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Solid argon as a possible substrate for quasi-freestanding silicene

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Abstract

We study the structural and electronic properties of silicene on solid Ar(111) substrate using *ab initio* calculations. We demonstrate that due to weak interaction, quasi-freestanding silicene is realized in this system. The small binding energy of only -32 meV per Si atom also indicates the possibility to separate silicene from the solid Ar(111) substrate. In addition, a band gap of 11 meV and a significant splitting of the energy levels due to spin-orbit coupling are observed.

Keywords: silicene, DFT calculation, substrate

1. Introduction

Silicene is based on a two-dimensional honeycomb Si lattice, similar to graphene, attracting interest by the predicted linear dispersion near the Dirac point and various potential applications in electronic devices. The structure is not perfectly two-dimensional, but a finite buckling mixes some sp^3 hybridization into the sp^2 states. The weaker Si–Si bonding, as compared to the C–C bonding in graphene [1], strongly complicates the synthesis. Still, silicene has been grown on thin film ZrB_2 , resulting in electronic properties that are different from the expectations for freestanding samples [2]. Both the buckling and the electronic properties can be modified by



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epitaxial strain, which hints at a strong interaction with the substrate. Silicene on Ir(111) has been investigated experimentally and theoretically in [3].

It has been demonstrated that Si nanoribbons can be grown on Ag(110) substrates [4, 5] and the electronic structure has been investigated by angular resolved photoelectron spectroscopy [6]. Epitaxial growth with a highly ordered honeycomb structure on Ag(111) has been confirmed by scanning tunneling microscopy [7]. The Si nearest neighbor distance of $1.9 \pm 0.1 \text{ \AA}$, obtained by line analysis of the microscopy data, also points to strong interaction with the substrate. A systematic study of Si superstructures on Ag(111) has been performed in [9] using low energy electron diffraction, scanning tunneling microscopy, and *ab initio* calculations. Further results from scanning tunneling microscopy have been reported in [10–12], confirming that the quasiparticles in silicene behave as massless Dirac fermions. However, experiments indicate that the Dirac nature is perturbed by symmetry breaking due to the substrate [13]. This argumentation is supported by *ab initio* results, which lack a Dirac dispersion for various stable and metastable structures of silicene on Ag(111) [14, 15].

Graphene has been separated from SiC(0001) substrates, on which the binding energy experimentally amounts to 106 meV [16]. Hexagonal boron nitride [17] and SiC(0001) [18, 19] are known substrates for graphene and therefore have also been studied for silicene by *ab initio* calculations, finding that the Dirac cone is preserved, though slightly doped in the case of hydrogenated SiC(0001) [20]. For a superlattice of silicene and hexagonal boron nitride, a binding energy of 57 meV per Si atom has been predicted theoretically [21]. The electronic properties of silicene on II–VI and III–V semiconducting (111) substrates, including AlAs, AlP, GaAs, GaP, ZnS, and ZnSe, have been investigated in some detail [22–24], finding n-doping on metal terminated and p-doping on non-metal terminated surfaces.

Ar exists as a solid at low temperature, with short range, weak, and attractive London dispersion forces responsible for the molecular bonding [25]. The temperature-pressure phase diagram has been studied in [26, 27], demonstrating that a face-centered cubic structure is stable below a temperature of 84 K. Despite various attempts, so far no suitable substrate could be identified such that the characteristic electronic structure of silicene would not be perturbed dramatically on it [28]. This is probably the consequence of too high binding energies on the tested substrates. For example, values of 89 and 76/84 meV per atom have been reported for hexagonal boron nitride and Si/C-terminated SiC(0001) respectively [20]. In this context, we study the possibility of utilizing solid Ar(111) as a substrate and analyze the consequences on the electronic properties of silicene. We will argue that silicene on solid Ar(111) is quasi-freestanding. In addition, in [29, 30] a buffer layer of solid noble gas has been used to deposit metal clusters by soft landing and subsequent evaporation of the noble gas. A similar approach with solid Ar(111) on top of the desired substrate can provide access to growth of silicene on essentially any substrate.

