Exotic forms of low-dimensional epitaxial silicon and Xenes

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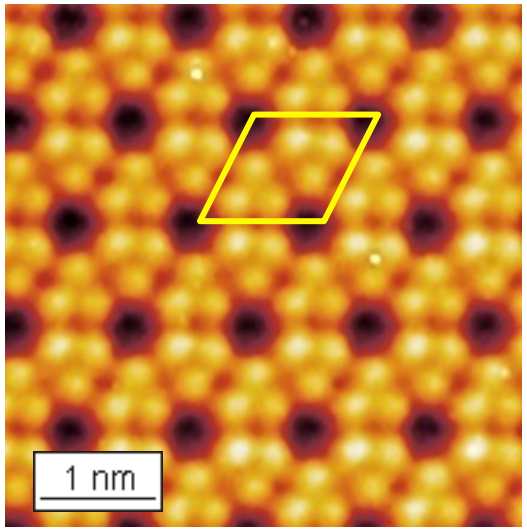
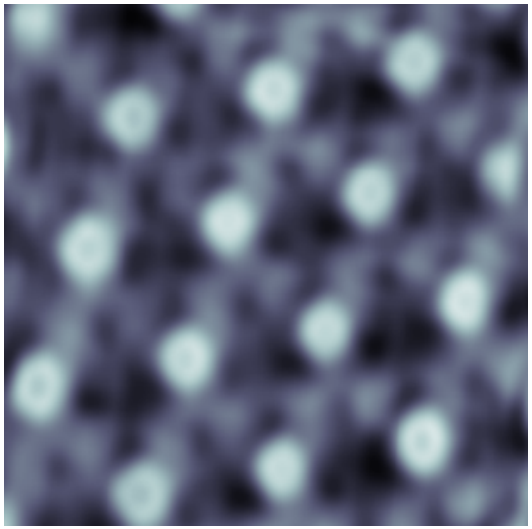
Aix-Marseille University, CNRS-PIIM, France

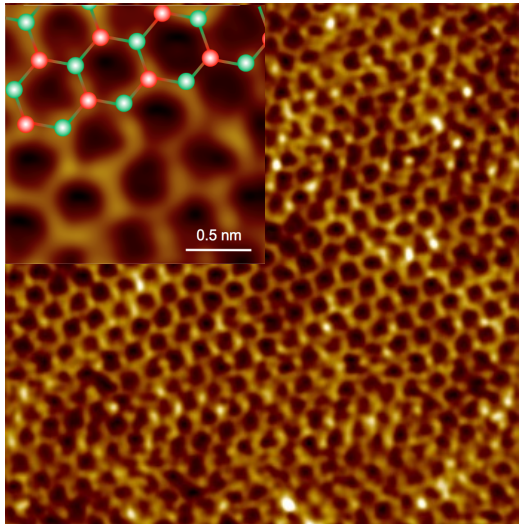
Workshop on Chiral Modes in Optics and Electronics of 2D Systems,
Aussois, France, Nov. 26-28, 2018



Epitaxial silicene archetype structure on Ag(111)4x4



Kagome silicene on Al(111)3x3 (3x3 nm^2)



Large area stanene on Ag(111)√3x√3

Co-workers

Europe

T. Angot and **E. Salomon**, Marseille, France

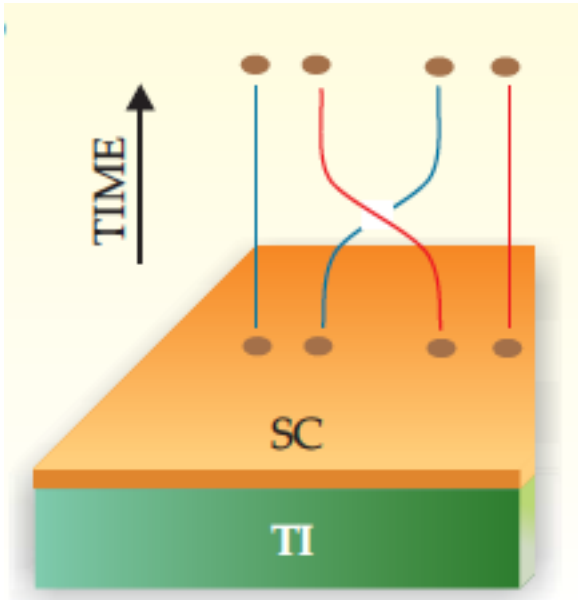
Y. Sassa and coll., Uppsala, Sweden

H. Sahin and **F. Iyikanat**, Izmir, Turkey

Japan

J. Yuhara and coll., Nagoya, Japan

The Hunt for the Topological Qubit



When a TI is coated by an s-wave superconductor (SC), the superconducting vortices are **Majorana fermions**—they are their own antiparticles. Exchanging or braiding Majorana vortices, as sketched here, leads to non-abelian statistics. Such behavior could form the basis piece of hardware (**Majorana Qubit**) for topological quantum computing.

Xiao-Liang Qi and Shou-Cheng Zhang, Physics Today Jan. 2010, 33

The Challenge: the Hardware

QSHE

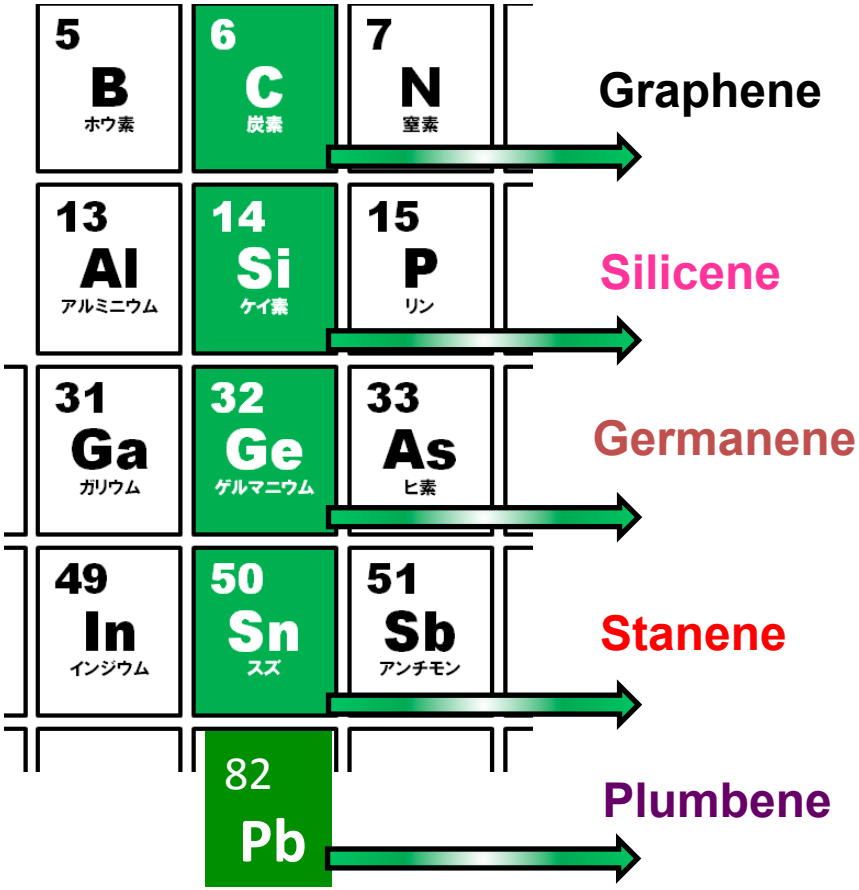
« Experimental synthesis and characterization of **2D Topological Insulators** remain a major challenge at present, offering outstanding opportunities for innovation and breakthrough. »

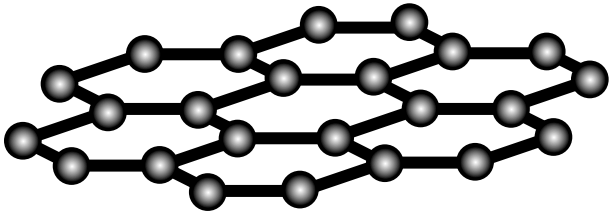
Kou et al., J. Phys. Chem. Lett. 2017, 8, 1905

The way: Nanoarchitectonics, i.e., create atomically controlled artificial structure by design

The artificial Xenes

What about Si, Ge, Sn, and Pb group 14 *artificial counterparts* of graphene?





Flat
No band gap
Minute SOC

Increasing Spin Orbit Coupling

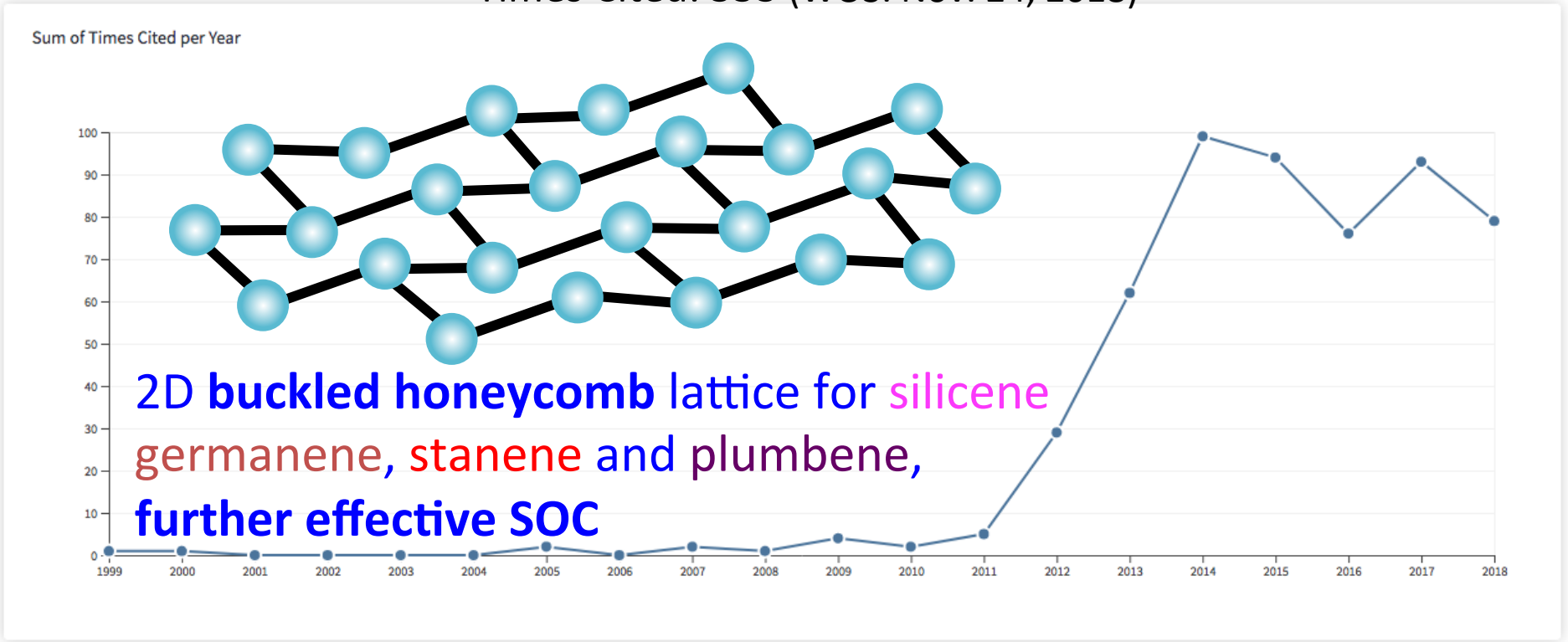
The hardware beyond graphene

First prediction in 1994, 10 years before the isolation of graphene!

"Theoretical Possibility of *Stage Corrugation* in Si and Ge Analogs of graphite"

⇒ **K. Takeda and K. Shiraishi,** Phys. Rev. B 50, 14916 (1994)

⇒ Times Cited: 553 (WOS: Nov. 24, 2018)



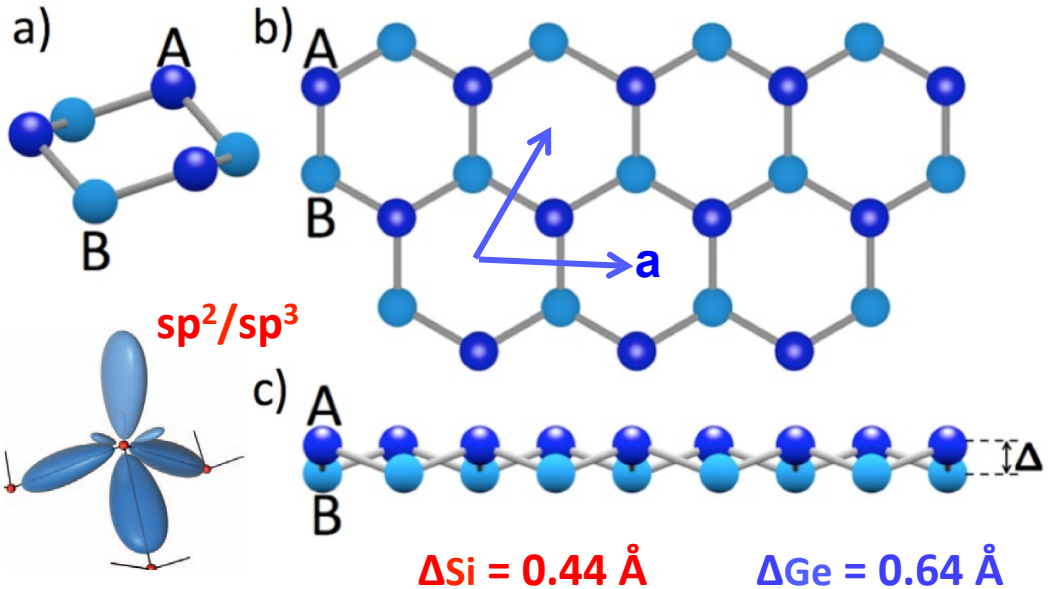
Only 18 citations until Dec. 31, 2011 !

Nobody believed that sp^2-like silicon or germanium could ever exist since there is no parent lamellar Si or Ge crystal in nature comparable to graphite!

Stability with respect to phonons confirmed !

