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Ab initio and empirical modeling of lithium atoms penetration into silicon

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A process of lithium atoms penetration into silicon (100) subsurface layers was investigated with the help of DFT method. It was shown that, while the concentration of lithium adatoms on reconstructed (100) silicon surface is low, the bonding energy of lithium atoms in the subsurface layers is smaller than the bonding energy on the surface, so lithium atoms are unlikely to migrate into the crystal. When the (100) silicon surface is covered by 2 layers of lithium, migration into the subsurface layer becomes favorable. In addition to this, the reconstruction of the surface changes to the form with symmetric dimers as the concentration increases. Thus, all possible lithium migration paths become energy-wise equal, so the rate of lithium atom transfer into silicon crystal rises.

In addition to the ab initio calculations, an ad-hoc empirical interatomic potential was developed and the kinetics of lithium diffusion into silicon were studied. It was shown that lithium penetration proceeds in a layer-by-layer way with a sharp border between undoped and lithiated silicon. This is accounted for the fact that, once a tetrahedral interstice is occupied by a lithium atom, the migration barriers between the adjacent interstices become lower and the rate of diffusion increases.

1. Introduction

Nowadays, silicon is considered as a promising novel material for Li-ion batteries anodes as it has the highest theoretical specific capacity (4200 mA h/g), which is 11 times higher than in graphite (372 mA h/g) [1–5]. Unfortunately, silicon lithiation is accompanied by a significant (up to 300%) increase in specific volume [2,6,7], as well as phase transitions between different Li_xSi phases. In this process, the change in volume causes large mechanical stresses and, consequently, a break-up of the crystal [8–11]. In addition to this, silicon has a low diffusion coefficient for lithium ions [12,13]. These limitations impede application of bulk silicon in modern Li-ion batteries.

To overcome this obstacle, nanostructured silicon-based materials were suggested, including thin films [14–16], silicon nanowires [17–19], nanoparticles [20–22], nanotubes [23–26] and porous structures [27–33]. Numerous preliminary experimental investigations show encouraging results for the usage of these materials as anodes in Li-ion batteries. Therefore, the theoretical investigations aiming at lithium diffusion in silicon structures and search for the way to overcome material limitations become utterly relevant.

At first, lithium atoms are adsorbed on the surface and subsequently penetrate subsurface layers. In [34], the average times Li adatom stays atop (100) and (111) surfaces were obtained for temperatures in the interval of 800–1250 K and it was shown that Li goes into silicon through (100) surface easier than through (111) surface.

The sorption of lithium is greatly affected by the reconstruction of the surface, where it takes place. It is common knowledge that silicon (100) surface is covered with silicon dimers, which reduces the number of dangling bonds and minimizes the surface energy, leading to the (2×2) reconstruction at room temperature. Theoretical investigations [35] showed that, when silicon (100) surface is covered with 1 monolayer of lithium, the (2×2) reconstruction is replaced by the (2×1) reconstruction with a symmetrical silicon dimers arrangement. Also, the potential barriers of a single lithium atom transition from surface to subsurface layers and from subsurface layers into the bulk were calculated at dilute lithium concentration (0.88 eV and 0.5 eV, correspondingly). However, the barriers for the diffusion at higher Li concentrations,

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when the surface reconstruction changes, have not been studied yet.

In this work, we have investigated the diffusion of lithium through Si (100) surface at different Li concentrations by means of density functional theory (DFT) methods and classical molecular dynamics (MD). First, the possible positions of Li on the surface were found and compared. Then, main paths of Li atom transition into bulk silicon were examined and the effect of Li concentration level on the potential barriers was studied. Finally, we performed MD simulations of Li diffusion through Si (100) surface and estimated the diffusion coefficient.

2. DFT calculations of lithium atoms behavior on silicon surface and their jumps into the subsurface layers

All the calculations of lithium sorption on the surface and the barriers of transition into the subsurface layers were conducted with VASP 5.3 (Vienna Ab-initio Simulation Package) [36–38] quantum-chemical software package using DFT [39,40] in plane-wave basis sets and with the help of projector augmented wave (PAW) method [41,42]. General gradient approximation (GGA) in Perdew–Burke–Ernzerhof (PBE) form [43] with Grimme van der Waals corrections was used [44]. The nudged elastic band (NEB) method [45] was applied for modeling transitional states and finding potential barriers for Li atom jumps.

Before the actual studies, a cubic unit cell of silicon was modeled. During its structural optimization, a $12 \times 12 \times 12$ Monkhorst–Pack mesh [46] was used for Brillouin zone (BZ) integrations. The resulting unit cell was used to build up a $4 \times 4 \times 3$ supercell in a form of a periodic slab, which was subsequently used for modeling silicon (100) surface with the $c(4 \times 2)$ reconstruction. The supercell dimensions were $a = 15.3724$ Å, $b = c = 21.54$ Å. Considering relatively large supercell sizes, the density of k-points was decreased, resulting in a $2 \times 2 \times 1$ BZ mesh. In order to prevent slabs from interacting with each other (supercell's periodic images), they were separated by 27 Å vacuum spacings.

