Effect of Electric Field on Lithium Ion in Silicene Channel. Computer Experiment

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Abstract—The molecular dynamics method is used to study the drift of Li^+ ions exposed to electric interactions in a planar channel formed by silicene sheets. The character of dynamics of the ion and also its effect on mechanical properties of silicene sheets are used to determine the optimum size of the planar channel clearance. Instability of the surface (4 × 4) structure of free bilayer silicene is demonstrated. Mobilities of Si atoms and distributions of the main stresses in silicene appearing in the course of lithium ion movement along the channel are calculated.

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INTRODUCTION

The prospect of replacement of a graphite electrode by a silicon one in a lithium-ion battery is imposed by the fact that silicon is characterized by a much higher theoretical capacity (4200 mA h/g vs. 372 mA h/g). Silicon nanoparticles have much lower bulk density and higher specific surface area than massive crystalline silicon [1-3]. Search for the honeycomb silicon structure (silicene) similar to the graphene structure consisting of carbon atoms is being performed lately. Stability of such a structure has been predicted theoretically [4]. As opposed to graphene with its planar geometry, silicene has a texturized geometry with bulging corresponding to certain atom groups, as if two sublattices were displacing each other in the vertical direction. Silicene sheets were synthesized on a Ag(111) support [5-7]. Charge carriers in monolayer silicene can act as massless Dirac fermions, as the valence and conductivity bands intersect linearly in the region of the Fermi level. Silicene is of considerable interest for electronics due to its compatibility with the existing electronic devices based on silicon [8, 9]. It is essential that transition from monolayer silicene to bilayer silicene was accompanied by preservation of its remarkable electronic properties [10].

The results show that bilayer silicene with AB packing can be characterized by a 2D lattice and is synthesized much more easily than a monolayer silicene of a similar size. Linear dispersion near points K and K' of the hexagonal Brillouin zone is observed for such bilayer silicene. Thorough analysis was carried out within the framework of strong bond approximation to elucidate the character if low-energy electron excitations of massless Dirac fermions in bilayer silicene [8]. The obtained characteristics imply the possibility of appearance of new phenomena favorable for development of high-performance electronic devices.

The honeycomb structure with a negligible distorted geometry can exist in the form of an AA or AB packing, each of which forms stable bilayer silicene. Each layer of bilayer silicene has the same effect on its stability. The structure of bilayer silicene is formed due to the combination of the sp^2 and sp^3 hybridization. Bonds in bilayer silicene contain more sp³ hybridization components that bonds in monolaver silicene. Bilayer silicene with the AB packing is characterized by a lower bond energy (5.32 eV) that silicene with the AA packing (5.25 eV) or multilayer silicene (5.13 eV) [11]. Flexibility the Si–Si bond results in obtaining various local nonplanar devices with slightly different energies. Different periodical structures are observed for silicene on Ag(111), such as (4 \times 4), ($\sqrt{7}$ \times $\sqrt{7}$) R19.1°, and ($\sqrt{13} \times \sqrt{13}$) R13.9° [12, 13].

The main problem revealed while using bulk silicon as an anode material is that silicon breaks down easily in the course of the charge–discharge cycles. The porous structure eliminates to a certain extent the problem of degradation when silicon is expanded in the course of absorbing lithium during the charging and when it is compressed during the discharge [14]. It is suggested to use chemical vapor deposition to apply carbon coatings of highly elastic carbon black onto Si [15]. Addition of carbon atoms allows maintaining a more stable electric contact between silicon particles. Degradation of deformed silicon can be related to reorganization of local atomic electric fields. A decrease in the silicon film thickness reduces variability of superposition in the change in atomic electric fields; stability with respect to lithium intercalation—deintercalation cycles is improved. Physical properties are also changed. Thus, a 16-fold decrease in thermal conductivity with respect to the bulk material is observed for a 9 nm thick Si membrane [16]. This is explained by a decrease in the free path length of phonons due to diffuse scattering at the edges.

