ELECTROCHEMISTRY. GENERATION AND STORAGE OF ENERGY FROM RENEWABLE SOURCES

Computer Test of a Silicene/Silicon Carbide Anode for a Lithium Ion Battery

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Abstract—Molecular dynamics is used to study the filling of an anode with lithium. The anode is a defective two-layer silicene on a thin silicon carbide substrate. Lithium ions are deposited from numerous places above the top sheet of the silicene perpendicular to its plane. Bi-, tri-, and hexavacancies serve as defects in the silicene. The silicene sheets deform during lithium intercalation, but the structure of the silicene is retained. None of the defects change their shape appreciably after intercalation is complete. The structure of the SiC substrate is investigated by constructing simplified polyhedra separately for the Si and C subsystems. The C subsystem in crystalline silicon carbide is found to be more disordered than the Si subsystem. It is shown that the type of vacancies in silicene has no appreciable effect on the structure of the substrate. It is concluded that the vertical filling of the anode with lithium can be done when using a combination of silicene and silicon carbide as the anode material of a lithium-ion battery.

Keywords: polyhedron, molecular dynamics, silicene, silicon carbide, lithization, structure

INTRODUCTION

Silicene has great potential for many different applications, mainly because it has amazing electronic properties [1]. The electronic structure of silicene is sensitive to interaction with a substrate. Its chemical composition and spin-orbit coupling allow the fabrication of silicene topological bits and quantum sensors. Silicene is also a material for the production of highly efficient energy devices.

A number of recent works focused on selecting substrates for silicene when it is used as a material for lithium-ion battery (LIB) anodes. It was found that silicene with vacancy defects should be used for this purpose, since the capacitance of a silicene electrode grows notably. In contast, the normal stresses caused by incorporating lithium atoms into the silicene channel are reduced [2–4]. However, the strong adhesion of silicene to metals (Ag, Al, Cu, and Ni) adversely affects the resistance of defective silicene to charge/discharge cycles [5–7]. Silicene with large defects (hexavacancies) is therefore destroyed. In earlier molecular dynamics studies of using silicene anodes, they were filled with lithium in the horizontal direction; i.e., Li$^+$ ions were deposited into a flat silicene channel parallel to its walls. Ions were removed from the channel in the same way, under the action of an electric field [8–10]. However, there is a high probability of crushing the unsupported silicene sheets

when using this way of intercalating lithium into the channel and deintercalating Li$^+$ ions. The vertical way of charging a silicene anode (i.e., by depositing Li$^+$ ions into the silicene channel perpendicular to its walls) was not considered earlier.

Silicon carbide (SiC) currently finds wide application in electronics [11]. It is used to make high temperature rectifier diodes, FETs, LEDs, and UV detectors. It is also a potential material for high-power microwave devices and heat- and radiation-resistant integrated circuits. It can be used on its own as an anode, but its capacity relative to lithium is quite low [12]. The capacitance of an electrode can be increased by combining a SiC film with two-layer silicene, (i.e., by using a combined silicene/SiC anode).

The aim of this work was to study the behavior of a combined silicene/SiC anode when it is filled with vertically directed lithium ions. Special attention is given to the structural changes that occur in the considered anode.

