Surface Thermodynamic Equilibrium Conditions and the Growth of Monolayer Graphene Films on SiC

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The Si side of SiC substrates is known for the epitaxial growth of large-scale, near-perfect monolayer graphene films by Si sublimation. Curiously, the same is not true for the C side of the substrate, where rotated few-layer graphene films are observed instead. In either case, straightforward theoretical simulations from first principles are made difficult by the lattice mismatch between graphene and the SiC substrate, leading to rather large, experimentally observed ($6\sqrt{3}\times6\sqrt{3}$)-*R*30° superstructures on the Si side of SiC. We here present accurate, all-electron simulations of graphene and competing phases on SiC that explain the observed high-quality monolayer graphene growth and its precursors on the Si side by the existence of a narrow range of (near) thermal equilibrium conditions [1], equivalent to specific settings of growth temperature and Si background pressure in experiment. These calculations are based on a van der Waals corrected generalized-gradient approximation to density functional theory, encompassing up to ~2,700 atoms in a slab model of graphene on SiC. In contrast, smaller model unit cell sizes in the surface energy calculations would introduce significant strain, enough to erroneously stabilize artificial defects. On the C side, we do not find a thermodynamic equilibrium regime for monolayer graphene. Instead, two non-graphene surface phases ((3×3) and $(2\times2)_C$) are found to coexist with a monolayer graphene covered surface right at the stability limit of bulk graphite, explaining the experimentally observed features. Overall, our results indicate that thermodynamic equilibrium conditions appear to govern the local atomic arrangements observed in the growth of graphene on SiC. Accurate, large-scale low-strain first-principles models of 2D materials on an intended substrate are thus indeed a desirable and viable way forward to distinguish which potential growth paths to near-perfect layers are promising and which are not.
Work carried out with Lydia Nemec, Patrick Rinke, and Matthias Scheffler at Fritz Haber Institute, Berlin.

[1] L. Nemec, V. Blum, P. Rinke, M. Scheffler, *Thermodynamic Equilibrium Conditions of Graphene Films on SiC.* Phys. Rev. Lett. **111**, 065502 (2013).