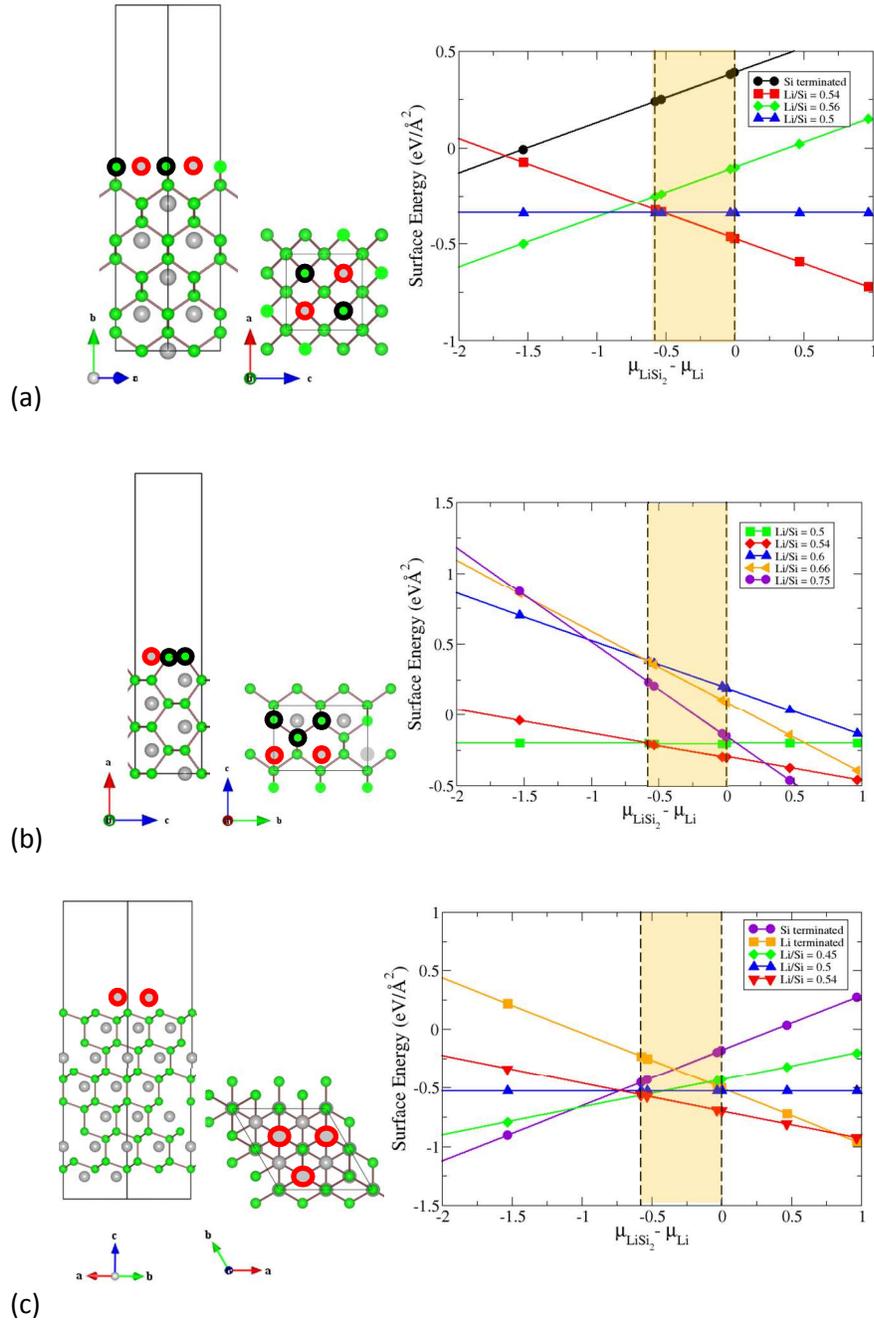


Fig. S1: Normalized surface energies for the different **(a)** (100), **(b)** (110) and **(c)** (111) surfaces as a function of $\mu_{\text{Li}}^{\text{LiSi}_2} - \mu_{\text{Li}}^*$, i.e., the difference between the Li chemical potential in the slab and its value for the pure metallic Li (highlighted region). Side and top view of the lowest energy configurations are presented on the left of each panel. Li atoms in bulk: grey circles, Li atoms on surface: red-grey circles, Si atoms in bulk: green circles, Si atoms on surface: green-black circles.