2. Computational method

All calculations are performed using density functional theory in the generalized gradient approximation (Perdew–Burke–Ernzerhof parametrization) and ultrasoft pseudopotentials, as implemented in the Quantum-ESPRESSO package [31]. The plane wave cutoff energy for pure Ar is set to 476 eV and for all other systems to 544 eV. In the self-consistent calculation of pure Ar, a Monkhorst-Pack $32 \times 32 \times 32$ k-mesh is employed, whereas for all other systems a

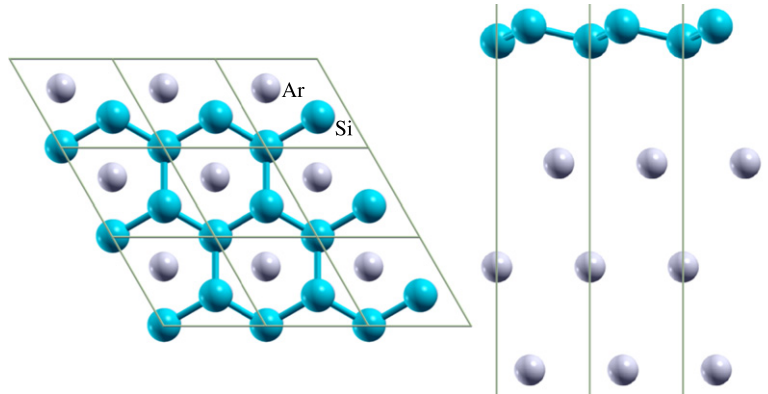


Figure 1. Top view (left: along c -axis) and side view (right: along x -axis) of silicene on Ar(111).

$32 \times 32 \times 1$ k-mesh is used. To achieve a high resolution, dense $64 \times 64 \times 64$ and $64 \times 64 \times 1$ k-meshes are used for calculating the density of states (DOS). An energy convergence of 10^{-5} Ry and a force convergence of 10^{-4} Ry/Bohr are achieved. Calculations are performed with and without spin-orbit coupling (SOC) and with and without van der Waals (vdW) interaction [32]. In the zoomed band structures shown in the following we use $\delta K = (0.002; 0.002; 0)$ with $K = (1/3; 1/3; 0)$. We consider a slab geometry with silicene on one side of an Ar(111) slab, which inherits hexagonal symmetry from the two subsystems.

3. Results and discussion

The optimized lattice parameter of solid Ar is 5.36 \AA , which leads to an Ar–Ar distance of $5.36/\sqrt{2} \text{ \AA} = 3.79 \text{ \AA}$. On the other hand, for freestanding silicene we obtain 3.86 \AA , in agreement with [33]. For the combined argon–silicene (ArSi) system we set the lattice parameter to 3.79 \AA , i.e., silicene is subject to a lattice mismatch of 1.9%. Figure 1 shows for the ArSi system a buckling of 0.53 \AA (distance between the bottom and top atomic layers), which is slightly higher than predicted for freestanding silicene (0.46 \AA) in [34]. We note that an artificially planarized structure with the same Si–Si bond length as the ground state buckled structure is only 32 meV per Si atom higher in energy. The Ar(111) substrate consists of six Ar layers. The top layer is arranged such that two thirds of the atoms are located below Si atoms and the last third is located below the center of a Si hexagon, which turns out to minimize the energy. After structural optimization without vdW interaction, the Si–Si bond length is 2.27 \AA with a bond angle of 115° , in agreement with [34–36]. We obtain a distance of 4.3 \AA between the top Ar layer and the silicene, whereas the interlayer spacing in the substrate amounts to 3.6 \AA . Taking into account the vdW interaction, we obtain the same buckling but reduced interlayer spacings of 3.4 \AA and 3.1 \AA respectively.

