Soft X-ray Li-K and Si-L\textsubscript{2,3} Emission from Crystalline and Amorphous Lithium Silicides in Lithium-Ion Batteries Anode

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Abstract

Silicon is a promising candidate for anode material in lithium-ion batteries (LIBs) because of its high theoretical Li capacity (4200 mAh/g for Li\textsubscript{4}Si) in comparison with the conventional graphite anodes (372 mAh/g). However a large volume expansion of about 400%, amorphization of Si and crumbling of the electrode hinders its use in practical applications.

To overcome this problem intense theoretical and experimental studies aiming at elucidation of the mechanisms of structural transformations in Si electrodes upon lithiation/delithiation processes have been performed worldwide. A number of theoretical studies have been devoted to the modeling of the lithiation of the crystalline c-Si, search for the stable crystalline Li\textsubscript{x}Si phases and investigation of the structural properties of amorphous a-Li\textsubscript{x}Si alloys. It has been demonstrated that room temperature lithiation of c-Si often results in formation of amorphous lithium silicides a-Li\textsubscript{x}Si, while the crystalline structures can be formed during the high-temperature lithiation. Interestingly the lithiation of the crystalline silicon, c-Si, occurs layer by layer, starting with the formation of a lithium enrichment zone during the first charge step. The lithiumated area of Li\textsubscript{x}Si can be divided into a highly lithiated zone at the surface with concentration x ~ 2.5 and a much less lithiated growth region with x ~ 0.1 formed deep into the crystal and separated from the pristine c-Si by a sharp reaction front with the thickness of about 1 nm. After the first cycle of lithiation and delithiation c-Si becomes amorphous. Recent experiments indicate that lithiation of the amorphous silicon, a-Si, also leads to formation of the boundary between lithiated and pristine areas in spite of the absence of the crystalline order in a-Si. Several groups have reported that at the high lithium concentration the crystalline c-Li\textsubscript{x}Si\textsubscript{4} phase can be formed through an amorphous Li\textsubscript{x}Si phase, however these results are controversial and only formation of the amorphous Li\textsubscript{x}Si phases was observed in other groups.

Recently, Aoki et al. investigated the process of the electrochemical lithiation of Si(111) using experimental methods of the soft X-ray emission spectroscopy (XES) combined with the scanning electron microscopy and X-ray diffraction with synchrotron radiation. It has been reported that three different phases of the electrochemically lithiated Si with a well-organized layered structure are likely formed on the Si(111) substrate. It was suggested that the first outermost layer consists of a crystalline c-Li\textsubscript{13}Si\textsubscript{4} phase; the second layer is a mixture of amorphous a-Li\textsubscript{13}Si\textsubscript{4} and/or a-Li\textsubscript{15}Si\textsubscript{4} phases; while the third layer is a mixed phase of a-Li\textsubscript{11}Si\textsubscript{4} and/or a-Li\textsubscript{15}Si\textsubscript{4} (52%) with the crystalline c-Si (48%). It has been found that the shape and peak position of the Si-L\textsubscript{2,3} emission band and its relative intensity in comparison with the Li-K emission vary considerably from layer to layer reflecting the differences in structure and composition of the lithiated silicon phases. However, the detailed theoretical analysis of the soft X-ray spectra of Li-Si alloys is lacking except our recent work on investigation of the lithiation products of a silicon anode.

In the present work we perform a systematic analysis of the soft X-ray Li-K and Si-L\textsubscript{2,3} emission spectra of crystalline and amorphous lithium silicides Li\textsubscript{13}Si\textsubscript{4} and Li\textsubscript{15}Si\textsubscript{4} forming in the outermost layer of the silicon anode in LIB upon electrochemical lithiation. We demonstrate that the energy position and shape of the considered X-ray emission bands strongly depend on the structure and composition of the lithiated silicon phases, while the intensities of Li-K and Si-L\textsubscript{2,3} bands provide information on Li concentration. Therefore we suggest that theoretical methods of soft XES can be used as a powerful tool for the detailed analysis of the electronic and structural properties of Li-Si alloys in LIBs.