MOLECULAR DYNAMICS MODEL

A thin film of silicon carbide (α-SiC) supporting a two-layer defective silicene when this silicon material is filled with lithium had a wurtzite structure (Fig. 1). The hexagonal surface of the α-SiC film or the cationic basal surface (0001) was oriented parallel to the
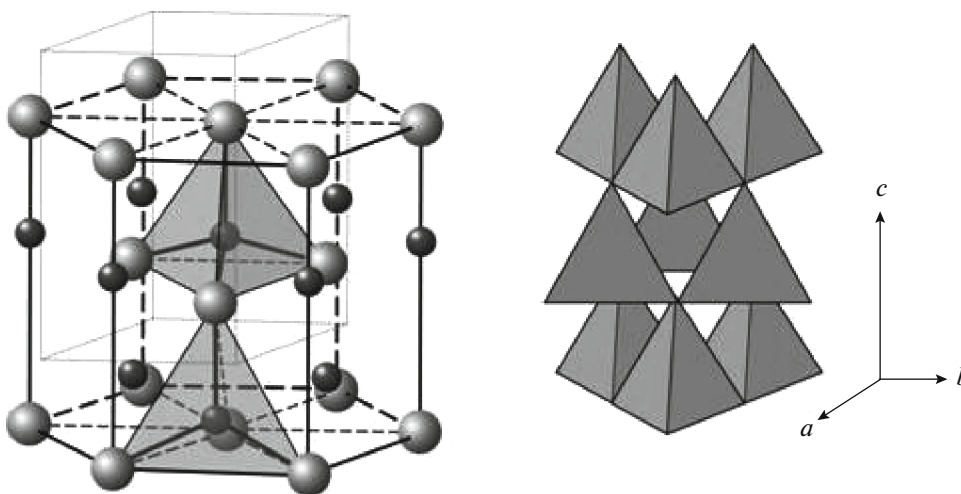
Fig. 1. Left, general view of the wurtzite structure with a α-SiC modification of silicon carbide. Right, tetrahedral nodes occupied by one type of atoms are highlighted. The system of coordinate axes is shown.

silicene sheets, which formed a flat channel with a gap of 0.75 nm. The film was formed by 6000 Si and C atoms. Each atom of one element in the wurtzite structure was surrounded by four atoms of another element. Replacing Si atoms in this structure with C atoms converts polymorphic α-SiC into hexagonal diamond, which can be obtained from the cubic diamond structure with a slight modification. (In nature, hexagonal diamond is found in some meteorites.) Each sheet of silicene contained nine polyvacancies, which were represented by bi-, tri-, and hexavacancies. The silicene sheet could contain 510, 501, and 474 Si atoms, depending on the type of vacancy defects. The corresponding sheet of perfect silicene contained 528 Si atoms.

The initial specified distance between the lower silicene sheet and the SiC substrate was 0.27 nm. Interactions between Si atoms inside the silicene sheets and interactions between Si and C atoms in the SiC compound were represented using the Tersoff potential [13, 14]. The interaction between Si atoms belonging to different silicene sheets, and between the Si atoms of silicene and the atoms of the substrate (C and Si), was described in terms of the Morse potential, using the parameters in [15]. The Lennard–Jones potential was used to describe Li–Li, Li–Si, Li–C interactions with the parameters in [16].

Each lithium ion was deposited in the silicene channel every 10 ps with time step $\Delta t = 10^{-16}$ s. New Li$^+$ ion was launched from a new position, while the previous ion lost its electric charge (i.e., became a neutral atom). A total of 151 ions were deposited. The last five attempts were unsuccessful (i.e., the deposited ions were never adsorbed by the system). As a battery charges, lithium ions acquire electrons on the anode, since it has a negative electrical potential. The Li$^+$ ions deposited in the model moved in electric field **E** with

a strength of 10^4 V/m. All calculations were made for a temperature of ~300 K in the NVE ensemble. Full free boundary conditions were used in whole SiC + Li system.

Constructing Voronoi polyhedra (VPs) is a natural way of using computers to study the structure of nanoscale systems. VPs create a direct geometric image of an atom's immediate environment. Statistically established topological characteristics are the distributions of VPs according to the number of faces and the distribution of faces according to the number of sides they contain. There are different ways of using statistical geometry based on constructing VPs or modifications of them. If a system consists of two or more types of atoms, we can construct partial polyhedra in which atoms of only one type participate. The thermal motion of atoms often makes it difficult to decipher the local structure. Small displacements of atoms produce small geometric elements (faces and edges) in VPs. It is therefore logical to exclude small elements in polyhedra from consideration in order to improve the efficiency of statistical geometry. In reality, this results in considering coarse or simplified polyhedra (SP) [17]. Both approaches are used in this work to perform a detailed analysis of the structure of a SiC substrate (i.e., partial simplified polyhedra are analyzed).

