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Single-layer Dual Germanene Phases on Ag(111)

Two-dimensional (2D) honeycomb lattices beyond graphene promise new physical properties such as quantum spin Hall effect. While there have been claims of growth of such lattices (silicene, germanene, stanene), their existences are still being debated and their preparation and characterization remain a difficult challenge. We provide definitive evidence that two distinct phases of germanene, the analog of graphene made of germanium (Ge) instead of carbon, can be grown on Ag(111) as observed by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), and angle-resolved photoemission spectroscopy (ARPES). One such germanene exhibits an atom-resolved alternatively-buckled full honeycomb lattice, which is tensile strained and partially commensurate with the substrate to form a striped phase (SP). The other, a quasi-freestanding phase (QP), also exhibits a honeycomb lattice with a lattice constant incommensurate with the substrate but very close to the theoretical value for freestanding germanene. The SP, with a lower atomic density, can be driven into the QP and coexist with the QP by additional Ge deposition. Band mapping and first-principles calculations with proposed SP and QP models reveal an interface state exists only in the SP but the characteristic σ band of freestanding germanene emerges only in the QP - this leads to an important conclusion that adlayer-substrate commensurability plays a key role to affect the electronic structure of germanene. The evolution of the dual germanene phases manifests the competitive formation of Ge-Ge covalent and Ge-Ag interfacial bonds, providing a vital insight into the growth of other 2D honeycomb lattices.