The band structure and DOS of solid Ar are shown in figure 2 and those of freestanding silicene in figure 3. Without SOC we obtain for silicene the characteristic linear dispersion of the π and π^* bands around the K point [1], reflecting massless Dirac fermions. The inclusion of SOC opens a band gap of 2 meV, which is small, but much larger than in the case of graphene

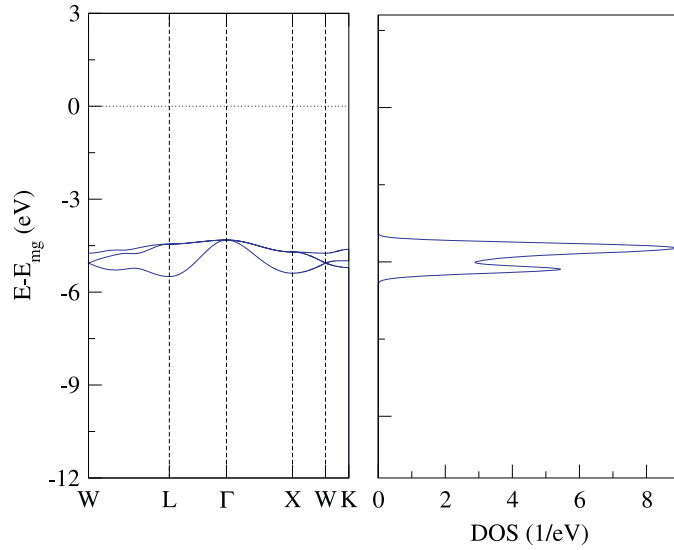


Figure 2. The band structure and DOS of solid Ar (mg: midgap).

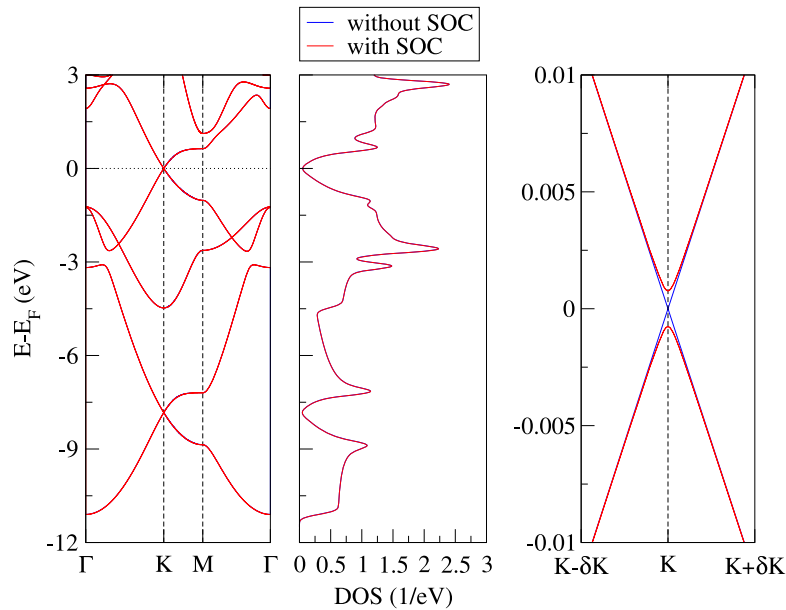


Figure 3. The band structure and DOS of silicene without vdW interaction (no band gap without SOC and $E_g = 2$ meV with SOC).

(due to the stronger SOC) and agrees with [21, 36]. When we turn on the vdW interaction we obtain virtually identical results to figure 3 both without and with SOC.

For the combined ArSi system, the band structure and DOS are presented in figure 4. Without vdW interaction and without SOC we obtain again a band gap of 2 meV, indicating the minor influence of the substrate despite the fact that the interlayer spacing between Ar and Si is large. SOC splits the bands near the K point, one forming a perfect Dirac cone and one showing a band gap of 2 meV. We note that the band gap of silicene can be tuned by applying an external electric field, because the insulating Ar does not screen electric fields. The binding

