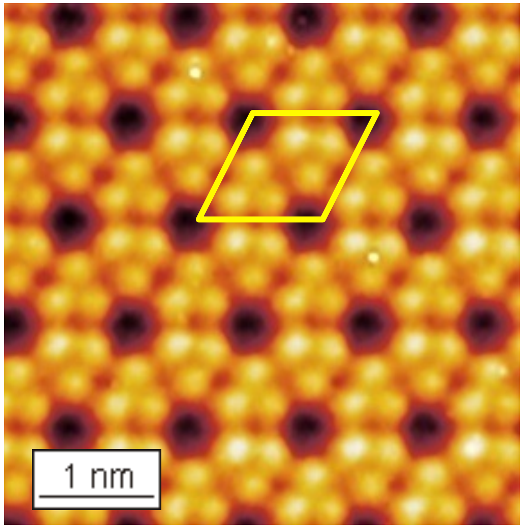
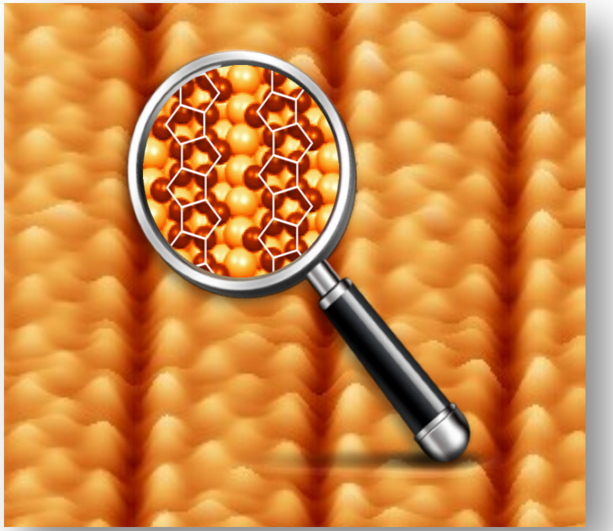
Exotic forms of low-dimensional artificial Xenes

Guy Le Lay
Aix-Marseille University, CNRS-PIIM, France

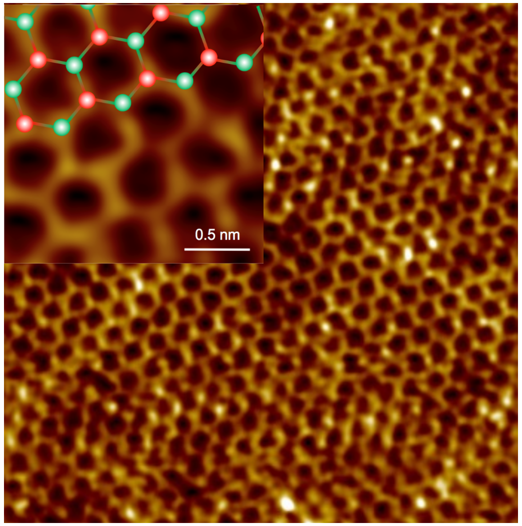
Workshop on Anyons in Quantum Many-Body Systems,
Dresden, Germany, Jan. 20-25, 2019



Epitaxial silicene archetype structure on Ag(111)



1D pentasilicene nanoribbons on Ag(110)



Large area stanene on Ag(111)

Co-workers (recently)

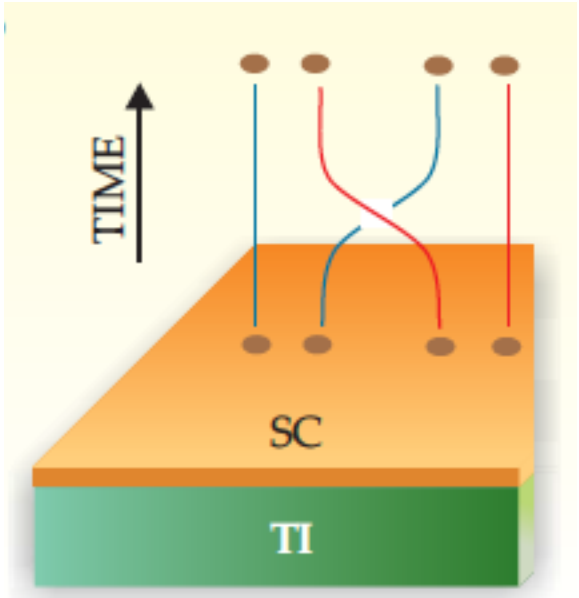
Europe

T. Angot and **E. Salomon**, Marseille, France
Y. Sassa and coll., Uppsala, Sweden
S. Cahangirov, Ankara, Turkey
H. Sahin and **F. Iyikanat**, Izmir, Turkey
P. Vogt and coll., Chemnitz, Germany
P. De Padova and coll., Rome, Italy,
M.E. Davila and **J.I. Cerda**, Madrid, Spain
A. Rubio and coll., Hamburg, Germany

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

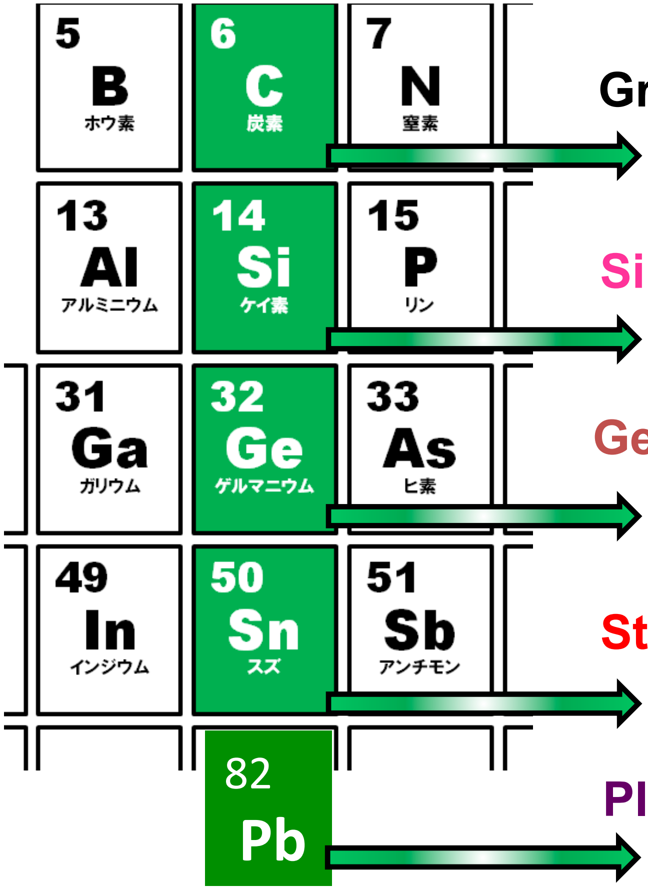
« Experimental synthesis and characterization of **2D Topological Insulators** remain a major challenge at present, offering outstanding opportunities for innovation and breakthrough. »

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 IV *artificial counterparts* of graphene?



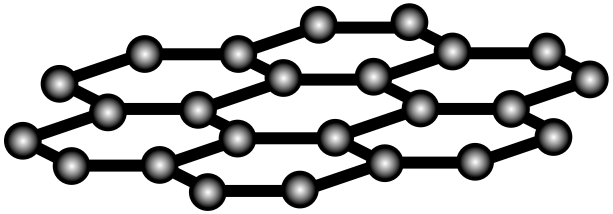
Graphene

Silicene

Germanene

Stanene

Plumbene



Flat
No band gap
Minute SOC

Increasing Spin Orbit Coupling

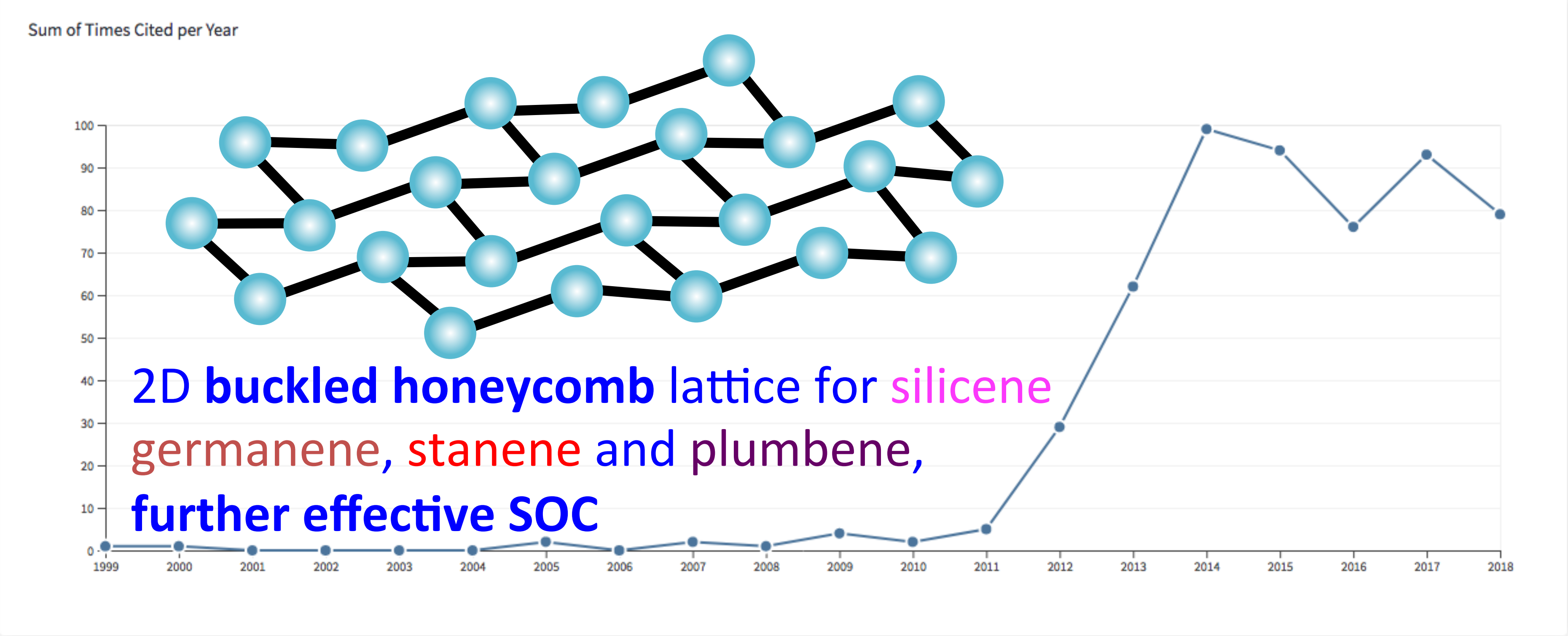
The hardware beyond graphene

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: 566 (WOS: Jan. 18, 2019)



2D **buckled honeycomb** lattice for silicene germanene, stanene and plumbene, **further effective SOC**

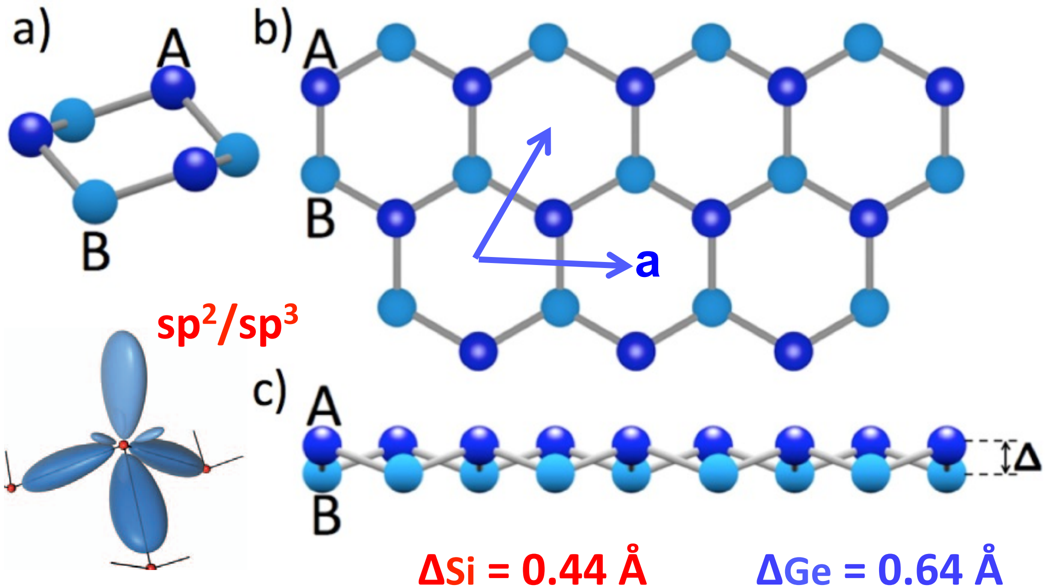
Only 18 citations until Dec. 31, 2011 !