Methods

The calculations were performed using the density-functional theory (DFT) within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) for the exchange-correlation functional as implemented in the pseudopotential-based CASTEP code. A plane wave (PW) basis set with the cutoff energy of 280 eV and the ultra-soft pseudopotentials (USPs) with two projectors for each angular momentum to describe the electron-ion interactions have been used. The 1s\textsuperscript{2}2s\textsuperscript{2} electrons of Li atom and the 3s\textsuperscript{2}3p\textsuperscript{2} electrons of Si atom have been treated as valence electrons.

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The reference structures of the metal Li and crystalline Si (c-Si)\textsuperscript{55} as well as two stable lithium silicide crystalline phases of c-Li\textsubscript{13}Si\textsubscript{4} with high concentration x of Li atoms, namely c-Li\textsubscript{x}Si\textsubscript{4} (Pbam(55))\textsuperscript{56} (x=3.25), and c-Li\textsubscript{12}Si\textsubscript{4} (I\textsubscript{4}3d(220))\textsuperscript{57} (x=3.75) have been fully optimized and relaxed. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) optimizer with line search has been used for optimization of cell parameters and the all-bands conjugate-gradient minimizer for determination of the relaxed atomic positions. The Monkhorst-Pack\textsuperscript{58} k-point meshes (15\times15\times15), (12\times12\times12), (6\times3\times11), and (5\times5\times5) have been used for Brillouin zone sampling of Li metal, c-Si, c-Li\textsubscript{x}Si\textsubscript{4}, and c-Li\textsubscript{x}Si\textsubscript{4} structures, respectively. The geometry optimization has been performed until the energy difference per atom, the forces on the atoms and all the stress components do not exceed the values 1\times10\textsuperscript{-6} eV/atom, 2\times10\textsuperscript{-3} eV/Å and 4\times10\textsuperscript{-3} GPa, respectively. The convergence of the self-consistent energy was achieved with a tolerance of 5\times10\textsuperscript{-7} eV/atom.

For modeling of the amorphous structures we constructed 2\times2\times2 supercell for Si and 1\times1\times2 supercell for Li\textsubscript{12}Si\textsubscript{4} phases in order to maintain the total number of atoms in the cell not less than 64. The numbers of Li and Si atoms in the simulation cell have been set to (Li:Si) = (64), (52:16) and (60:16) for Si, Li\textsubscript{12}Si\textsubscript{4} and Li\textsubscript{12}Si\textsubscript{4} phases, respectively. The amorphous structures were generated by the first-principles molecular dynamics simulations via the melt-and-quench scheme, where we used the CP2K package\textsuperscript{59} with the mixed Gaussian and plane-waves (GPW) approach. The PBE functional was employed as the exchange and correlation functional. The double-\zeta and plane-waves (GPW) approach. The PBE functional was employed as the exchange and correlation functional.

Further details of calculations are described in the previous work.\textsuperscript{49}

The intensity \( I(E) \) of an X-ray emission spectrum (XES) is given by the following expression:\textsuperscript{63}

\[
I_0(E) = E \sum_{n,k} P_n(k) \sigma(E - E_n(k) + E_c),
\]

where the summation over \( k \) is performed over occupied states of the Brillouin zone, \( E = \hbar \omega \) is the energy of the X-ray photon, \( E_n(k) \) is the one-electron energy of the \( n \)th valence band, \( E_c \) is the energy of the core level, \( N \) is the number of points in the Brillouin zone, and \( P_n(k) \) is the probability of transition from \( n \)th valence band to the core level \( c \) per unit time. Atomic system of units \( \hbar = \alpha = m = 1 \) is used throughout unless specified otherwise. The probability \( P_n(k) \) of the radiative electron transition in the one-electron dipole approximation is given by

