
STRUCTURE OF MATTER
AND QUANTUM CHEMISTRY

Calculating from First Principles the Interaction between Li, Na, and K Atoms and Silicene

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Abstract—Interaction between Li, Na, and K atoms and autonomous silicene and is investigated using the first-principles means of density functional theory. The energies of adsorption and bond distances of Si–Me for different positions of adsorbed alkali-metal atoms are calculated. The band structure of the silicene–Me systems is counted in a generalized gradient approximation. It is found that metallic conductivity can result from either substituting an atom of Si for an atom of Li, or the one-sided absolute adsorption of silicene by atoms of Na. It is shown that the adsorption of atoms of K does not result in the formation of metallic conductivity, but it does ensure lower values of the energy gap that can be obtained via the adsorption of atoms of Li or Na.

Keywords: bond distance, band structure, potassium, lithium, sodium, silicene, energy of adsorption

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INTRODUCTION

The consumption of energy grows along with the capacity of electronic devices, which negatively impacts their operating time. The new supercapacitor should have high electric output and receive and return stored energy at a high rate. Such properties make it a perfect choice for use in batteries for electricity-powered automobiles, remotely piloted vehicles, and all electronic devices. The transition from lithium-ion batteries to sodium- and potassium-ion batteries will allow the capacity of electrochemical power sources and the rate at which they charge to be increased. The theoretical capacity of devices based on such large ions as Na⁺ is substantially greater than that of the lithium ones widely used today. Test samples of new storage batteries already have capacities as high as 600 mA h/g—2.5–6 times higher than for commercial lithium batteries. It is important that sodium is ~30 times less expensive, and batteries made of it will be far cheaper than those with lithium. Potassium (K⁺) ions can intercalate electrochemically into such materials as graphite and the reduced oxide of graphene (RGO) at ambient pressures and temperatures.

Experiments show [1] that graphite can provide a reversible capacitance of 207 mAh/g. The process of intercalating K⁺ ions into graphite is assumed to consist of three phases. K⁺ ions also can integrate themselves into an RGO film with even higher reversible

capacitance (222 mAh/g). The intercalation of K⁺ ions reduces absorption, so it can effectively increase the optical transparency of an RGO film from 29.0 to 84.3%. It is becoming possible to develop K-ion technologies for use in creating new nonaqueous electrochemical storage cells and in optical applications. The use of asymmetric intercalation batteries with K₂NiFe(CN)₆ cathodes and commercially produced graphite as anodes, in combination with of an organic electrolyte containing mixed salts of lithium and potassium, was proposed in [2]. The battery works via the reversible intercalation of K⁺ ions from the cathode side, along with the simultaneous reversible intercalation of Li⁺ ions on the anode. The coordination medium of π -electrons in K₂NiFe(CN)₆ ensures the preferred reversible intercalation of K⁺, and the short ionic radius allows the preferred reversible intercalation of Li⁺ ion in the graphite. The battery has high service voltage (~3.6 V) and a long lifetime with a minimal loss of capacity even after 5000 cycles.

Graphite anodes have relatively low capacity because of the limited number of places for storing ions in the hexagonal structure of carbon [3]. The current power of an anode battery can theoretically be increased by replacing the carbon-based material with new anodic material such as silicene [4, 5]. The intercalation of ions of alkali metals in a silicon-based material starts with the reduction of these ions to atoms at the boundary between the anode and electro-

lyte. The alkali-metal atoms then diffuse into the anode material.

The aim of this work was to study the interaction between Li, Na, and K atoms and autonomous (without a substrate) silicene to determine the adsorption and electronic properties of the silicene. These are important when investigating Si-based anodes and producing a physical interpretation of the energy of adsorption of the considered alkali metals in storage batteries.