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)



ΔSi = 0.44 Å

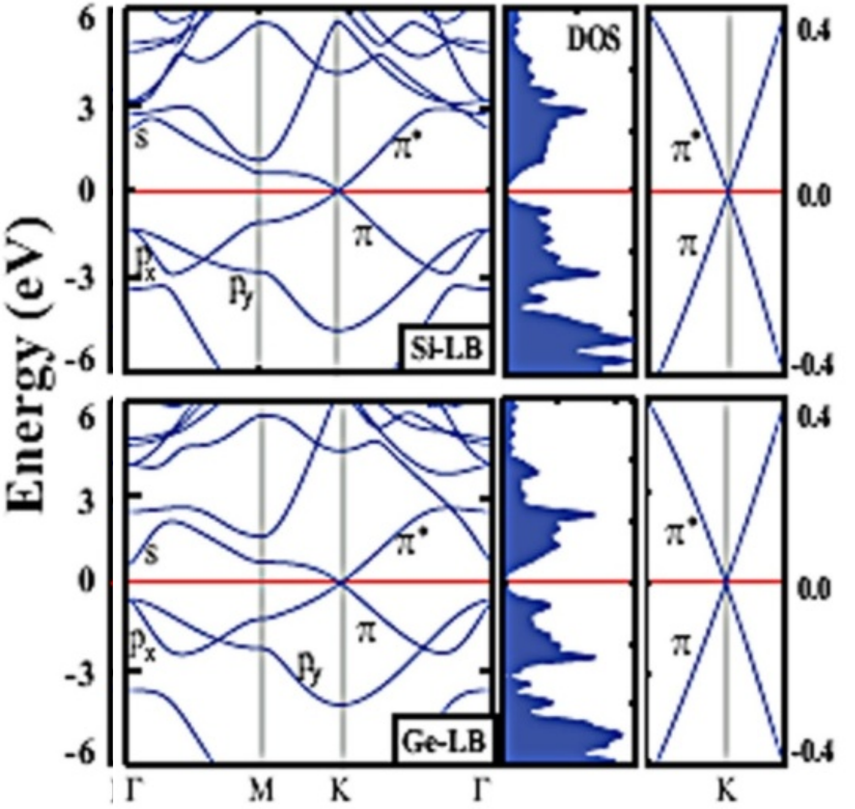
ΔGe = 0.64 Å

$\Delta_{Si(111)}$ = 0.78 Å

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

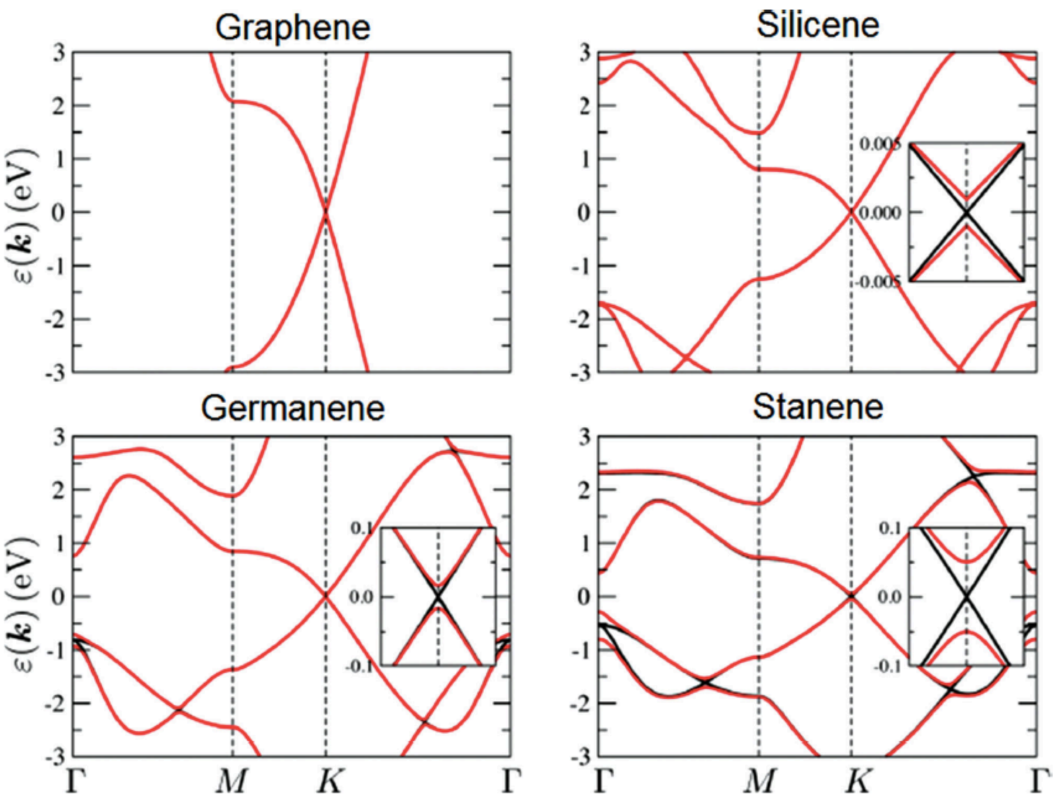
a_{Si} = 3.9 Å

d_{Si-Si} = 2.25 Å



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

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**

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)

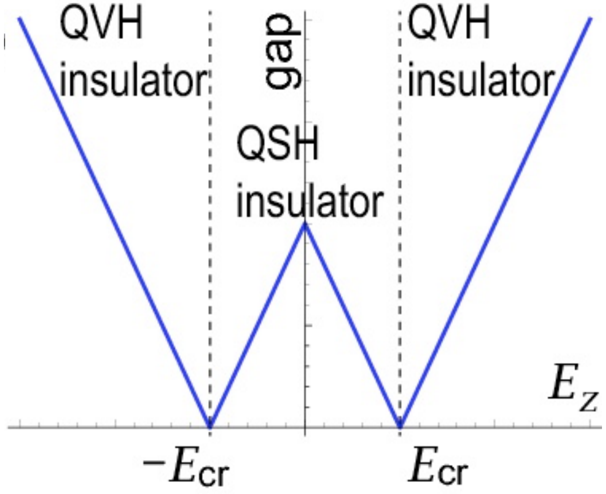
Few predicted properties

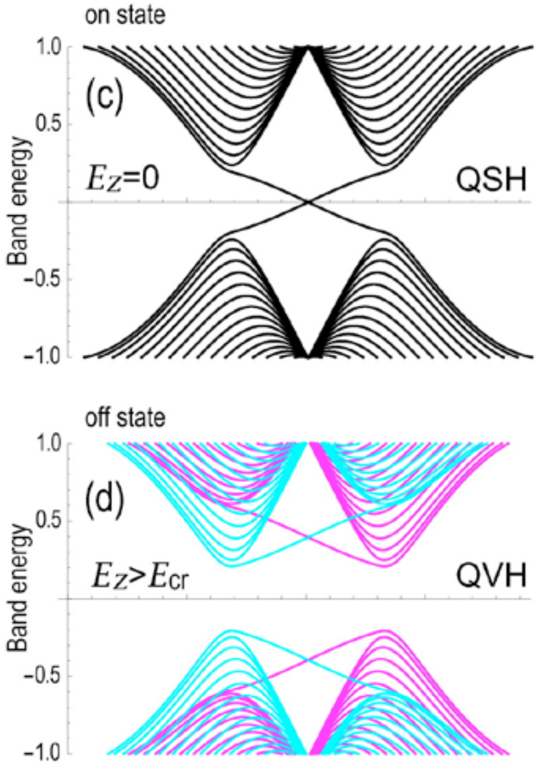
Electrically tunable band gap

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)





Extremely high mobilities

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

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

Phonon mediated superconductivity

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

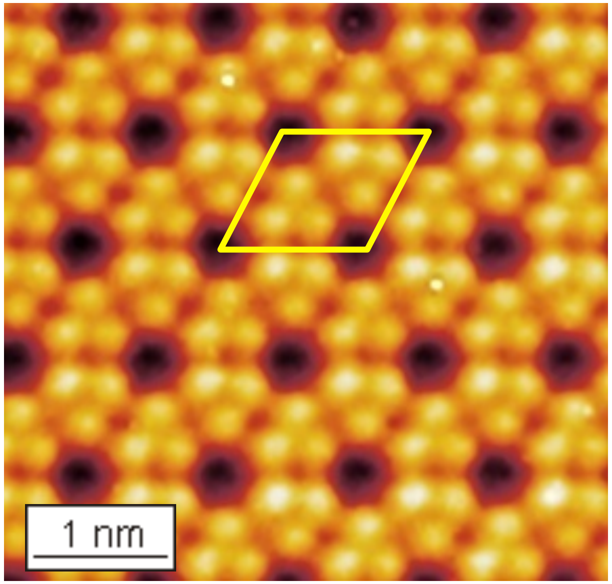
In situ silicon deposition onto the Ag(111) surface

Silicene: graphene’s Lightweight brother

Scanning Tunneling Microscopy image

INSPIRATION:
a hidden underlying honeycomb structure

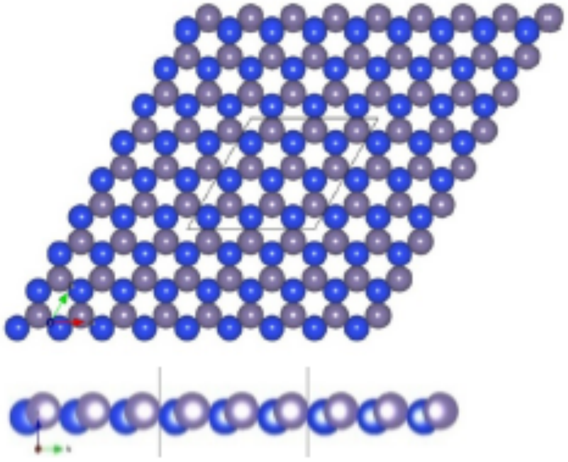
3x3 reconstructed silicene matching a 4x4 Ag(111) supercell



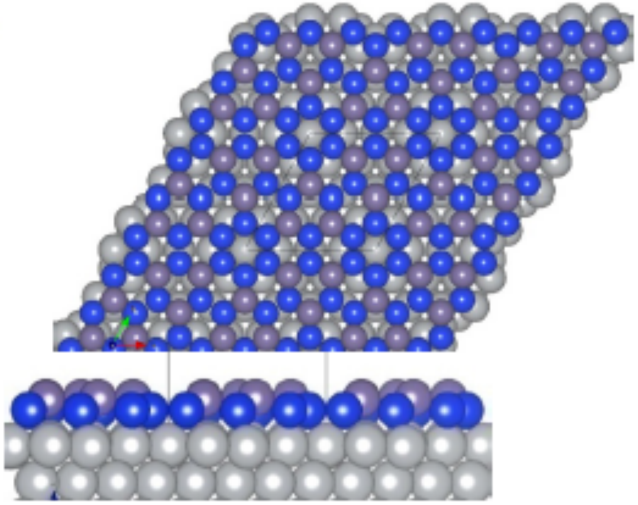
Vogt *et al.*,
Phys. Rev. Lett.108, 155501 (**2012**)
WOS citations: 1859 on Jan., 18, 2019

Density Functional Theory calculations

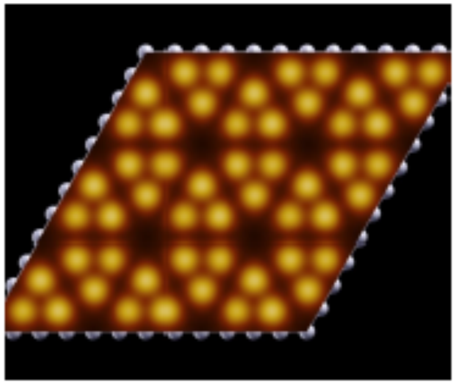
Standalone silicene (buckling ~0.38 Å)