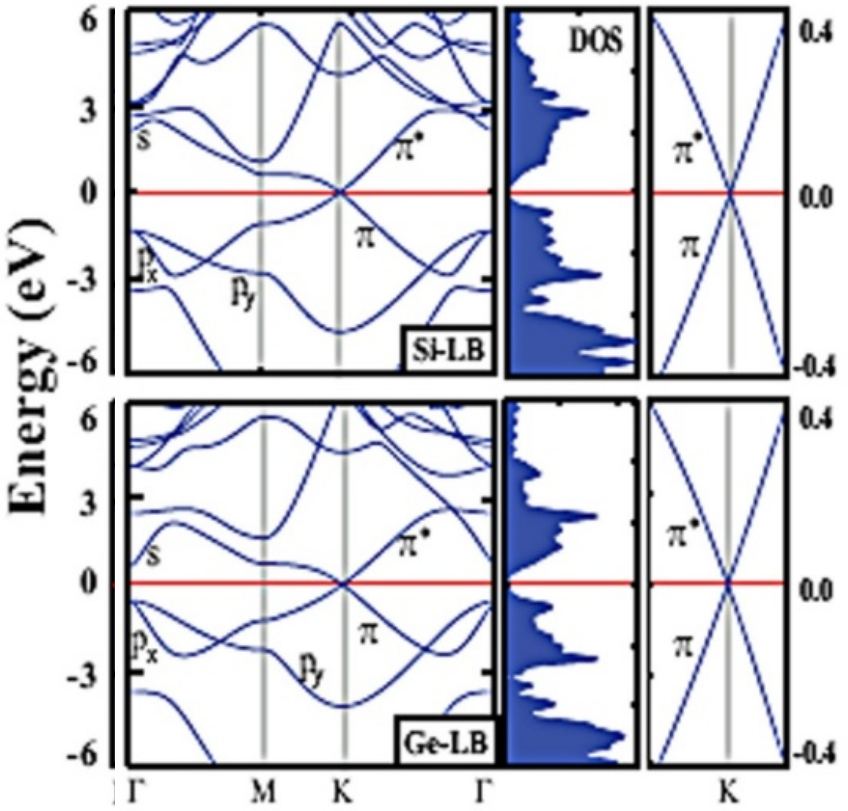
DFT-GGA calculations on free standing Silicene and Germanene

S. Cahangirov *et al.*, PRL 102, 236804 (2009)



$\Delta Si = 0.44$ Å $\Delta Ge = 0.64$ Å

$\Delta_{Si(111)} = 0.78$ Å

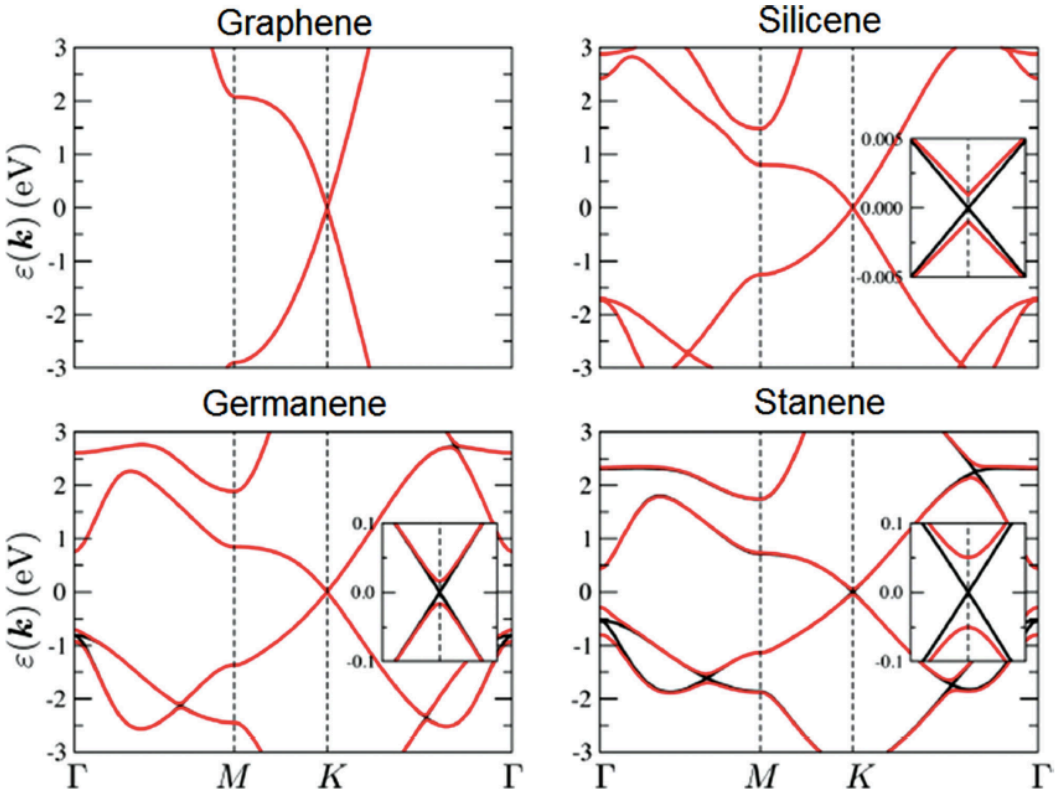


Band structures of silicene/germanene in the low-buckled (LB) geometry

The hybridization of silicene sp^D (D = 2.27) is closer to sp^2 than to sp^3.

$a_{Si} = 3.9$ Å $d_{Si-Si} = 2.25$ Å

Monolayer topological insulators **C.-C. Liu, W. Feng, Y. Yao** PRL 107, 076802 (2011)



Spin-orbit coupling (SOC) opens up a bandgap at the Dirac point which facilitates the 2D material transition from semi-metallic to a QSH insulator

SOC gaps of over 23 meV and 73 meV in germanene and stanene (compared to 1.55 meV in silicene and 8 μeV in graphene), lead to the possibility of RT 2D topological insulators.

L. Matthes, O. Pulci and F. Bechstedt,
J. Phys.: Condens. Matter 25 (2013) 395305

Silicene/Germanene/Stanene ↔ **Graphene**

Buckled **Flat**

2D Topological insulators

QSHE at 15 K / ~RT / > RT **too low T**

S. Cahangirov et al., PRL 102, 236804 (2009)
M. Ezawa Euro. Phys. J. B 85, 363 (2012)
L. Matthes et al., Phys. Rev. B 94, 085410 (2016)
L. Matthes et al., Phys. Rev. B 93, 121106(R) (2016)

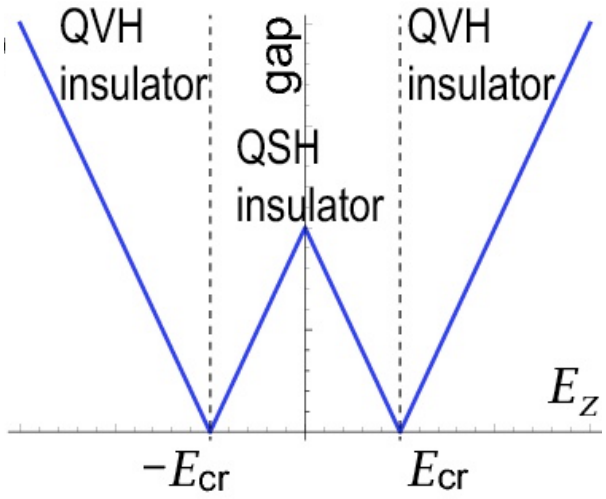
Few predicted properties

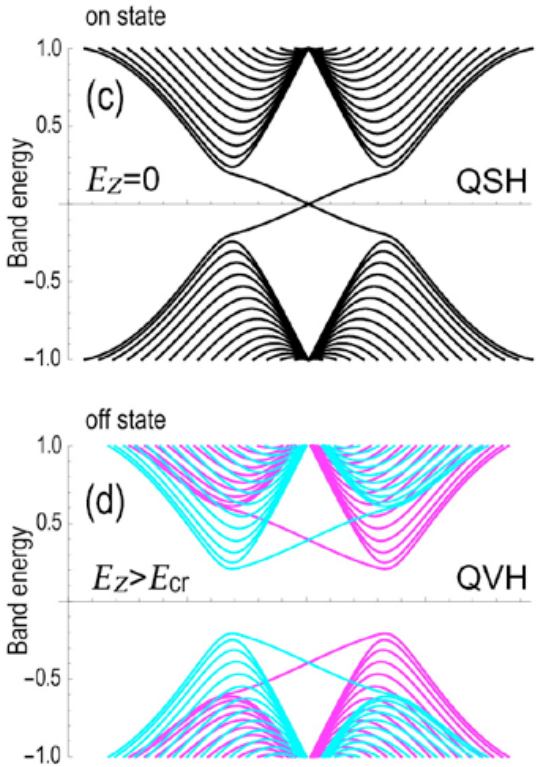
Electrically tunable band gap

V. Fal'ko et al., Phys. Rev. B 85, 075423 (2012)

Electric field controlled topological phase transition

M. Ezawa, J. Phys. Soc. Japan 84, 121003 (2015)





Predicted mobilities at 300K (10^5 $cm^2/V.s$)

along the zig-zag and armchair directions

	μe	μh
Germanene	6.09	6.39
	6.24	6.54
Silicene	2.58	2.23
	2.57	2.22
Graphene	**3.39**	**3.22**
	3.20	**3.51**

Extremely high mobilities

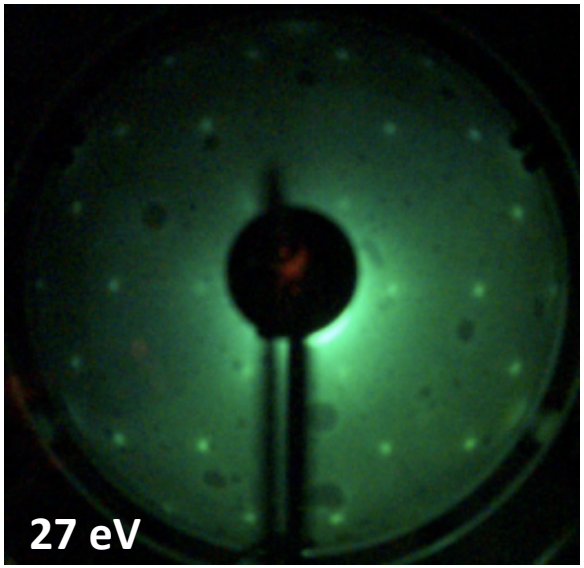
X.-S. Ye *et al.*, RSC Adv., 4, 21216 (2014)

Phonon mediated superconductivity

Liu *et al.*, Europhys. Lett., 104, 36001 (2013)

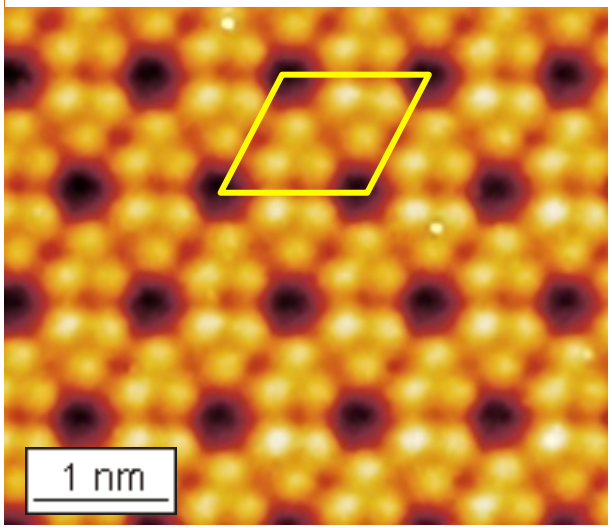
Silicene

4x4 LEED pattern

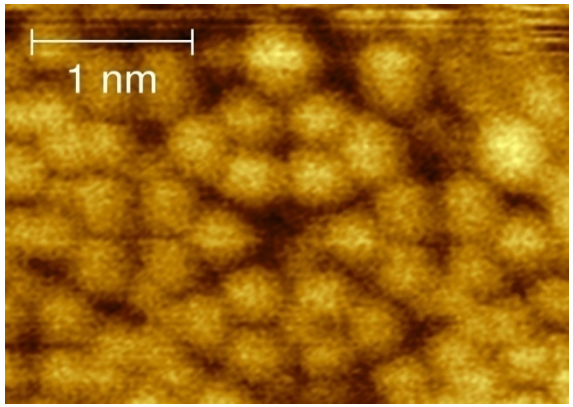


STM image at RT

The "flower pattern"



Non Contact AFM image at 77 K (2013)



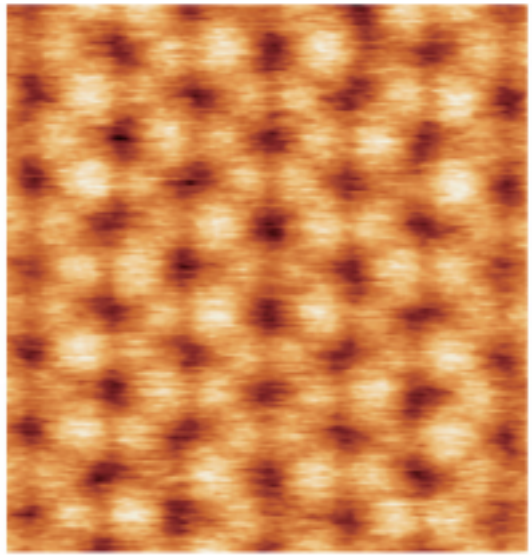
Resta *et al.*, Sci. Rep., 3, 2399 (2013)

Silicon deposition onto a Ag(111) substrate held at 200-220°C

3x3 reconstructed silicene matching a 4x4 Ag(111) supercell

Θ = 18/16 = 1.125

Nothing looking like a honeycomb structure !



DIRECT OBSERVATION of the honeycomb structure by near Contact AFM with a CO terminated tip(2017)

Onoda *et al.*, PRB 96, 241302(R) (2017)

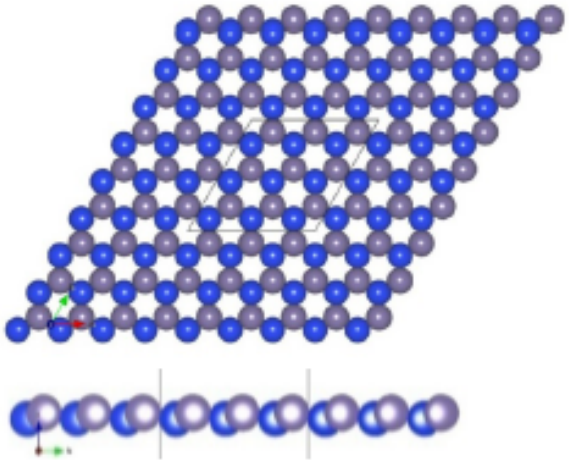
INSPIRATION: a hidden underlying honeycomb structure

Vogt et al., PRL108, 155501 (2012)

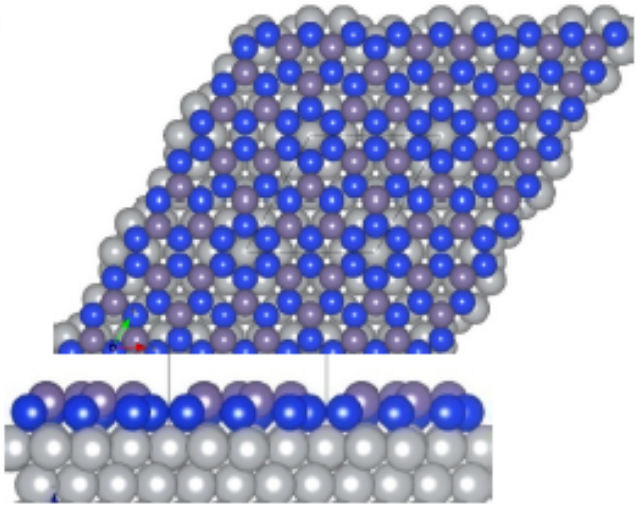
WOS citations: 1760 on Oct. 25, 2018

Single Layer Silicene on Ag(111)

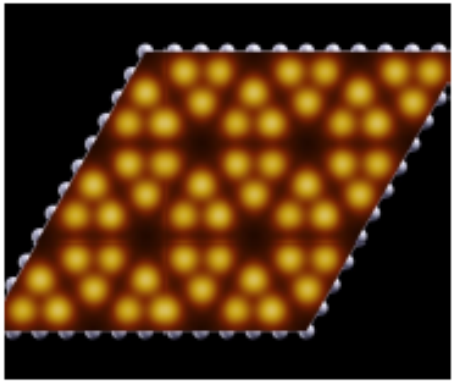
Standalone silicene
(buckling ~0.38 Å)



Si atoms atop Ag atoms
protrude by 0.4 Å



Simulated STM



- 18 atoms of Si and 16 atoms of Ag in the 4 x 4 unit cell → θ = 1.125.
- Silicene adapts to the substrate (at variance with graphene which forms Moiré patterns).
- On all metallic substrates, it is reconstructed