Electric fields on the atomic scale are characterized by much higher values of field strength than the usually applied fields. Interatomic forces used in molecular dynamics simulations are ultimately determined by the properties of electrons, according to which atomic units are chosen. The atomic unit of electric field strength is the $E_h/ea_0 = 5.14220652 \times 10^{11} \text{ V/m},$ where $E_h = 4.35974417(75) \times 10^{-18}$ J, the Hartree unit, e is the elementary electric charge, a_0 is the Bohr radius. Studying multiple electron scattering in the SrTiO₃ ceramic and electron momentum transfer allowed determining the quantitative characteristics of the atomic electric field [17]. The maximum field strength near the oxygen atoms as measured by a probe was 4×10^{11} (V/m) and that in the vicinity of Ti and Sr atoms was 10^{12} (V/m). The measurement accuracy is determined by the microscope resolution.

An important characteristic of the anode is intercalation capacity, i.e., the charge that can be accumulated on the electrode after full charging per unit mass or volume. Full carbon electrode charging leads to formation of the LiC_6 compound, so that intercalation capacity is 0.167. The corresponding value for silicon is much higher (theoretically, by 26.4 times), because silicon can form lithium compounds containing up to 4.4 Li atoms per 1 Si atom. Intercalation of lithium into crystalline silicon causes an intense increase in specific volume resulting in degradation of the electrode. However, thin films of amorphous silicon are not destroyed during intercalation of lithium [18–20].

With account for similarity to graphene, it is natural to consider silicene as a potential material for application in lithium—ion batteries. The almost 4-fold swelling in the bulk of a crystalline silicon anode ultimately results in its degradation in the course of the lithium ion intercalation—deintercalation cycles. Analysis showed that a change in the volume of monolayer and bilayer silicene as a result of full lithiation corresponds to the increase of 13 and 24%, respectively. Besides, silicene is restored to the initial state after delithiation, unlike crystalline Si [21].

The aim of this work is to study the movement of the Li^+ ion between the sheets of bilayer silicene in a constant electric field, to determine the optimum value of field strength and the minimum clearance

value that does not hinder the ion motion in the planar channel.

COMPUTER MODEL

Calculations are carried out using the method of classical molecular dynamics. Interactions in silicene are represented using Tersoff potential [22]:

$$U^{\mathrm{Ter}} = \frac{1}{2} \sum_{i} \sum_{j \neq i} f_{c}(r_{ij}) \{ f_{R}(r_{ij}) + b_{ij} f_{A}(r_{ij}) \},$$

$$f_{R}(r) = A \exp(-\lambda_{1}r),$$

$$f_{c}(r) = \begin{cases} 1, & r < R, \\ \frac{1}{2} + \frac{1}{2} \cos \frac{\pi(r - R)}{S - R}, & R < r < S, \\ 0 & r > S, \end{cases}$$
(1)

$$f_{A}(r) = -B \exp(-\lambda_{2}r), \quad b_{ij} = (1 + \beta^{n} \zeta_{ij}^{n}),$$

$$\zeta_{ij} = \sum_{k \neq i,j} f_{c}(r_{ik})g(\theta_{ijk}),$$

$$g(\theta) = 1 + \frac{c^{2}}{d^{2}} - \frac{c^{2}}{d^{2} + (h - \cos \theta)^{2}}.$$

Here, indices *i*, *j*, *k* indicate silicon atoms, r_{ij} is the length of the *i*–*j* bond, θ_{ijk} is the angle between bonds *i*–*j* and *j*–*k*. The parameters of this potential are provided in the table.

This potential describes sufficiently accurately interactions of particles in semiconductors, in which the structure largely affects the properties of the materials. It is an empirical potential with parameters chosen on the basis of experiments. The analytical expression for Tersoff potential function can be expressed in the form of modified isotropic Morse potential.

Interaction between Si atoms belonging to different silicene sheets was described by Morse potential [23]:

$$\Phi(r) = D_e \left[\exp\{-2\alpha(r - r_e)\} - 2\exp\{-\alpha(r - r_e)\} \right], (2)$$

where D_e is the potential well depth, α is the rigidity parameter, r_e is the equilibrium bond length. Morse potential was also used to represent interaction between the Li⁺ ion and Si atoms [16, 17]. Parameters of this potential were determined on the basis of the corresponding data for description of Li–Li [23] and Si–Si interactions [24]. If parameters of Morse potential for representing interactions between atoms of type *i* and between atoms of type *j* are known, then parameters of *i*–*j* interactions are obtained from simple interpolation relationships [24]:

$$D_{e}^{ij} = (D_{i}D_{j})^{1/2}, \quad \alpha^{ij} = \frac{1}{2}(\alpha_{i} + \alpha_{j}),$$

$$r_{e}^{ij} = (r_{e}^{i}r_{e}^{j})^{1/2}.$$
(3)