Si atoms atop Ag atoms protrude by 0.4 Å



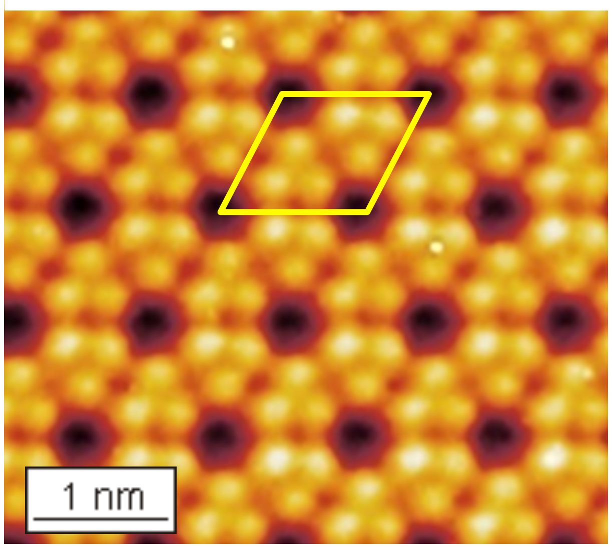
Simulated STM



Silicene: graphene's Lightweight brother

(2012)

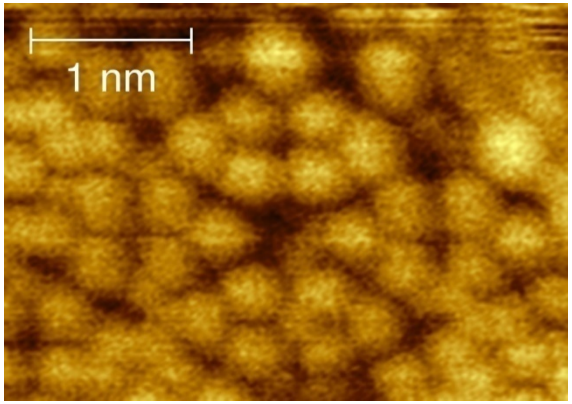
STM image: the "flower pattern"



Vogt et al.,
Phys. Rev. Lett.108, 155501 (**2012**)
WOS citations: 1859, on Jan., 18, 2019

(2013)

NonContact AFM Image

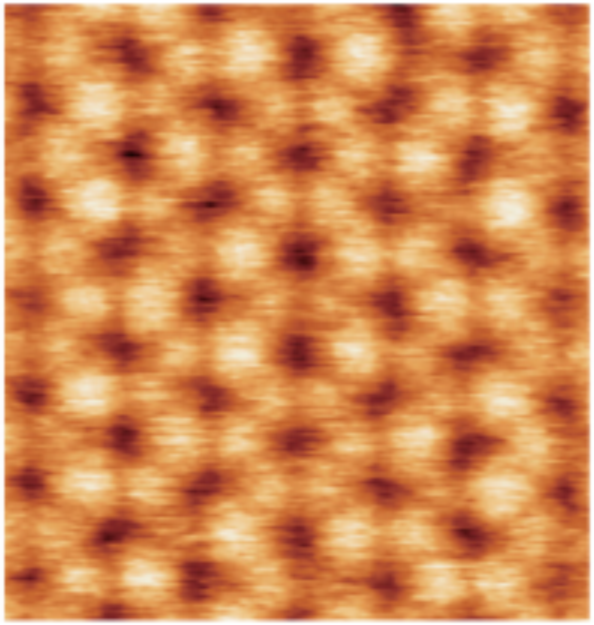


Resta *et al.*,
Sci. Rep., 3, 2399 (**2013**)

(2017)

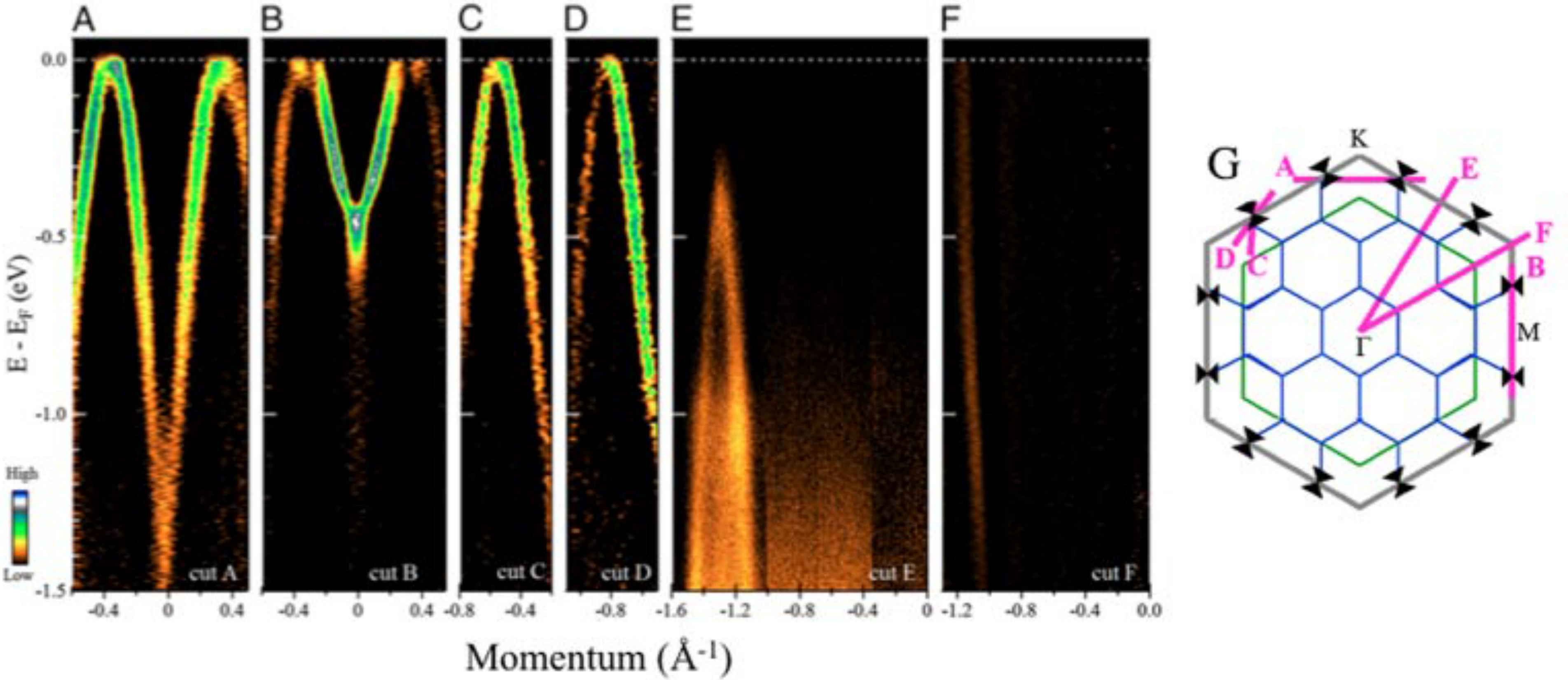
Observation of the internal honeycomb structure

Near Contact AFM image



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

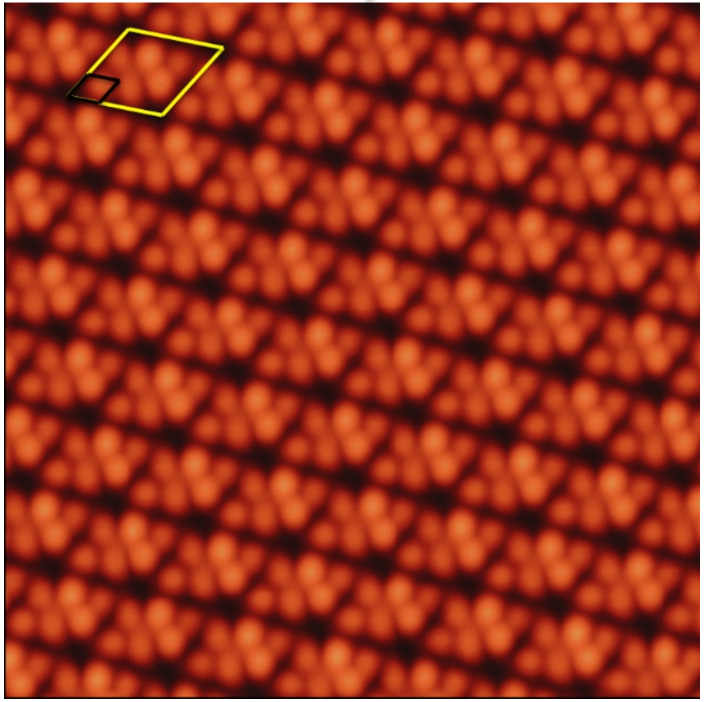
Interaction-induced Dirac cones in the monolayer silicene/Ag(111) system



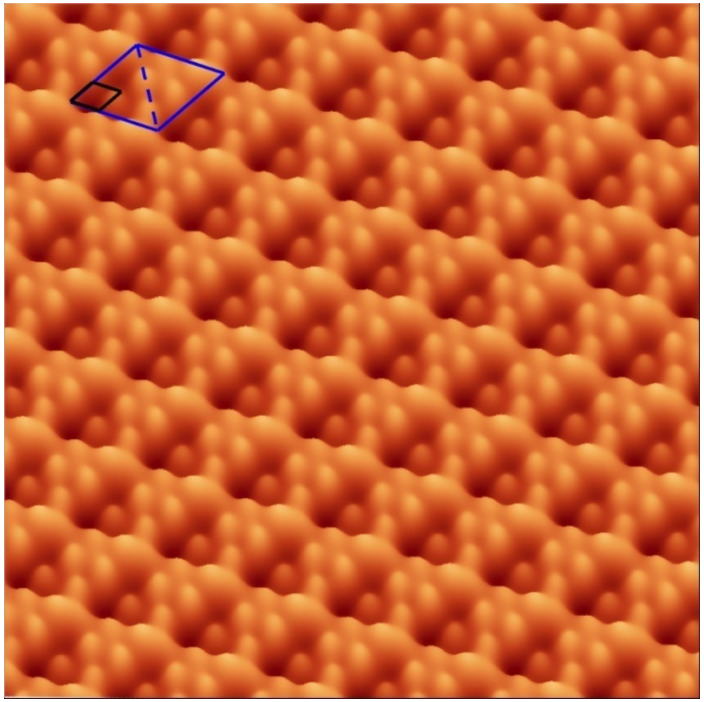
(A–D) Band structures measured along six typical momentum cuts of the (3x3)/(4x4) silicene phase on Ag(111). The six momentum cuts are shown in G.

Feng *et al.*, PNAS, 113 (2016) 14656

Silicene functionalization with H, breaking the symmetry ⇒ 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)

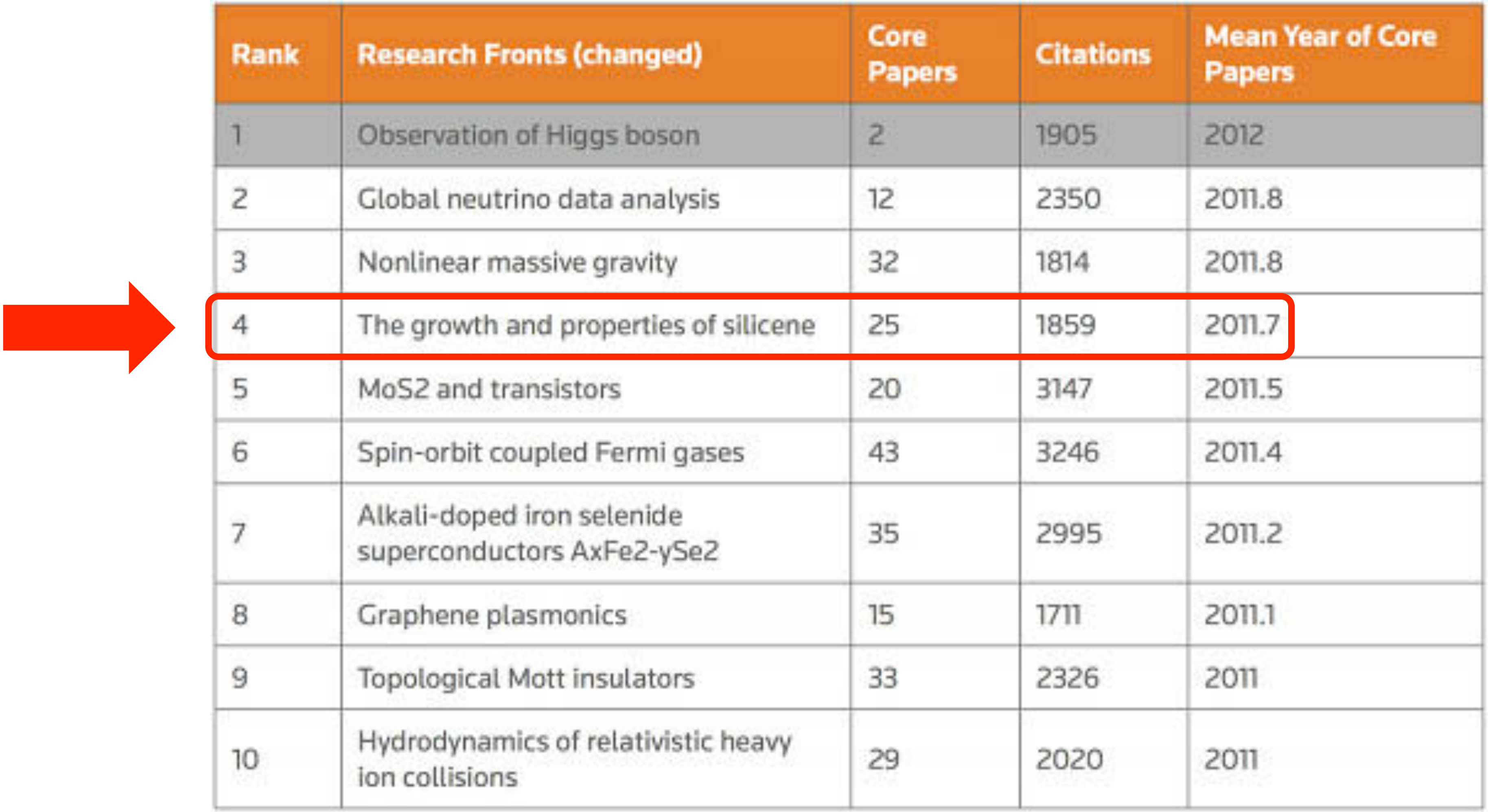
First realized by Qui *et al.*, PRL 114, 126101 (2015)

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

HOT RESEARCH FRONT.

