Kinetic test of a doped silicene-graphite anode element in a computer experiment

A Ye Galashev[1,2]**, O R Rakhmanova**[1,2] **and Yu P Zaikov**[1,2]

[1]Institute of High-Temperature Electrochemistry UB RAS, Akademicheskaya Str., 20, 620990, Yekaterinburg, Russia
[2]Ural Federal University, Mira Str., 19, 620002, Yekaterinburg, Russia

alexander-galashev@yandex.ru

Abstract. The stability of the system "bi-layer silicene on the graphite substrate" is studied in the molecular dynamics simulation. Silicene sheets are doped with phosphorus, and graphite sheets are doped with nitrogen. Lithium ion moves along a silicene channel with a gap in the range of 0.6–0.8 nm. The time for the ion to pass the channel and leave it decreases with an increase in the channel gap. There is a tendency of the silicene sheets roughness growth with an increase in the gap between silicene sheets (except, 0.75 nm). Doping phosphorus and nitrogen atoms stabilize the silicene and graphite structure.

1. Introduction

Doping is an effective way to improve the properties of semiconductor materials. According to [1], at a phosphorus concentration level of 10^{18}–10^{19} cm^{-3} a significant effect of P doping on the tensile strength of silicon does not reveal. In [2], it was shown that the implanted phosphorus ion increases Young's modulus of the silicon crystal. It was reported in [3] that, at a phosphorus concentration in silicon of the order of $5 \cdot 10^{19}$ см$^{-3}$, the breaking strength of the crystal increases, and Young's moduli decrease. Molecular dynamics (MD) simulation is a convenient tool for investigating the mechanism of the doping phosphorus effect on silicon. In the MD calculation [4] (using the modified potential of the immersed atom MEAM), it was shown that in the α-silicon film with increasing concentration of doping phosphorus, an increase in the tensile stress resistance is observed. A transition from a brittle pure silicon film to a flexible Si structure doped with phosphorus occurs.

Neutron transmutation doping of semiconductor materials is a good method for precise control of the amount of dopant and its uniform distribution over the material. The method is based on nuclear reactions. The nucleus of a semiconductor material captures thermal neutrons and forms an unstable radioactive nucleus. As a result of beta decay, they pass into the nucleus of another element. Phosphorus produces as a result of neutron irradiation of silicon, and nitrogen forms when carbon is irradiated.

The aim of the present work is the MD study of the behavior of Li$^+$ ion in the system "two-layer silicene on a graphite substrate" subjected to transmutation doping. It is a very important computer experiment for understanding the possibility of future using of silicene modified by neutron irradiation for the anode of a new generation of lithium-ion batteries.

2. Computer model

Tersoff potential is used to describe the Si-Si and C-C interactions in both the pure and doped silicene and graphene [5,6]. The interactions of lithium ion with Si, C, P, and N atoms are defined with the help of Morse potential [7]. The Si-X and C-X interactions (where X = P or N) are also taken into account using Morse potential. The Morse potential parameters for some interactions are calculated by us in the quantum-mechanical models according to the method of work [8-9]. The obtained parameters are shown in table 1. The parameters for the cross interactions that are absent in table 1 are obtained using simple interpolation relations [10]. The interactions between the atoms of different graphite and silicene sheets, as well as the Si–C interactions for these sheets, are calculated using the Lennard-Jones potential with the parameters of work [11].

Table 1. Morse potential parameters.

Interaction	D_e, eV	α, Å^{-1}	r_e, Å
P–P	1.001	2.322	2.263
Si–P	4.479	2.301	1.3
N–N	2.775	2.233	1.342
C–N	4.44	2.096	1.350

The bilayer silicene formed by the method of work [12] is located on the graphite substrate. The gap between the silicene sheets varied from 0.6 to 0.8 nm with a step of 0.5 nm. The silicene sheets are doped with phosphorus (the doping degree is 3%), and graphite sheets are doped with nitrogen (the doping degree is 5%). The distance between the channel and the substrate is r_{Si-C} = 0.286 nm, it is obtained from the *ab initio* calculations [13]. Lithium ion moves through the channel under the influence of a constant electric field of 10^5 V/m. The calculation length for each system is 1 million time steps ($\Delta t = 1 \times 10^{-16}$ c), i.e. 100 ps. The calculations are executed using the LAMMPS program code for parallel computing in the MD method [14] on the cluster-type hybrid computer URAN with a peak frequency of 216 Tflop/s and 1864 CPU.