2012, Silicene's Annus Mirabilis

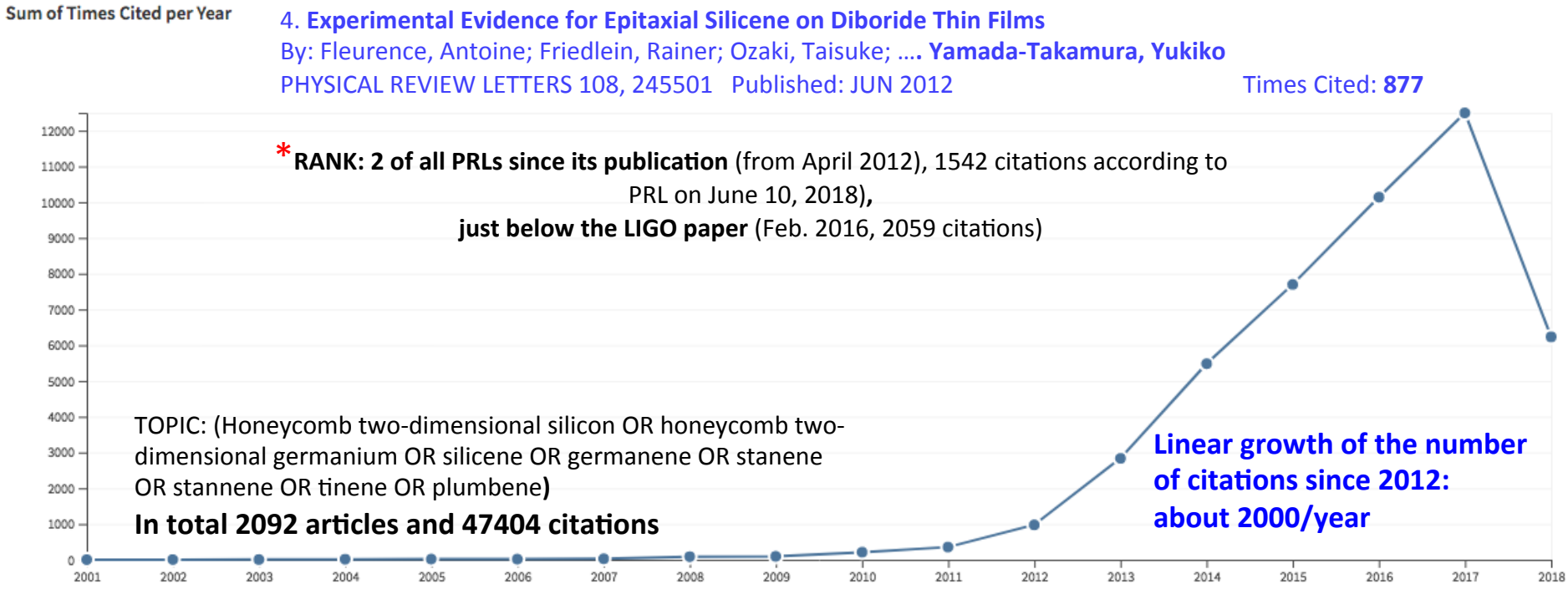
Original 2D Si, Ge, Sn, Pb papers with more than 800 citations on Nov. 27, 2018, according to WOS: 4 Phys. Rev. Lett.'s !

1. **Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional** Silicon*
By: Vogt, Patrick; De Padova, Paola; Quaresima, Claudio; …; **Le Lay, Guy**
PHYSICAL REVIEW LETTERS 108, 155501 Published: APR 2012 Times Cited: **1,797**

2. **Two- and One-Dimensional Honeycomb Structures of Silicon and** Germanium
By: Cahangirov S., Topsakal M., Arturk E., Sahin H., **Ciraci S.**
PHYSICAL REVIEW LETTERS 102, 236804 Published: JUN 2009 Times Cited: **1,519**

3. **Quantum Spin Hall Effect in Silicene and Two-Dimensional Germ**anium
By: Liu, Cheng-Cheng; Feng, Wanxiang; **Yao, Yugui**
PHYSICAL REVIEW LETTERS 107, 076802 Published: AUG 2011 Times Cited: **1,169**

4. **Experimental Evidence for Epitaxial Silicene on Diboride Thin Films**
By: Fleurence, Antoine; Friedlein, Rainer; Ozaki, Taisuke; …. **Yamada-Takamura, Yukiko**
PHYSICAL REVIEW LETTERS 108, 245501 Published: JUN 2012 Times Cited: **877**

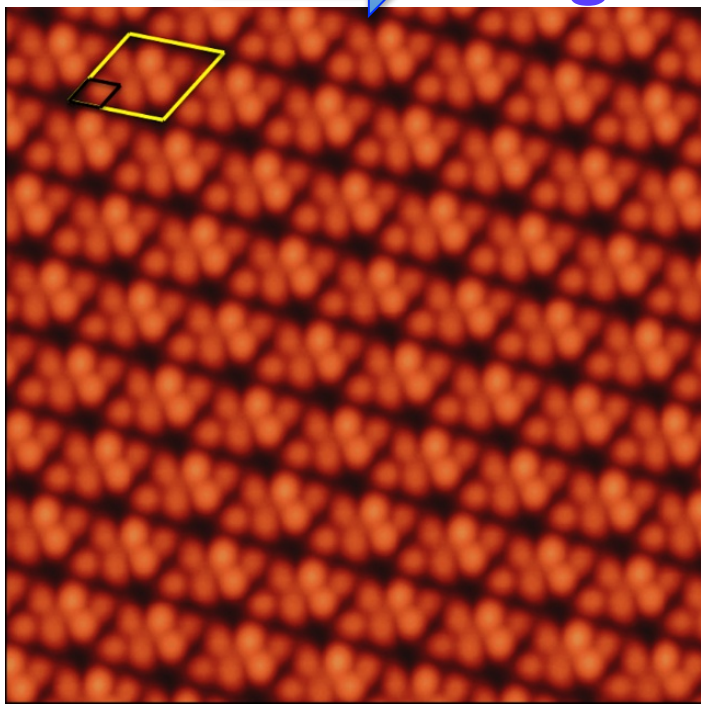


*__RANK: 2 of all PRLs since its publication__ (from April 2012), 1542 citations according to PRL on June 10, 2018),
just below the LIGO paper (Feb. 2016, 2059 citations)

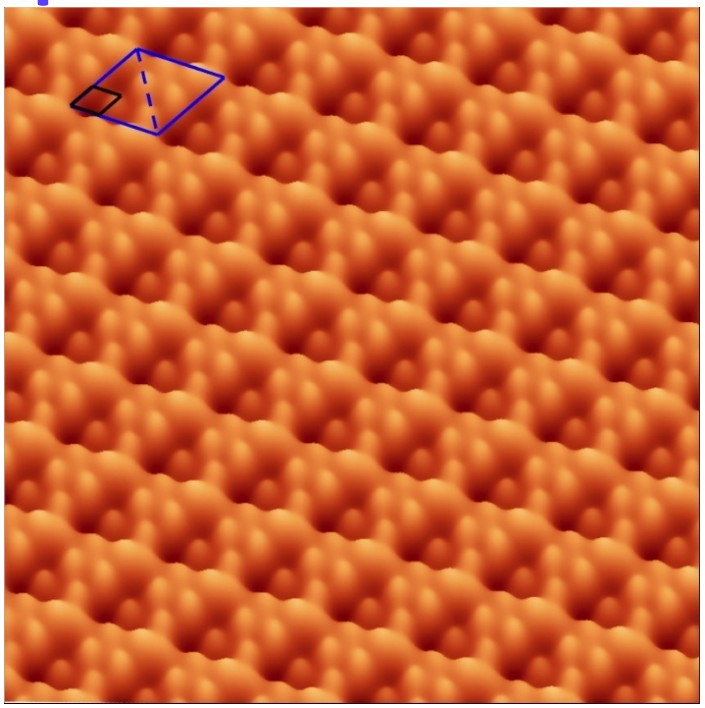
TOPIC: (Honeycomb two-dimensional silicon OR honeycomb two-dimensional germanium OR silicene OR germanene OR stanene OR stannene OR tinene OR plumbene)
In total 2092 articles and 47404 citations

Linear growth of the number of citations since 2012: about 2000/year

Silicene functionalization: hydrogenation → magnetic properties?



Filled states STM image of **pristine silicene** 3×3 reconstructed (yellow cell, while the primitive 1×1 is in black) matching a 4×4 Ag(111) supercell 9 nm × 9 nm tunnel current 0.55 nA, sample bias -520 mV



Filled states STM image; **after hydrogenation the 3×3 silicene super cell is preserved**, **but the H atoms saturate the Si dangling bonds in a manner that favors one of the sublattices** (6 H atoms on one sublattice on the left half of the supercell) over the other (a single H atom on the other sublattice on the right half of the supercell). 9 nm × 9 nm, 0.33 nA, -200 mV . **Beato Medina** *et al.*, J. Electron Spectrosc. Rel. Phenom., 219, 57 (2017)

First realized by Qui *et al.,* PRL 114, 126101 (2015)

H is released at ~200°C: toward hydrogen storage

Pentasilicene

J. I. Cerdá *et al.*,
Nature Comm., **7,** 13076 (2016)

Hidden atomic structure: 1D crystals formed only of pentagonal Si tiles !

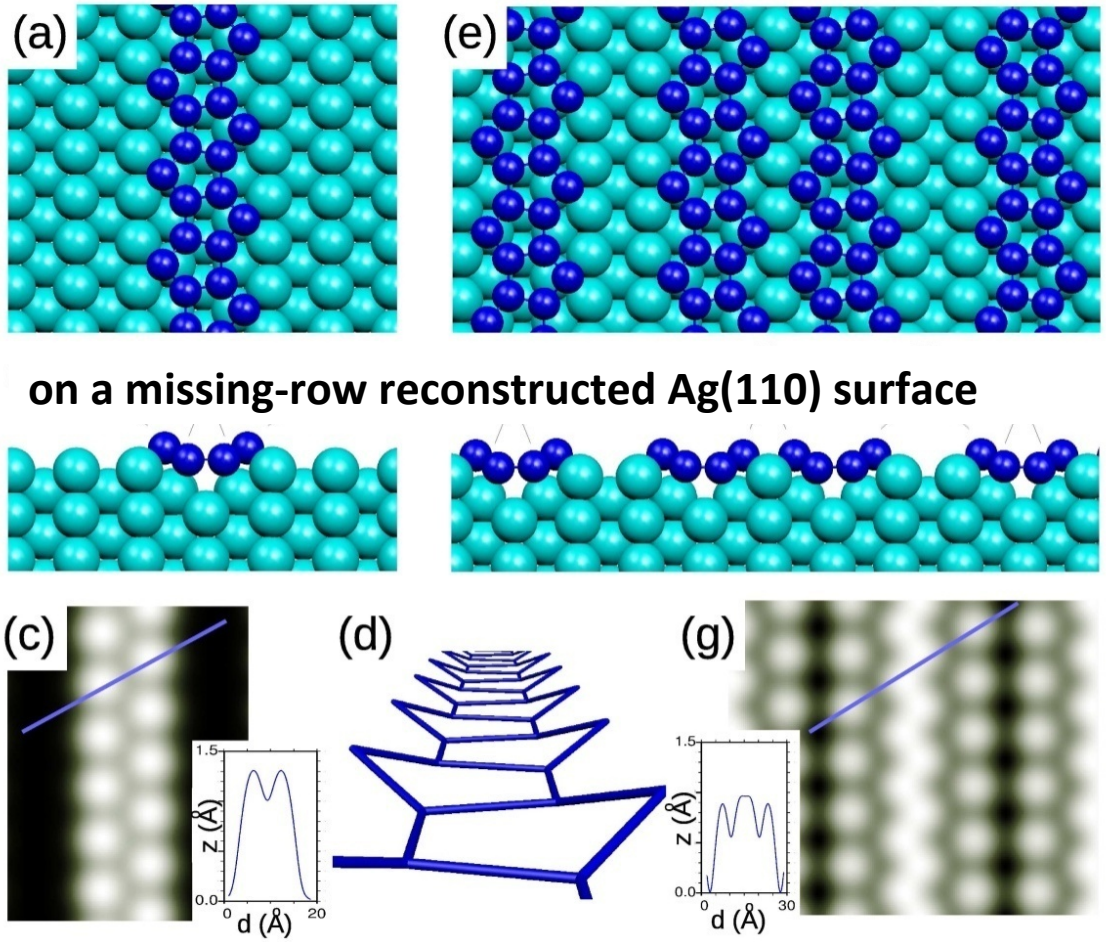
DFT LDA/GGA approximations;
van der Waals corrections yielded negligible changes

The theoretically determined pentasilicene-like structure has been further confirmed experimentally by Grazing-Incidence X-Ray Diffraction
G. Prévot et *al.*,
Phys. Rev. Lett., **117**, 276102 (2016)

and by Photoelectron Diffraction
P. Espeter *et al.*,
Nanotechnology, **28**, 455701 (2017)

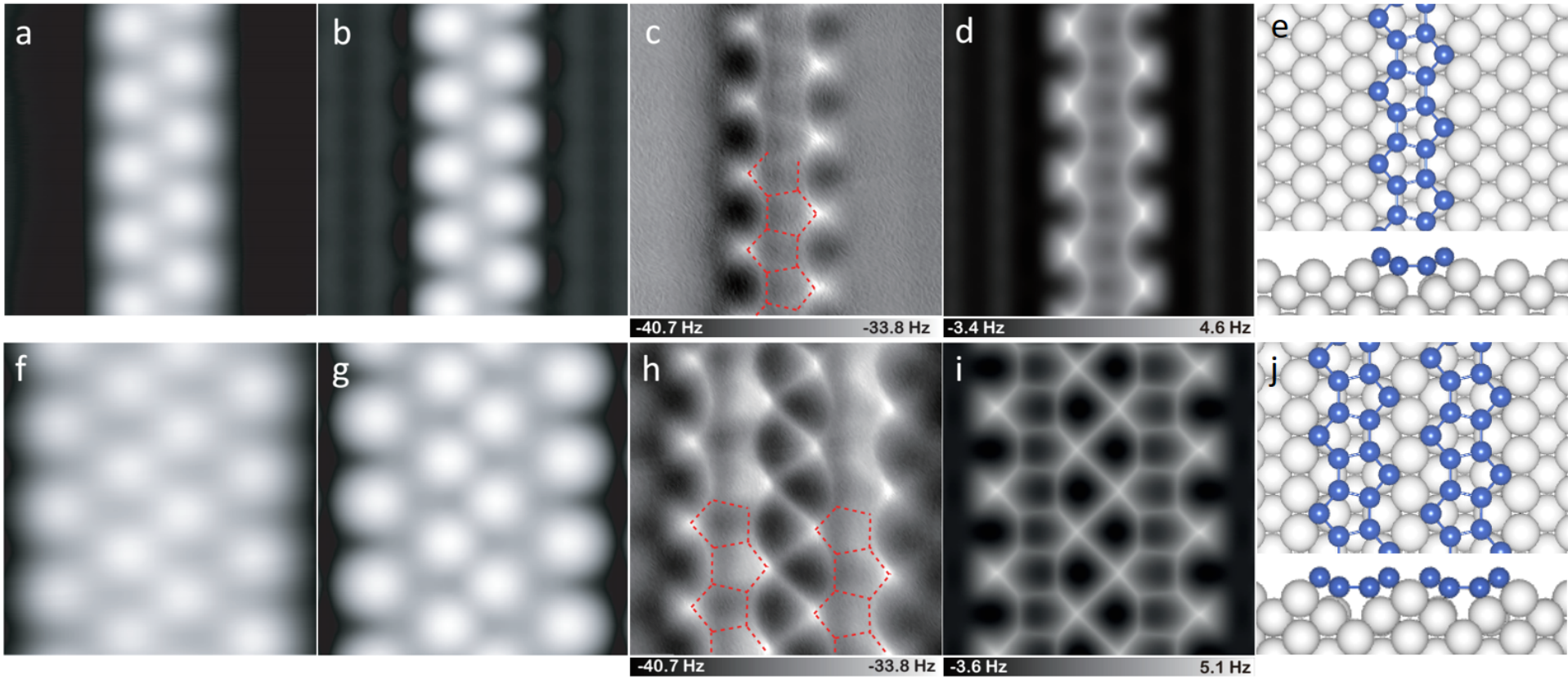
Si nanoribbons and nanodots

Single strand & Double strand SiNRs



Optimized geometry
(a-c) Top, side and simulated topographic STM image for the SNR phase.
(d) Perspective view of a **penta-silicene** strand without the silver surface.
(e-g) Top, side and simulated topographic STM image for the DNR array.
Insets in (c) and (g) show line profiles along the blue lines indicated in the topographic maps. All STM simulations employed a sharp Si ended tip apex and set points V = −0.2 V and I = 1 nA.

