

International Workshop on Computational Nanotechnology

Session: Electronic Structure/First Principles Calculations

(Invited) Structural diversity of silicene

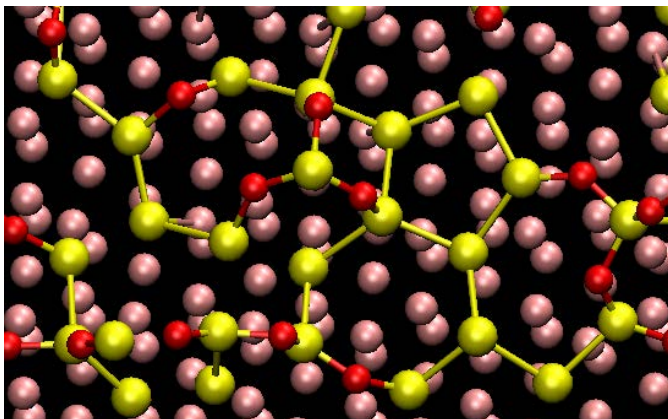
T Morishita

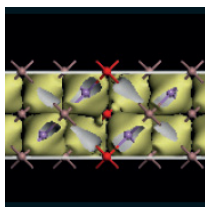
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A silicon (Si) monolayer, which is a graphene analogue and is called silicene, has recently been successfully formed on metallic substrates. Silicene possesses a similar honeycomb structure to that of graphene though it is corrugated due to its sp^3 hybridisation. The two-dimensional nature of silicene and the fact that Si forms the basis for most semiconducting devices today make it a promising material for use in future nanoscale electronic devices. However, in contrast to graphene, free-standing pristine silicene has never been synthesised thus far, partly because its structural stability is degraded by unsaturated sp^3 bonds. It is thus highly demanded to elucidate how the two-dimensional honeycomb silicene behaves (with or without a substrate) under various conditions. We have thus carried out a series of first-principles molecular-dynamics simulations to investigate the stability of the silicene structure.

In the first part of my talk, I will discuss the atomistic mechanism of the oxidation process of the silicene overlayer on the Ag(111) surface [1] when exposed to highly dense oxygen gas. I will demonstrate that there exist barrier-less oxygen chemisorption pathways around the outer Si atoms of the silicene overlayer, indicating that oxygen can easily react with a Si atom to form an Si-O-Si configuration. In the reaction process involving multiple O_2 molecules, a synergistic effect between the molecular dissociation and subsequent structural rearrangements was found to accelerate the oxidation process. This effect enhances self-organized formation of sp^3 -like tetrahedral 3D configurations (consisting of Si and O atoms), which results in collapse of the two-dimensional silicene structure and its exfoliation from the substrate, thus indicating that silicene is highly unstable upon exposure to air.

This theoretical investigation suggests that capping the unsaturated sp^3 bonds (dangling bonds) is a key to stabilising the silicene structure. In the latter part of my talk, I will talk on a bilayer silicene covered by atomistic walls [2,3] and on a organommodified monolayer silicene [4,5]. In both cases, we found that saturating the dangling bonds strongly affects the structural stability and the electronic properties. In particular, the structure of bilayer silicene can be controlled by tuning the degree of the saturation of the dangling bonds. I will also demonstrate that these modified silicene have non-zero band gap, being able to work as a semiconducting material, which is in stark contrast to graphene.





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Figure 1: A snapshot from the first-principles MD simulation of the oxidation process of silicene (Si; yellow, O; red, Ag; pink).

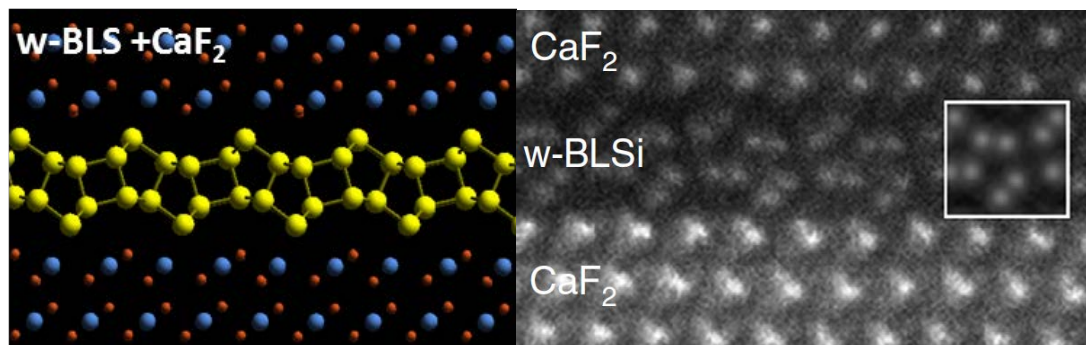


Figure 2: A bilayer silicene formed in a slit pore sandwiched by CaF_2 layers (left: theoretical prediction, right: experimental synthesis).

- [1] T. Morishita and M. J. S. Spencer, *Sci. Rep.* 5, 17570 (2015).
- [2] T. Morishita *et al.*, *Phys. Rev. B* 77, 081401(R) (2008); *Phys. Rev. B* 82, 045419 (2010).
- [3] R. Yaokawa, T. Ohsuna, T. Morishita, Y. Hayasaka, M.J.S. Spencer, H. Nakano, *Nat. Comm.* 7, 10657 (2016).
- [4] M.J.S. Spencer, T. Morishita, M. Mikami, I.K. Snook, Y. Sugiyama, and H. Nakano, *PCCP* 13, 15418 (2011).
- [5] M.R. Bassett, T. Morishita, H.F. Wilson, A.S. Barnard, and M.J.S. Spencer, *J. Phys. Chem. C* 120, 6762 (2016).

General atomistic approach for modeling metal-semiconductor interfaces and surfaces

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Metal-semiconductor (M-SC) contacts play a pivotal role in a broad range of technologically relevant devices. Still, their characterization at the atomic-scale remains a delicate issue. One of the reasons is that the present understanding relies either on simplified analytical models often parametrized using experimental data [1], or on electronic structure simulations describing the interface using simple slab calculations [2]. Here we propose a general strategy to model realistic M-SC interfaces by using density functional theory (DFT) in combination with the non-equilibrium Green's function (NEGF) method as implemented in the Atomistix ToolKit (ATK) simulation software [3]. An accurate description of both sides of the interface is achieved by using a meta-GGA functional [4] optimally tuned to reproduce the SC measured band-gap, and a spatially dependent effective scheme to account for the presence of doping in the SC side. Compared to previous computational methods [2], the present approach has the important advantages of (i) treating the system using the appropriate boundary conditions and (ii) allowing for a direct comparison between theory and experiments by simulating the I-V characteristics of the interface. We apply this methodology to an Ag/Si interface relevant for solar cell applications, and test the reliability of traditional strategies [1,2] to describe its properties [5]. Finally, we will describe a novel surface Green's function (SGF) method where the surface is described as a true semi-infinite system and present a number of examples to