COMPUTER SIMULATION OF THE APPLICATION OF THE TWO-LAYER SILICENE ON COPPER SUBSTRATE IN THE ELECTROCHEMICAL DEVICES


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ABSTRACT

The processes of lithization/delithization in a flat channel formed from defective sheets of silicene and located on a copper substrate are considered in the molecular dynamic experiment. Depending on the type of defects (mono-, bi-, tri-, and hexavacancy), the channel can hold 67, 86, 60, 23 lithium atoms without destroying. As a result of the intercalation/deintercalation cycle, the structure of the defective silicene has changed, especially in the presence of tri- and hexavacancies. With an increase in the size of defects, the diffusion of lithium atoms in the silicene channel also increases. After the delitization, the shape of the silicene sheets is not restored, and the volume of the space enclosed between sheets changes slightly. The effective use of silicene in the lithium-ion batteries assumes that only mono- and bivacancies can present in its sheets.

INTRODUCTION

Batteries with high energy density, long life and low cost are key factors for consumer electronics, electric vehicles and energy storage in networks [1-3]. The operation of lithium-ion batteries is based on the phenomenon of lithium intercalation into the electrode material. When the battery is charged, lithium is extracted from the positive electrode material and introduced into the negative electrode material, most often made of graphite. When it is discharged, these processes are reversed. One of the main characteristics of an electrode is its intercalation capacitance. It is defined as the amount of electricity imparted to the electrode when fully charged per unit mass or volume. In particular, when the carbon electrode is fully charged, the intercalation capacity is 372 mA·hour/year. This characteristic for a silicon electrode is 4200 mA·hour/year [4]. The rate of the intercalation/deintercalation reaction is determined by the diffusion rate of lithium in the solid phase. The diffusion coefficient of lithium in the process of lithization/delithization, for example, in two-layer graphene at room temperature is $7 \times 10^{-5}$ cm$^2$/s [5]. To avoid a significant change in volume (almost four times in the case of crystalline silicon) during lithium intercalation, it is proposed to use negative electrodes made of thin-film materials [6-10]. There are no significant structural changes in the autonomous bilayer silicene during the lithization/delithization cycles. Its volume change is no more than 25% and the energy barrier for diffusion of lithium is rather low (<0.6 eV) [11]. The silicene on a copper substrate is the semimetal. In this case, the hybridization between the two-dimensional structure and the substrate is rather strong, so, the Dirac cone almost disappears in the band structure of silicene [12]. However, Dirac fermions can be restored, when alkali metal atoms intercalating into the system. There is a lot of data on the properties of silicene on a silver substrate [7, 13, 14], but other materials of the substrates are still to be investigated. Copper is the most widely used metal in electrochemical devices. It has
a relatively low cost and high prevalence in the crust (compared with silver). Experiment [15] and MD studies [16] indicate the formation of an amorphous structure at the Cu/Si (001) interface of two bulk phases. Depending on the substrate temperature, their mutual diffusion can reach a depth of 10 nm [17]. The properties of silicene on a Cu substrate are insufficiently studied.

The goal of this work is to simulate the behavior of functionalized bilayer silicene on the copper substrate during lithization/delithization processes by the molecular dynamic and quantum-mechanical study, to determine the kinetic and dynamic properties of the system and to estimate of its applicability as an anode for the lithium-ion battery.

**COMPUTER MODEL**

The silicon atoms in silicene are interacted via the Tersoff multiparticle potential [18] with the parameters of [19]. To describe the interatomic interactions in the copper substrate, the EAM potential of the immersed atom was used [20]. Between the Cu – Si, Si – Si pairs (belonging to different sheets), Cu – Li, Si – Li, Li – Li, the Morse potential acted with the parameters of [21–23] and the parameters calculated through interpolation relations [4].

The considered model of silicene is a 4 × 4 surface reconstruction. The unit cell contains 18 Si atoms arranged in the form of a rhombus, 6 of them are displaced by a distance of 0.074 nm perpendicular to the surface upward for the top silicene sheet and downward for the bottom one. A flat channel formed by two sheets of silicene located on the Cu (111) substrate was modeled. The channel gap size (the distance between the sheets) was 0.75 nm. The earlier calculations of the lithium ion behavior in the silicene channel [6] showed that it is precisely with such a gap that the Li⁺ entering the channel can be in it at least 100 ps interacting with the channel walls.

Silicene sheets had a rectangular shape measuring 4.7 × 4.0 nm. In the presence of a perfect structure, they contained 300 Si atoms. In silicene, defects of various sizes were created. 1, 2, 3, and 6 silicon atoms were removed in silicene sheets and mono-, bi-, tri-, and hexavacancies were formed. Experimental data show that mainly, irrespective of the method, defective silicene structures are obtained [24].