Direct evidence of Pentagonal silicon chains in AFM imaging with a CO terminated tip*

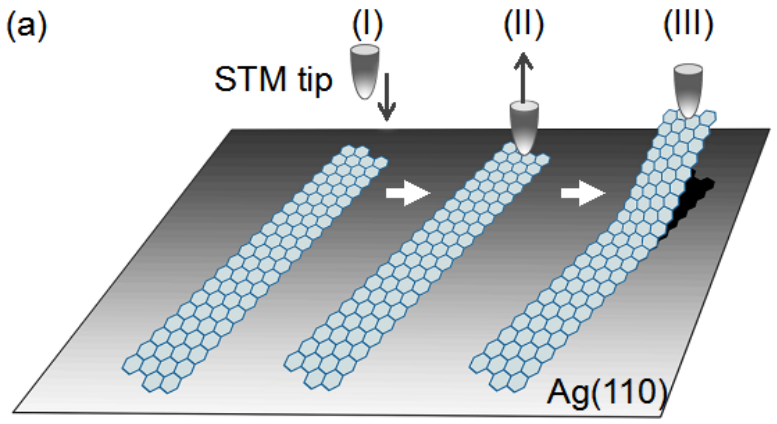


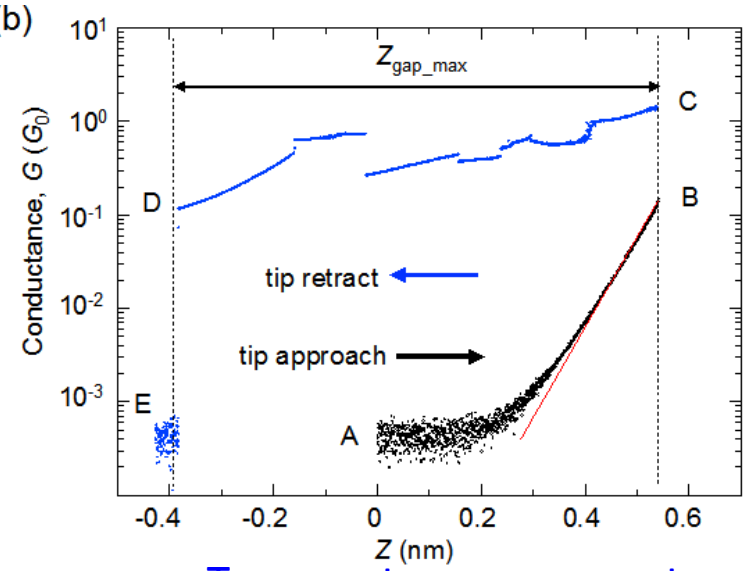
S-SiNRs and D-SiNRs on the Ag(110) surface. a-d, STM (a) and AFM images (c) of S-SiNRs, and the corresponding simulated ones (b, d). e, Atomic structure of the SNR on Ag(110) in top and side views. Ag, Si atoms are denoted as white and blue spheres respectively. f-i, STM (f)and AFM (h) images of D-SiNRs, and the corresponding simulated ones (g, i). j, Atomic structure of the DNR on Ag(110) in top and side views.

Shaoxiang Sheng *et al.*, Nano Letters 18, 2937 (2018)

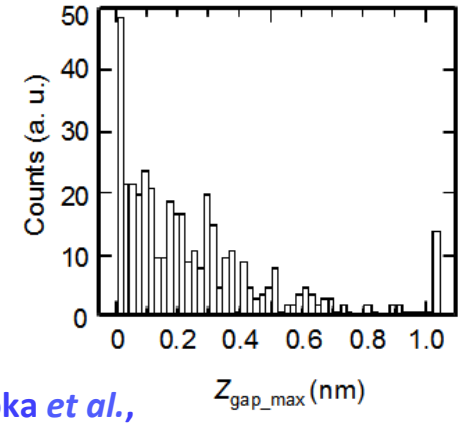
***Very similar results by R. Pawlak, E. Meyer, G. Le Lay and P. Jelinek (unpublished)**

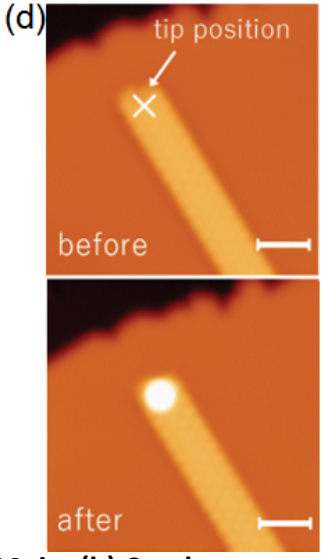
Free standing double strand SiNRs lifted off from the Ag(110) substrate

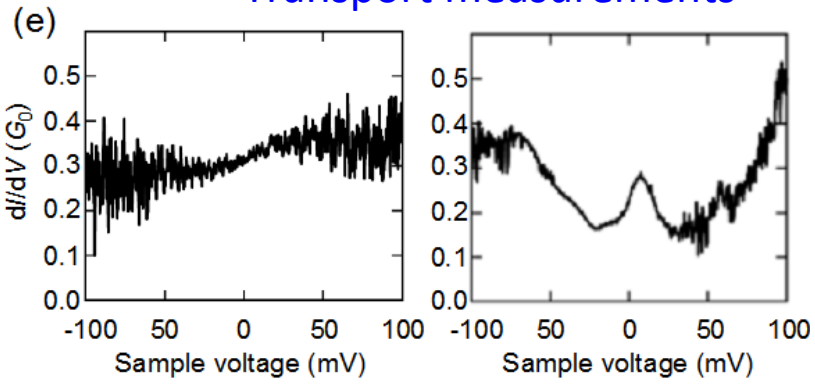




Transport measurements





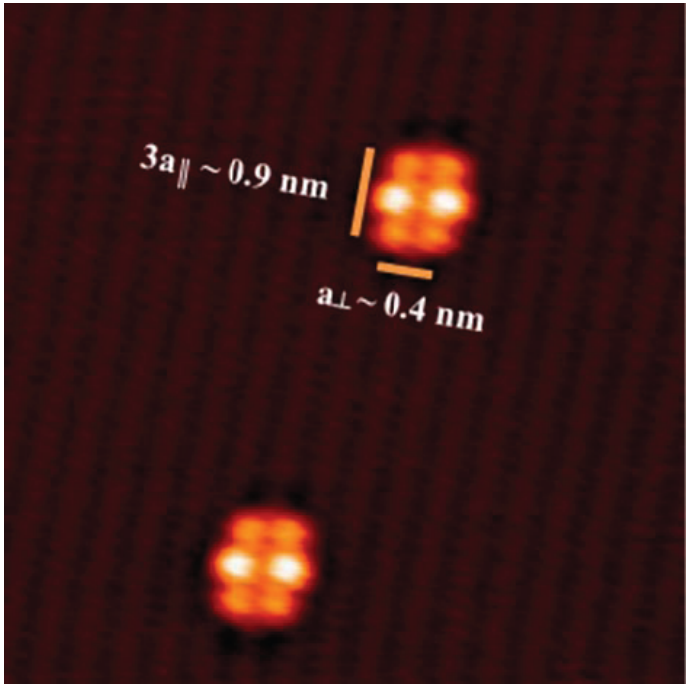


R. Hiraoka *et al.*,
Beilstein J. Nanotechnol. 2017, 8, 1699

(a) Scheme of the lift off of a SiNR with an STM tip. (b) Conductance trace measured as a function of tip vertical position (Z). G0 is the conductance quantum (7.75 Å~ 10−5 S). The feedback is turned off at VS = 100 mV and It = 20 pA and the conductance is measured at VS = 100 mV. The conductance measured during the tip approach/retraction are plotted with black/blue circles; red curve: least-squares fitting. In the conductance measurement, the gain of the current amplifier is switched from 10^9 (in the STM measurements) to 10^5 for measuring the large variation of the current in the tip approach /retraction processes. The currents in the almost flat region around label A in (b) are too small to be measured with this gain so that the conductance around A is nominally different from the value (2.6 Å~ 10^{-6} G0) taken for VS = 100 mV and It = 20 pA**. (c) Histogram of Zgap_max, the maximum distance the tip travels before the SiNR nanojunction is broken** after contacting the tip to the SiNR. (d) STM images before and after the conductance measurement (scale bars: 2 nm. **(e) Two types of measured dI/dV spectra of the SiNR nanojunction** (modulation 4 mV at 312.6 Hz).

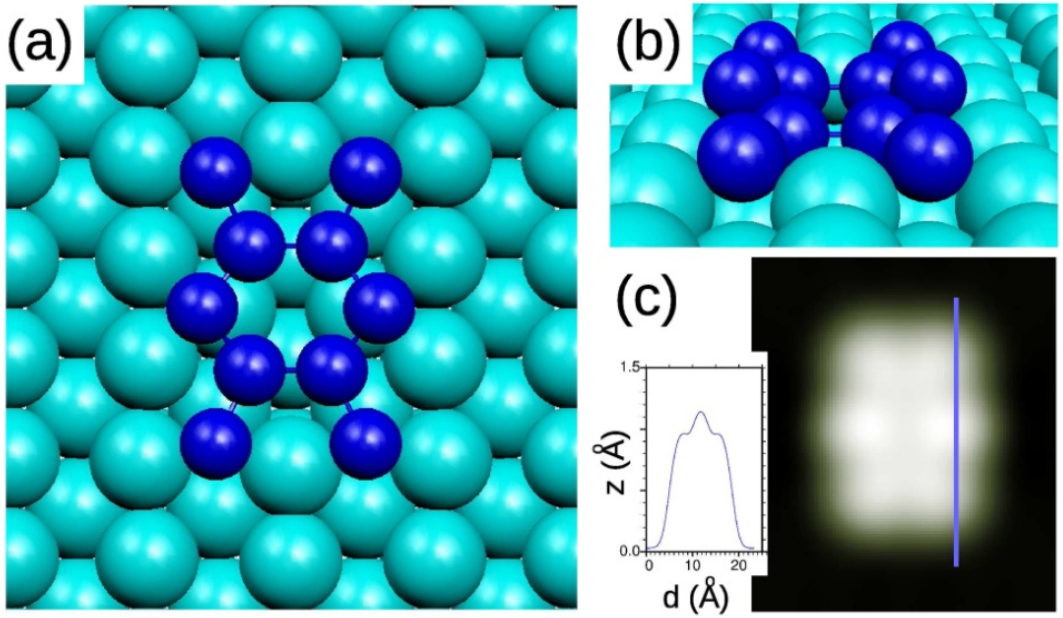
Zero Dimension: Symmetric, *benzene-like (?)* nanodots on Ag(110)

DFT-GGA with vdW, SIESTA-GREEN package



***Symmetric* Si nanodots**

F. Ronci, S. Colonna, A. Cricenti,
P. De Padova, C. Ottaviani,
C. Quaresima, B. Aufray, and Guy Le Lay,
Phys. Status Solidi C 7, 2716 (2010).



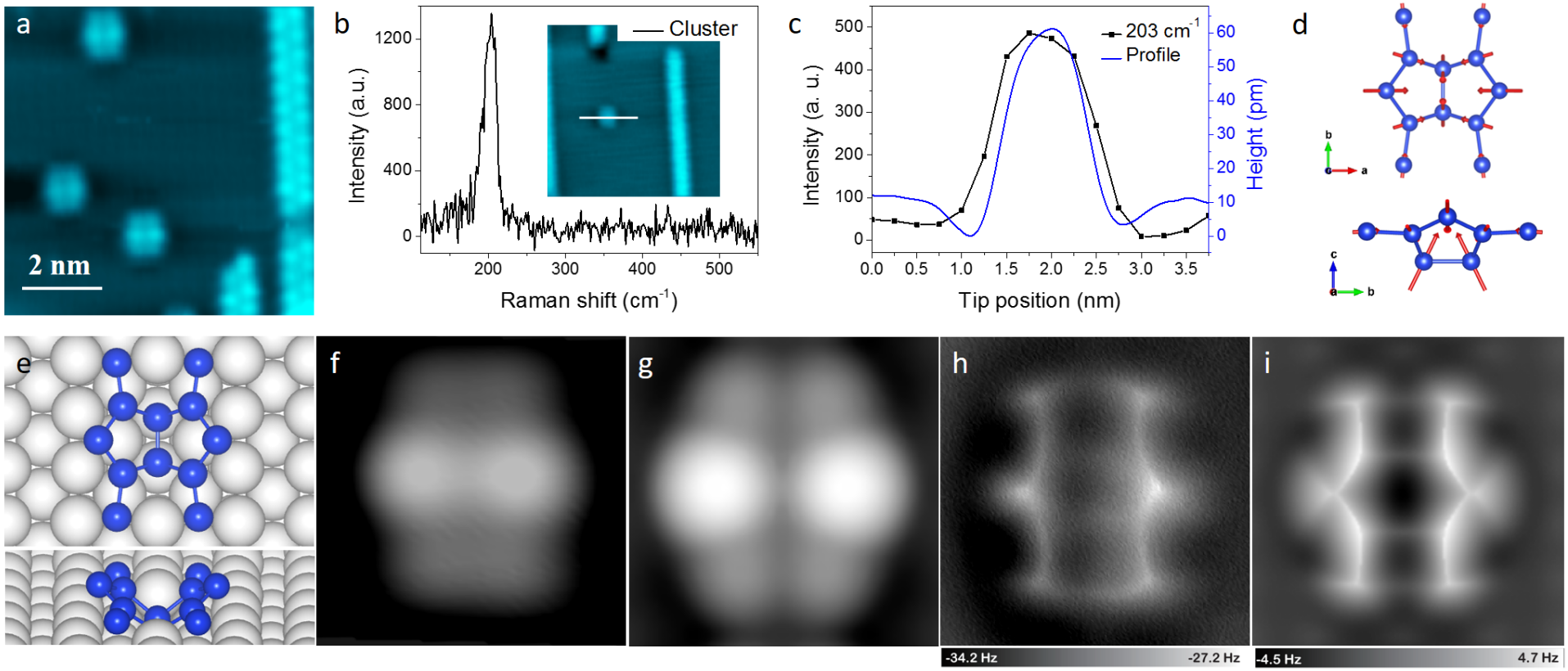
(a & b) Top and perspective views of the nano-dot structure over 2 Ag vacancies. (c) Simulated STM topographic image and line profile along the solid line.

J. I. Cerdá, J. Sławińska, G. Le Lay, A. C. Marele,
J. M. Gómez-Rodríguez, and M. E. Dávila,
Nature Comm., 7, 13076 (2016)

Pentasilicene-like nanoribbons: a symmetry breaking polymerisation of nanodots !

Direct evidences of Pentagonal Si nanodots:

AFM imaging & Tip Enhanced Raman Spectroscopy



TERS spectrum and structure of Si nanodots. a, STM of the Si dot and S-SiNRs at low Si coverage (1 V, 50 pA). b, TERS spectrum of the dot in the inset. c, TERS intensity of the 203 cm-1 mode along the line in (b) with an interval of 0.25 nm every step, and the STM topography height profile. d, Atomic vibration schematic of the 203 cm-1 mode of the dot. e, Atomic structure of the Si dot on a Ag di-vacancy Ag(110) surface, with top and perspective views. f, High resolution STM images of the dot (100 mV, 50 pA). g, Simulated STM image of the dot (1 V). h, Corresponding AFM image of the dot in (f). tip (k = 0.5 N/m, Q = 0.0 e).

