Supplementary information

I. CORE-LEVEL SPECTROSCOPY

Here, we present experimental details during the high-resolution Scanning Tunneling Microscopy and synchrotron radiation core-level spectroscopy studies of Germanium grown on Au(111) in situ.

Samples were prepared *in situ* in two separate ultrahigh vacuum (UHV) systems, i.e. one with Low Energy Electron Diffraction and STM and one with LEED and Angle Resolved PhotoElectron Spectroscopy (ARPES). STM images were recorded at room temperature using an Omicron variable temperature STM at Aix-Marseille University and the ARPES experiments were first performed on the Surface/Interface Spectroscopy (SIS) X09LA beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland, then repeated (with confirmation) at the APE beamline of the Italian synchrotron radiation facility, Elettra in Trieste. At the SLS (data presented here), the beamline was set to Linear polarized light with a photon energy, hv = 135 eV with an energy resolution of 80 meV, and data were acquired at Room Temperature using a VG-Scienta R4000 electron analyzer. The binding-energy scale was calibrated with a copper reference sample in direct electrical and thermal contact with the film. The base pressure of the UHV systems was below 5×10^{-11} mbar during the entire measurement and no sign of sample and/or data quality degradation was observed. Our results were reproduced on several occasions, using different samples grown under the same conditions. A single crystal Au(111) substrate was cleaned in vacuum by 1.5-keV Ar ion sputtering for 30 min at $5x10^{-5}$ mbar. Subsequently, annealing in vacuum at 500° C for 30 min was performed to cure Ar ion sputtering damage and obtain flat and well-ordered surface. The annealing-sputtering cycle was repeated as many times as necessary to obtain a clean surface free of C and O contaminants as verified by *in situ* x-ray photoelectron spectroscopy (XPS). Here, slightly less than 1 ML of Ge was deposited on the substrate at 200° C by a resistance heated crucible resulting in sharp LEED patterns. A series of experiments was undertaken to determine the rate of germanium evaporation in vacuum as a function of temperature.

The Au 4f and Ge 3d core-levels (CLs) have been fitted using standard methods with the following parameters:

<u>Clean Au(111) Normal Emission (NE) : Au 4f</u>
Areas: B 15,02 ; S 15.83
Spin-orbit split: 3.678 eV,
Branching ratio: 0.6,

Gaussian widths: 121 (S) and 200 (B) meV,
Lorentzian width: 300 meV.
The asymmetry parameter of the Doniach-Sunjic line Profile is α = 0.012,
The energy difference between the two components Surface and bulk is 0.31 eV.
Ge/Au(111) NE : Au 4f
Areas: B 14,9 ; S 3,12 ; I 3,11
Branching ratio: 0.6,
Gaussian widths: (B) 204 ; (S) 294 ; (I) 311 meV,
Lorentzian width: 300 meV.
α = 0.012,
The energy difference between the two components Surface and Bulk is 0.31 eV and B to I: 0.3 meV
Ge/Au(111) 50° Off Normal: Au 4f
Areas: B 6.54 ; S 1.4 ; I 1.9
Spin-orbit split: 3.678 eV,
Branching ratio: 0.58,
Gaussian widths: 180 (S) ; 150 (B) ; 200 (I) meV,
Lorentzian width: 300 meV.
α = 0.012 The energy difference between the two components Surface and bulk is 0.31 eV
and (B) to (I) 0.3 eV
Ge/Au(111) NE : Ge 3d
Areas, Peak1: 1.80713 ; Peak2: 0.18152
Spin-orbit split: 0.551 eV
Branching Ratio: 0.69
Gaussian widths: 112 and 370 meV, respectively,
Lorentzian width: 150 meV.
α = 0.12,
Energy difference between the two components is 0.245 eV.
Ge/Au(111) 50° Off Normal: Ge 3d
Areas: Peak1: 1.7816; Peak2 : 0.00
Branching ratio: 0.65,
Gaussian widths: 114 and 370 meV, respectively.

II. COMPUTATIONAL METHODS

We have performed first principle calculations based on density functional theory (DFT) as implemented in the VASP code [1]. The exchange-correlation potentials are treated with the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [2]. Ionic cores of atoms are modeled with the projector-augmented wave (PAW) pseudopotential method [3]. Plane wave basis set with a energy cutoff of 310 eV are employed for the valence electron wave functions. The calculations are

performed in a √7x√7 Au supercell on the Au(111) surface with theoretical optimized bulk Au-Au distance 0.294 nm. The supercell Brillouin zone is sampled with 9 x 9 x1 k-point grids. The Au surface is modeled with a 6-layer slab and a vacuum region larger than 1.6 nm in the z direction perpendicular to the surface. The bottom three Au layers are kept fixed, while all the other atoms are relaxed in the calculations until all forces are converged within 0.01 eV/$Å^{-1}$. Dipole correction is added along the z direction to eliminate the artificial long range interaction between periodic slab images [4]. STM simulations are performed base on the Tersoff-Hamann model [5]. Core level shift for the Au 4f and Ge 3d electrons are calculated within the final state approximation [6]. Considering the lattice constant for germanene and Au surface, we have examined several possible candidates for monolayer germanene on top of the Au (111) surface, including 2 x 2 and √3 x√3 germanene on top of the √7 x √7 Au surface.

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