DEVELOPMENT TREND OF THE TOP 10 RESEARCH FRONTS IN PHYSICS

Roughly speaking, a top-10 physics front in 2014 ended up being one whose core papers, published no earlier than 2011, had already generated about 2000 citations



Rank	Research Fronts (changed)	Core Papers	Citations	Mean Year of Core Papers
1	Observation of Higgs boson	2	1905	2012
2	Global neutrino data analysis	12	2350	2011.8
3	Nonlinear massive gravity	32	1814	2011.8
4	The growth and properties of silicene	25	1859	2011.7
5	MoS2 and transistors	20	3147	2011.5
6	Spin-orbit coupled Fermi gases	43	3246	2011.4
7	Alkali-doped iron selenide superconductors AxFe2-ySe2	35	2995	2011.2
8	Graphene plasmonics	15	1711	2011.1
9	Topological Mott insulators	33	2326	2011
10	Hydrodynamics of relativistic heavy ion collisions	29	2020	2011

From a Thomson-Reuters citation-based study covering years 2011 to 2014. **See also PHYSICS TODAY, The Dayside : Hot physics** C. Day 25 September 2015

2012, Silicene's Annus Mirabilis

Original 2D Si, Ge, Sn, Pb papers with more than 800 citations on Jan. 18, 2019, according to WOS: 4 Phys. Rev. Lett.'s !

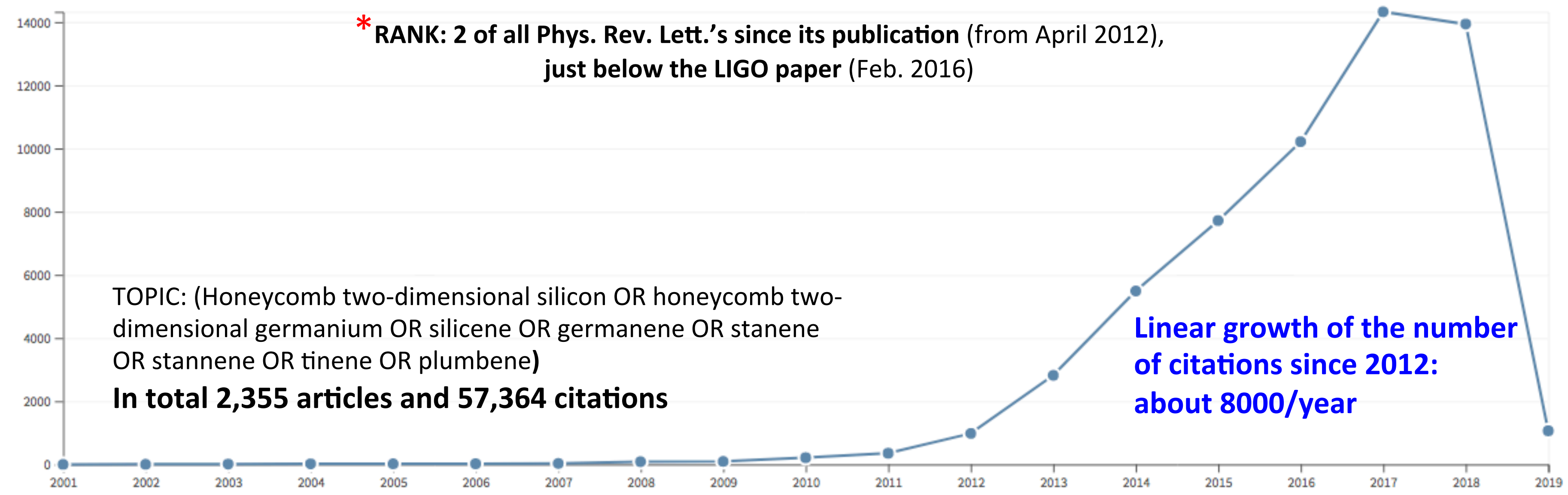
1. **Silicene: Compelling Experimental Evidence for Graphenelike Two-Dimensional** Silicon*
By: Vogt, Patrick; De Padova, Paola; Quaresima, Claudio; …; **Le Lay, Guy**
PHYSICAL REVIEW LETTERS 108, 155501 Published: APR 2012 Times Cited: **1,859**

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: **1,576**

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: **1,204**

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: **897**

Sum of Times Cited per Year



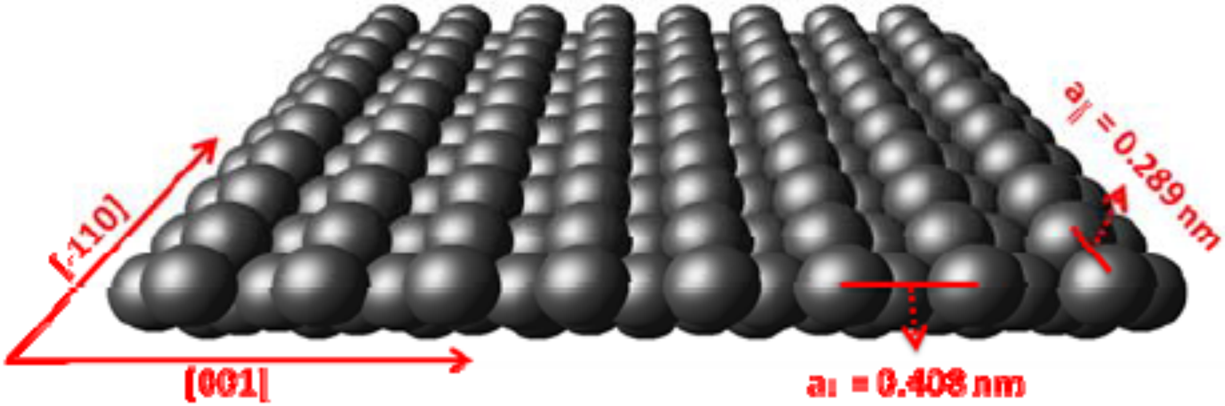
***RANK: 2 of all Phys. Rev. Lett.'s since its publication** (from April 2012),
just below the LIGO paper (Feb. 2016)

TOPIC: (Honeycomb two-dimensional silicon OR honeycomb two-dimensional germanium OR silicene OR germanene OR stanene OR stannene OR tinene OR plumbene)

In total 2,355 articles and 57,364 citations

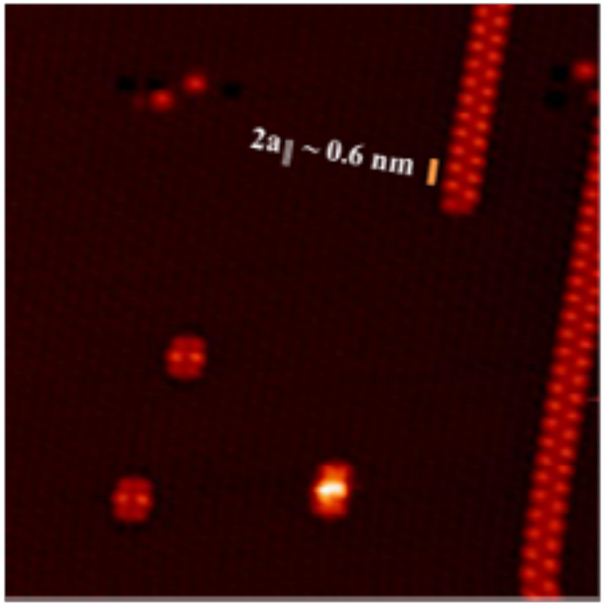
Linear growth of the number of citations since 2012: about 8000/year

In situ silicon deposition onto the Ag(110) open surface (rectangular unit cell)

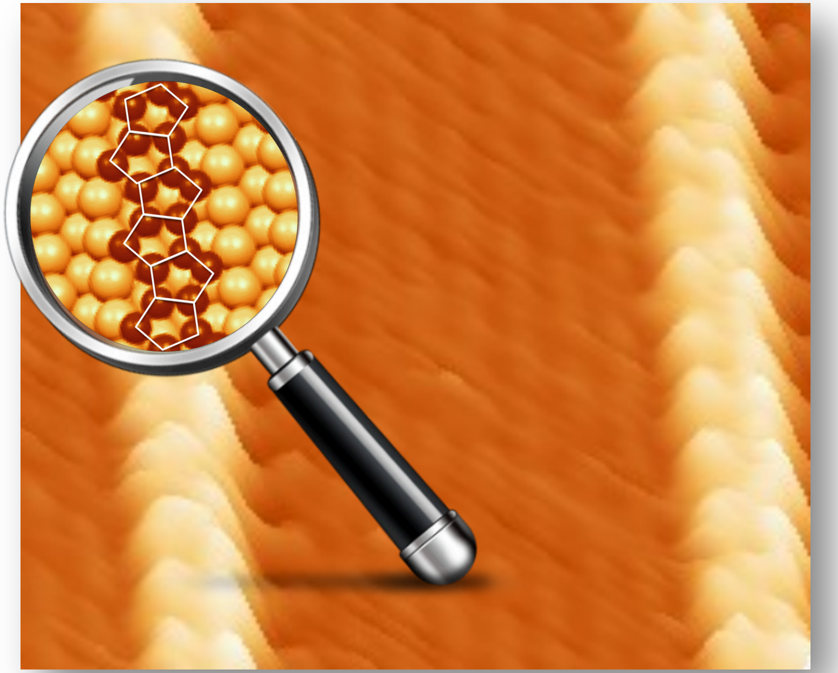


Ball model of the Ag(110) surface

Si nanodots and **massively parallel Si nanoribbons**

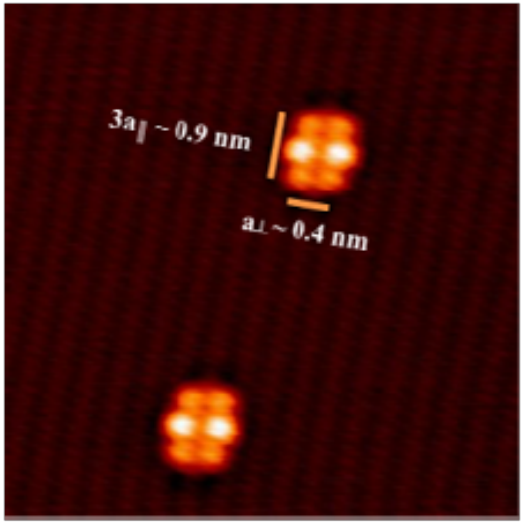


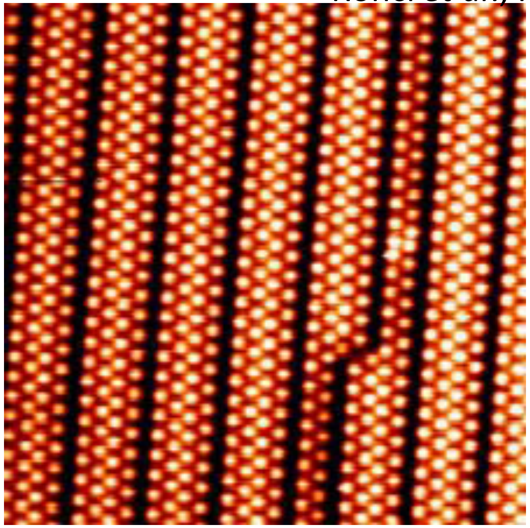
Nanodots, all identical, have mirror symmetry