Shaoxiang Sheng *et al.*, Nano Letters 18, 2937 (2018)

Kagome silicene on Al(111)

The "other side" of the Schottky barrier formation process: Si 3×3 overlayers on Al(111)

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(Received 20 August 1987; accepted 26 October 1987)

We present a photoemission and electron diffraction study of Si overlayers on Al(111). The overlayers exhibit 3×3 electron diffraction patterns at submonolayer coverages, and become disordered at higher coverages. The core-level photoemission spectra indicate that the interface is sharp, like those obtained by depositing Al on Si. The interface position of the Fermi level, however, is different with respect to the case of Al on Si.

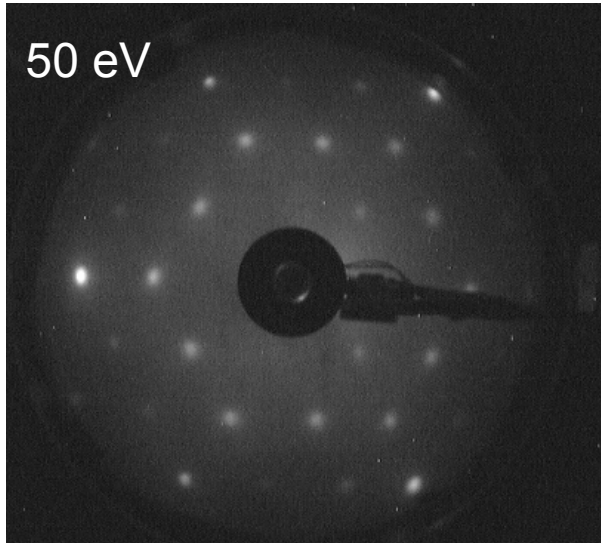
JVST 6, 1971 (1988)

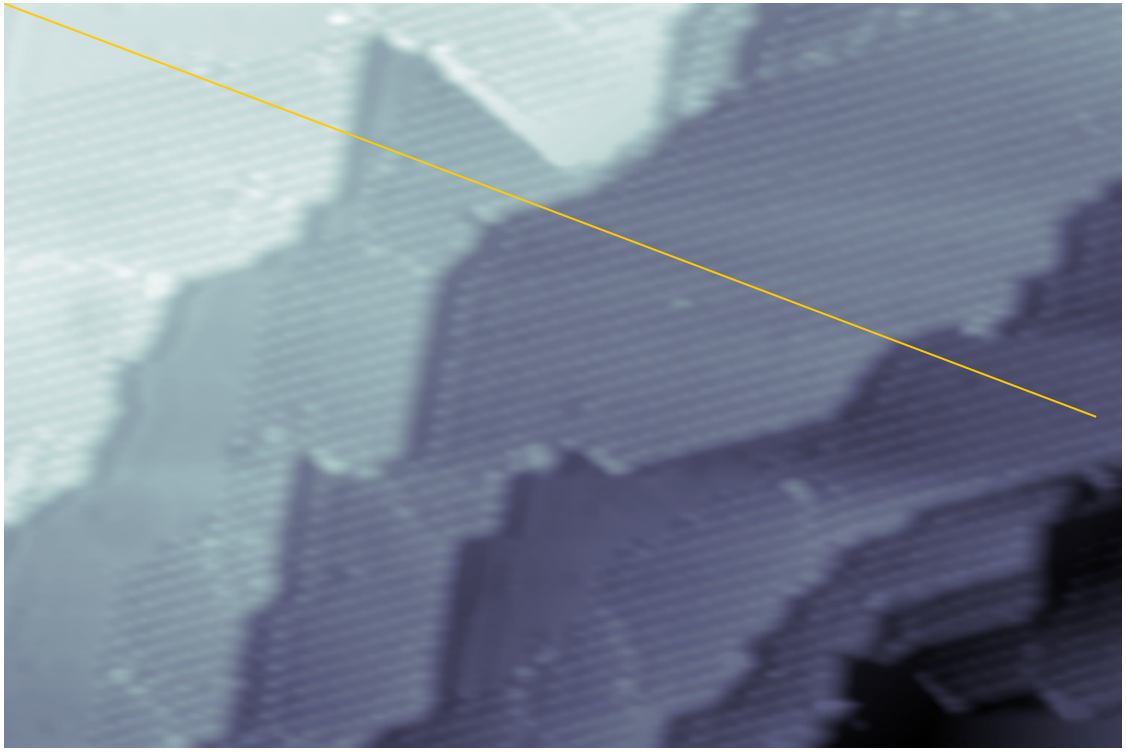
Although Ag and Al have nearly the same lattice parameter,
the 2D structures formed upon Si deposition differ drastically:

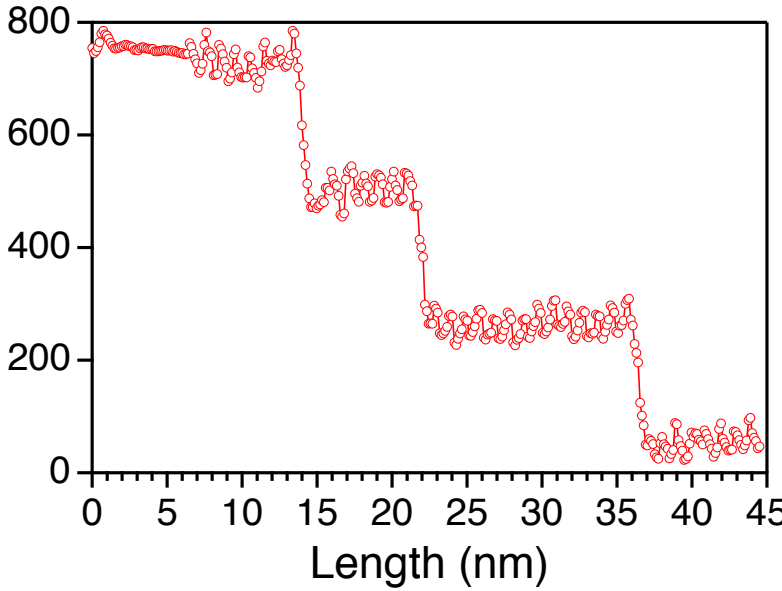
4x4 wrt Ag(111) ⟺ 3x3 silicene

3x3 wrt Al(111) ⟺ **???**

3x3 LEED pattern and STM image of Si deposited onto Al(111) at RT







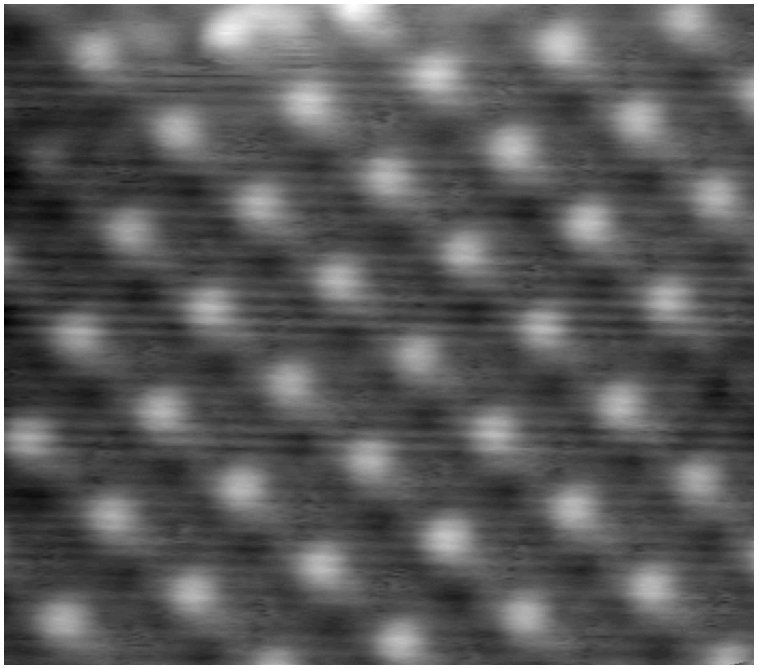
44 nm x 29 nm

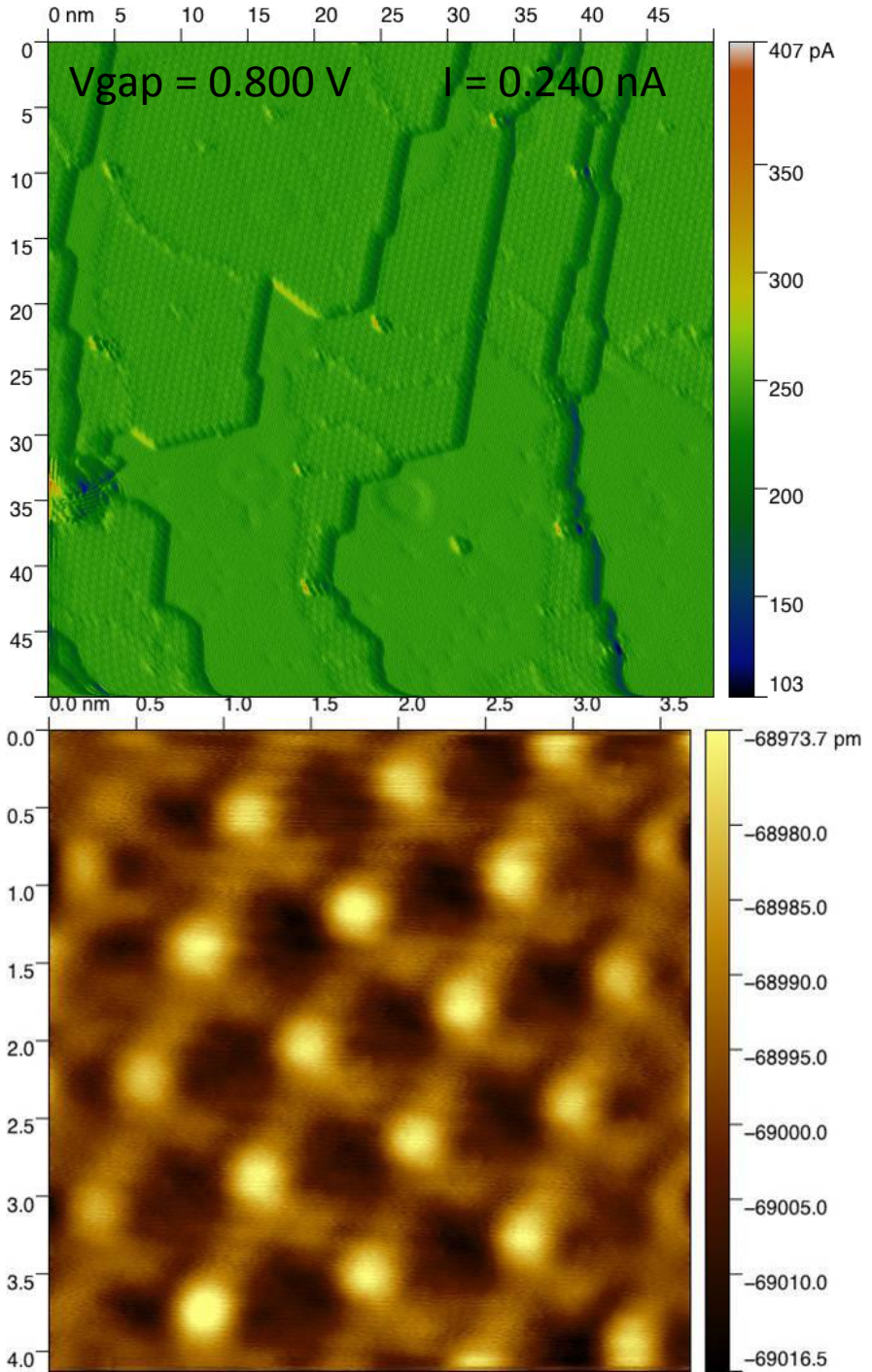
V_{GAP} = + 80 mV (empty states), I_T = 170 pA

Y. Sassa *et al.*, in preparation

2D Si weird structure epitaxially formed on Al(111) at RT in a single orientation