The two-layer silicene was located in accordance with the Bernal packing (ABAB ...) on the fixed but interacting Cu (111) substrate. The fixing of the edges of the silicene sheets eliminates their non-physical turns associated with the presence of uncompensated local rotational moments [1–2]. Calculated according to the density functional theory, the distance $r_{\text{Cu-Si}}$ between the two-layer silicene and the metal substrate is 0.2481 nm [25]. However, preliminary calculations showed the instability of silicene sheets on a copper substrate in the presence of lithium between the sheets. Therefore, the value $r_{\text{Cu-Si}}$ was increased to 0.27 nm, which corresponds to the data of [26]. In the center of the channel, between the sheets of silicene, two six-link rings were placed vertically one above the other at the equal distance (in the form of a “column”) to prevent the strong bending of the sheets.

The process of lithization of the bilayer silicene on the substrate was carried out using the periodic pairwise addition of lithium ions to the system. The initial position of the Li⁺ ion pair was chosen randomly on a line parallel to the axis and located near the channel entrance at the level $\frac{h}{2}$. Lithium ions were launched into the channel at intervals of 10 ps, or $10^5 \Delta t$, where $\Delta t = 1 \times 10^{-16}$ s is the time step value. An electric field of $10^3$ V/m had an intensity vector directed along the axis $\hat{o}x$. The charges (ions) moved through the channel under the action of this electric field with Coulomb repulsion. After 10 ps, these ions filled the channel became atoms, and later remained electrically neutral during intercalation. A new pair of ions
was launched every 10 ps, i.e. the time interval required for the calculation of the stress tensor of silicene and the self-diffusion coefficient of Li atoms. When the system began to destroy (in the presence of hexavacancies) or the lithium ions and atoms began to leave the channel actively, the process of lithiation stopped. For example, the saturation process for a silicene channel constructed from sheets with monovacancies lasted 0.75 ns. In addition to visual observation of the system, a jump in the total energy of the system was the channel filling indicator.

The process of delitization occurred in the opposite direction by pairwise removal of lithium ions from the channel. After the removal of Li\(^{+}\) ions from consideration, already leaving the channel at the previous stage, a new pair of ions began to move under the action of the electric field of 10\(^5\) V/m, directed in the opposite direction along the \(\alpha\) axis. The electric field strength supporting the deintercalation process was increased to overcome the energy barrier by ions associated with their exit from the channel. The observation time for the system in this case was increased up to 200 000 time steps.

In the calculations, we used the modified LAMMPS software packaged [27]. It was run on the hybrid cluster type calculator URAN located at IMM UB RAS with the peak productivity of 216 Tflop/s and 1864 CPU.

The self-diffusion coefficient of lithium atoms in the channel was calculated through the average square of the displacement of atoms \(\langle [\Delta \mathbf{r}(t)]^2 \rangle\)

\[
D = \lim_{t \to \infty} \frac{1}{2\Gamma t} \langle [\Delta \mathbf{r}(t)]^2 \rangle,
\]

where \(\Gamma = 3\) is the dimension of space, \(\langle \ldots \rangle\) denote the average over time.

The nature of the interaction of silicene with the copper substrate was investigated with the help of the ab initio calculations. The generalized gradient approximation PBE in the Siesta software package was used [28]. To study the band structure of a silicene monolayer sheet on a copper substrate, a 2×2 silicene supercell consisting of 8 silicon atoms was constructed. The metal substrate was specified by 8 copper atoms located at two possible distances from the lower silicene sublattice (0.27 nm and 0.42 nm). The initial difference between the silicon atoms of the lower and upper silicene sublattices was 0.074 nm. This system was geometrically optimized. Dynamic relaxation of atoms was carried out until the change in the total energy of the system became less than 0.0001 eV. The electronic structure was calculated by integrating in the Brillouin zone using the \(k\)–grid constructed using the Monkhorst–Pack method. The dimension of the \(k\)–grid was 10×10×1. The band structure was calculated in the direction of \(\Gamma\)-K-M-\(\Gamma\). Cutoff energy of the plane wave basis was set equal to 200 Ry.

For the system of monolayer silicene–copper substrate the cohesion energy was calculated according to the formula:

\[
E_{\text{Coh}} = E_{\text{Cu}} + E_{\text{Si}} - E_{\text{Cu-Si}}.
\]

where \(E_{\text{Cu-Si}}, E_{\text{Cu}}, E_{\text{Si}}\) are the total energies obtained as a result of calculations for a monolayer silicene on the copper substrate, a silicene, and the copper substrate, respectively.
RESULTS AND DISCUSSION

The silicene channel on the Cu (111) substrate after complete intercalation with lithium is shown in Fig. 1 in the form of a thin net to show all Li atoms deposited on the channel walls. It is seen that the location of Li atoms in the channel is uneven. The first half of the channel in the direction of the $ox$ axis is filled with Li atoms much more densely than the second half: 33 Li atoms have a coordinate $x \leq 2.6$ nm and only 15 Li atoms are placed in space with a coordinate $x > 2.6$ nm. The bulge relative to the substrate in the middle part of the bottom silicene sheet is observed. The concavity is observed in the same part of the top silicene sheet. A significant narrowing of the channel in the middle part makes it difficult to passage by Li$^+$ ions and limits the channel occupancy by lithium.