3. Simulation results

Figure 1 shows a configuration of the investigated system «bi-layer silicene on the graphite substrate» with a gap between sheets of silicene of h_g = 0.8 nm. The configuration corresponds to the moment when the ion leaves the channel, i.e. 24 ps. The buckles of the bottom silicene sheet are almost smoothed. The shape of the sheet becomes similar to the surface shape of the graphite substrate. The top silicene sheet has a buckled surface. The nonfixed doped sheets of the graphite substrate are rather mobile in the *z*-direction. They have the deformation distortions, but they are not destroyed and do not lose their integrity. The given trajectory of lithium ion shows that ion can pass through the silicene channel with a gap of 0.8 nm without any difficulties. It should be noted, there is a significant energy barrier (~ 0.6 eV) for the ion to enter the doped silicene channel. In our previous calculations, for pure silicene modified by vacancies of various sizes and located on metal substrates, an energy barrier was 5–7% lower [15]. Li$^+$ ion leaves the channel at all gaps under consideration except for h_g = 0.7 nm.
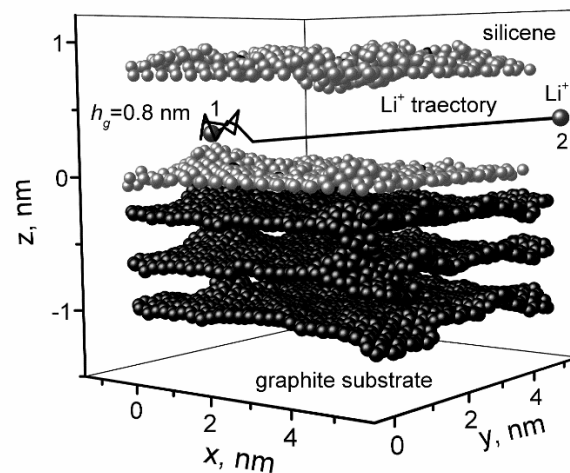
Figure 1. Configuration of the system "bi-layer silicene on the graphite substrate" with a channel gap of h_g = 0.8 nm; 1 and 2 – initial and final points of lithium trajectory.

It is shown in [16], that the silicene sheets modified with monovacancies on the Ag(111) substrate are deformed significantly, including buckling. Despite the partial destruction, the vacancy defects generally keep their shape. Lithium ion could enter the channel only starting with a gap of 0.75 nm. The doping of the system "bi-layer silicene on the graphite substrate" strengthens the system and makes it flatter and more stable. The doping does not create significant obstacles for Li$^+$ ion to pass through the channel. The velocity of the channel passage by lithium ion increases with a further increase in the gap h_g.
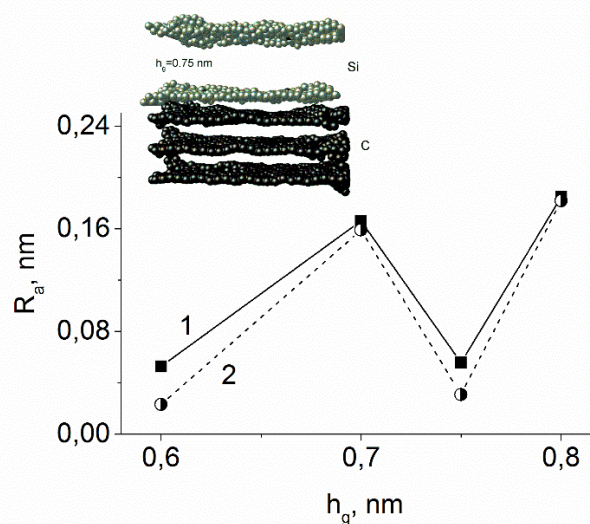

Figure 2. The roughness of the top (1) and bottom (2) silicene sheets; insert shows zx-projection of the system configuration with a channel gap of 0.75 nm.

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The surface roughness R_a of the top (polyline 1) and bottom (polyline 2) silicene sheets (calculated as the mean arithmetic deviation of z coordinate of Si atoms) is shown in figure 2. In general, one can note the presence of slightly higher R_a values of the top sheet, which is also seen in figure 1. The bottom silicene sheet has a smoother form due to its close position to the graphite substrate. In the case when the undoped silicene channel is located on the metal (Ag, Cu, Al, and Ni) substrates (data from our earlier calculations), a significant influence of the substrate on the roughness of Si sheets is established. Moreover, the obtained roughness exceeds the present R_a data by 15-20% [17,18].

The zx-projection of silicene sheets with a gap of 0.75 nm on the graphite substrate is shown in the inset to figure 2. The most severe deformation of graphite sheets extends along the edges of the sheets. It is due to the presence of the uncompensated C–C bonds. The distance between the bottom silicene sheet and the top graphite one does not change during the calculation. The buckles of the bottom doped silicene sheet become flat and the sheet imitates the shape of the top graphite one. A similar effect was discovered in our calculations while studying the behavior of the bilayer silicene between graphene sheets [17]. In that case, the forms of two-dimensional honeycomb structures of the silicon and carbon crystals imitated each other completely.

4. Conclusion

Using the molecular dynamics method, the behavior of lithium ion in the silicene channel on the graphite substrate is investigated. The results of silicene doping with phosphorus and graphite doping with nitrogen (for example, as a result of transmutation doping) is the hardening of both structures. An increase in the channel gap (from 0.6 to 0.8 nm) mostly leads to a decrease in the time for the ion to pass through the entire channel and leave it. Significant distortion of the sheets of the substrate and silicene is not observed. Doped silicene sheets don't lose their integrity and don't destroy while lithium ion moving along the channel. The roughness of silicene sheets is not an unambiguous function of the channel gap. Silicene doped with phosphorus can be considered as a promising material for the anode of lithium-ion batteries of a new generation.

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