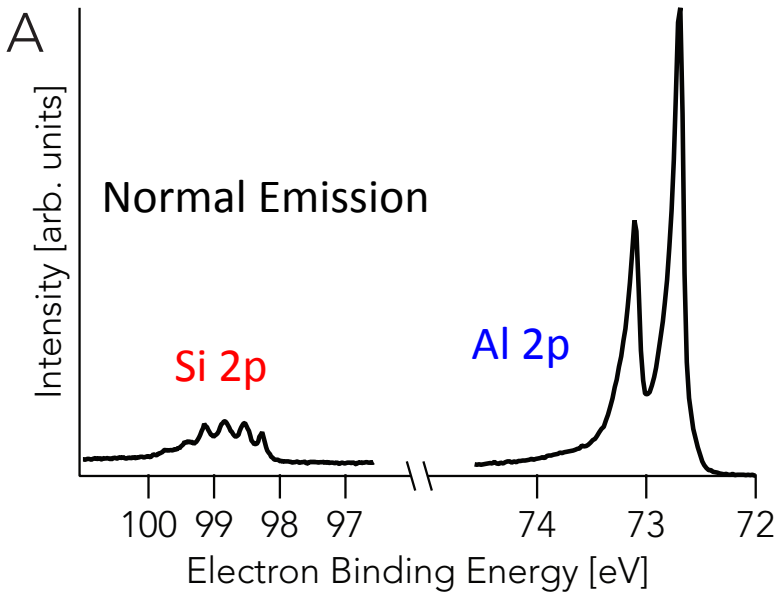
Y. Sassa *et al.*, in preparation



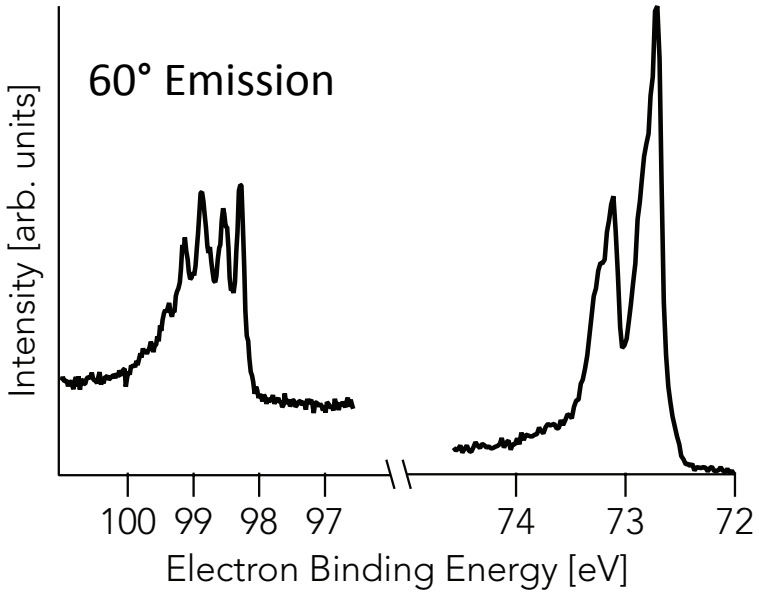


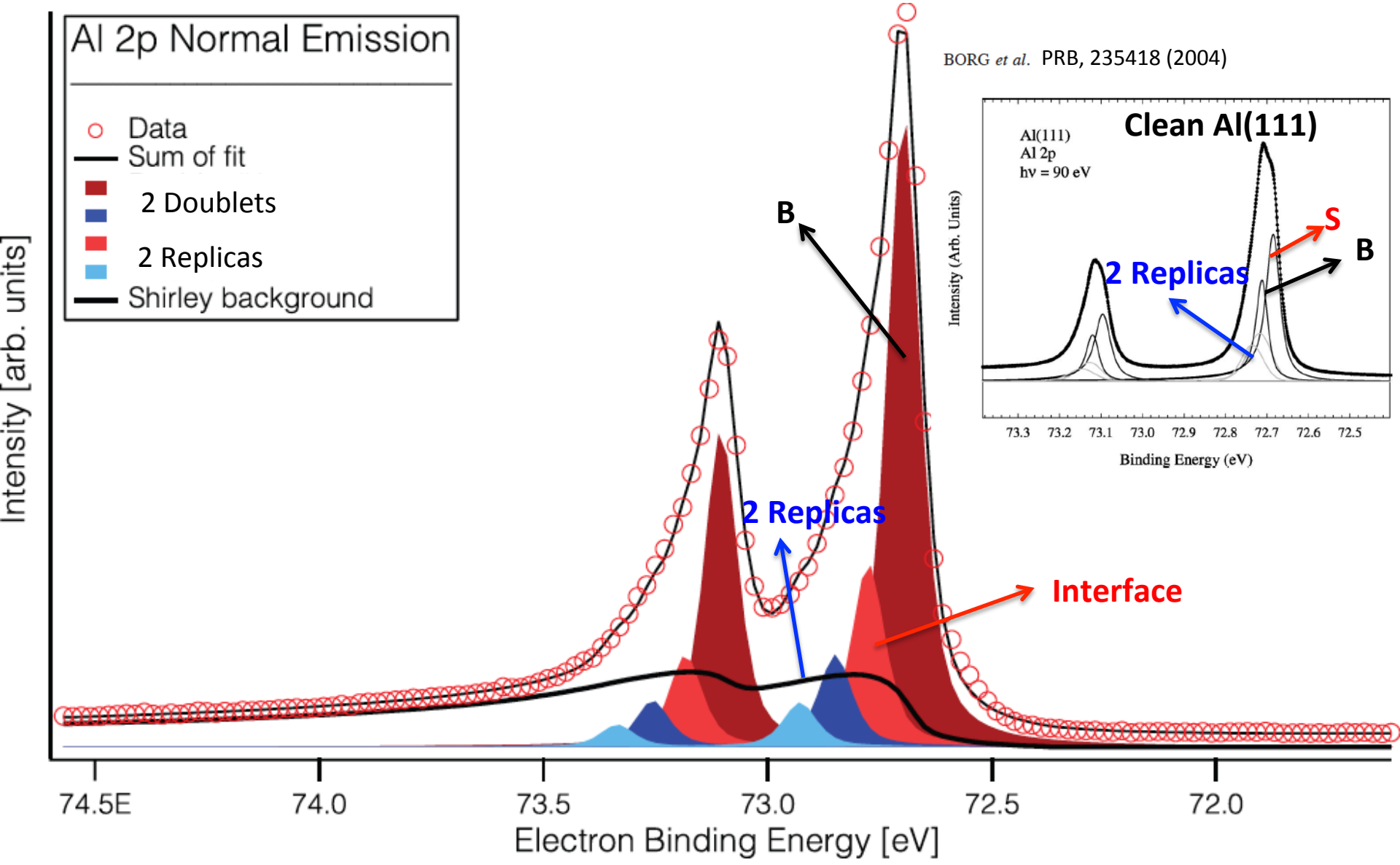
In accord with the 1rst STM images obtained by H. Brune in the early 90's (PhD thesis, 1992, unpublished)

Si 2p & Al 2p Core-levels hv = 136 eV acceptance 4°



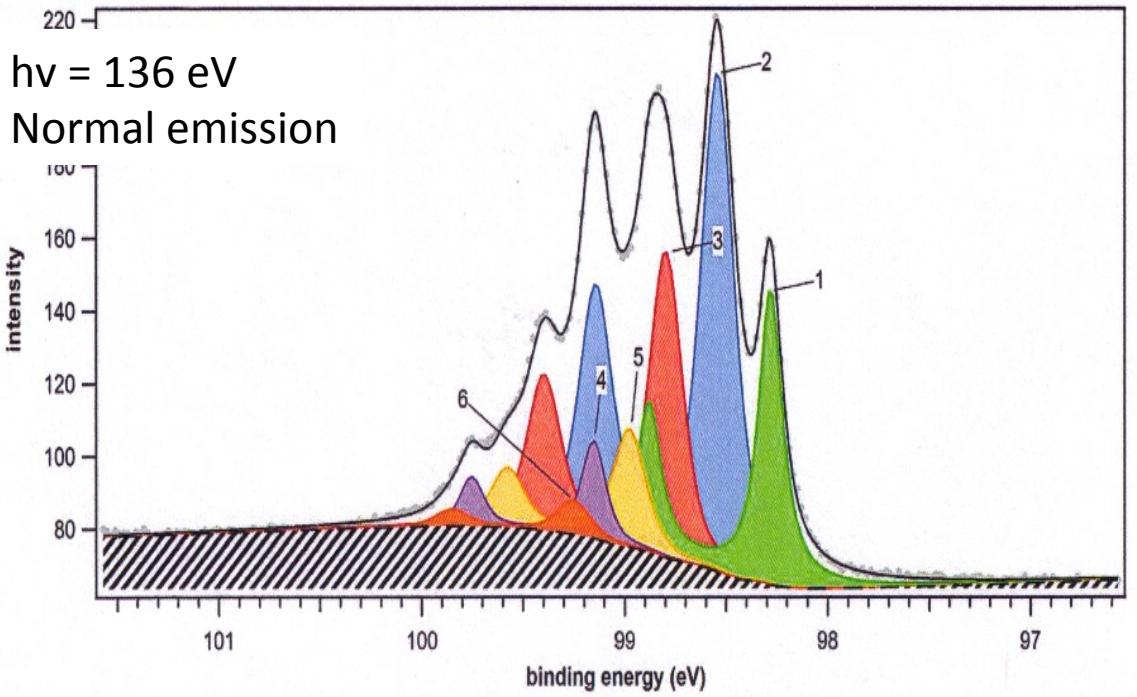
Si is on top!

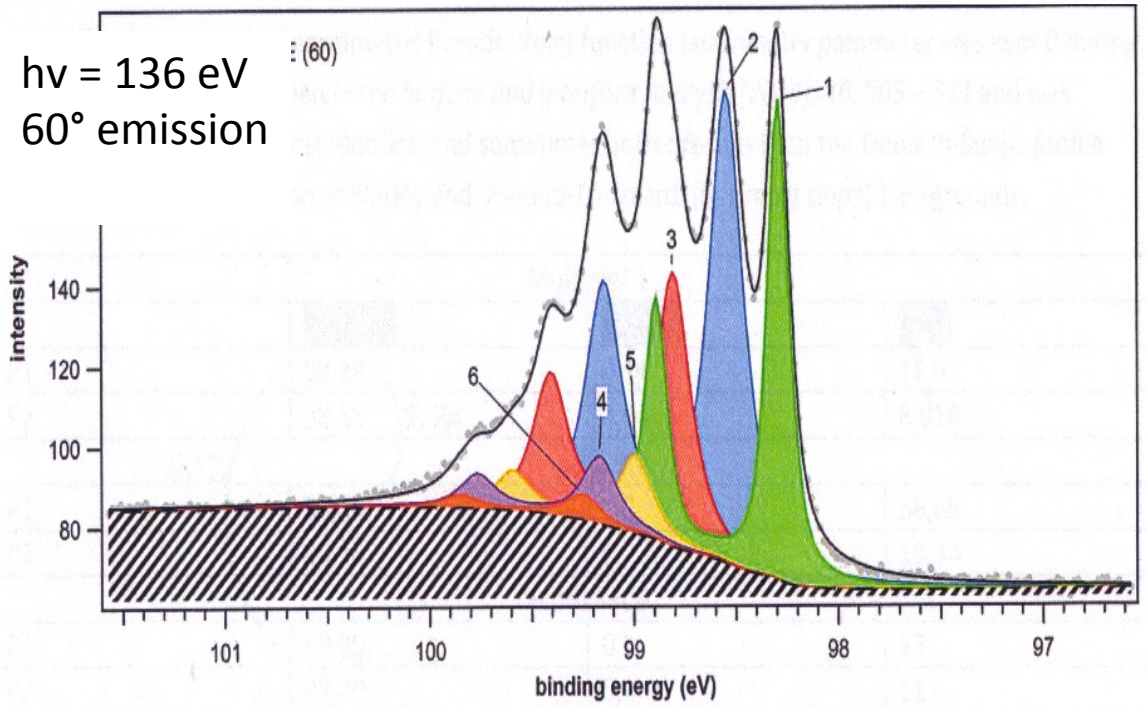




Narrow Al 2p core-levels with their phonon replicas (hν = 136 eV)

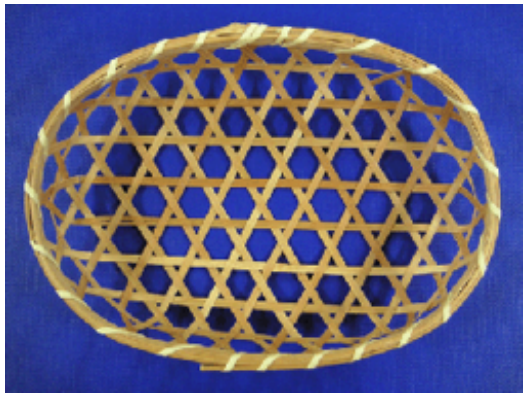
Extremely narrow Si 2p CLs fitted with 3 components + 3 phonon replicas

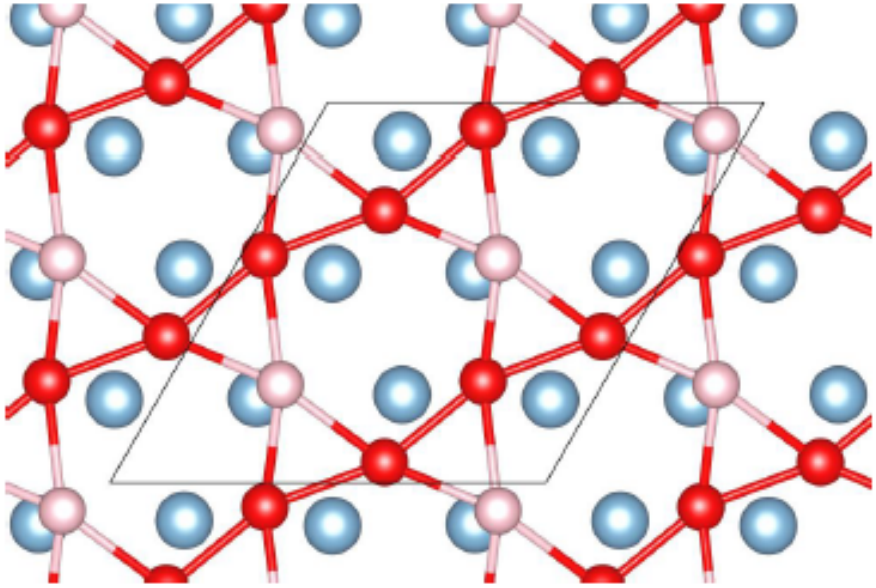


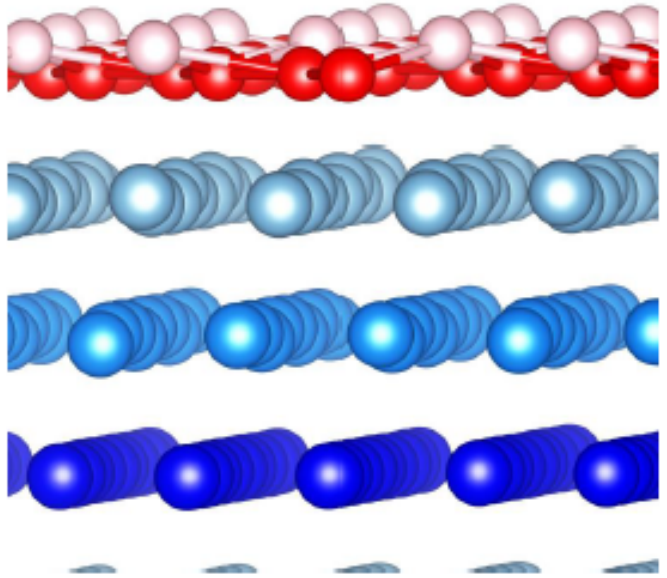


Kagome Silicene

in fact 1x1 Kagome silicene / Al(111)√3x√3 !!!







Top View

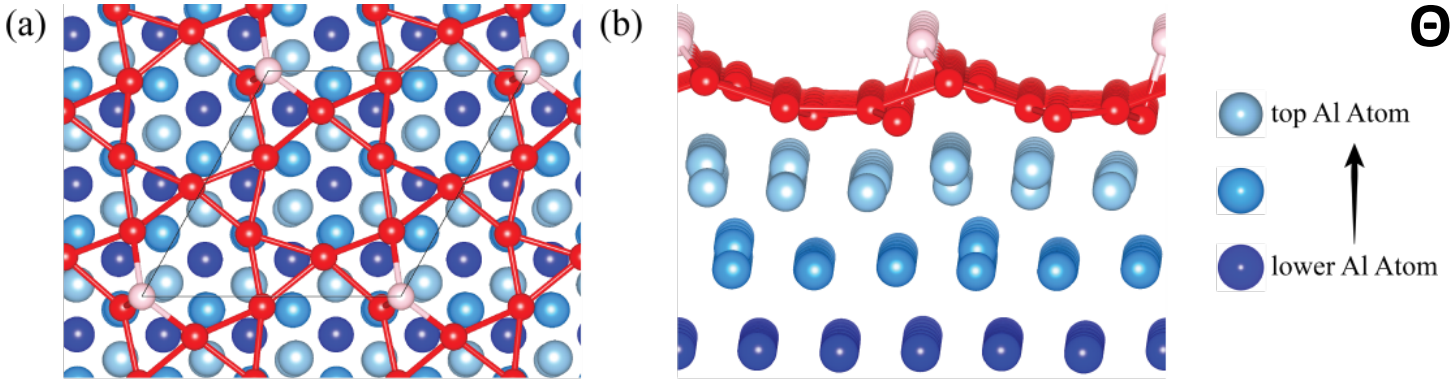
Θ = 1

Tilted Side View

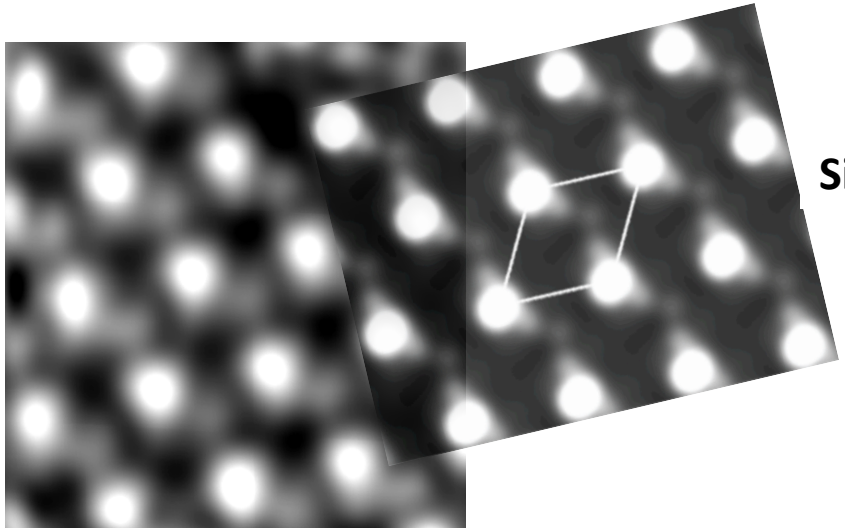
For clarity only the last Al plane is displayed in the left figure.