\[
P_n(k) = \frac{4}{3} \left( \frac{\omega_{mc}(k)}{c} \right)^3 \frac{1}{2l+1} \sum_{m,n} \left| \langle \psi_{ak} | r_m | \phi_c \rangle \right|^2,
\]

where \( \omega_{mc}(k) \) is the transition frequency, \( l \), is the orbital quantum number of the core vacancy and \( c \) is the speed of light, \( \psi_{ak}(r) \) and \( \phi_c(r) \) are the wave functions of the \( n \)th band and the hole, respectively, \( m \), is the quantum number of the projection of the core hole angular momentum and index \( \alpha = -1, 0, 1 \) enumerates cyclic components of the position operator \( r_m \). To calculate the dipole matrix elements and intensity of XES we have used the projector augmented wave (PAW) reconstruction method\textsuperscript{48} and the on-the-fly generated (OTFG) ultrasoft pseudopotentials developed by Pickard as implemented in CASTEP code.\textsuperscript{51,52} In order to present theoretical XES Li-K and Si-L\textsubscript{2,3} spectra in the energy scale of photons avoiding explicit ab initio calculations of the energies of core levels of atoms in solids we have adjusted the Fermi level to the experimental values of the edge energy of the emission Li-K and Si-L\textsubscript{2,3} spectra, respectively. Further details of calculations and methods are described in the previous work.\textsuperscript{49}

\( I_0(E) \) is the X-ray emission spectrum of metal Li. The theoretically obtained Li-K spectrum of metal Li possesses a single intensive asymmetric spectral line at 54.3 eV with a width of 1.8 eV. In the dipole approximation the Li-K soft X-ray emission is formed as a result of electron transitions from the p states of the valence band to the 1s vacancy at the core level of Li atom. A single Li atom has an unoccupied 2p-level at about 2 eV.

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above the half-filled 2s-level. When metal Li is formed the unoccupied 2p-level transforms in a wide p-band which hybridizes with the partially occupied s-band resulting in formation of the high density of p-electronic states near the Fermi level. The above effect is illustrated in Figure 3a where we present the partial density of electronic states (PDOS) of the metal Li. Solid black, dashed blue and solid red curves represent contribution of the s, p, and d states, respectively. Thus the partly occupied p-band of the metal Li is responsible for the formation of the intensive X-ray Li-K emission band shown in Figure 2a. The experimental Li-K emission spectrum of the metal Li reported by Aoki et al. exhibits intensive spectral line at 54.2 eV as shown in Figure 2a by black dots. As one can see the theoretical results excellently reproduce the experimental data.

Experimental Si-L\textsubscript{2,3} spectrum of c-Si exhibits two pronounced peaks at the photon energies 89.95 eV and 92.05 eV and broad shoulder at 95.2 eV with the fast decrease in slope at 97.5 eV. Figure 2b demonstrates that the Si-L\textsubscript{2,3} emission spectrum of c-Si calculated in this work reproduces very well the experimental one\textsuperscript{46} represented by dots. We would like to emphasize that the Si-L\textsubscript{2,3} X-ray emission is formed as a result of radiative transitions of the valence electrons to the 2p vacancy of Si atom. Therefore in the dipole approximation the Si-L\textsubscript{2,3} spectrum reflects the energy distribution of s- and d-states of the valence band mainly localized nearby the Si atoms. It is clearly seen that the low-energy peak in the XES of c-Si (Figure 2b) is mainly associated with the low-lying valence 3s states in the energy range of −12 eV −8 eV below the Fermi level, as shown in Figure 3b by black line. The second peak at 92.05 eV in XES of c-Si shown in Figure 2b corresponds to the valence states with s-p hybridization, represented by a sharp peak in PDOS with the maximum at −6.78 eV below the Fermi level. The high energy broad shoulder in the Si-L\textsubscript{2,3} X-ray emission from c-Si at 95.2 −97.5 eV is associated with the transitions from the 3d valence states appearing at the energies of −4 −1 eV below the Fermi level as a result of p-d hybridization.