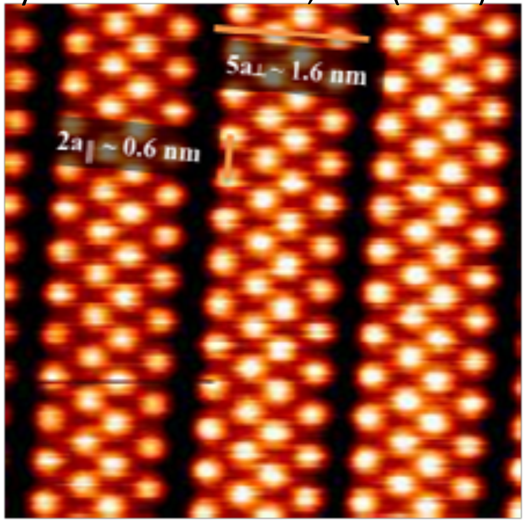


Nanoribbons either single- or double-strand, i.e., either 0.8 or 1.6 nm in width, break the symmetry

Ronci *et al*., Phys. Status Solidi C 7, 271 (2010)



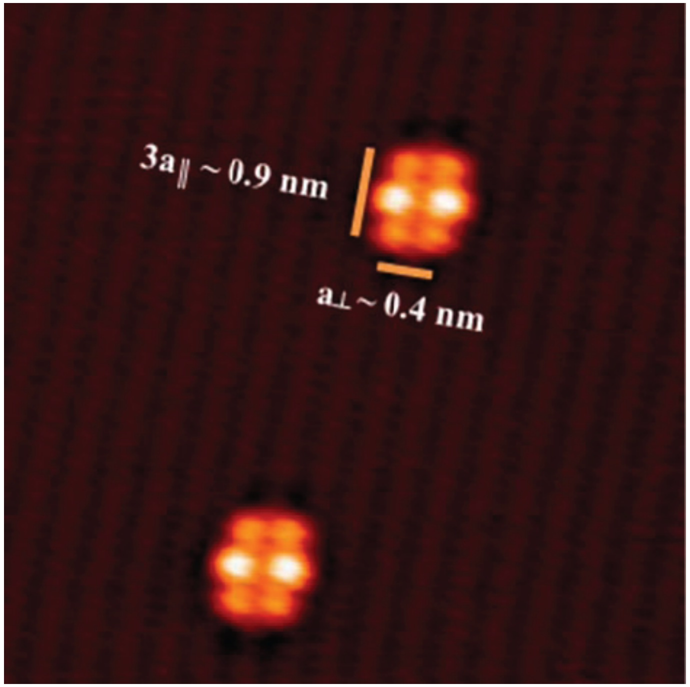




Nanoribbons: a symmetry breaking polymerisation of nanodot building blocks !

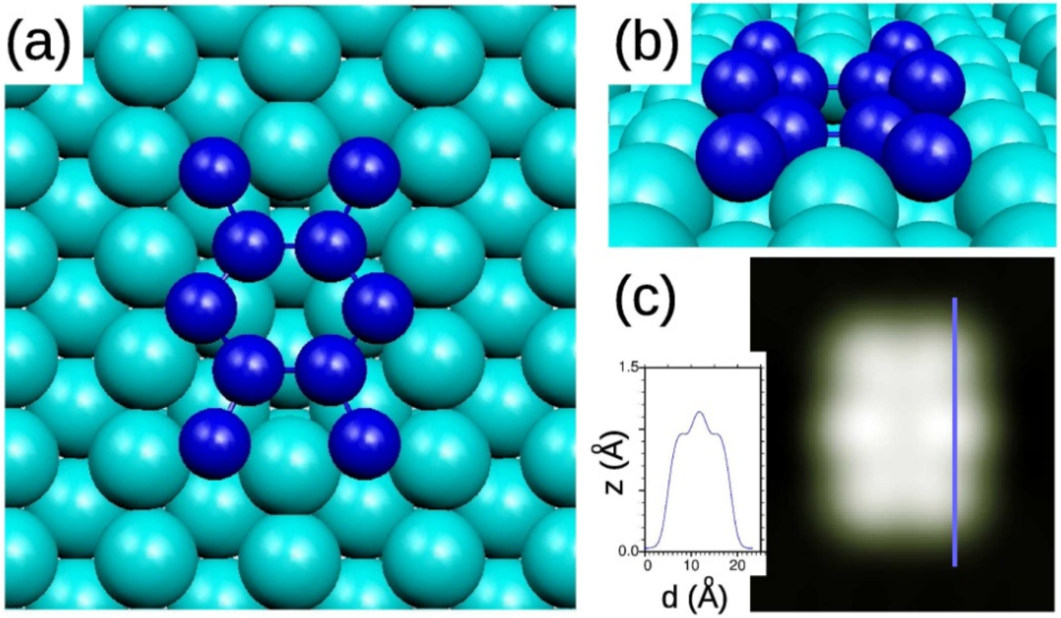
Zero Dimension: Symmetric, *benzene-like (?)* nanodots on Ag(110)

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).

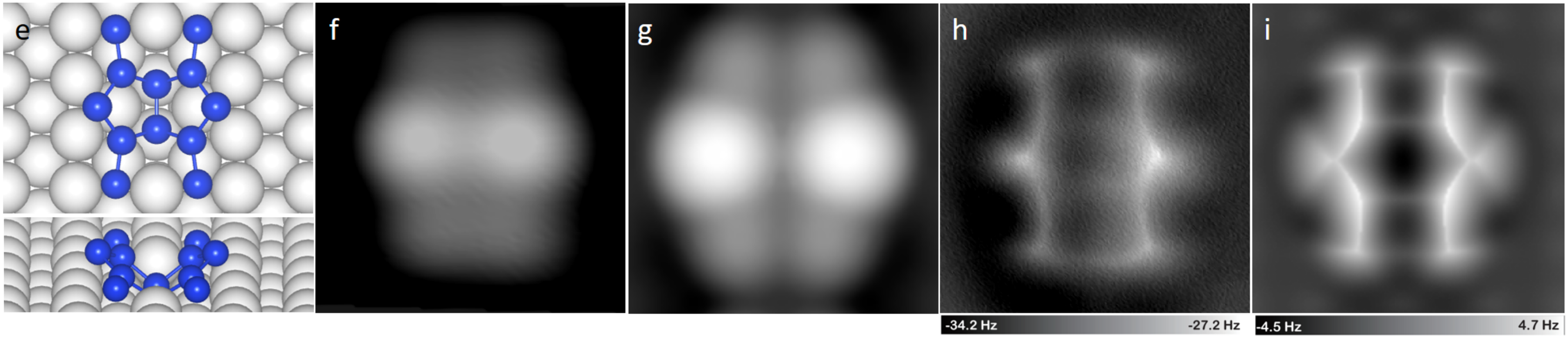


(a & b) Top and perspective views of the nano-dot structure over 2 Ag vacancies. (c) Simulated STM topographic image and line profile along the solid line.

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

Direct evidences of Pentagonal Si nanodots

By AFM imaging



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)

Pentasilicene: silicene’s cousin

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

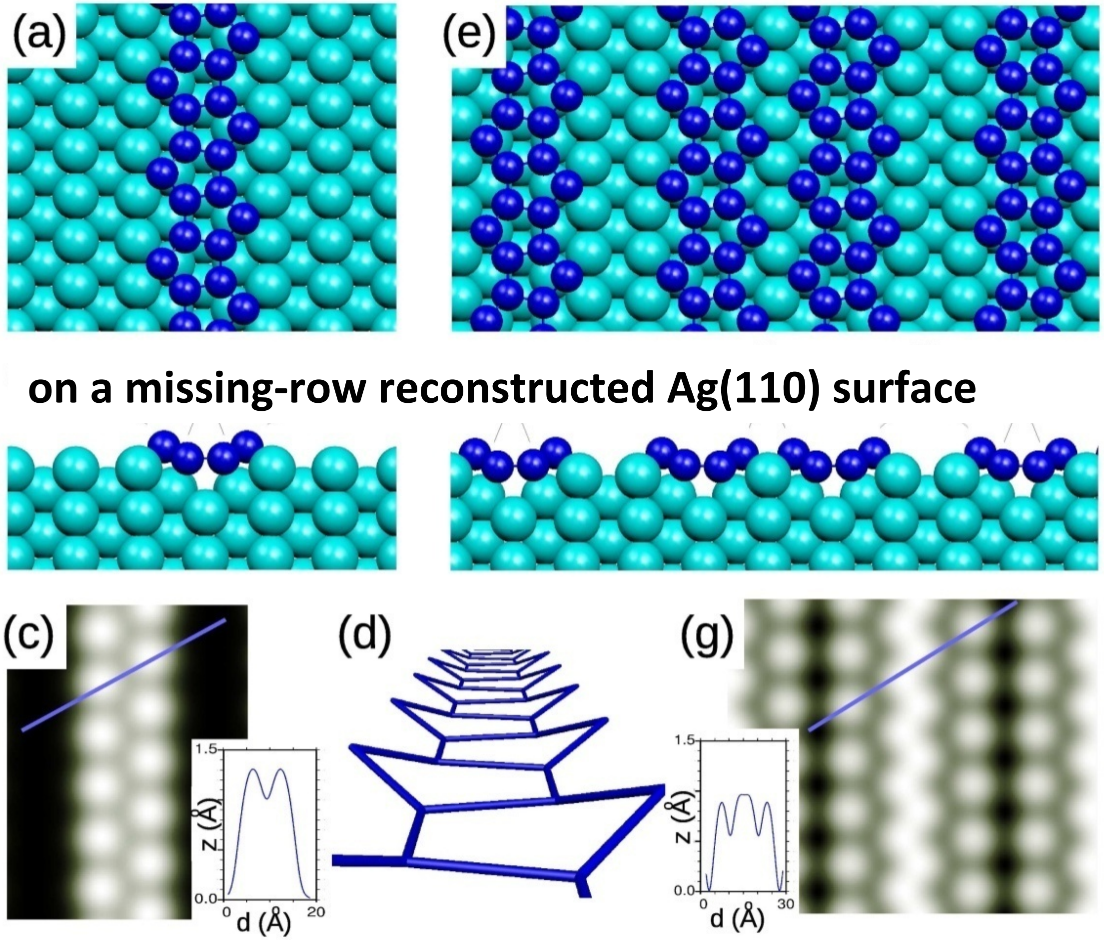
G. Prévot et *al.*,
Phys. Rev. Lett., **117**, 276102 (2016)

and by Photoelectron Diffraction

P. Espeter *et al.*,
Nanotechnology, **28**, 455701 (2017)

Si nanoribbons and nanodots

Single strand & Double strand SiNRs

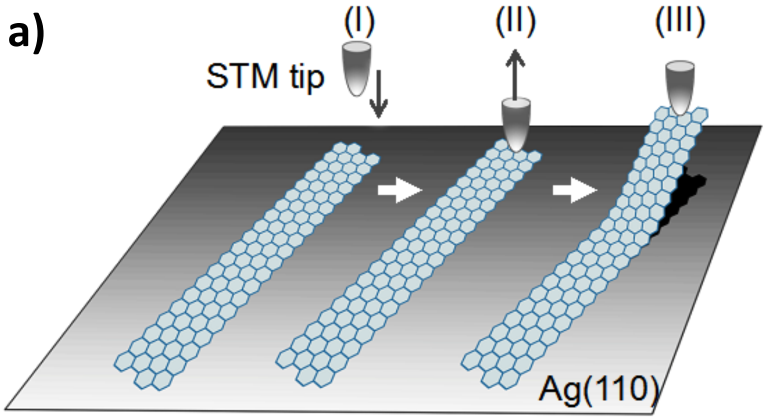


on a missing-row reconstructed Ag(110) surface

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.