The thickness of the slab was selected so as the surface energy estimate would comply with known values. For a 15.3724 Å thick slab (12 atomic layers) the surface energy was 151.6 meV/Å^2, which agrees with the values calculated in [47,48]: 155.9 meV/Å^2 and 149.2 meV/Å^2, respectively. In order to ensure, that the slab of the chosen thickness reasonably represents the properties of macroscopic crystal surface, it was additionally tested for convergence of Li binding energies. The binding energy of a lithium atom in T3 position (see Fig. 1) was calculated with the slabs of 12 and 11 layers thickness. The values occurred to be 1.24 eV and 1.201 eV respectively, making difference of only 3.15%.

A plane-wave energy cut-off of 245.3 eV was used in the calculations. All structural optimizations were carried out until the forces, acting on atoms, fell below 0.01 eV/Å.

At first, the behavior of Li atoms on the surface was investigated. A set of structures with different lithium atom positions were calculated, and after that the most energetically favorable positions of lithium on Si (100) were determined (Fig. 1).

The lithium binding energies (Table 1) were calculated as:

$$E = (E_{\mathrm{SiLi}} - E_{\mathrm{Si(100)}} - nE_{\mathrm{Li}})/n, \quad (1)$$

where E_{SiLi} is the full energy of Si (100) surface with lithium atoms adsorbed, $E_{\mathrm{Si}}(100)$ – the full energy of a silicon supercell with two reconstructed (100) surfaces, E_{Li} – potential energy per atom in lithium crystal, n – the number of lithium atoms adsorbed.

As can be seen in Table 1, the most energetically favorable position is T3, with lithium atom placed in a valley between silicon dimers (Fig. 1), which is in agreement with other theoretical studies [49]. It is worth noting that lithium binding energy decreases

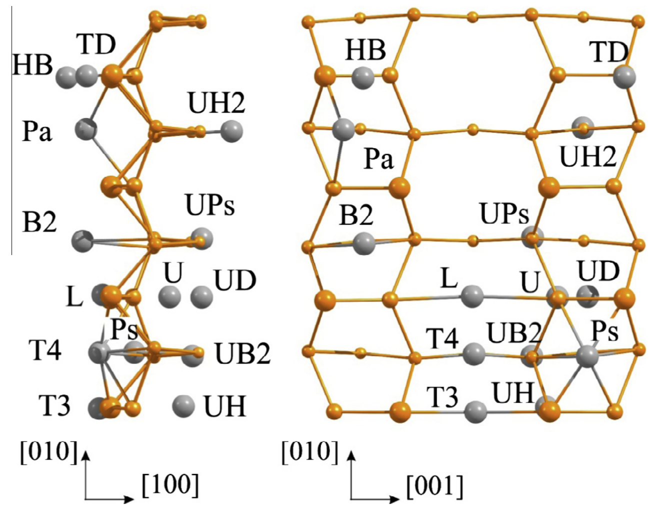

Fig. 1. Different positions of lithium atom on Si (100) surface and in subsurface layers. Silicon atoms are in orange color, lithium – light gray. Left panel - side view, right panel - top view.

Table 1
Binding energies of lithium atom adsorbed on Si (100) surface at different positions.

Li position	Li atom on Si (100) surface binding energy, eV
Surface	
T3	−1.240
L	−1.177
T4	−1.160
Ps	−1.045
B2	−1.045
Pa	−1.040
HB	−0.518
TD	−0.517
Subsurface	
UPs	−1.037
UH	−0.810
UB2	−0.809
U	−0.793
UH2	−0.761
UD	−0.110

when lithium atom propagates into silicon (positions UD, UH, UH2, UB2, U) or goes out of the valley (positions HB, TD). Hence, the position between silicon dimers can be considered as the preferable initial lithium atom location. To support this thesis, transitions between surface and subsurface positions were simulated (Fig. 2).

The heights of the potential barriers shown in Fig. 2 argue that lithium can easily migrate on the surface at room temperature, but is unlikely to go below the surface. So lithium atoms are kept in the surface-adsorbed positions by the high potential barriers. It is worth noting that the barriers of migration under the surface are lower and are comparable with the migration barriers in bulk silicon, obtained from theoretical calculations (0.85 eV for a cubic silicon supercell containing 64 atoms) and experiment (0.8 eV [13]).

At small lithium concentrations, two different paths of migration from surface to subsurface layers can be figured out:

(1) T3 → UH → UB2, further referred as [T3 → UB2]
(2) L → U → UB2, further referred as [L → UB2]

The initial positions are considered to be T3 and L, with a possibility of hopping between them (the activation energies are 0.43 eV from T3 to L and 0.37 eV backwards). The energy of the system is 0.063 eV lower, when lithium is in T3, and the barriers for lithium going below the surface T3 → UH and L → U are much