In the case of amorphous silicon the Si-L\textsubscript{2,3} band exhibits a wide maximum at the photon energies 90.5 eV with a shoulder at ∼96.5 eV as it is shown in Figure 2c. The main Si-L\textsubscript{2,3} emission band of the a-Si becomes broader if compared with the one for c-Si and the second peak in the spectrum corresponding to the s-p hybridized states disappears. Indeed, PDOS of a-Si presented in Figure 3c demonstrates absence of the s-p hybridization. Therefore in the Si-L\textsubscript{2,3} spectrum of a-Si the main peak corresponds to the transitions from the s states of the valence band, while the high energy shoulder maps the d states of the valence band. The calculated Si-L\textsubscript{2,3} spectrum of a-Si excellently reproduces the experimental one, showing that the theoretical approach used in the present work is reliable.

As the next step we have performed analysis of the soft X-ray Li-K and Si-L\textsubscript{2,3} emission spectra calculated for the crystalline (a) and amorphous (b) phases of lithium silicides Li\textsubscript{15}Si\textsubscript{4} and Li\textsubscript{13}Si\textsubscript{4} with the high concentration of lithium formed in the outermost layers of Si anode in LIB battery upon Si lithiation (Figure 4). The experimental Li-K and Si-L\textsubscript{2,3} emission spectra reported by Aoki et al.\textsuperscript{46} for the first and the second outermost layers of the electrochemically lithiated Si(111) are shown in Figure 4 by circles.

Figure 4 demonstrates that Li-K emission spectra of Li\textsubscript{15}Si\textsubscript{4} and Li\textsubscript{13}Si\textsubscript{4} lithium silicides consists of two peaks: the low intensity emission A\textsuperscript{′′} in the energy region of 45–50 eV and the intensive peak A’ in the region of 50–56 eV. In the case of c-Li\textsubscript{13}Si\textsubscript{4} as well as amorphous a-Li\textsubscript{15}Si\textsubscript{4} and a-Li\textsubscript{13}Si\textsubscript{4} alloys the low energy peak has more complicated structure with the small maximum A’\textsuperscript{″} or extended low energy shoulder at ∼46 eV. This differs considerably from the Li-K emission of the metal Li where only one intensive peak with the maximum at 54.3 eV is observed. In order to understand the mechanism of formation of the low energy peaks A’\textsuperscript{′} and A’\textsuperscript{″} in the Li-K emission of lithium silicides we analyze the PDOS projected on Li and Si atoms in crystalline phases of c-Li\textsubscript{15}Si\textsubscript{4} and c-Li\textsubscript{13}Si\textsubscript{4}, as shown in Figures 5a–5d. As a general feature we would like to note that the calculated PDOS projected on Si atoms of Li rich lithium silicides manifest

![Figure 2](https://example.com/figure2.png)  
**Figure 2.** Soft X-ray Li-K and Si-L\textsubscript{2,3} emission spectra calculated for the metal Li (a), crystalline (b) and amorphous (c) Si, respectively. Black dots: experimental spectra of metal Li,\textsuperscript{48} c-Si\textsuperscript{65} and a-Si\textsuperscript{66}.