COMPUTER MODEL

Our calculations were performed with the SIESTA software, using an ab initio pseudopotential based on the density functional theory (DFT) [6, 7]. Calculations with nonlocal potential were performed within the generalized gradient approximation (GGA) [8]. The geometry was optimized according to the Perdew Burke Ernzerhof (PBE) procedure [9] to increase the speed of calculations. The tolerances for geometry optimization according to total energy were within 5.0×10^{-6} eV/atom. The maximum Hellmann–Feynman force was within 0.01 eV \AA^{-1} , the maximum atomic displacement did not exceed 5.0×10^{-4} \AA , and the maximum level of stress was within 0.02 GPa. The geometry of all structures was completely optimized. An elementary cell of the silicene composed of eight atoms was used to calculate all properties. The initial coordinates of the four atoms of Si of the elementary cell were displaced perpendicular to the surface to a distance of 0.064 nm, and the other atoms of Si were on the same (initial) plane. This structure of the silicene sheet was similar to the surface of the silicene observable on the Ag {111} substrate in [10]. In other words, reconstructing a surface of $\sqrt{3} \times \sqrt{3}$ [11] was considered.

The energy of adsorption of metal atoms (Me = Li, Na, and K) on surfaces of silicon was calculated using the expression

$$E_{\text{ad}} = (E_{\text{Si}} + nE_{\text{Me}} - E_{\text{Si+Me}})/n, \quad (1)$$

where $E_{\text{Si+Me}}$ and E_{Si} are the total energies of a silicene surface with and without Me adatoms, respectively; E_{Me} is the energy of alkali-metal atoms, calculated with spin polarization; and n is the number of adsorbed atoms of Me.

A plane wave basis with a truncation energy of 300 eV was used to represent the wave functions of silicon and the investigated metals. This was enough to ensure high convergence. The Brillouin zone was defined by a matrix of $20 \times 20 \times 1$ k -points in the Monkhorst–Pack module. Diagonalization was used in performing all calculations. The energy band structure was obtained in direction K- Γ -M of the critical points of the Brillouin zone in all of the considered systems.

The investigated systems had no direct band gap. We therefore determined the value of band gap (BG)

as $E_g = \min(E_c - E_v)$, where E_c and E_v are the current energies of the conduction band and valence band, respectively. The values of E_c and E_v were examined in direction K- Γ -M-K. We assumed that on the Fermi level, the total number of electrons in the conduction band was equal to the total number of holes in the valence band. It should be noted that although the DFT underestimates forbidden gap E_g , this approach can yield the true values of E_g for many semiconductors [12, 13]. It was also used to describe the electronic properties of materials based on graphene with accuracy comparable to GW (a combination of Green's function G and screened coulomb interaction W) [14]. To confirm the certainty of this technique, we performed calculations for the volume Si as a standard, due to the dearth of experimental data for silicene. $E_g = 1.034$ eV for the volume silicon, which is close to the experimental value of 1.17 eV [15].

Seven positions of alkali-metal atoms relative to the supercell of silicene were examined: I and II, where an adatom of metal is over the silicon atoms of the top and bottom sublattice respectively; III, where an adatom of metal is over the geometric center of a six-bond ring; IV, where the adatom of metal is positioned at the point in the middle between two divided neighboring atoms; V, where an atom of metal displaces one of the silicon atoms; VI, where silicene is doped with atoms of metal in the ratio 2Si : 1Me (all atoms of Me were placed in the positions of II); and VII, where the system has a 1Si : 1Me ratio of atoms. The system where a metal adatom is over the point in the middle of the bond between two neighboring atoms was also considered, but the metal adatom changed its position during geometrical optimization, and occupied the position over the atom of silicon of the upper sublattice; i.e., a system that coincided with system I formed.

Our calculations were performed using the URAN Hybrid Cluster Computer at the Institute of Mathematics and Mechanics, Ural Branch, Russian Academy of Sciences, which has a peak capacity of 216 Tflop/s and 1864 CPU.

RESULTS AND DISCUSSION

As we move down along the (Li, Na, K, Rb, Cs) group, we observe a reduction in ionization energy and a rise in the reactive capability of metals. The energies of the initial ionization of Li, Na, and K are thus 5.41 , 5.16 , and 4.36 eV, respectively. These metals form positive ions during a reaction, and the lower the energy of ionization, the more easily these ions are formed. However, the formation of positive ions is only one stage of the process. We may therefore conclude one reaction or another is preferable by studying the overall situation instead of one small part of it. Nevertheless, the elements' energies of ionization are the main factors that influence a reaction's energy of activation, i.e., the minimum amount of energy needed to initiate