Kagome Silicene further stabilized by dumbells

Top (a) and side (b) views of the Kagome silicene lattice (red balls) with dumbells (pink balls) on Al(111)3x3



Θ = 10/9 = 1.11



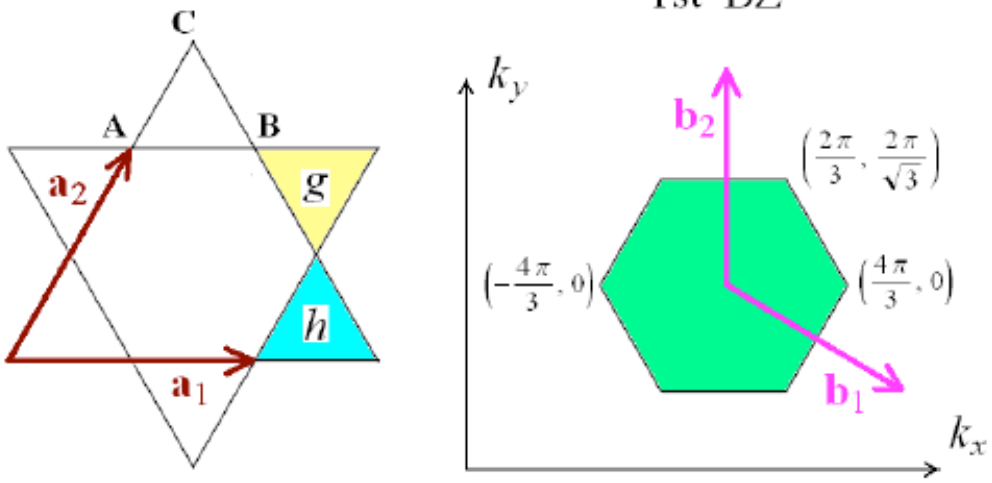
Simulation -10 meV

STM image 11 nm x 11 nm

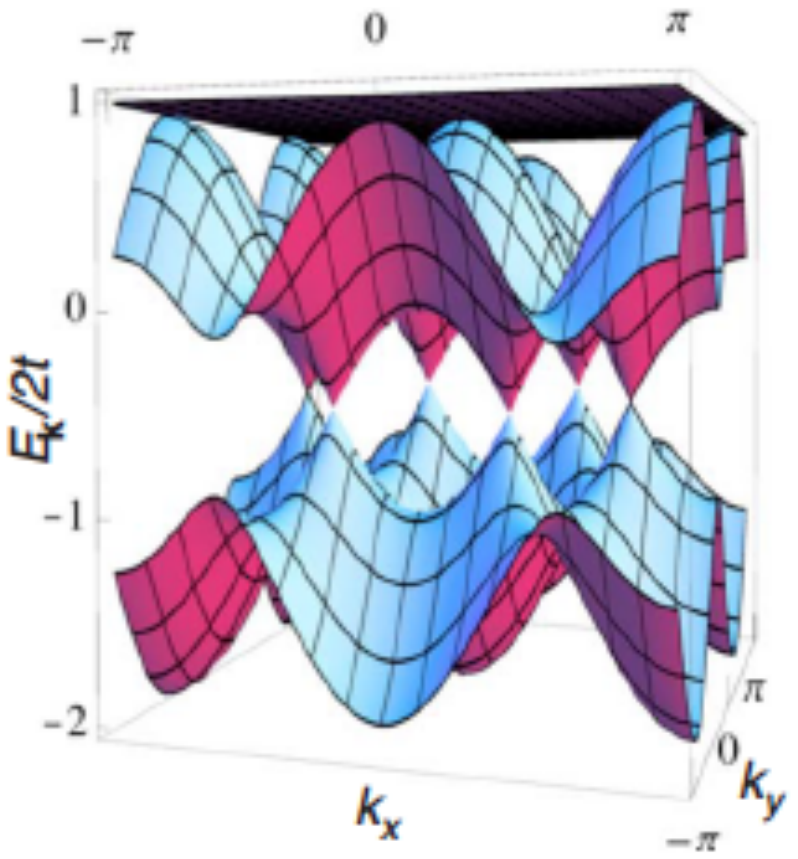
V_{GAP} = - 10 mV (filled states), I_T = 150 pA

Y. Sassa *et al.*, in preparation

Kagome lattice special electronic structure: Dirac cones and flat band



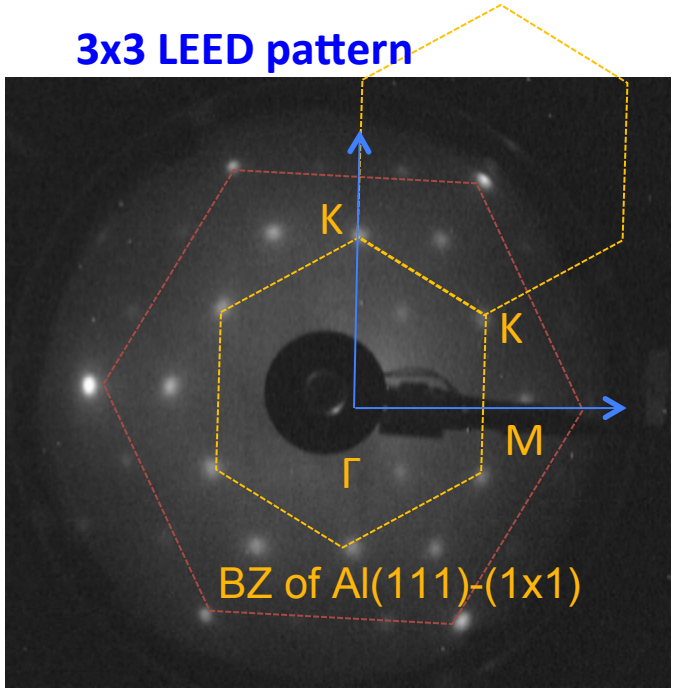
Kagome lattice and 1rst Brillouin zone

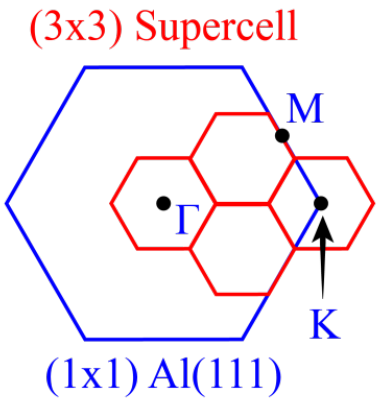


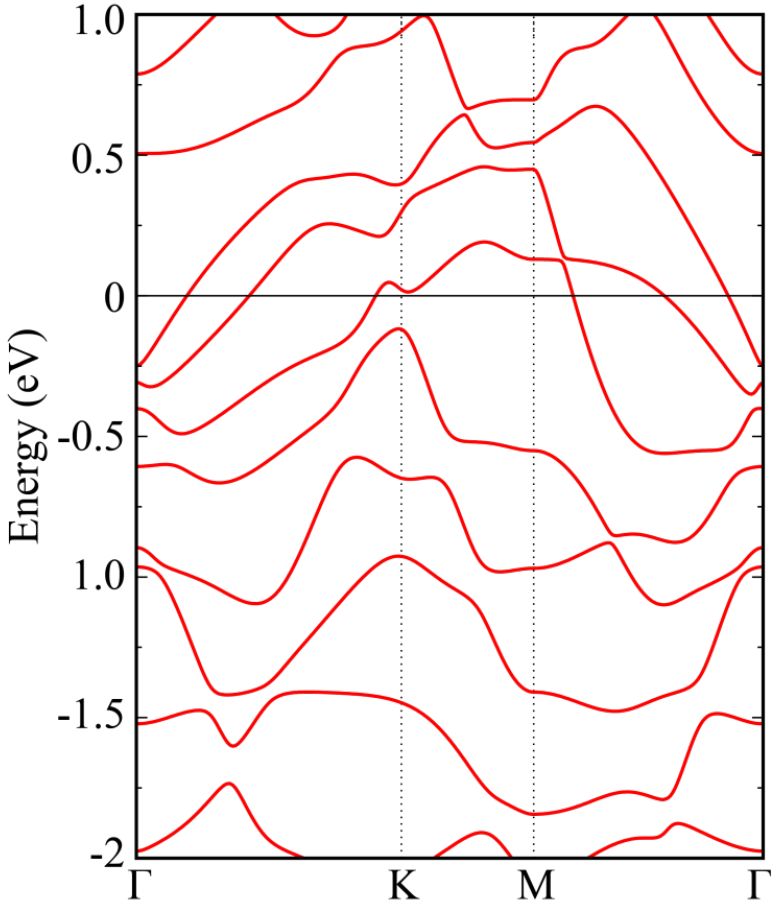
Tight binding band structure

Guo and Franz PRB 80, 113102 (2009)

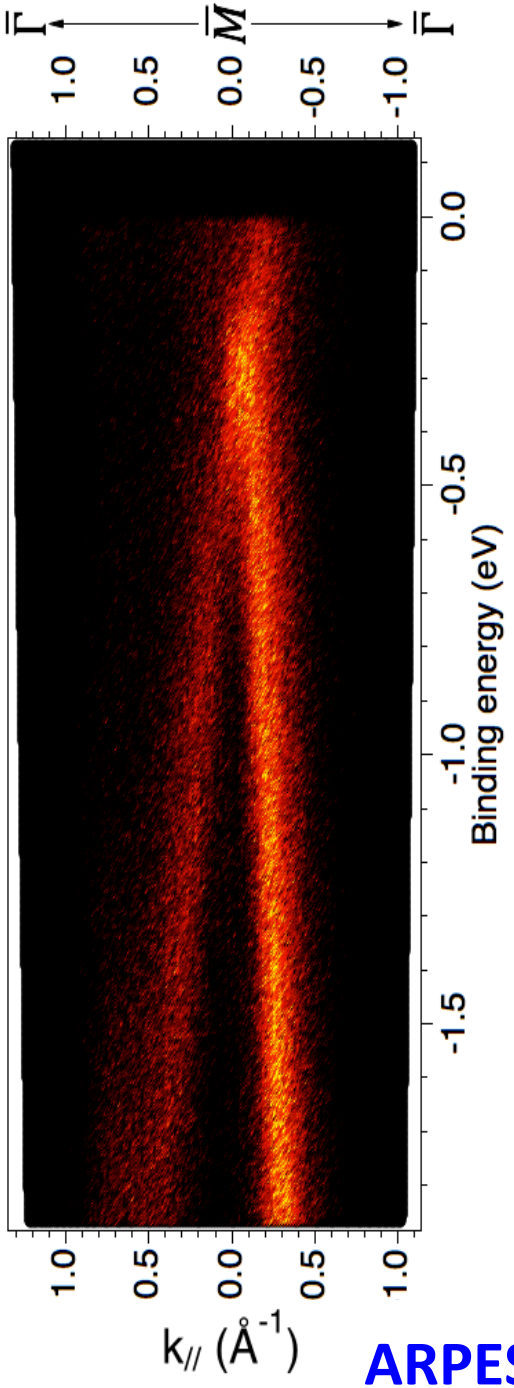
Calculated band structure of the extracted layer

