Functionalized silicene from first principles

Abstract

Graphene and other two-dimensional crystals have been the subject of intense research over the last few years. One of these materials is silicene – a single layer of silicon atoms arranged in the honeycomb structure, i.e. a hexagonal lattice with diatomic basis. The characteristic feature of the silicene electronic structure is the linear dispersion of the bands around the K points of the Brillouin zone, derived from orbitals π and π^*. These bands merge at the Fermi level, forming a Dirac cone. In this respect, silicene is analogous to graphene. However, these materials differ in their structure – graphene is flat on the atomic scale due to the formation of bonds between C atoms by sp^2 hybridization, while mixed sp^2-sp^3 hybridization in silicene leads to its low-buckled structure, in which sublattices are spatially separated in the direction perpendicular to the plane of the material.

Previous research on silicene was focused mainly on two aspects. The first problem was to produce a quasi-freestanding silicene layer on an appropriately selected template. The second aspect of these studies was the functionalization of freestanding silicene. The dissertation is focused on these two issues, in particular its third part, which presents the main findings of the study, and the included scientific papers.

Using the Density Functional Theory (DFT) calculations of silicene on thin layers of lead was performed. The results indicate that the Pb(111) surface may be a suitable material to produce quasi-freestanding silicene, since the binding energy per silicon atom is three times lower than in the case of silver, commonly used as a substrate. The electronic structure with the Dirac cone, to which the main contribution make $3p_z$ states of silicon atoms, indicates the presence of Dirac fermions in silicene on Pb(111) surface.

The use of thin metal layers – quantum wells – allows controlling the binding energy, the energy gap and position of the Dirac cone. Studies have shown that the additional corrugation of silicene on the lead surface plays a key role in protecting electrons forming the Dirac cone from the negative influence of the substrate.

As far as the functionalization of freestanding silicene is concerned, the study was focused on determining its most effective method. The calculations were carried out for silicene with small coverage of hydrogen atoms. This system was subjected to external electric field, charge doping and uniaxial or biaxial compression and stretch. Each of the applied mechanisms can increase the binding energy between silicene and hydrogen. The most efficient method of

functionalization is the charge doping as it allows the electronic and magnetic properties of the system to be varied in a wide range. The system in equilibrium is a ferromagnetic insulator, but it can be driven to a non-magnetic insulator, metal (with or without magnetic order) and a semi-metal with total spin polarization. Uniform stretch of the system by small values (2.5-5%) switches the energy gap from indirect to direct.

The last part of the study involves freestanding silicene subjected to a long-range (several or more lattice parameters) corrugation in one of the two characteristic directions of the honeycomb structure. Such modification of the structure makes the silicene properties dependent on direction – along the wrinkles they are close to the freestanding silicene, but in the perpendicular direction they can vary widely, in particular when the corrugation is very intense. This leads to the anisotropy of the group velocity of electrons. The long-range modulation of the silicene atomic structure leads to the charge density oscillation combined with polarization of the sublattices. This is the result of the rehybridization of Si-Si bonds caused by the destruction of planar symmetry in the curved part of silicene. The low-buckled structure of silicene is crucial to induce the charge density oscillations, so it is expected that also other two dimensional materials of an analogous structure will exhibit such behavior.

27.09.2017 r. Agata Podniadły-Paskowska