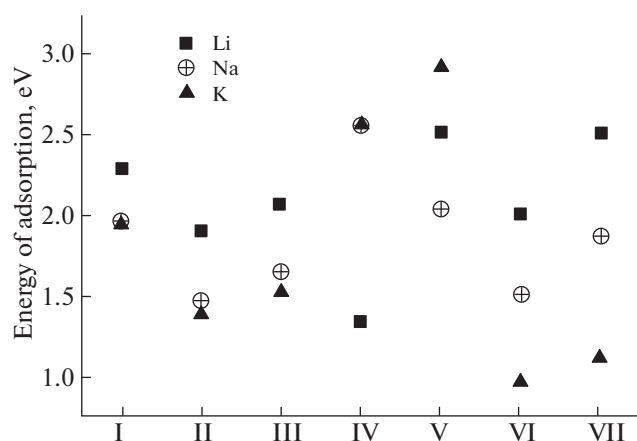


Fig. 1. Energy of adsorption of atoms of Li, Na and K, optimized via GGA and depending on the location of these atoms relative to a supercell of silicene. For the notations with Roman numerals, see text.

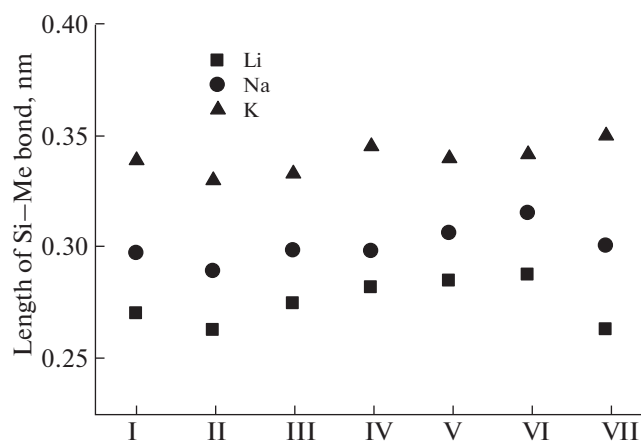


Fig. 2. Lengths of Si-Me bonds for atoms of Li, Na, and K, optimized via GGA depending on the location of these atoms relative to a supercell of silicene. For the notations with Roman numerals, see text.

it. The lower the energy of activation, the faster the reaction will proceed.

The calculated energies of activation of Li, Na and K atoms relative to silicene are presented in Fig. 1. In five of the seven investigated cases, the energy of activation falls as the atomic number of the element rises (i.e., from Li to K). The IV and V variants, which are highly improbable upon the intercalation of alkali metals in a silicene anode, were found to be atypical. The value of E_{ad} for Li atoms in a silicene anode was found to be the highest among the investigated metals. The dependence between the values of E_{ad} shows that the rate of intercalation and deintercalation of atoms of Na and especially K is higher than that of atoms of Li. At a faster effective speed of ion migration per unit time, a stronger charge will be transmitted. A battery operating on larger ions will thus be more powerful.

As a consequence of the appreciable difference between sizes of atoms of the investigated alkali metals, lengths L_{Si-Me} of the Si-Me-bonds for the considered variants of Me atom arrangement were found to be substantially more ordered than the values of E_{ad} (Fig. 2). As is evident from Fig. 2, strict dependence $L_{Si-K} > L_{Si-Na} > L_{Si-Li}$ is observed for all of the considered variants. For each of the investigated metals, the lowest value of L_{Si-Me} is observed when an Me atom is over an atom of silicon of the lower sublattice. The highest value of L_{Si-Me} was obtained upon the deposition of atoms of Li or Na on to silicene in a ratio of two atoms of silicene to one Li (Na) atom. With the adsorption of atoms of K, however, the highest value of L_{Si-K} was observed when adsorption on silicene proceeded at a ratio of one atom of K to one atom of Si. Note that this type of adsorption with atoms of Li results in one of the lowest values of L_{Si-Li} . The greater distance of atoms of Na and especially K from the silicene results in faster adsorption and desorption for

them than for atoms of Li. It also increases the effective charge-transfer velocity in an electrochemical power source, and thus the capacity of a battery.