RESULTS AND DISCUSSION

Defective silicene on a SiC substrate is fairly stable when the silicene/SiC system is filled vertically with lithium. Figure 2 shows horizontal projections of fragments of both silicene sheets with polyvacancies after deposition and moving to system 151 of Li$^+$ ions. The figure also reflects the Li atoms adsorbed on each fragment of the silicene sheets. We can see the defects in
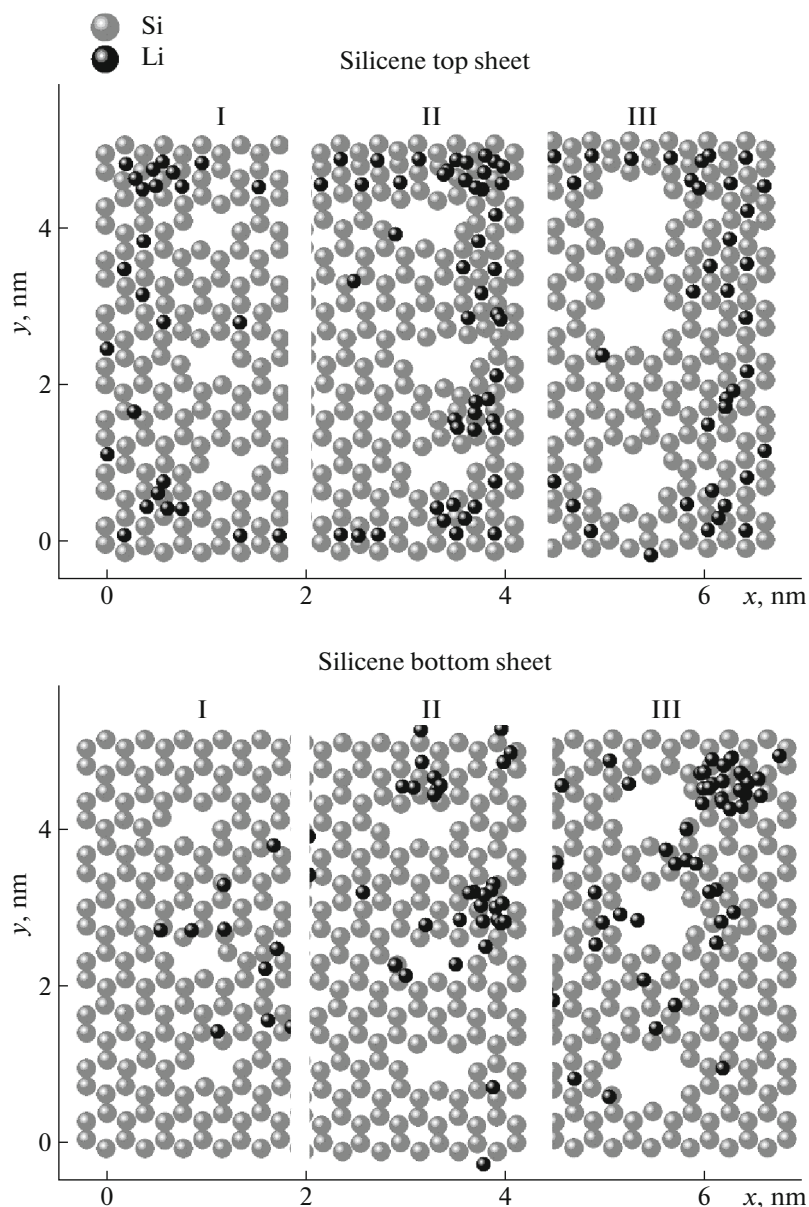
Fig. 2. *xy*-Projections of fragments of the upper and lower sheets of silicene with bi- (I), tri- (II), and hexavacancies (III) when the silicene channel is deposited on the SiC substrate after lithium adsorption ($t = 1.51$ ns). The numbers on the coordinate axes reflect the length and width of the full silicene sheet.

silicene retained their shape quite well up to 1.51 ns, especially in the top sheet of silicene. Regardless of the type of vacancy defects, the Li atoms on the outside of the top sheet tended to be along its perimeter. At the same time, Li atoms trapped in the channel were on the lower silicene sheet, either in the form of clusters near and along the boundaries of polyvacancies or scattered in the middle.

The top sheet and the silicene channel were not yet completely filled with lithium. The top sheet of silicene bent upon the vertical deposition of Li atoms, while the bottom one became convex. The silicene channel thus narrowed, keeping new Li atoms from

penetrating into it. A small fraction of Li atoms still passed under the bottom sheet, however, but lithium did not get inside the SiC substrate. The resulting deformation of silicene sheets was similar to the deformation observed when a channel located on a graphite substrate was horizontally filled with lithium [18].