A, eV	<i>B</i> , eV	λ_1, nm^{-1}	λ_2, nm^{-1}	λ_3 , nm ⁻¹	п
1830.8	471.18	2.4799	1.7322	0	0.78734
С	d	<i>R</i> , nm	<i>S</i> , nm	β	h
1.0039×10^5	16.217	0.27	0.30	1.1×10^{-6}	-0.59825
$D_e^{\mathrm{Si-Si}}$, eV	α^{Si-Si}, nm^{-1}	$r_e^{\text{Si-Si}}$, nm	$D_e^{\mathrm{Li-Si}}$, eV	α^{Li-Si} , nm ⁻¹	$r_e^{\text{Li-Si}}$, nm
0.2274	15.390	0.44992	0.30932	11.6445	0.36739

Parameters of Tersoff and Morse potentials for representation of the Si–Si and Li–Si interactions [15–17]

The parameters of Morse potential are given in the table.

Here, we consider the case of reconstruction of a 4×4 surface area. A unit cell in such a silicene structure (contained in the rhombus in Fig. 1) includes 18 Si atoms. Six Si atoms in the unit cell are shifted to the distance of 0.074 nm normally to the surface, while other Si atoms are located on a common (initial) plane. Such a silicene sheet structure is close to the silicene surface observed on a Ag(111) support [25]. While atoms bulging from the initial surface in the



Fig. 1. Schemes of arrangement of atoms at time t = 0: (1) frontal view of plane y0z; (2) side view of plane x0z with the Li⁺ ion before the channel. (3) Top view of the 4×4 silicene structure at the initial moment of time. Open circuits are Si atoms displaced normally to the surface, solid circles are Si atoms in the initial plane. An outline shows a unit surface cell of the silicene sheet. Electric field strength is directed along axis 0x. At the initial moment of time, the Li⁺ ion was located before the y0z plane on the outside of the channel.

upper bilayer silicene sheet are shifted upwards, such atoms in the lower sheet are projecting downwards. We used 6 values of distances h_g between the silicene sheets: 0.50, 0.55, 0.60, 0.65, 0.70, and 0.75 nm. These distances exceed by far the distance of 0.2481 nm between the sheets of bilayer silicene with the AB packing obtained in calculations using the density functional theory¹. However, such a set of distances covers the range of clearances used for studying movements of the Li⁺ ion in the electric field between the graphene sheets [26] and through porous graphene membranes [27].

Silicene sheets containing 406 atoms each are rectangular, 5.5×4.7 nm (14 atoms along each sheet edge). High electrode capacity is attainable when ions of electrolyte move fast, so that the self-diffusion coefficient of the ion would be in the range of 10^{-10} to 10^{-13} cm²/s [28]. We showed in computer experiments [27] with the clearance of 0.50-0.65 nm between graphene sheets that such an effect is obtained starting with electric field strength of about 10^3 V/m. Constant electric field with the strength of 10^3 V/m drove the Li⁺ ion along the *ax* axis oriented along the "zigzag" direction of the graphene sheets. Graphene sheets were arranged according to the Bernal packing (ABAB...) in exactly the same way as in bulk graphite.

Numeric solution of motion equations was obtained using the fourth order Runge–Kutta method with time step $\Delta t = 2 \times 10^{-16}$ s. Duration of each calculation with clearance h_g was 0.5 million time steps. In calculations, a modified code for parallel calculations using the molecular dynamics method, LAM-MPS, was used [29]. Program segments were added for calculation of kinetic and mechanical properties of the system. We used no scale modeling of time events, despite the fact that the character of the movement of Si atoms and the Li ion is quite different. An increase in the time step for modeling the ion movement could result in the significant overlapping of volumes of different kinds of particles and therefore in an increase in the system temperature. Besides, owing to intensive

¹ Wang R., Wang S., Wu X. arXiv:1305.4789v2 [cond-mat.meshall] 23 May 2013. http://www.researchgate.net/publication/236871722.

interaction of the ion with Si atoms, periodical skipping of accounting for a number of interactions at a larger time step could greatly distort the true ion path. Calculations were carried out using a URAN cluster type hybrid computing machine in Krasovskii Institute of Mathematics and Mechanics, Ural Division, Russian Academy of Sciences, with the peak performance of 216 Tflop/s and 1864 CPU.