The value of band gap of the autonomous silicene is equal to or near zero, and its dispersion is linear at point K [16, 17]. Our calculations show that silicene with adsorbed Li or Na becomes a semiconductor. In case III, i.e., with an Li adatom over the center of a six-bond ring, the calculated value of the band gap was 0.246 eV (Fig. 3). The value of band gap of silicene varied from 1.111 eV upon adsorbing atoms of lithium in a ratio of 2Si : 1Li to 0.388 eV with complete adsorption (1Si : 1Li). The value of E_g obtained in [17] for silicene completely adsorbed by lithium was $E_g = 0.368$ eV. Note that fully lithiated silicene is the most stable material of the silicene-Li systems [17] among the investigated compounds. In case III, the value of band gap for adsorbed Na was wider ($E_g = 0.279$ eV) than for the adsorption of Li. Continuous adsorption of Na on the silicene can lead to the formation of a fairly wide band gap for a silicene-Na system. So with VI (i.e., when one atom of Na is on two atoms of Si), the value of the band gap was 0.792 eV (Fig. 4). However, a state in which a silicene-Na system acquires the properties of a metal is possible. So with VII (1Si: 1Na), we observe overlapping of the energies of the valence and conduction bands, and the forbidden gap is found to be $E_g = -0.144$ eV. A system of silicene-Na in this case exhibits metallic properties with visible evidence of *n*-type conductivity (by far, most of the overlap area lies above the Fermi level).

The adsorption of one atom of K to the position over the center of the six-bond ring of silicene results in the formation of forbidden gap $E_g = 0.094$ eV. This value is 3 times lower than for the adsorption of an atom of Na, and 2.6 times lower than for an atom of Li. The value of the band gap upon the adsorption of

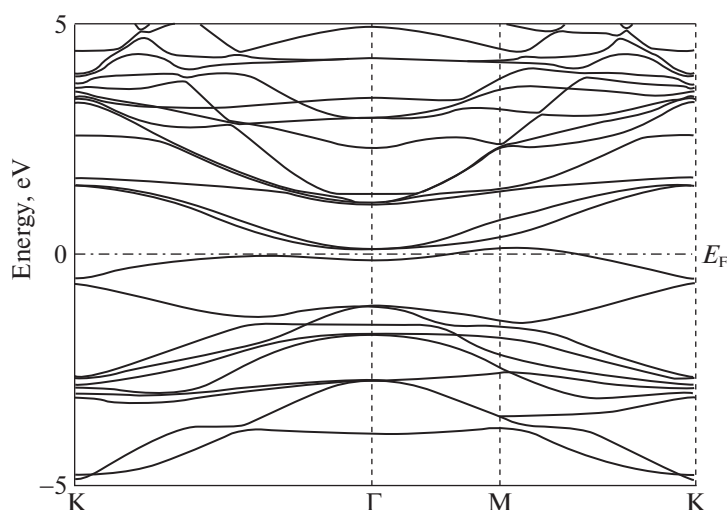


Fig. 3. Energy band structure of silicene with lithium adatoms deposited over the geometric center of a six-bond ring, obtained via GGA. Bond length $L_{\text{Si-Li}} = 0.274$ nm. The Fermi energy was set to zero.

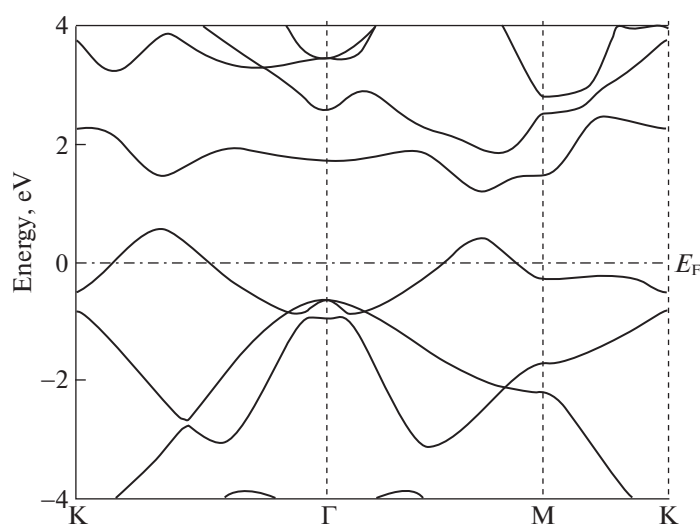


Fig. 4. Energy band structure of the silicene–Na system with a 2Si : 1Na ratio of atoms, obtained via GGA. Bond length $L_{\text{Si-Na}} = 0.315$ nm. The Fermi energy was set to zero.