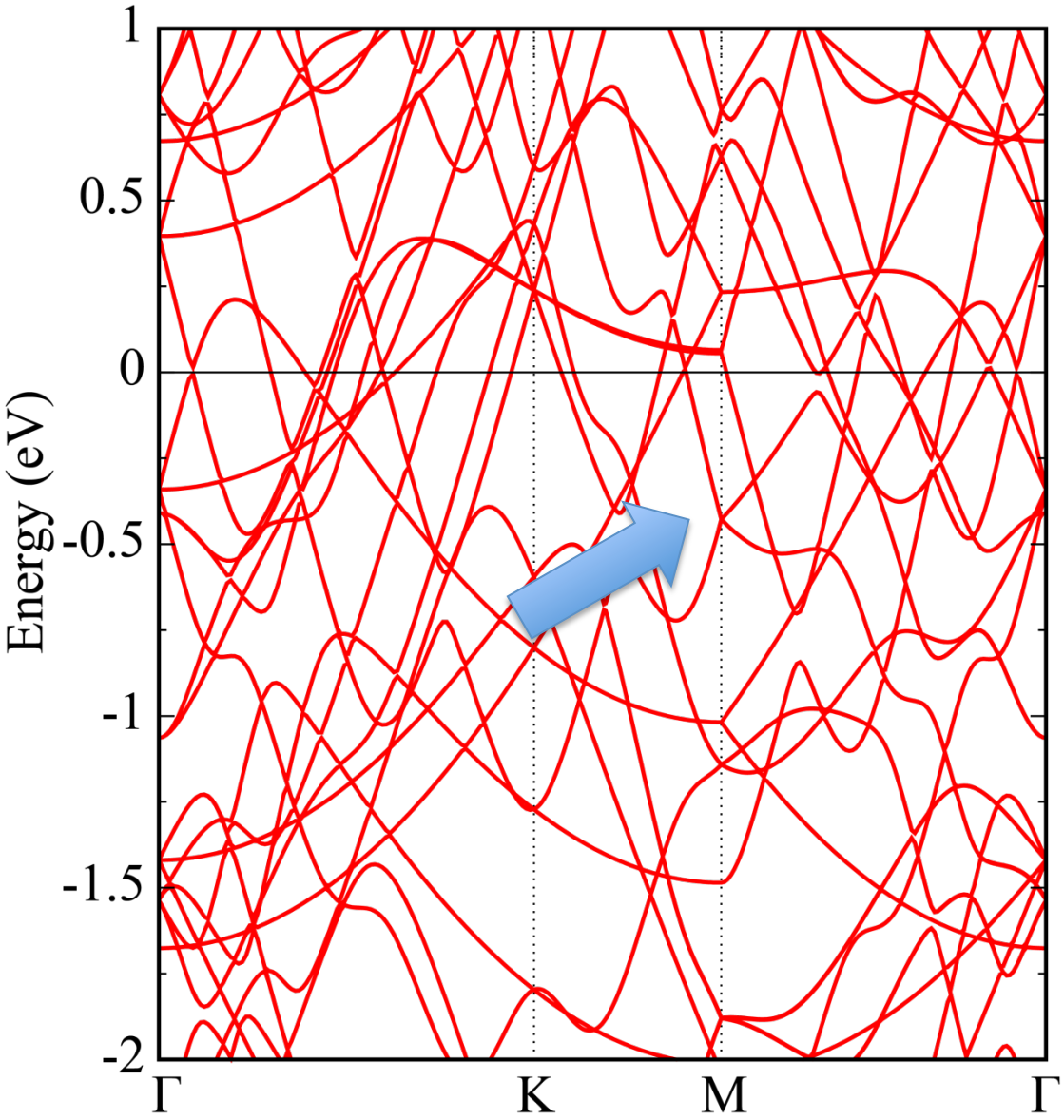






Conelike dispersions at M points

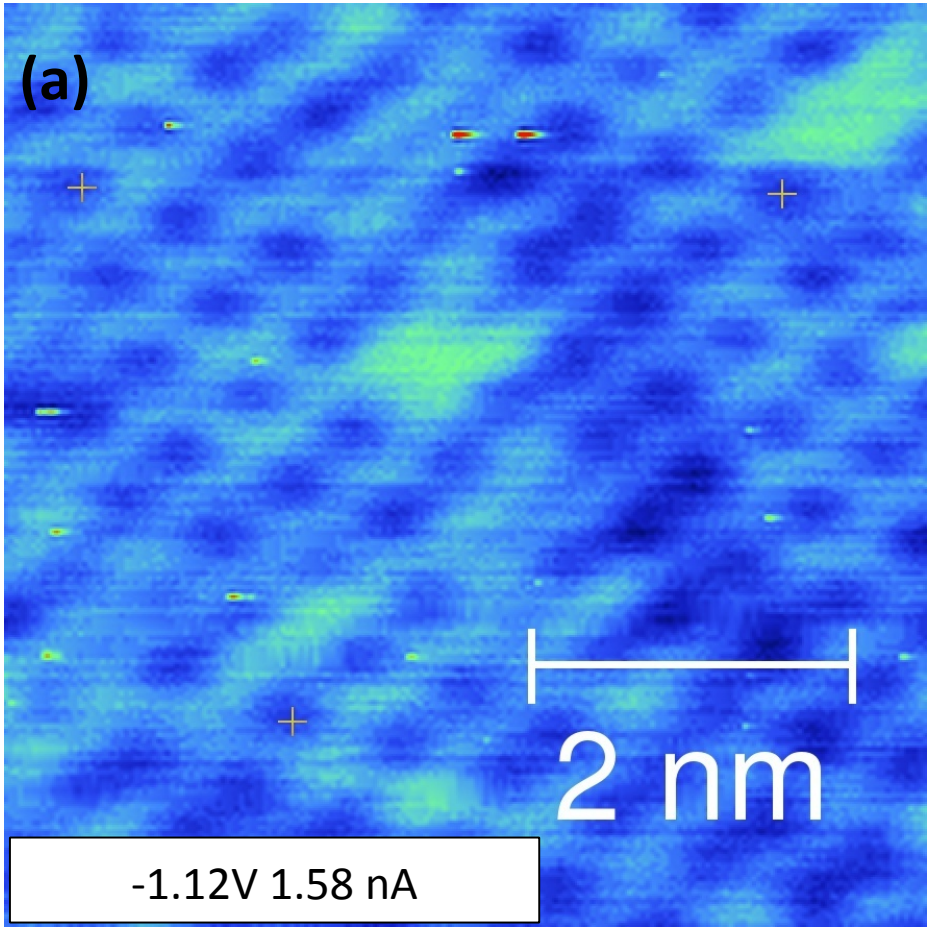




ARPES spectrum He I 21.2 eV

Germanene

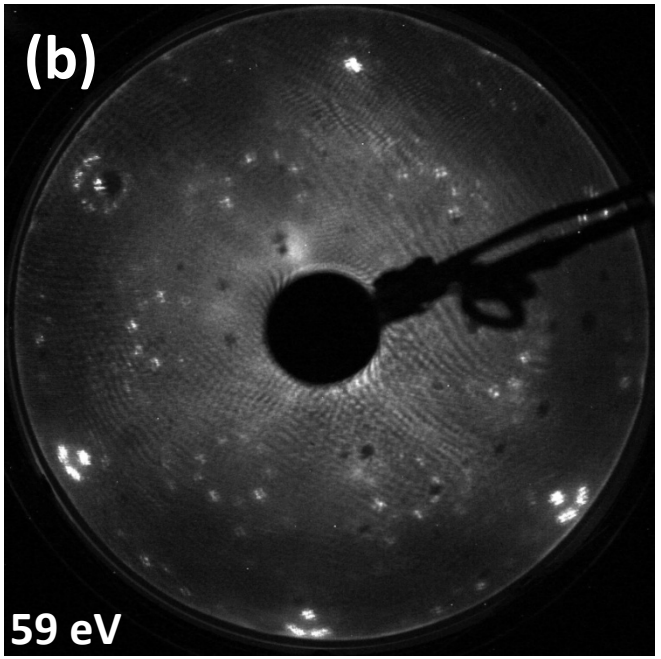
111)

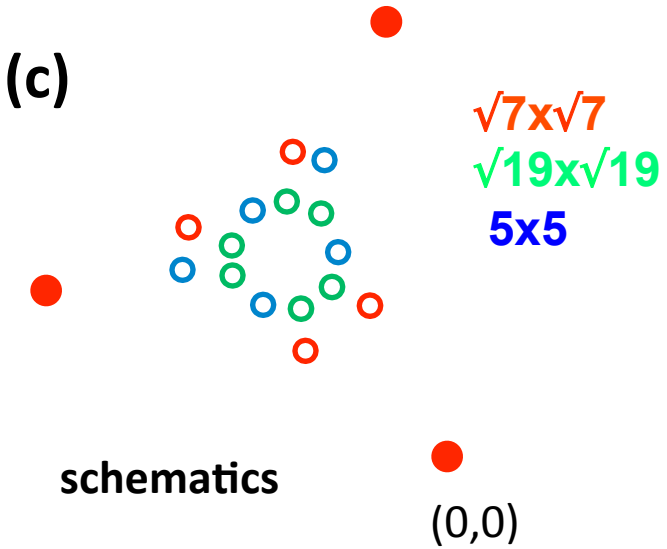


STM image of single layer germanene on Au(111) : one of the phases with modulated honeycomb Appearance in a Au(111)√7x√7 supercell

M. E. Davila *et al.*, *New. J. Phys.* 16, 095002 (2014)

Composite LEED pattern: 3 phases





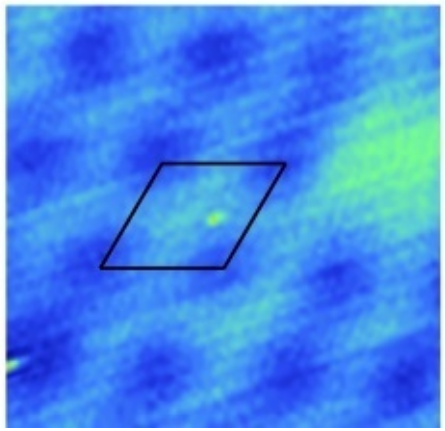
Germanene on Au(111)

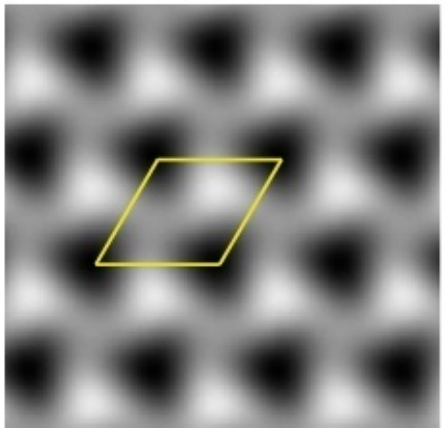
VASP, DFT-GGA

Dávila *et al.*, *New J. Phys.* **16**, 095002 (2014)

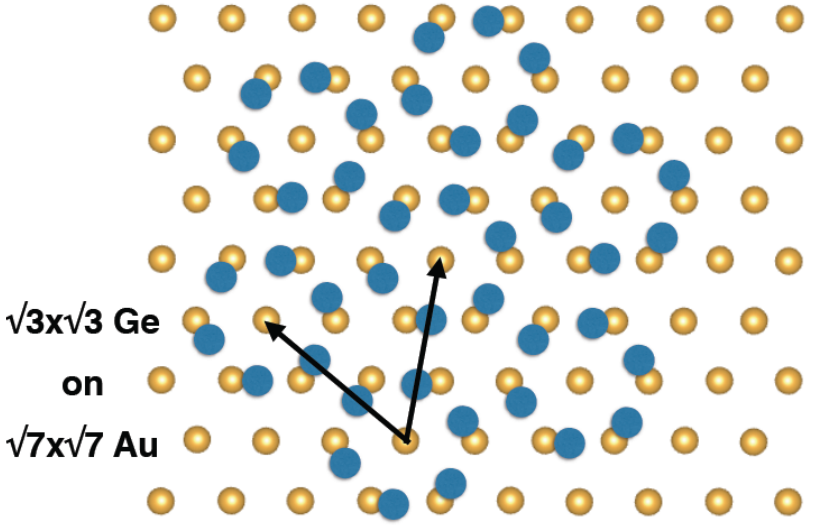
In plane d_{Ge-Ge} = 2.55 Å

Calculations by Cahangirov et al. for free standing germanene: 2.38 Å





Weak corrugation ~0.2 Å



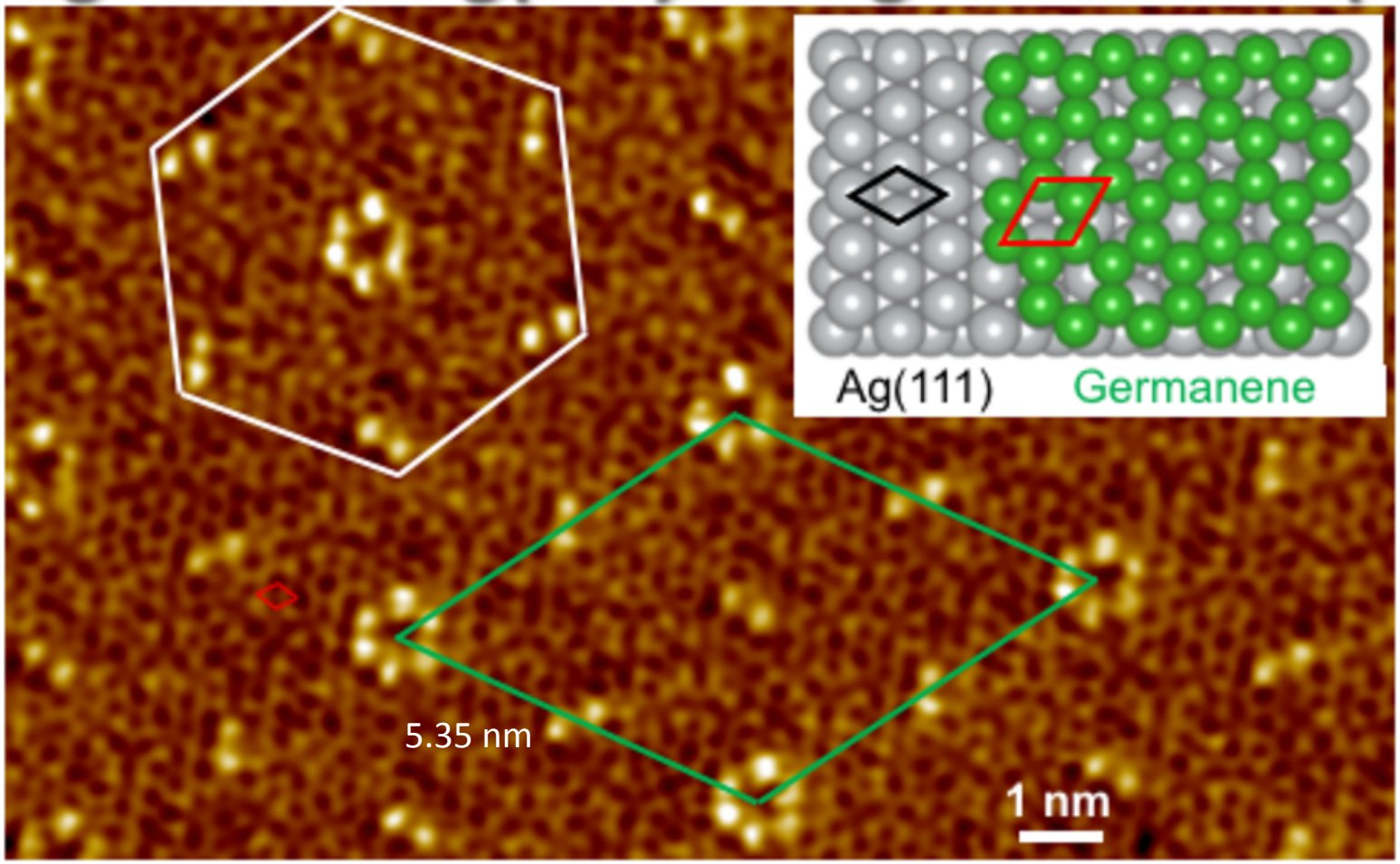
Atomic model : **√3x√3 germanene** on Au(111)√7x√7*R*(±19.1°)

DFT calculations

	Energy per Ge atom (eV/atom)	N_{Ge}
Structure 01	-3.641	8
Strcuture 02	-3.628	8
Structure 03	-3.744	6
Diamond Ge (bulk)	-3.727	-

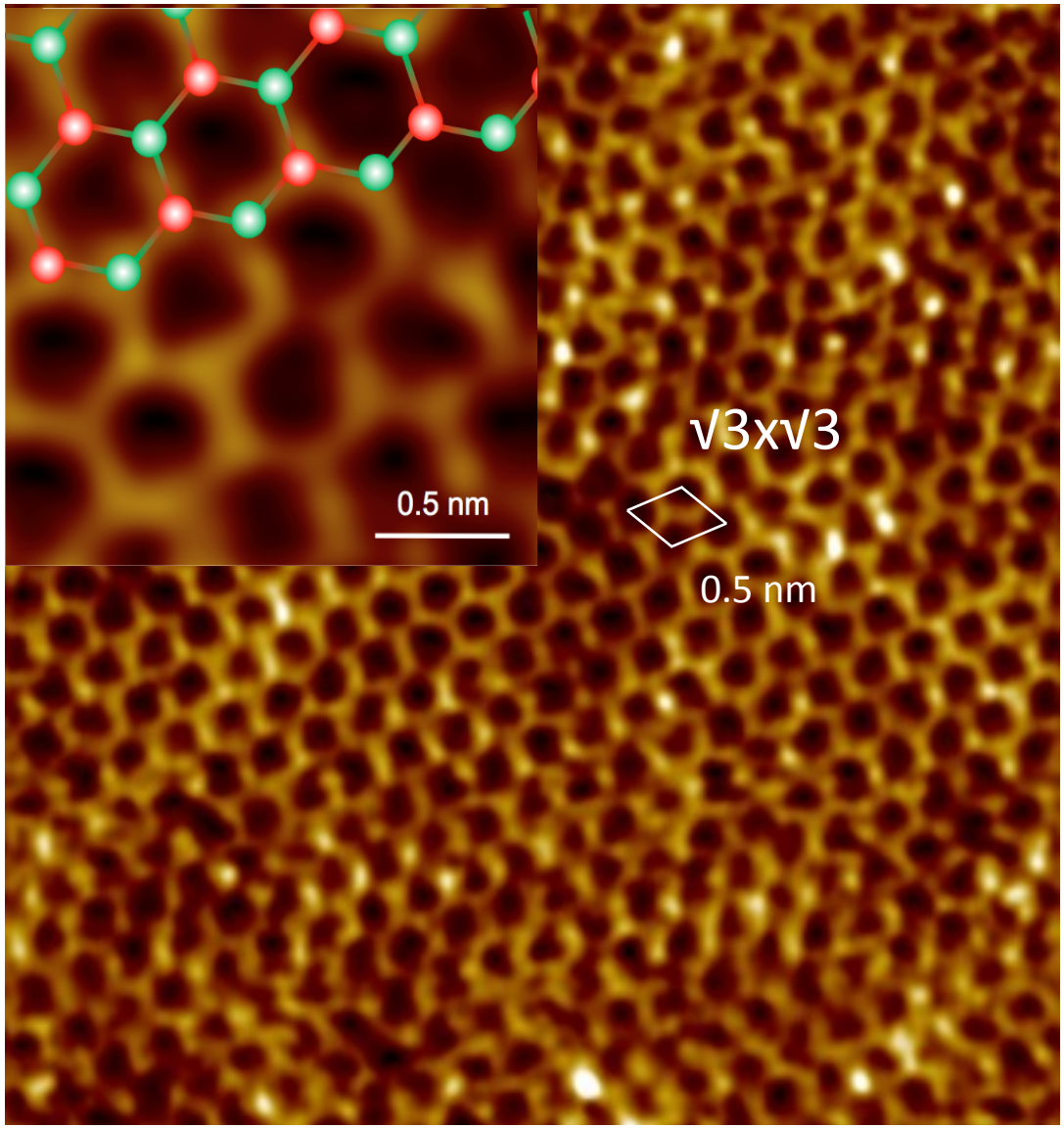
TABLE I: Absorption energy for different germanene structures on Au (111) surface.

STM image: germanene by segregation through a thin Ag(111) film grown on Ge(111)



Single phase: $3\sqrt{21}\times3\sqrt{21}$ germanene matching a $7\sqrt{7}\times7\sqrt{7}R\pm19°1$ Ag(111) supercell Yuhara et al., ACS Nano, in press

Stanene



Yuhara *et al.*, 2D Mater., 5, 025002 (2018)

Large area epitaxial stanene on Ag(111)

Summary and outlook

Silicene (2012), PentaSilicene (2016), Kagome Silicene (2018)

Germanene (2014),,Stanene (2017)

These novel group IV low dimensional allotropes have been synthesized using a bottom-up, directly scalable, method

→ **Prototypical 2D Topological Insulators with a sizeable band gap.**

→ **Evidence of layered silicene, germanene and stanene**

→ **The first silicene-based FET operating in air at RT was fabricated in 2015**

Prospects → **Plumbene!**

The quest → **Majorana fermions, anyons…**