The initial location of the ion corresponded to the height of $h_g/2$. At t = 0, the ion was located across from the hollow formed by rows of Si atoms of the lower silicene membrane closest to the sheet middle (Scheme 1, Fig. 1).

Despite the fact that interaction between the parallel silicene sheets decreases fast at an increase in the distance between them and becomes weak in the distance range under consideration (0.50-0.75 nm), the

movement of the Li⁺ ion in this interplanar clearance is not free. This is related to the fact that strong covalent bonds acting in the silicene plane allow only for

insignificant corrugation of the sheets when the Li⁺

ion moves. When the Li⁺ ion is affected by van der Waals forces from close–packed Si atoms of silicene sheets, it becomes slower.

The self-diffusion coefficient is determined by the mean square of atomic displacement $\langle [\Delta \mathbf{r}(t)]^2 \rangle$ [30]:

$$D = D_{xy} + D_z = \lim_{t \to \infty} \frac{1}{2\Gamma t} \left\langle \left[\Delta \mathbf{r}(t) \right]^2 \right\rangle, \tag{4}$$

where $\Gamma = 3$ is the space dimension. $\langle ... \rangle$ denotes time averaging.

For calculation of stresses appearing in silicene, the semiconductor sheets were divided into elementary areas. Stresses $\sigma_{u\alpha}(l)$ appearing under direction forces α (= x, y, z) are calculated in each area with number *l* with orientation *u*. In these calculations, products of projections of atom velocities and projections of forces

 f_{ij}^{α} acting on area *l* on the side of other atoms are used under the corresponding conditions [31]:

$$\sigma_{u\alpha}(l) = \left\langle \sum_{i}^{k} \frac{1}{\Omega} \left(m v_{u}^{i} v_{\alpha}^{i} \right) \right\rangle + \frac{1}{S_{l}} \left\langle \sum_{i}^{k} \sum_{j \neq i}^{(u_{i} \leq u, u_{j} \geq u)} \left(f_{ij}^{\alpha} \right) \right\rangle.$$
(5)

Here, k is the number of atoms on area l, Ω is the vol-

ume per atom, *m* is the atom mass, v_{α}^{i} is the α -projection of the velocity of atom *i*, S_{l} is the area of area *l*. Conditions of summation over *j* in the last sum in expression (5) are reflected both in the lower and upper sum indices; the force resulting from interaction of atoms *i* and *j* passes through area *l*; u_{i} is the current coordinate of atom *i*; in the upper sum index, *u* corresponds to the coordinate of the point of intersection of the straight line passing through centers of atoms *i* and *j* with area *l*.



Fig. 2. Trajectory of movement of the Li⁺ ion in a planar channel formed by silicene sheets at the clearance of 0.70 nm and electric field strength of 10^5 V/m: (1) the initial point of the trajectory, (2) final point. The coordinates are given in nm.

CALCULATION RESULTS

Electric field strength of 10^3 V/m proved to be insufficient for the Li⁺ ion to enter the planar channel formed by silicene sheets with the clearance of 0.50 nm. In this case, the ion, having walked for some time in front of the entrance to the channel, descended and passed on the outer side of the channel to its exit in the direction of the field (axis 0x) interacting with the Si atoms of the lower sheet. Then it leaves the exit behind and went forward and upward. After long walking around the entrance, the Li⁺ ion finally entered the channel at $h_{\rm g} = 0.50$ nm and at field strength of 10^4 V/m. But its slow motion inside the channel was limited to reaching coordinate x = 0.8 nm near which it remained at t = 100 ps. When field strength was increased to 10^5 V/m, the ion spent half the assigned time searching for the possibility to enter the channel. Having entered it, it advanced to almost the same distance (0.8 nm) along axis 0x, changed its direction while walking and having passed along the 0y axis exited the channel.

The Li⁺ ion could not pass the whole channel in the field direction and exit it on the opposite side at h_g from 0.50 to 0.75 nm, when the field strength was 10^3 to 10^4 V/m. Almost the same pattern was observed at $E = 10^5$ V/m, to the exclusion of $h_g = 0.70$ nm. The trajectory of the Li⁺ ion corresponding to this phenomenon is shown in Fig. 2. In this case, when the ion reaches the exit at the opposite side of the channel, it leaves the channel moving in a straight line forward and downwards. An increase in clearance to 0.75 nm at the same field strength (10^5 V/m) yielded no such



Fig. 3. Configuration of the system of "the lithium ion in bilayer silicene" obtained up to the time of 100 ps at the electric field strength of 10^5 V/m with the clearance between the sheets of 0.55 nm.

effect: the ion walked in the channel during the whole period of 100 ps.

