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Theoretical aspects of graphene-like group IV semiconductors

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ABSTRACT

Silicene and germanene are the silicon and germanium counterparts of graphene, respectively. Recent experimental works have reported the growth of silicene on (1 1 1)Ag surfaces with different atomic configurations, depending on the growth temperature and surface coverage. We first theoretically study the structural and electronic properties of silicene on (1 1 1)Ag surfaces, focusing on the (4 × 4)silicene/Ag structure. Due to symmetry breaking in the silicene layer (nonequivalent number of top and bottom Si atoms), the corrugated silicene layer, with the Ag substrate removed, is predicted to be semiconducting, with a computed energy bandgap of about 0.3 eV. However, the hybridization between the Si 3p orbitals and the Ag 5s orbital in the silicene/(1 1 1)Ag slab model leads to an overall metallic system, with a distribution of local electronic density of states, which is related to the slightly disordered structure of the silicene layer on the (1 1 1)Ag surface. We next study the interaction of silicene and germanene with different hexagonal non-metallic substrates, namely ZnS and ZnSe. On reconstructed (0 0 0 1)ZnS or ZnSe surfaces, which should be more energetically stable for very thin layers, silicene and germanene are found to be semiconducting. Remarkably, the nature and magnitude of their energy bandgap can be controlled by an out-of-plane electric field, an important finding for the potential use of these materials in nanoelectronic devices.

1. Introduction

Very recently, the formation of silicene, the silicon counterpart of graphene, was reported on (1 1 1)Ag surfaces [1–3], as well as on (0 0 0 1)ZrB_2 [4] and (1 1 1)Ir [5] surfaces. The electronic properties of the silicene layer on (1 1 1)Ag was investigated using angle-resolved photoemission spectroscopy. These measurements revealed the presence of a linear dispersion in the band structure of silicene (so called Dirac cones) with a Fermi velocity of about 1.3×10^6 m/s (3), as theoretically predicted for free-standing silicene [6].

Several possible phases of silicene on (1 1 1)Ag were recently identified [1–3], using a combination of surface characterization techniques, including the (4 × 4), $(\sqrt{13} \times \sqrt{13})$, $(2\sqrt{3} \times 2\sqrt{3})$, and $(\sqrt{7} \times \sqrt{7})$ superstructures. While most of the theoretical studies on silicene have been performed on free-standing layers [6–9], not much work has been devoted to (1 1 1)Ag/silicene superstructures [10–12], more specifically concerning their electronic properties.

The possible existence of silicene was so far only reported on these metallic substrates. However, the characterization of the electronic and electrical properties of silicene on metallic substrates is very challenging, since these properties are then largely dominated by the metal. The growth of silicene on semiconducting or insulating substrates is required for its identification and complete characterization. In addition, potential applications of silicene in nanoelectronic devices will also require the use of non-metallic substrates.

We first theoretically study the structural and electronic properties of the specific (4 × 4)Ag/silicene superstructure, using density functional theory (DFT). The silicene supercell, with the Ag substrate removed, is predicted to be semiconducting, with a computed energy gap of about 0.3 eV. The opening of an energy gap in the silicene supercell is essentially due to the substrate-induced broken symmetry (non-equivalent number of top and bottom Si atoms) in the silicene layer [11,12]. However, the mixing between the 5s states of Ag and the 3p states of silicene leads to a metallic character for the whole Ag/silicene superstructure [11,12]. The

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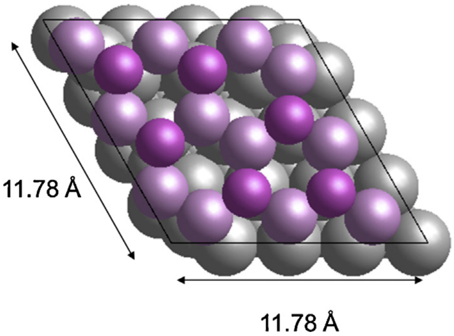

Fig. 1. Slab model of the (4 × 4)silicene/(1 1 1)Ag structure. Dark purple, light purple and gray spheres are top Si, bottom Si and Ag atoms, respectively.

distribution of bond lengths, bond angles and buckling distances in the silicene layer leads to a distribution of electronic density of states, as recently observed experimentally at (1 1 1)Ag/silicene interfaces [3].

We next investigate the interaction of silicene and germanene (2D hexagonal germanium) with semiconducting substrates, namely (0 0 0 1)ZnS and ZnSe surfaces. These materials crystallize in the wurtzite (hexagonal) phase, which appears to be compatible with the possible growth of 2D hexagonal silicon and germanium. The charge transfer at the silicene/(0 0 0 1)ZnS and germanene/(0 0 0 1)ZnSe interface leads to the opening of an indirect energy band gap in silicene or germanene. Very interestingly, it is found that the nature (indirect or direct) and magnitude of the energy band gap can be controlled by an external electric field: the energy band gap is predicted to become direct for electric fields larger than about 0.4–0.5 V/Å, and the direct energy gap decreases approximately linearly with the external electric field; the predicted electric field control of the energy gap of silicene and germanene is very promising for their potential applications in nanoelectronic devices.

