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Accurate Quantum Mechanics for slab calculations of semiconductor surfaces: The elusive case of the Si (111)-7x7 Surface

Surfaces play a fundamental role in all materials processes, in most chemical processes and in the growth or formation of all solid-state materials, especially semiconductors and new 2-D materials. Over the years our ability to rigorously calculate their properties has improved, starting from simple model systems to more complicated systems. Computational advances aimed at handling larger and more complex systems and more accurately solving the wave equation for them is necessary to make progress in understand such systems. That is the case for the Si(111)-7x7 surface since it represents a complex large unit cell structure combining 49 primitive cells whose nature still remains elusive.

The Dimer-Adatom-Stacking fault model or DAS model for the 7×7 surface was proposed in 1985 and validated using Density Functional theory a dozen years later. Indeed, a Machine Learning Force Field demonstrated formation of the DAS structure by first melting the 2D slab to 1500K and then cooling it. [1] Recently the nature and our understanding of the Si (111)-7x7 surface has been questioned [2-4] due to the failures of all DFT calculations to describe a wide range of properties of this system [5]. The most obvious is the ground state of the widely accepted DAS structure that shows a metallic electronic structure whereas numerous experiments show a ˜0.1 eV (semiconducting) gap at Ef. In addition, several structural measures including X-ray measurements show that the height of the adatoms predicted is at least 0.2 Å smaller than those measured, an error well beyond the accepted accuracy of DFT calculations.

Here we present all electron DFT calculations using CRYSTAL that more accurately describe the exchange-correlation, k-pt sampling, and the surface point group symmetry of the 7x7 than considered previously to evaluate the DAS structure. We discovered that preserving the quantum mechanical nature of a slab model of our surface is essential to correctly describing the quantum mechanical elements of the substrate as well as the adlayer to avoid introducing unnecessary 'spurious' boundary conditions. Our Hybrid DFT (B3LYP) calculations reveal that the starting DAS structure from a VASP PBE calculation relaxes to a new lower energy structure with distinctly different properties for the Si(111)-7x7 surface. This changes many of the structural features found using semi-local non-hybrid functionals (PBE, PBEsol and PBE-D3) calculated with VASP. Indeed, this resolves some of the paradoxes of this complex system. This work demonstrates the need for more accurate calculations and modeling of surfaces to reliably calculate their properties, their role in chemical processes, and to evaluate features in such novel 2-D materials.

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