As a rule, the ion remains within the channel in the period under consideration. A typical configuration of the system of "Li⁺ ion in bilayer silicene" obtained by time moment 100 ps is shown in Fig. 3. The Li⁺ ion forms a much stronger bond with silicene than with graphene. Therefore, the predicted behavior consisting in the lithium ion passing the whole sheet in the direction of the applied electric field and leaving the channel on the opposite side from the entrance occurs here at much higher field strength (10^5 V/m against 10^3 V/m) and greater clearance (0.70 nm against



Fig. 4. Interaction energy of the lithium ion with silicene at the electric field strength of 10^5 V/m and clearance h_g between the layers being: (1) 0.5 nm, (2) 0.6 nm, (3) 0.7 nm.

0.60 nm) than in the case of intercalation of such an ion into bilayer graphene. Thus, the field strength of 10^5 V/m and clearance of 0.70 nm are determined as the optimum values for movement of the lithium ion in a planar silicene anode.

Energy U of interaction of the Li^+ ion with silicene depends directly on the position of the ion in the silicene channel or beyond it. Therefore, the value of Uindirectly depends on the electric field strength determining the motion of the ion in the channel. Figure 4 shows function U(t) for the case of $E = 10^5$ V/m for clearances between Si layer being $h_{\rm g} = 0.5, 0.6,$ and 0.7 nm. At such field strength, the Li^+ ion can enter the channel even at $h_{\rm g} = 0.5$. However, movement in a narrow channel proves to be very constrained and occurs at sufficiently high interaction energy U. Having overcome not more than a quarter of the channel length in the direction of ox and having undergone significant energy fluctuation, the ion leaves the channel up to the time of 80 ps. From this moment, the potential energy of the ion becomes zero. Considerably lower values of ion energy U are obtained at the channel clearance of 0.6 and 0.7 nm. In the case of $h_{\rm g} =$ 0.6 nm, the low energy values are preserved during the whole time of observation of the system, as the ion does not leave the channel in 100 ps. At $h_g = 0.7$ nm, the Li⁺ ion remains in the channel for only 40 ps. In this time, it passes the whole channel. Its potential energy becomes zero when t > 40 ps.

Self-diffusion coefficients D of Si atoms don't depend on Li⁺ ion velocity or field strength E. Mobility of Si atoms in the bottom silicene layer almost at all h_g is higher than that in the top layer (Fig. 5). Decreasing Si atoms mobility along with increasing the clearance from 0.50 to 0.65 nm is due to slackening of



Fig. 5. Self-diffusion coefficient of the Si atoms in bilayer silicene: (1) in the top layer, (2) in the bottom layer, (3) average for both layers.



Fig. 6. Horizontal components of the self-diffusion coefficient of the Si atoms in bilayer silicene: (*1*) in the top layer, (*2*) in the bottom layer.

mutual influence of the silicene sheets with $h_{\rm g}$ rise. Sharp increase of D value upon going of h_g from 0.65 to 0.70 nm is due to sufficient enhancement of the channel passability by Li⁺ ion, and therefore increase of the intensity of the ion interaction with Si atoms. By virtue of Li⁺ ion does not leave the flat channel with h_{g} of 0.75 nm, and upon its movement for the observation time it covers much than half of silicene area decelerating Si atoms, the average mobility of Si atoms decreases but insufficiently. As it seen in Fig. 6 the behavior of horizontal components of Si atoms mobility is analogous to above described. According to quantitative values of D and its components it is precisely horizontal mobility of atoms is the factor determining the behavior of Si atoms. This fact can be explained by existence of oriented covalent bond between silicon atoms.

The presence of the Li⁺ ion creates additional stress in silicene. This is mainly reflected in considerable enhancement of stress component σ_{zz} that grows by tens of times. In silicene free of the Li⁺ ion, components σ_{zx} , σ_{zy} , and σ_{zz} are of about the same order of magnitude. Distribution of the analyzed stresses over elementary areas elongated along axis oy in the case of intercalation of the Li⁺ ion in bilayer silicene with the clearance of 0.7 nm is shown in Fig. 7. As seen from distributions in the figure, the direction of growth of stresses is strongly reoriented towards vertically directed forces (0z). And the greater the surges of stress σ_{zz} correspond to the middle part of the sheets. But peak stresses σ_{zz} are still lower than similar surges of the corresponding stress appearing during the motion of the Li⁺ ion through the channel formed by graphene sheets [27].