The substrate made of a dense material (silicon carbide) did not bend when the system was filled vertically with lithium. However, the structure of the SiC substrate material itself changed. These structural rearrangements can be described by performing a structural analysis based on constructing simplified polyhedra (SPs).
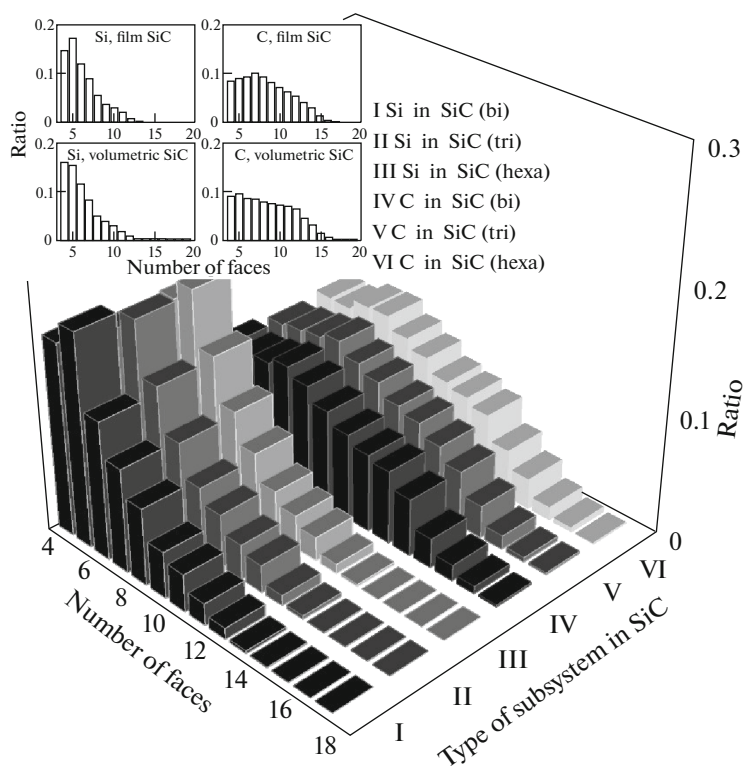
Fig. 3. Fraction of faces of simplified polyhedra constructed for Si and C atoms in a silicon carbide substrate containing a silicene channel with defective walls, filled vertically with lithium. The inset shows the corresponding SP distributions obtained for the carbon and silicon subsystems when there is an empty defect-free silicene channel on the SiC substrate, along with the SP n-distributions calculated for bulk SiC.

Excluding small geometric elements (faces and edges)—i.e., moving from Voronoi to simplified polyhedra—allows us to simplify a structural analysis of the considered atomic packings. The distributions (Figs. 3 and 4) resulting from the vertical filling of the system with lithium were obtained at 1.51 ns. To test the reliability of our results, we extended our MD calculations by another 1 million time steps (by 0.1 ns) without adding lithium ions to the system. The distributions shown in Figs. 3 and 4 did not change appreciably (by more than 1%), so the calculated distributions of SPs according to the number of faces (the n-distribution), and those of faces according to the number of sides (the m-distribution), are reliable. Each subsystem of the SiC substrate had specific n-distributions. The n-distributions of the Si subsystem are characterized by maxima at $n = 5$, while the maximum of such distributions for the C-subsystem falls when $n = 7$. To clarify the cumulative effect produced by defects in the silicene and filling the channel with lithium, we calculated the n-distributions of SPs for Si and C subsystems of bulk silicon carbide with identical structures and the SiC substrate when the silicene channel on it had no defects and was not filled with lithium. Each of these calculations were for a duration of 0.15 ns. Results from these calculations are presented in the insets in Figs. 3 and 4. The n-distribu-

tions for Si and C subsystems with no lithium filling of the system were generally similar to ones obtained for systems filled with lithium and having defects in the silicene channel. Small differences between them were expressed by a slightly higher main peak (at $n = 5$) in the distribution for the Si subsystem and a smoother drop (after passing the maximum at $n = 7$) in the distribution for the C subsystem with no lithium filling. Greater differences appeared in the n-distributions obtained for bulk SiC, where the main peaks shifted by $n = 4$ and 5 for the n-spectra of the Si and C subsystems, respectively.