Lift off of a SiNR with an STM tip

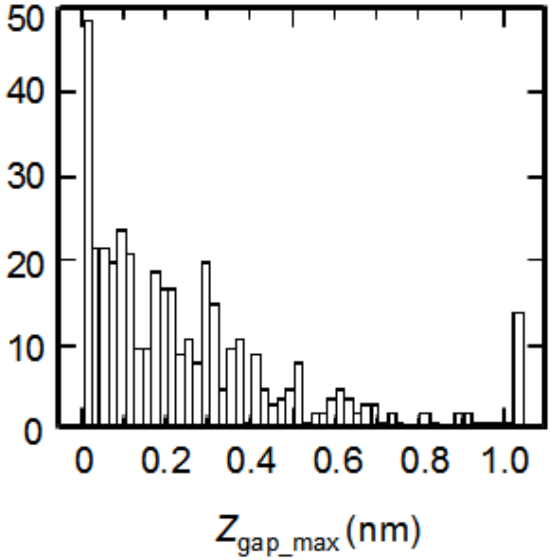
a)



a) Scheme of the process

→ **Standalone SiNR**

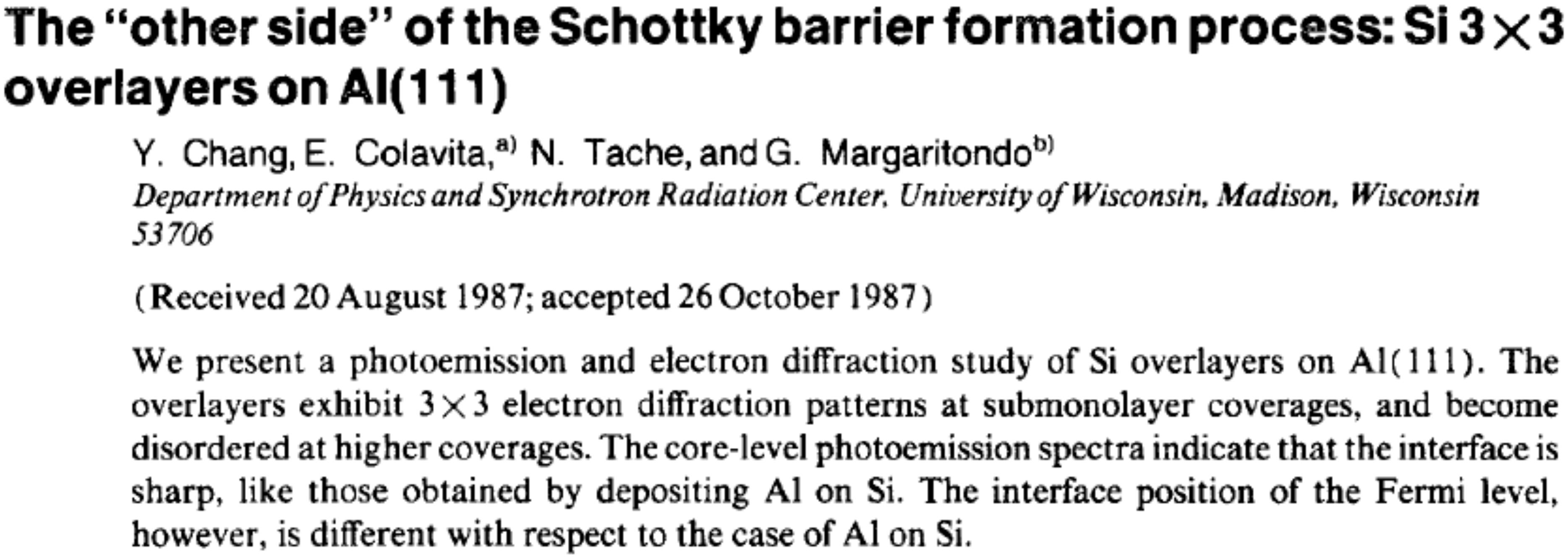
b)



b) Histogram of Zgap_max, the maximum distance the tip travels before the SiNR nanojunction is broken after contacting the tip to the SiNR.

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

Silicon deposition onto Al(111)



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

Y. Chang, E. Colavita,[a] N. Tache, and G. Margaritondo[b]
Department of Physics and Synchrotron Radiation Center, University of Wisconsin, Madison, Wisconsin 53706

(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:

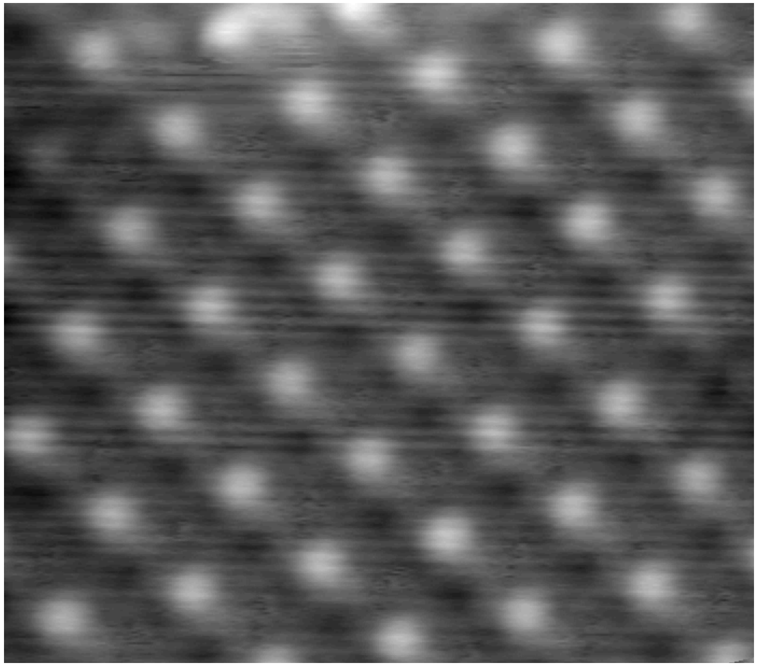
4x4 wrt Ag(111) ↔ 3x3 silicene

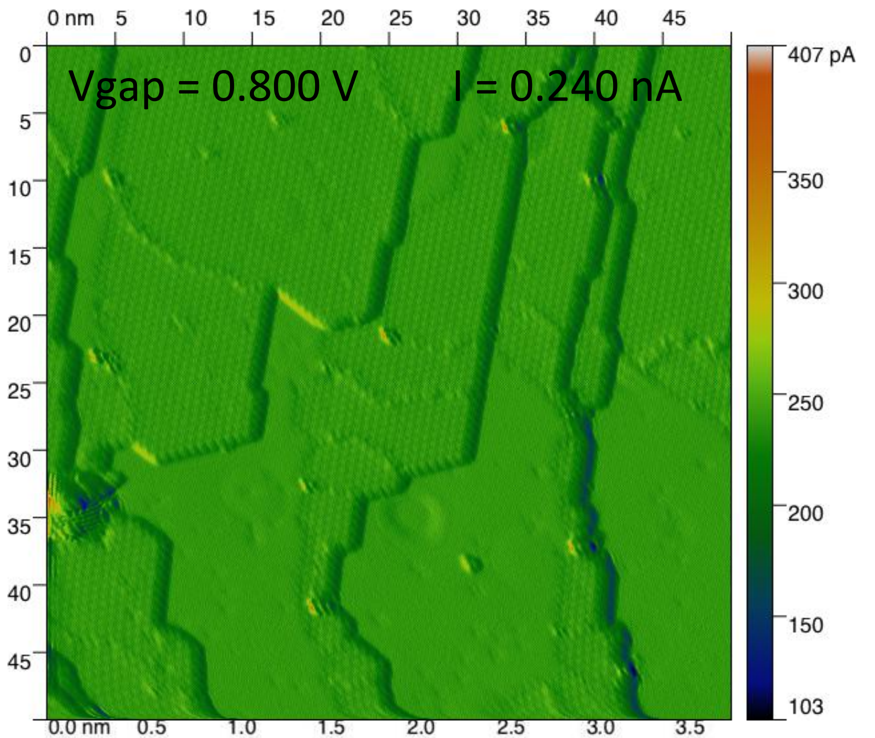
3x3 wrt Al(111) ↔ ???

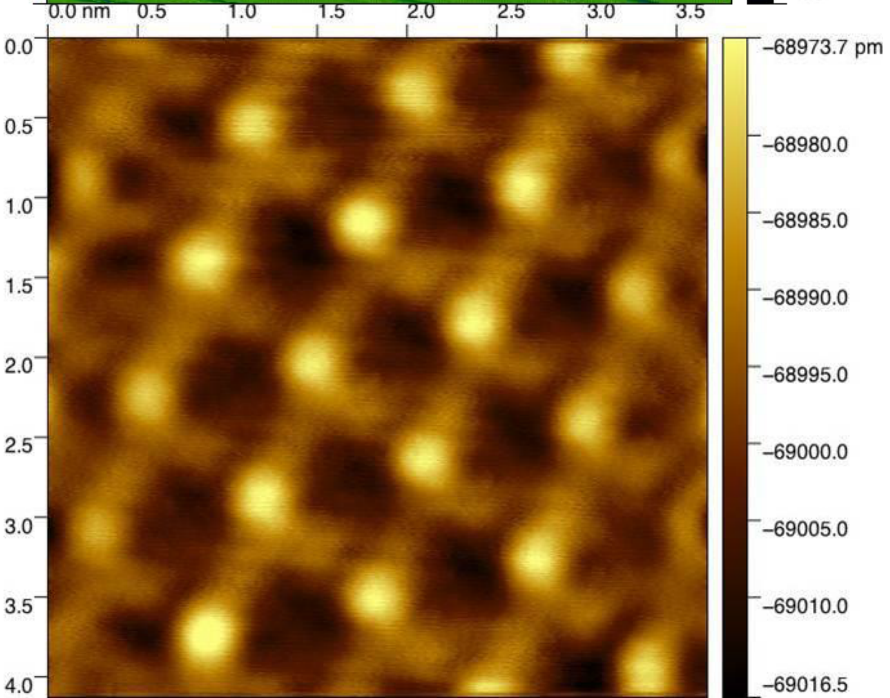
Kagome silicene: silicene's sister

2D Si weird structure epitaxially formed on Al(111)3x3 at RT in a single orientation

Y. Sassa *et al.*, submitted





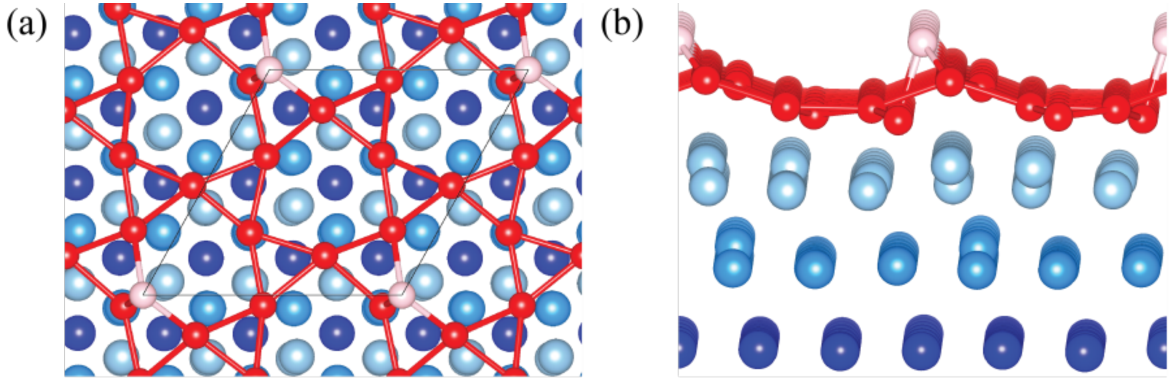


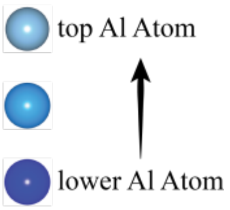
In accord with the 1rst STM images obtained by H. Brune in the early 90's (PhD thesis, 1992, unpublished)

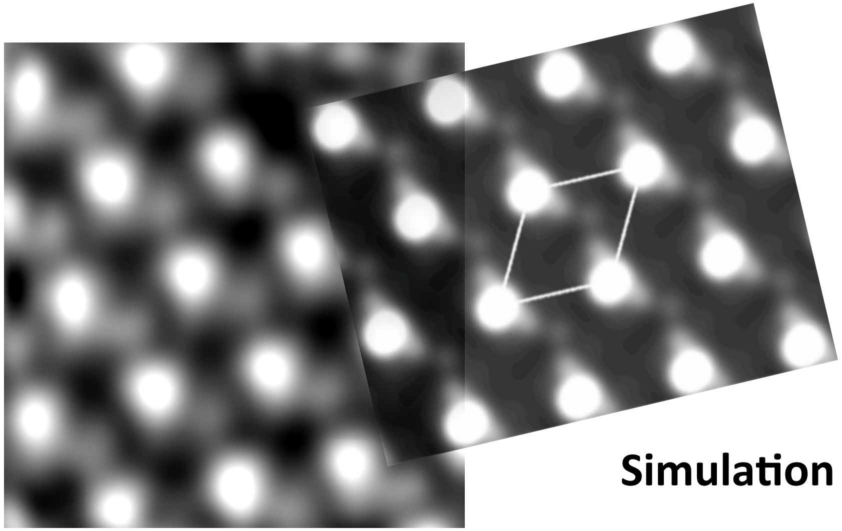
Kagome Silicene stabilized by **dumbells**