2. Theoretical methods

First-principles simulations were performed using density functional theory (DFT). The generalized gradient approximation (GGA) was used for the exchange-correlation functional [13], as implemented in the Siesta package [14]. The core electrons were implicitly treated using norm-conserving pseudopotentials [15], with the following electronic configurations of the elements: Si (Ne) $3s^2$ $3p^2$, S (Ne) $3s^2$ $3p^4$, Zn (Ar) $3d^{10}$ $4s^2$, Ge (Ar) $4s^2$ $4p^2$, Se (Ar) $4s^2$ $4p^4$, and Ag (Kr) $4d^{10}$ $5s^1$, with the core configurations indicated in parenthesis. The valence electrons were described by using a double zeta singly polarized basis set. An energy cutoff of 300 Ry and a (10 × 10 × 1) k-point mesh were used for the computations, allowing convergence of the total energy of the systems below typically 10 meV. The atomic structure optimization was carried out by relaxing the forces on all atoms until a 0.05 eV/Å force tolerance was reached, using a conjugate gradient method. The computations were performed on periodic slab models, with about 15 Å of vacuum between the periodic cells, in order to minimize the interaction between neighboring cells. To study the effect of an external electric field on the electronic properties of the silicene/(0 0 0 1)ZnS and germanene/(0 0 0 1)ZnSe interfaces, a periodic zigzag electric potential was applied in the direction perpendicular to the interface.

3. Results and discussion

3.1. (4 × 4)silicene/(1 1 1)Ag structure

Several atomic arrangements of Si on (1 1 1)Ag surfaces have been recently identified by scanning tunneling microscopy [1–3], one of the most observed being the so called (4 × 4)silicene/Ag structure. This structure corresponds to a (3 × 3)silicene supercell on a (4 × 4)Ag supercell. This supercell contains 18 Si atoms (see Fig. 1), with 2 sublattices [1,10–12]: 6 atoms at top position, at about 2.93 Å from the Ag surface and 12 atoms at bottom positions, at about 2.18 Å from the Ag surface. A slab model with 5 layers of Ag atoms, each containing 16 atoms was considered for the DFT simulations; the lattice parameter of Ag was calculated to be 4.16 Å, about 2% above the experimental value.

We first calculated the electronic density of states (DOS) and energy band structure of the (3 × 3)silicene supercell, stripping-off the underlying (1 1 1)Ag substrate. As shown in Fig. 2, the silicene layer is semiconducting, with a (direct) energy band gap of about 0.3 eV, in agreement with recent theoretical reports [11,12]. The opening of this band gap results from the breaking of the symmetry in the silicene layer, i.e. from the non-equal number of top (6) and bottom (12) Si atoms in the supercell, as well as from the distribution of Si—Si buckling distances (Δz, in the direction perpendicular to the silicene layer) and distribution of Si—Si bond lengths and angles, as shown in Fig. 3; Note also that the average buckling distance of the silicene layer of the (1 1 1)Ag surface is larger than the one predicted for free-standing silicene, which is about 0.4 Å [16,17]. The symmetry breaking/disorder in the silicene layer induces a charge transfer between the top and bottom Si atoms, leading to the opening of an energy band gap. From the analysis of the energy band population, shown in Fig. 2, it appears that the bottom Si atoms (from the planar hexagons) essentially contribute to the valence (π) band and the top Si atoms are mainly contributing to the (π^*) conduction band of the system.

We next computed the electronic density of states (DOS) of the (4 × 4)silicene/(1 1 1)Ag system. The mixing between the 3p orbitals of Si atoms and the 5s orbitals of Ag atoms results in an overall metallic system [11,12], as shown in Fig. 4. The distribution of the buckling distances, bond lengths and bond angles also leads

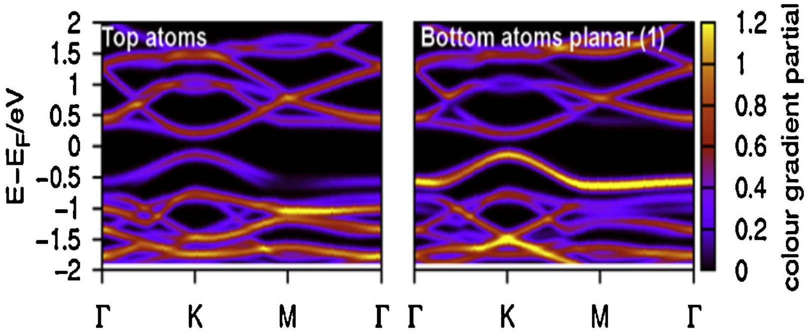

Fig. 2. Energy band population of the top and bottom Si atoms of the (3 × 3)silicene supercell. The highest electron density is shown in yellow and the lowest one in black.