atoms of K on silicene with a ratio of 2Si : 1K was 0.507 eV. This is 1.5 times lower than with the same Si/Me ratio for deposited atoms of Na and 2.2 times lower than with the adsorption of the corresponding number of Li atoms on silicene. With the complete adsorption of atoms of K on silicene, however, a silicene–K system acquires properties of a semiconductor with hole-type conductivity, and $E_g = 0.509$ eV (Fig. 5).

CONCLUSIONS

Among the investigated lithium systems, nos. V and VII had the highest energies of adsorption (the corresponding sodium system was no. IV; the corre-

sponding potassium system, no. V). The last system had the highest energy of adsorption (2.917 eV), while $E_{\text{ad}} = 0.97$ eV of potassium system VI was the lowest of all the considered systems. According to our calculations, lithiation can be considered a unique way of setting the value of the band gap of silicene only for certain positions of atoms of Li on the surface of this 2D material. For V, when an atom of Li displaces a silicon atom, there is a partially occupied band in the structure that occupies the niche immediately above the occupied (valence) band; i.e., the energy band structure characteristic of metals is formed.

Between the concentrations of free electrons in metals Li, Na, and K we observe a ratio of 1 : 0.54 :

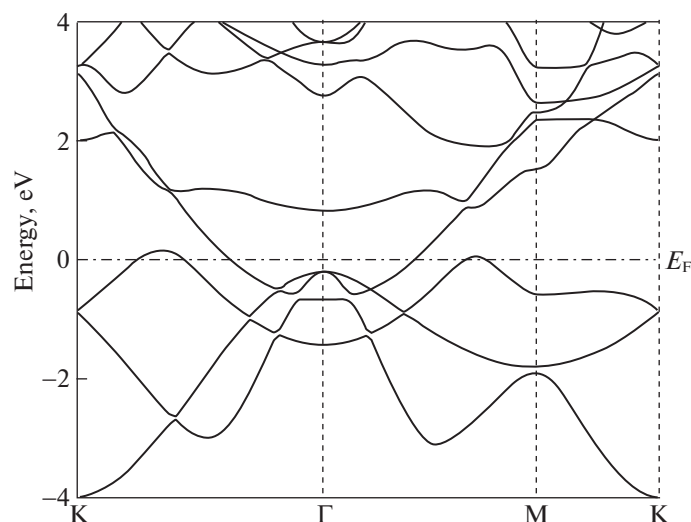


Fig. 5. Energy band structure of a silicene–K system with a 1Si : 1Na ratio of atoms, obtained via GGA. Bond length $L_{\text{Si-K}} = 0.349$ nm. The Fermi energy was set to zero.

0.29. For the Fermi energies, the ratio is 1 : 0.65 : 0.44; for the relative electronegativities, it is 1 : 0.9 : 0.8. The difference between these properties for atoms of Li, Na, and K, together with the differences between the sizes of atoms, is responsible for their differentiated effect on the energy band structure when they are adsorbed on silicene. It is known that the surfaces of semiconductors are susceptible to reconstruction that can change sharply when adsorbed atoms of metals are present [18]. The Fermi level can shift to the band gap upon suitable doping, and the state of a degenerated gas can in some cases be achieved in the conduction or valence band. The Fermi energy can easily be displaced by several electron volts in semiconductors, especially ones with a wide band gap. The Fermi level can be vacant or fixed by surface states, entailing the transfer of charge to or away from a surface. The mean electric field inside silicene can be changed via the directed manipulation of adatoms by changing their position or charge. A special case of obvious overlapping of valence and conduction bands was observed as the result of the adsorption of Na atoms on silicene at a ratio of 1 : 1. A set of closely osculating states exceeding the number of electrons contained in them was formed; i.e., the silicene–Na system acquired metallic properties. The Fermi level position is associated with the energy of adsorption of different atoms or ions. Variation of the Fermi level as a result of doping creates great problems in interpreting the band structure of a semiconductor.

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