Y. Sassa *et al.*, submitted

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



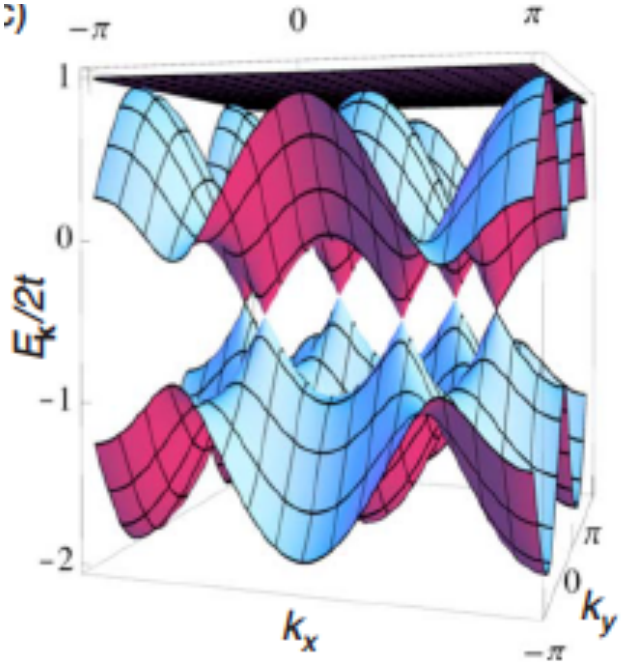




Simulation -10 meV

STM image 11 nm x 11 nm

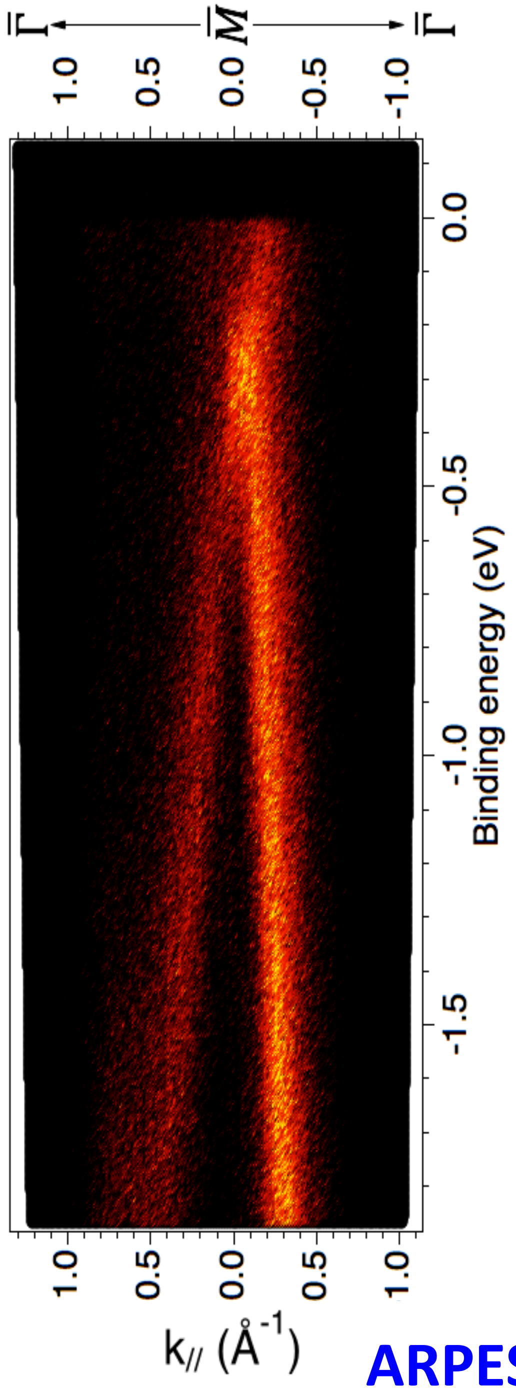
V_{GAP} = - 10 mV (filled states), I_T = 150 pA

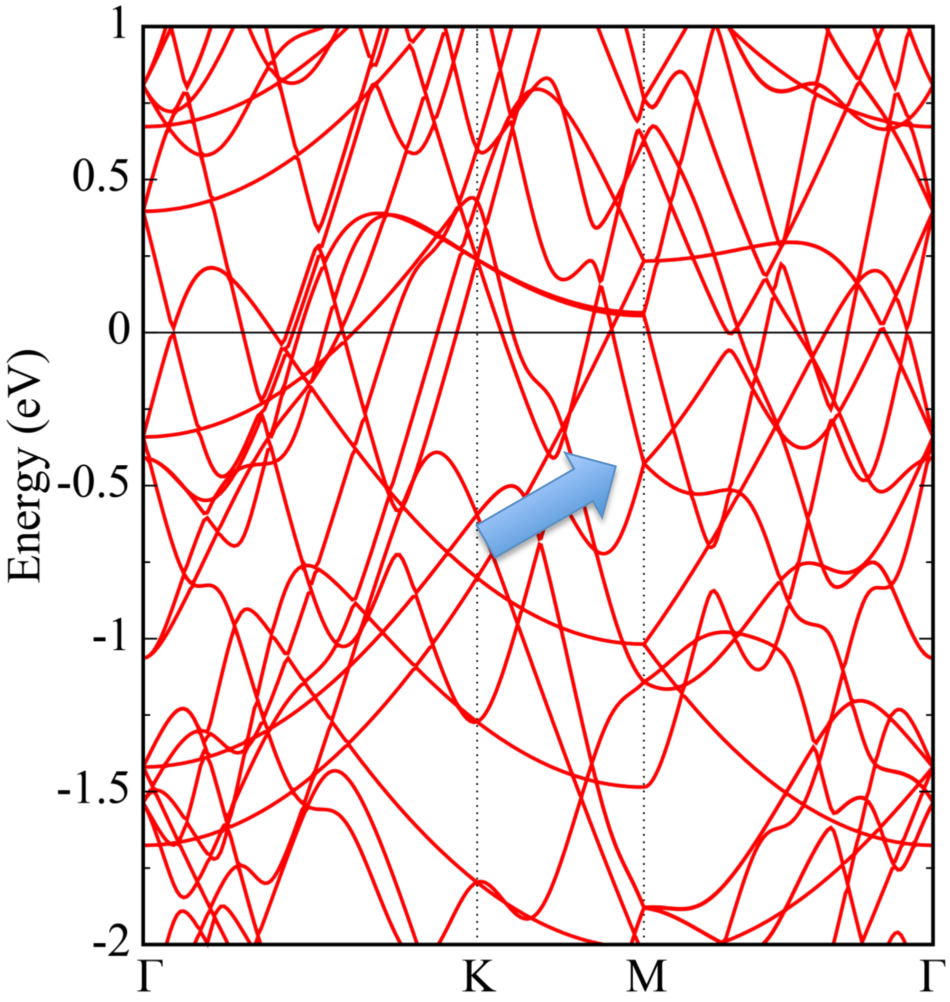


Tight binding band structure

Guo and Franz PRB 80, 113102 (2009)

Conelike dispersions at M points



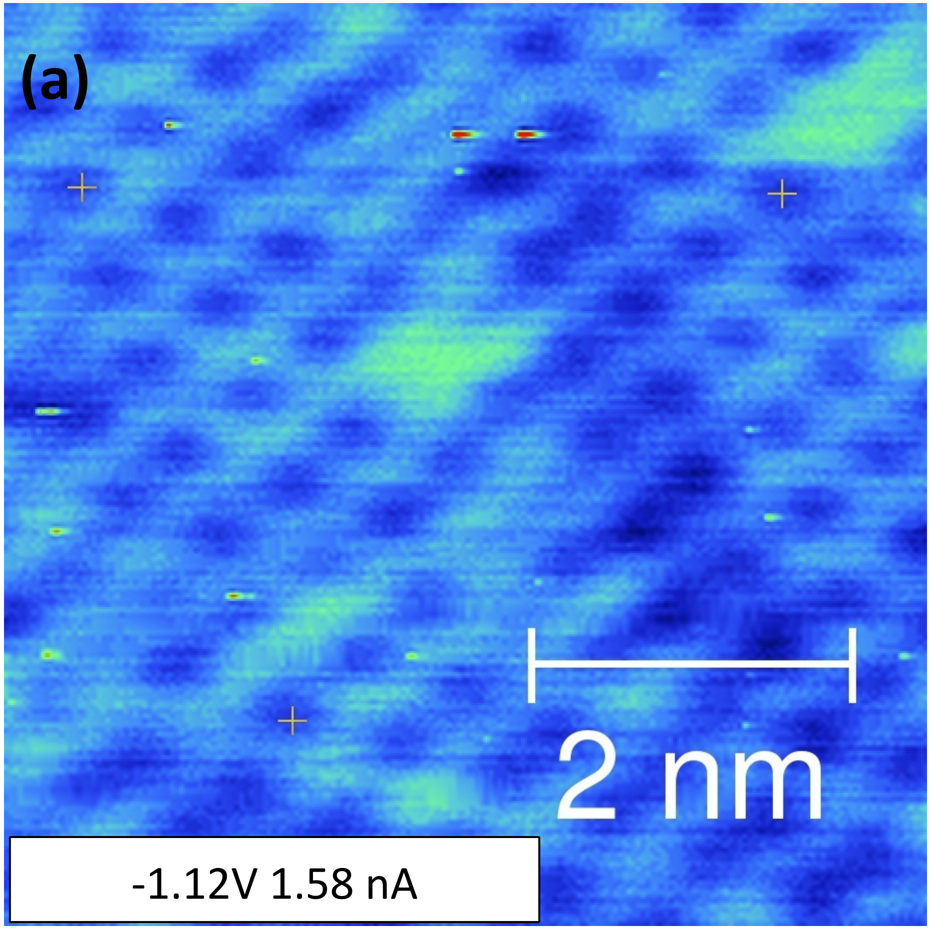


Calculated band structure

ARPES spectrum He I 21.2 eV

Germanene: silicene's Middleweight brother

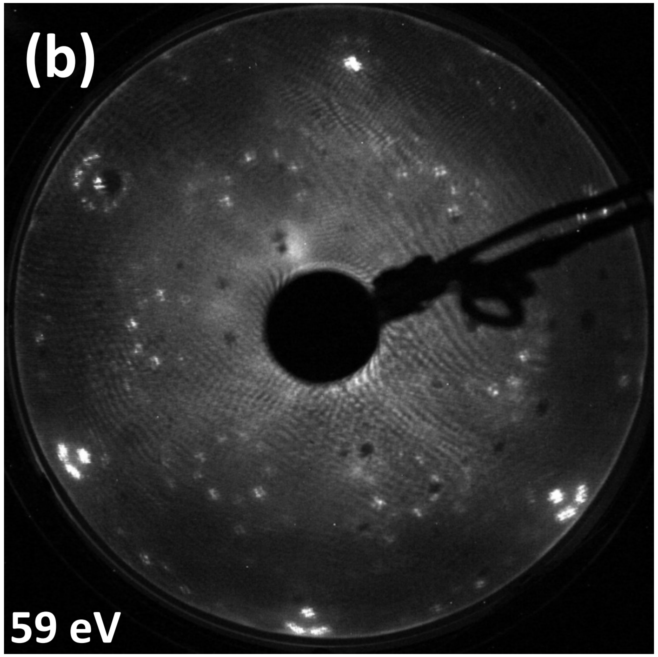
111)

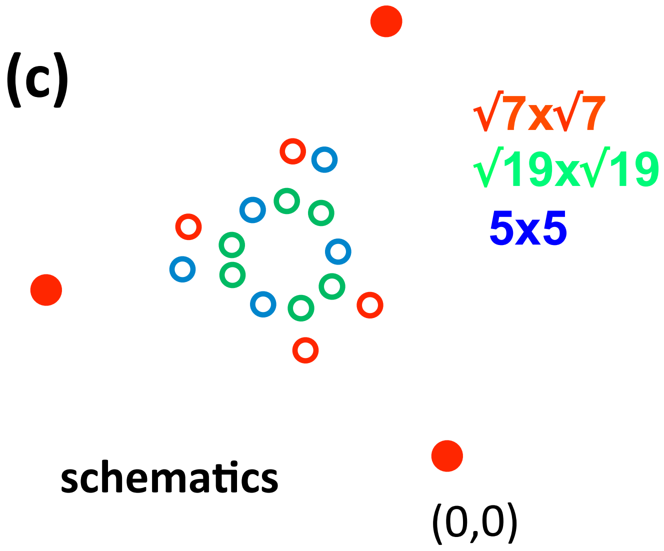


STM image of single layer germanene on Au(111) :
one of the phases with modulated honeycomb
Appearance in a Au(111)√7x√7 supercell