![Figure 3](https://example.com/figure3.png)  
**Figure 3.** Partial density of electronic states (PDOS) projected on Li and Si atoms in metal Li (a), crystalline (b) and (c) amorphous Si structures. Solid black, dashed blue and solid red curves represent contribution of the s, p, and d states, respectively. Gaussian broadening of half-width 0.1 eV has been used.
Therefore the low energy peak A results of mixing of the p-band of Li with the occupied s-states of Si. The high density of p-states at −6.5 eV below the Fermi level originates from Si dimers, while the double peak structure in the energy region 7–5 eV below the Fermi level corresponds to the contribution of single Si atoms and dimers. Similar structure appears in the PDOS of p states projected on Li atoms in c-Li15Si4 as a result of mixing of the Li p states with the Si s states, as shown in Figure 5c. These p states appear in the Li-K emission spectrum as low energy peaks A′ and A′′ in the region of 45–50 eV resembling the spectral shape of the main Si-L2,3 emission band. The high energy Li-K emission peak at 57.8 eV is shifted by 0.3 eV toward smaller photon energies if compared with the Li-K emission from the pure Li metal, indicating influence of the Si content in Li-Si alloy on the position of the main Li-K line. This decrease in Li concentration results in a shift of the position of the main peak in Li-K emission.

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Figure 4b demonstrates Li-K and Si-L2,3 emission spectra calculated for amorphous a-Li15Si4 and a-Li13Si4 structures. It has been shown that in amorphous Li-Si alloys, Si atoms tend to cluster, forming Si-Si covalent bonds even at the high lithium concentration.49 This feature affects the shape of the Si-L2,3 emission bands which depends on the relative contribution of X-ray radiation from Si atoms having different coordination numbers and hence can be used for the analysis of the Si lithiation of LIB’s anodes.

The Si-L2,3 emission spectrum of the amorphous a-Li15Si4 (Figure 4b) demonstrates low energy structure with pronounced peaks B′ and B′′ at 91.6 eV and 90.1 eV mainly corresponding to radiation from the isolated Si atoms and dimers, respectively. Presence of the Si dimers and trimers in amorphous a-Li15Si4 structure results in broadening of the the Si-L2,3 emission band in comparison with c-Li15Si4 structure, where all Si atoms are well separated without formation of the Si–Si covalent bonds. In the amorphous a-Li15Si4 structure X-ray emission from the single and double coordinated Si atoms makes considerable contribution to the total Si-L2,3 spectrum, as shown in Figure 4b. Therefore the main Si-L2,3 emission band of a-Li15Si4 becomes broader in comparison with the spectrum of the corresponding crystalline phase. The high energy wide bump C at photon energies 95–99 eV in Si-L2,3 emission from a-Li13Si4 and a-Li15Si4 corresponds to the transitions from the d states localized in the vicinity of the single coordinated Si atoms.

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Amorphization of L12Si4 and L13Si4 lithium silicides also affects the Li-K emission spectra of the corresponding structures. The main Li-K emission peak A′ becomes broader with the width of 2.6 eV and 2.8 eV for a-Li13Si4 and a-Li15Si4 structures, respectively. As it was observed experimentally, the energy position of the Li-K emission peak from the outermost layer of the lithiated silicon which most likely consists of the superposition of Li15Si4 and Li13Si4 phases is located at 53.5 eV, while for the metal Li this peak is observed at 54.2 eV.48 Our calculations demonstrate that for the amorphous a-Li15Si4 and a-Li13Si4 phases of the lithiated silicon and metal Li the Li-K peak A′ is observed at 53.7 eV, 53.6 eV, and 54.3 eV, respectively, in a very close agreement with experiment. Figure 4b clearly demonstrates that the overall shape and energy position of the theoretically obtained Li-K and Si-L2,3 emission bands of a-Li15Si4 and a-Li13Si4 phases are in an excellent agreement with experimentally obtained spectra from the second outermost layer of the electrochemically lithiated silicon.48 Indeed, it was suggested by Aoki et al, that the second layer is a mixture of the amorphous a-Li15Si4 and a-Li13Si4 phases. Our calculations confirm this suggestion. On the other hand it should be noted that analysis of the experimental XRD patterns obtained from the first layer of the electrochemically lithiated Si suggests presence of the crystalline c-Li15Si4 phase.48 In addition the scanning electron microscopy (SEM) images showed that the Li-Si alloys exhibit considerably more discrete structure than the calculated PDOS of the pure Si (Figures 3b and 3c) as a result of decrease in coordination of Si atoms and Si–Si interaction with increase in Li concentration.