CONCLUSIONS

Changes in the shape of the n-distributions indicate that the main structural differences between the systems presented here occurred upon moving from a $3d$ to a $2d$ SiC structure. Structural changes caused by defects in the silicene channel and its lithium filling can be considered secondary. The form of the n-distributions indicates the C subsystem in the SiC substrate was more disordered than the Si subsystem. This was due to the higher mobility of C atoms, the mass of which is 2.3 times less than that of Si atoms. We can also see from the n-distributions that the structure of
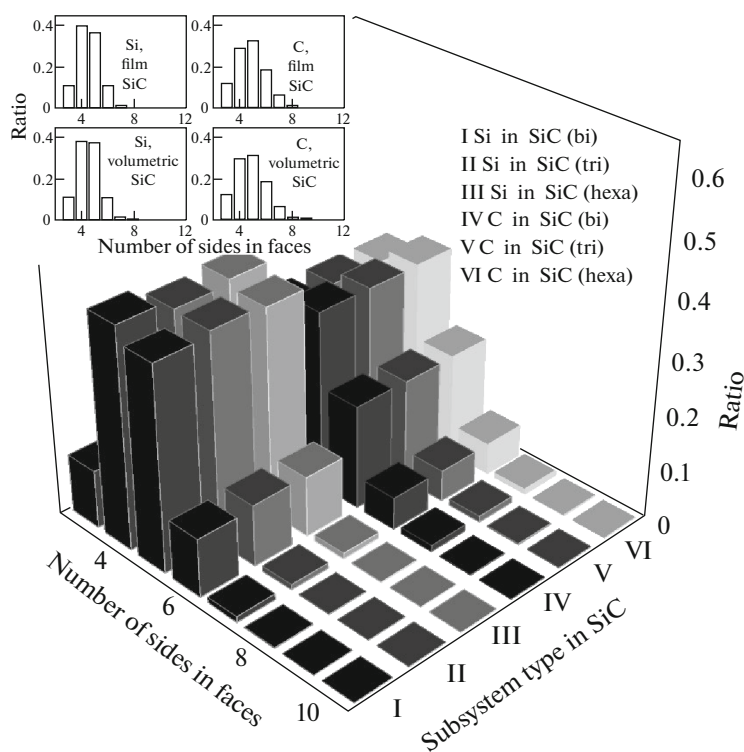
Fig. 4. Fraction of sides in faces of simplified polyhedra constructed for Si and C atoms in a silicon carbide substrate containing a silicene channel with defective walls, filled vertically with lithium. The inset shows the m-distributions obtained for a SiC substrate with a defect-free silicene channel when there is no lithium filling of the system, along with the corresponding distributions for bulk SiC.

the SiC substrate depends weakly on the type of vacancies in the walls of the silicene channels.

The distributions of the number of sides in the SP faces obtained for the Si and C subsystems of the SiC substrate differ in the shape of the spectra and the location of their maxima. In the Si subsystem, the maximum of the m-distribution is observed at $m = 4$. In the C-subsystem, it is at $m = 5$. The considerable fraction of fifth-order symmetry in the structure of the C-subsystem indicates there is more disorder than in structural arrangement of the Si subsystem. We can see the dependence of the m-distributions on the type of vacancy defects in the walls of the silicene channel is very weak. The locations of the maxima of the m-distributions for the Si and C subsystems do not change if the system is not filled with lithium and there are no polyvacancies in the walls of the silicene channel (see inset in Fig. 4). This is also true of m-distributions obtained for the bulk SiC system. Changes in the m-distributions that occur upon moving to systems not filled with lithium (including bulk SiC) are less noticeable than for n-distributions. The considered n-distributions of the studied systems are therefore a more accurate indicator of structural changes than the corresponding m-distributions.

Computer tests show that a two-layer defective silicene and a thin SiC substrate supporting it can be con-sidered a potential material for the anode of a lithium-ion battery at a vertical lithium intercalation. The type of defects in the walls of the silicene channel has little effect on the structure of the SiC substrate.

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CONFLICT OF INTEREST

The author declares he has no conflicts of interest.

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