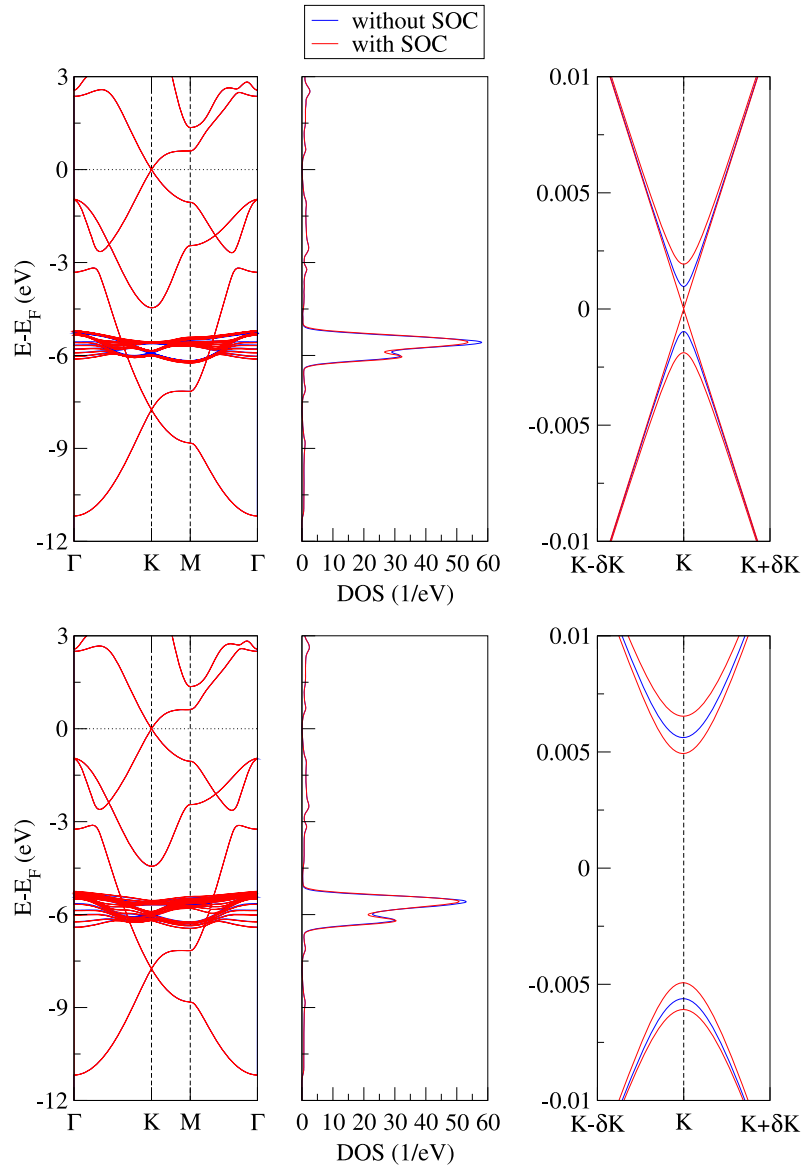


Figure 4. The bandstructure and DOS of the ArSi system. Top: without vdW interaction ($E_g = 2$ meV without SOC and no band gap with SOC). Bottom: including vdW interaction ($E_g = 11$ meV without SOC and $E_g = 10$ meV with SOC).

energy $(E_{\text{ArSi}} - E_{\text{Ar}} - E_{\text{Si}})/2$ per Si atom between silicene and the substrate amounts to -3 meV, both without and with SOC.

Switching on the vdW interaction enhances the band gap to 11 meV without and 10 meV with SOC. This is much larger than in graphene, but for many potential device applications still too small. For example, for metal-oxide-semiconductor field-effect transistors, a sizeable band gap is required for a good on-off ratio and low power dissipation [37]. If SOC is included, both split bands show energy gaps, where the splitting at the K point is of similar magnitude as seen in the top part of figure 4. The larger band gap reflects the relevance of the vdW interaction in the hybrid system, in contrast to freestanding silicene, while SOC splits the bands near the

Fermi level. The binding energy per Si atom accordingly is enhanced to -32 meV, which, however, is still very small. In particular, it is much less than reported for silicene on inert hexagonal boron nitride [21]. Due to the weak interaction, we conclude that solid Ar(111) will support quasi-freestanding silicene.

4. Conclusion

In conclusion, we have discussed the structure and electronic properties of silicene on solid Ar (111). It turns out to be critical to take into account the vdW interaction in order to obtain realistic results. We have shown that the Dirac cone of freestanding silicene remains intact on Ar(111), which points to a weak interaction with the substrate. In fact, we obtain for the binding energy a small value of -32 meV per Si atom, indicating a quasi-freestanding nature of silicene on Ar(111). Any other substrate employed so far has resulted in fundamental perturbations of the Dirac states, which is not the case on solid Ar according to our simulations. It is likely that the separation of silicene from this substrate is possible.

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