

Quantum-mechanical study of the substitution and adsorption of P atoms on silicene

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Abstract

The behavior (substitution and adsorption) of the phosphorus atom on the surface of silicene has been studied using quantum mechanical calculations. The most favorable positions, binding energies and the value of the activation barrier for phosphorus diffusion have been established. The change in the local magnetic moment on the phosphorus atom is described depending on its position and the positions of the surrounding silicon atoms.

Introduction

Silicene is of great interest for fundamental physics and practical applications. It has a stronger spin-orbit interaction [1], in contrast to graphene, which will make it possible to observe the spin Hall effect at not too low temperatures [2]. Theoretical studies have also reported such unique properties as a mechanically adjustable band gap [3] and a metal phase with valley polarization [4]. Experimental observations and synthesis of silicene [5-9] showed the prospects of nanosized materials that can be easily functionalized chemically or mechanically and introduced into modern electronics [10]. The study of the interaction of phosphorus atoms with the surface of silicene, presented in this work, may be of interest in the prospect of creating qubits for quantum computers based on this material, by analogy with crystalline silicon doped with phosphorus.

Experiment

The Quantum Espresso software package [11] based on the density functional theory and the pseudopotential method was used to perform quantum mechanical calculations. The calculations were performed taking into account the spin-orbit non-collinear interaction. Fully relativistic pseudopotentials for silicon and phosphorus were selected from the Quantum Espresso program library [12]. The cutoff energy of the plane wave basis was 476 eV. Calculations of Si:P structures were carried out with a homogeneous grid of k-points $9 \times 9 \times 1$, constructed according to the Monkhorst-Pack scheme. The analysis of the values of charges on atoms was carried out using the Bader partitioning method.

Results and discussions

To study substitution, one silicon atom in the silicene structure was replaced by phosphorus. The binding energy is calculated as follows: $E_B = E_{\text{system}} - [E_{\text{silicene}}(N_{\text{Si}} - 1)/N_{\text{Si}} + E_P]$, where E_{system} is the total energy of the P-doped silicene, E_{silicene} is the total energy of the perfect silicene, N_{Si} is the number of Si atoms in a supercell of pristine silicene, E_P is the total energy of an isolated P atom. The binding energy of the resulting system is -3.34 eV. To study adsorption, key variants of the location of the phosphorus atom were considered (Fig. 1).

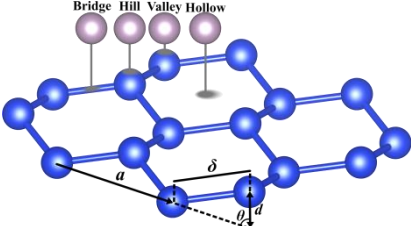


Fig. 1. Structure of silicene and possible sites of adsorption of the phosphorus atom.

Binding energy for adsorption: $E_B = E_{\text{system}} - (E_{\text{silicene}} + E_P)$.

The most favorable is *Hill* site with a binding energy of -3.84 eV. The local magnetization and charge on the phosphorus atom is determined by the silicon environment — the number of neighboring silicon atoms, the distances to them. The magnetic moment of the phosphorus atom in the *Bridge* site is 0.210 μ_B/cell and decreases to 0.020 μ_B/cell in the *Hill* position. The charge value varies in the range from -1.20 e in the case of substitution to -0.83 e in the *Hollow* site. The magnitude of the charge on the phosphorus atom does not correlate with the magnitude of the magnetization. The Nudged Elastic Band (NEB) method was used to determine the energy barrier when a phosphorus atom moves over the silicene surface from the *Hill* position through the hexagonal ring to the next *Hill* position. The activation energy to overcome the barrier, which is located between the *Hill* and *Hollow* sites, was 1.51 eV.

The adsorption of a phosphorus atom onto a silicene surface already containing either one substituting (Fig. 2a) or one adsorbed (Fig. 2b) phosphorus atom was considered.

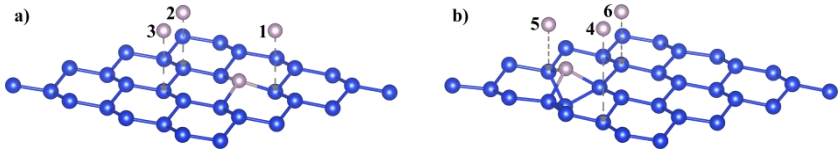


Fig. 2. Options for the location of the adsorbed P atom next to a) a substituting one; b) adsorbed.

In the 2nd and 3rd cases, in the region of adsorption of the second phosphorus atom, shifts occur in the arrangements of neighboring silicon atoms, similar to the *Hill* and *Valley* sites considered earlier; in this case, the binding energies become lower, the *Hill* site (-4.17 eV) is the most favorable. In the case of two adsorbing atoms, according to the binding energies, configuration 5 can be distinguished as the most favorable (-4.23 eV), the location of the second phosphorus atom near the first reduces its binding energy in configuration 4, and in configuration 6 leads to a spontaneous displacement from the already existing adsorbed atom. The charge on phosphorus atoms deviates insignificantly from the previously considered cases of single substitution or absorption of a phosphorus atom on silicene. Local magnetic moments on phosphorus atoms are not expressed.

Conclusions

A complex of quantum mechanical calculations made it possible to determine the optimal positions of one and two phosphorus atoms on the silicene surface. Adsorption has been shown to be more beneficial than substitution; the energy gain is 0.5 eV. The binding energy during the absorption of the second P atom decreases while maintaining the distance between the phosphorus atoms; the formation of dimers from phosphorus atoms is energetically unfavorable. The dependences of the local magnetization on phosphorus atoms on the silicon environment are established. Using the NEB method, the activation energy for the transfer of an adsorbed P atom over the silicene surface was determined.

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