Let us consider in more detail the behavior of defects and the belonging of Li atoms to the silicene sheets. Here is the silicene channel with monovacancies filled with lithium completely. The studied configurations refer to the time point of 0.75 ns (or $7.5 \times 10^6 \Delta t$). $Xy$-projections of the top and bottom layers of the channel cut by the middle plane ($z = h_g / 2$) are shown in fig. 2 (view from the $z = h_g / 2$ plane). One of the monovacancies of the bottom sheet was transformed into a large hollow formation. This is a demonstration of the destructive effect of the copper substrate on silicene. In the top sheet, there is a transformation of some monovacancies into cyclic ellipse-shaped formations containing from 7 up to 9 Si atoms. The eight monovacancies of the bottom silicene sheet and the seven monovacancies of the top sheet were deformed but they saved their original shape. The top and bottom parts of the channel have equal volumes. But the number of Li atoms in them is different: 37 Li atoms are in the top part and 30 Li atoms are in the bottom one. The lithium atoms in the channel are located predominantly above the centers of six-membered silicon rings.
Fig. 2. Xy-projections of the top and bottom silicene sheets with monovacancies on the Cu (111) substrate at the time of full lithiation (67 lithium atoms were in the channel).

The behavior of the self-diffusion coefficient $D$ of Li atoms in the channel in the processes of intercalation and deintercalation is unpredictable (Fig. 3). The common features of the behavior of $D$ in all cases under consideration are the high values at the initial part of the intercalation. This is natural, because with a small number of Li atoms in the channel, they are transferred from the Li$^+$ ions to a larger specific value of the impulse, which leads to an increase in the value of the coefficient $D$. However, when the number of Li atoms in the channel becomes more than 20, the relief of the channel walls influences strongly on the mobility of Li atoms. In this regard, the $D$ value as decrease (in the presence of monovacancies), as increase (in the case of bivacancies). The $D$ coefficient behaves also quite unpredictable during deintercalation. The $D$ coefficient can also decrease its values during deintercalating with fluctuation changes (as it happens in the presence of bivacancies in silicene) or almost continuously (when trivacancies are present in silicene). In the case of silicene with trivacancies, a sufficiently strong structural rearrangement is observed in both
silicene sheets. So, in the top sheet some of the defects save their shape. Vertical deformation of the sheets after the process of lithization/delitization is not so significant.

![Image of self-diffusion coefficient](image)

**Fig. 3.** Self-diffusion coefficient of lithium atoms in the process of intercalation (left) and deintercalation (right) in the silicene channels with perfect silicene and silicene having mono-, bi- and trivacancy.

The calculation of the band structure and the density of states (DOS) of a monolayer silicene on the copper substrate show the existence of conductivity (Fig. 4). The silicon atoms in the silicene sheet interact with the copper substrate. This interaction leads to the change in the copper valence from +1 to +2, due to the transition of one electron from the 3d-level to the 4p-level. As a result of the change in the valence, copper behaves as an element of the Fe group. That leads to a stronger interaction of the silicene sheet with the copper substrate because of the hybridization of the metal p-orbital with the silicon p-orbital. The cohesion energy between the silicene sheet and the copper substrate is $-0.48$ eV/atom. As a result of this interaction, the silicon atoms displaced, so that the distance between the lower and upper sublattices increased up to 0.13 nm. At the same time, the distance between the lower sublattice of the nearest metal atoms decreased up to 0.193 nm.
CONCLUSION

Molecular dynamics calculations show that the silicene used in the lithium-ion batteries should have defects only in the form of mono- and bivacancies. The use of perfect silicene and silicene structures with such defects increases by an average of 20% the number of adsorbed Li atoms, compared with the use of the silver substrate to support silicene. The use of silicene with defects in the form of tri- and hexavacancies on the copper substrate as an anode material leads not only to a reduction (relative to small vacancy defects) in the number of adsorbed Li atoms, but also to the destruction of the anode material. Ions and atoms of lithium intercalated into a perfect silicene channel and a channel with mono- or bivacancies on the copper substrate have approximately the same diffusion rate. The diffusion rate increases by more than an order when silicene with tri- and hexavacancies are used. However, the instability of suchsilicene structure does not allow us to take advantage of this. The preferred arrangement of the Li atom in the silicene channel is located above the center of the hexagonal Si ring. At the edges of the silicene sheets, Li atoms tend to be above (or below) Si atoms.

A sufficiently strong interaction of the copper substrate with a silicene monolayer is shown in the quantum mechanical calculations. As a result, silicene is transferred from a semiconductor with a very narrow band gap to a semimetal.

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REFERENCES