The dependence of the character of stresses σ_{zz} in silicene along axis 0y on the clearance in the case of



Fig. 7. Average distribution of stresses in the silicene plane: (1) σ_{xz} , (2) σ_{yz} , (3) σ_{zz} in the case of intercalation of the Li⁺ ion at the field strength of 10^5 V/m into the planar channel with the clearance of 0.70 nm. Elementary areas are elongated along axis 0y.

motion of the Li⁺ ion at the field strength of 10^5 V/m can be seen in Fig. 8. Stress peaks σ_{zz} can appear on both edges of silicene sheets in direction 0y normal to field strength. These oscillations are significant at low clearances ($h_g = 0.50$ and 0.60 nm) and undergo a decrease by half at $h_g = 0.70$ nm.

Initial roughness R_a corresponding to the profile formed by bilayer silicene on an Ag support decreases fast to practically zero values (Fig. 9), i.e., silicene sheets flatten before the Li⁺ ion enters the planar channel. In other words, the experimentally observed [25] profile of bilayer silicene on a silver support proves to be unstable, as soon as silicene leaves the support. As the Li⁺ ion moves inside the planar channel, R_a grows fast and reaches relatively stable values already in approximately 20 ps. But these values are lower than the initial roughness characteristic for silicene formed on an Ag support. Further, in 40 ps, R_a somewhat decreases (up to 11%) in the case of small clearances ($h_g = 0.50$ nm) and increases (by ~3%) for larger clearances ($h_g = 0.70$ nm).

In this work, the molecular dynamics method was used to study the motion of the Li⁺ ion between the silicene sheets exposed to constant electric field with the strength of 10^3-10^5 V/m. The clearance of 0.50 to 0.75 nm was formed between the graphene sheets with



Fig. 8. Average distribution of stress σ_{zz} in the silicene plane at the field strength of 10^5 V/m at clearances h_g between the top and bottom layers being (1) 0.5 nm, (2) 0.6 nm, (3) 0.7 nm. Elementary areas are elongated along axis 0x.

a (4×4) reconstructed surface. The bilayer silicene structure corresponded to the AB packing. The Li⁺ ion completely passed the planar channel in 100 ps in the field direction at the clearance of 0.70 nm and field strength of 10^5 V/m. In other cases, the ion either passed around the channel, or left the intersheet space in the direction differing from the direction of the field, or got stuck in the channel. The roughness of silicene corresponding to the Ag support completely disappeared even before entering the channel. When the ion moves along the channel, the value of $R_{\rm a}$ assumes a new value (lower than the initial one) that changes in time as dependent on the clearance between the silicene sheets. The ion entering the channel corresponds to the time periods of negative values of the silicene-Li interaction energy. Mobility of Si atoms tended to decrease at an increase in the clearance to 0.65 nm and then grew drastically at the further increase in the clearance. The similar behavior was characteristic of horizontal mobility components of Si atoms in the silicene sheets. When the ion moved along the channel, significant fluctuation in stresses σ_{zz} exceeding by tens of times fluctuation of stresses σ_{zx} and σ_{zv} appear in the distributions along the length and width of the silicene sheets. The location and range of strong fluctuations of σ_{zz} depend on the clearance between the graphene sheets.



Fig. 9. Roughness of bilayer silicene for intercalation of the Li⁺ ion at the field strength of 10^5 V/m and clearances h_g between the layer being (1) 0.5 nm, (2) 0.7 nm.

RESULTS AND DISCUSSION

Let us turn out attention to the movement of the Li⁺ ion in silicene and compare it with the movement of an electrically neutral Li atom. Two motion types are distinguished for a freely diffusing (in the absence of external field) Li atom: in the direction parallel to the silicene sheet surface and in the direction normal to the surface. When a lithium atom jumps to a free node (vacancy) on the silicene surface, it passes between two adsorbing nodes overcoming the energy barrier of 0.23 eV [32]. This barrier is almost three times lower than the energy barrier calculated for diffusion in bulk crystalline and amorphous silicon $(\sim 0.6 \text{ eV})$ [33]. The Li atom also can diffuse from the node it occupies to the free node across the silicene layer. Such a path implies passing the energy barrier of 1.07 eV [32]. Here, the Li atom passes through the center of a hexatomic Si ring, i.e., it turns out at some point to be surrounded by 6 Si atoms.