In c-Li15Si4 the PDOS of p states projected on Li atoms (Figure 5a) exhibits an intensive peak at about −6.5 eV below the Fermi level. This peak corresponds to the sharp peak in the PDOS of the valence s-states of Si as it is seen from Figure 5b. Therefore formation of the high density of p-states at −6.5 eV below the Fermi level occurs as a result of mixing of the p-band of Li with the occupied s-states of Si. Therefore the low energy peak A′ in the Li-K emission spectrum of c-Li15Si4 at 48.4 eV is formed as a result of radiative electron transitions from the partially occupied p states of Li mixed with the s states of Si and hence it contains direct information on Li-Si interaction. On the other hand the s states of Si at −6.5 eV are responsible for formation of the sharp intensive spectral line B′ in the Si-L2,3 emission spectrum of c-Li15Si4 at 92 eV (Figure 4a). In this respect shape of the low energy peaks in Li-K emission spectra mimics the shape of the main peak of the Si-L2,3 band. The intensive high energy peak A′′ in Li-K emission of c-Li15Si4 at 54.1 eV appears as a result of population of the Li p-band due to hybridization with the partially occupied s-band of Li similar to the case of the pure metal as well as a result of partial contribution of the p-states of Si. In addition, mixing the p and d states of Si results in a small presence of the d states in the valence band at −0.5 to −3 eV below the Fermi level which appears as a small bump C in Si-L2,3 emission spectrum of c-Li15Si4 at 96.8 eV.

The Li-K and Si-L2,3 emission spectra of c-Li15Si4 demonstrate several important differences if compared with X-ray emission spectra of c-Li15Si4. The c-Li15Si4 structure contains an equal number of the isolated Si atoms and Si atoms forming dimers.46 The X-ray emission from these two groups of atoms shows different spectral dependence: the Si-L2,3 emission spectrum from the isolated Si atoms possesses sharp line, while the spectrum from Si dimers demonstrates the double peak structure. Therefore the total Si-L2,3 emission spectrum of c-Li15Si4 shows sharp peak B′ at 92 eV which corresponds mainly to the emission from the isolated Si atoms and the low energy peak B′′ at 89.9 eV corresponding to the radiation from the Si dimers, as it is seen from Figure 4a. This spectral feature can be also seen in the c-Li15Si4 PDOS projected on Si atoms (Figure 5d), where the peak in density of s states at −8.6 eV below the Fermi level originates from Si dimers, while the double peak structure in the energy region 7–5 eV below the Fermi level corresponds to the contribution of single Si atoms and dimers. Similar structure appears in the PDOS of p states projected on Li atoms in c-Li15Si4 as a result of mixing of the Li p states with the Si s states, as shown in Figure 5c. These p states appear in the Li-K emission spectrum as low energy peaks A′ and A′′ in the region of 45–50 eV resembling the spectral shape of the main Si-L2,3 emission band. The high energy Li-K emission peak at 53.8 eV is shifted by 0.3 eV toward smaller photon energies if compared with the Li-K emission from the pure Li metal, indicating influence of the Si content in Li-Si alloy on the position of the main Li-K line. This decrease in Li concentration results in a shift of the position of the main peak in Li-K emission.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Soft X-ray Li-K and Si-L2,3 emission spectra calculated for crystalline (a) and amorphous (b) phases of Li15Si4 and Li13Si4. Circles: experimental emission spectra of the first (a) and second (b) outermost layers of the electrochemically lithiated Si(111).

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Figure 5. PDOS projected on Li and Si atoms for crystalline phases of Li$_{15}$Si$_4$ (a and b) and Li$_{13}$Si$_4$ (c and d). Solid black, dashed blue and solid red curves represent contribution of the s, p, and d states, respectively. Gaussian broadening of half-width 0.1 eV has been used.

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