Energy $U_{\text{Li}-\text{Si}}$ of interaction between the Li^+ ion and silicene in a silicene channel with constant electric field (10⁵ V/m) directed along the channel is negative (Fig. 10a). The minimum value of energy $U_{\text{Li}-\text{Si}}$ is reached at clearance $h_g = 0.65$ nm and the maximum of the $U_{\text{Li}-\text{Si}}(h_g)$ function is observed at $h_g = 0.70$ nm. In this case, the ion meets more favorable conditions for passing the channel and interacts with silicene to a lesser degree. Besides interactions of the Li^+ ion with Si atoms, a factor hindering the movement of the ion in the channel is attraction between the silicene sheets. The values of energy $U_{\text{Si1}-\text{Si2}}$ of interaction between the top and bottom silicene sheet per atomic pair are shown in Fig. 10b. The value of $U_{\text{Si1}-\text{Si2}}$ increases nonmonotonously at an increase in clearance h_g . The dimensionless parameter reflecting the mutual effect



Fig. 10. Characteristics of motion of the Li⁺ ion in the field strength of 10^5 V/m: (a) $U_{\text{Li-Si}}$, (b) $U_{\text{Si1-Si2}}$ are partial energies, indices "1" and "2" correspond to the top and bottom silicene sheets, respectively; (c) dimensionless parameter of obstacles for ion motion.

of obstacles to the ion movement in the channel and determined by the ratio of $U_{\text{Sil-Si2}}/U_{\text{Li-Si}}$ is shown in Fig. 10c. The effect of interaction between the silicene sheets weakens at an increase in clearance h_{g} and the ratio of $U_{\text{Sil-Si2}}/U_{\text{Li-Si}}$ decreases. Energy obstacles related to the motion of the Li⁺ ion in the silicene channel under exposure to electric field as a whole exceed the energy barriers for diffusion of the Li atom in silicene.

The behavior of the Li^+ ion intercalated into silicene in the external field is even less predictable than the behavior of this ion intercalated into bilayer graphene. This is related to the complex profile of the silicene surface, while graphene better corresponds to 2D geometry. More rigid bonds in graphene compensate the lower mass of C atoms as compared with Si atoms, so that the mobility coefficients of C and Si atoms for the lithium ion moving along the planar channel prove to be close. In the case of a narrower

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channel, when movement of the Li⁺ ion is much hindered, fluctuations of the highest stress σ_{zz} in graphene can significantly exceed the corresponding fluctuations in silicene also appearing when the lithium ion passes through the channel. But if the Li⁺ ion moves along the channel freely enough, the range of fluctuations of σ_{zz} in graphene and silicene are comparable. Owing to topological regularities (the presence of the initially nonsmooth profile of the silicene surface), we do not compare roughness due to movement of the lithium ion in bilayer graphene and silicene. A decrease in roughness of silicene when the lithium ion moves between its layers with respect to the corresponding characteristic of bilayer silicene on an Ag support agrees with the conclusion as to improvement of its electronic properties caused by Li [26].

CONCLUSIONS

The results show that bilayer silicene with an AB packing has the geometry deviating from an ideal 2D lattice. It is more easily synthesized experimentally than monolayer silicene. Bilayer silicene does not tend to undergo irreversible structural changes during the lithiation and delithiation cycles. Textured geometry of silicene can be formed in the course of the drift of the Li⁺ ion between its sheets. Apart from the combination of sp^2 and sp^3 hybridization, the possible effect of the textured geometry of silicene is formation of Dirac-type electron dispersion. The doping of bilaver silicene by hydrogen or bromine results in appearance of anti- or ferrimagnetism at the room temperature [34]. Therefore, new possibilities appear for development of high-performance electronic devices based on bilayer silicene. Abundance of Si, its rare ability to retain Li, flexibility of atomic layers, and a small energy barrier for diffusion of Li⁺ ions make application of silicene attractive for development of lithiumion batteries. It can be used to provide high energy density and improve the battery life cycle. Thus, the obtained results can be used in development of silicene anodes for lithium-ion batteries.

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