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

Composite LEED pattern: 3 phases





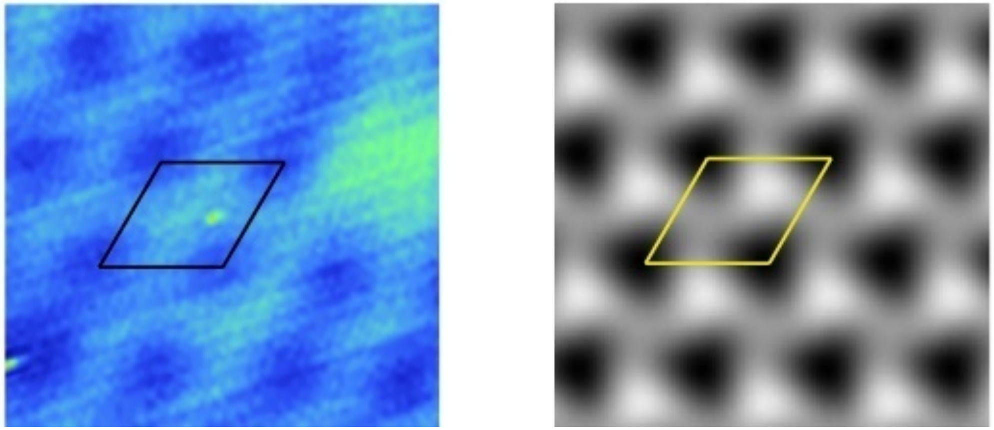
Germanene on Au(111)

VASP, DFT-GGA

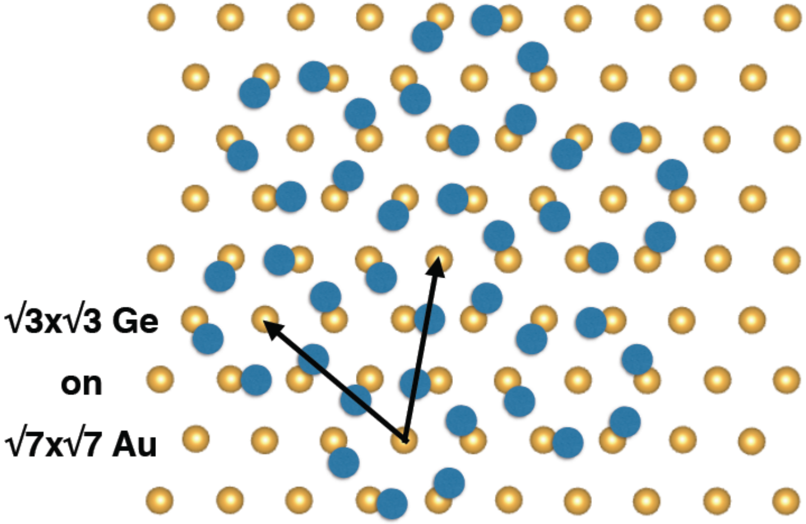
Dávila *et al.*, *New J. Phys.* **16**, 095002 (2014)

In plane d_{Ge-Ge} = 2.55 Å

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

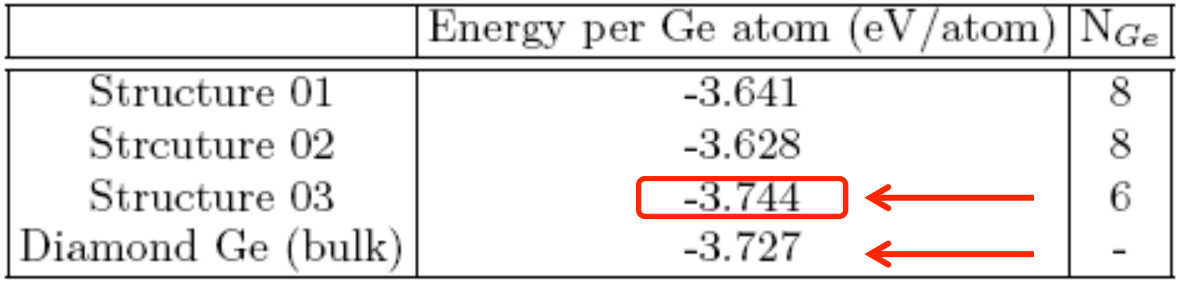


Weak corrugation ~0.2 Å



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

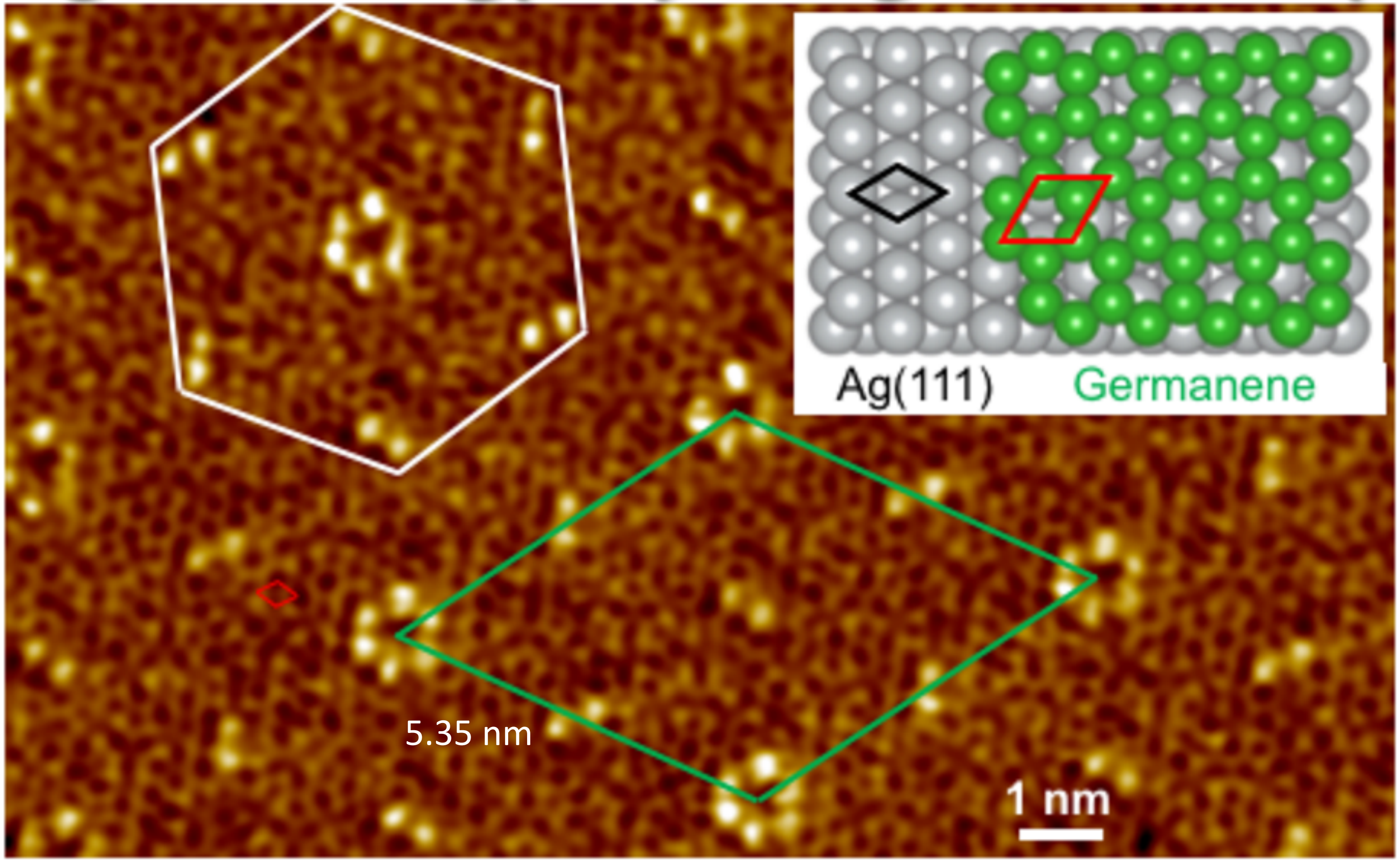
DFT calculations



	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	-

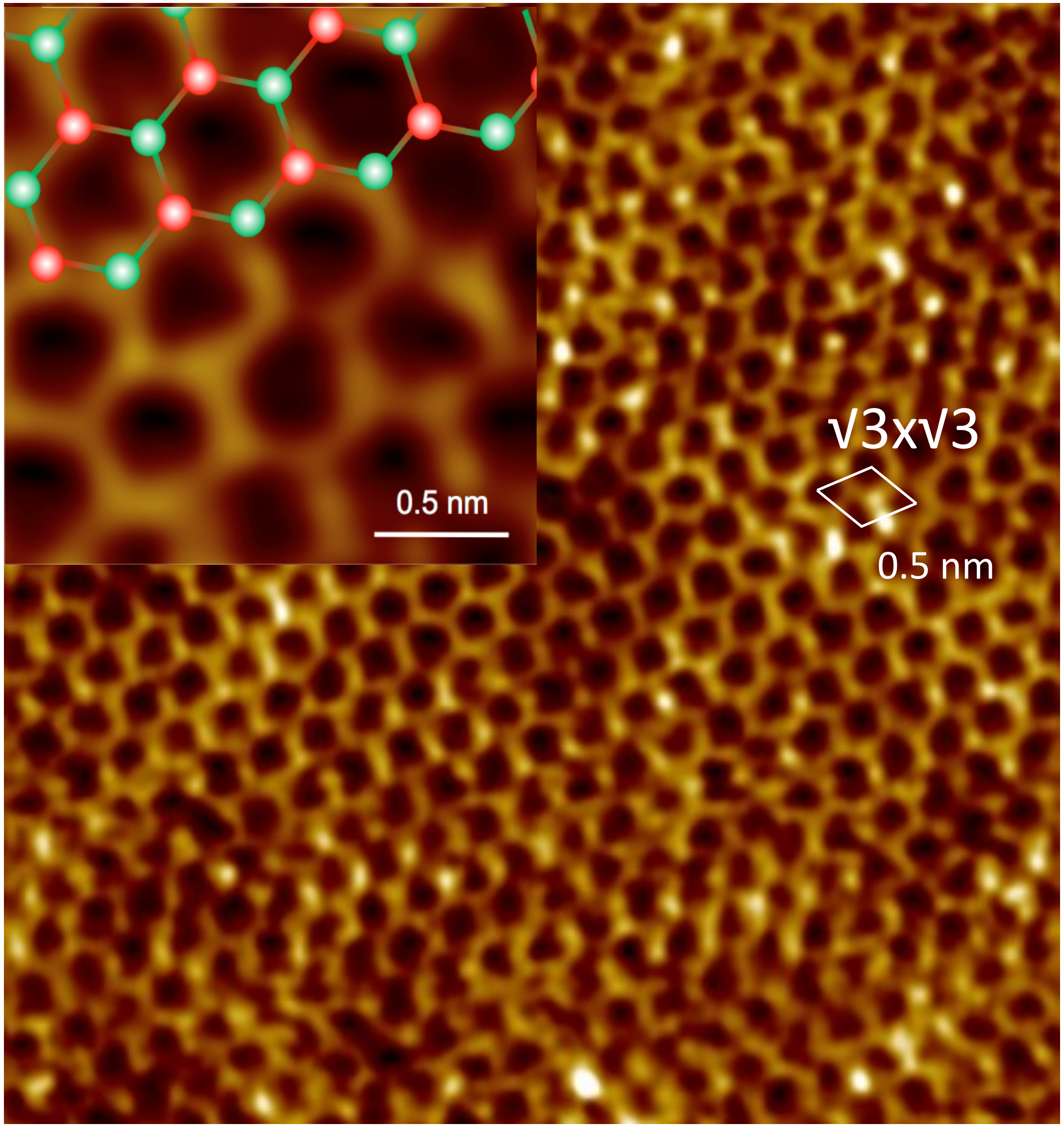
TABLE I: Absorption energy for different germanene structures on Au (111) surface.

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



Single phase: 3√21x3√21 germanene matching a 7√7x7√7*R*±19°1 Ag(111) supercell Yuhara et al., ACS Nano, 12, 11632 (2018)

Stanene: silicene's Light Heavyweight brother

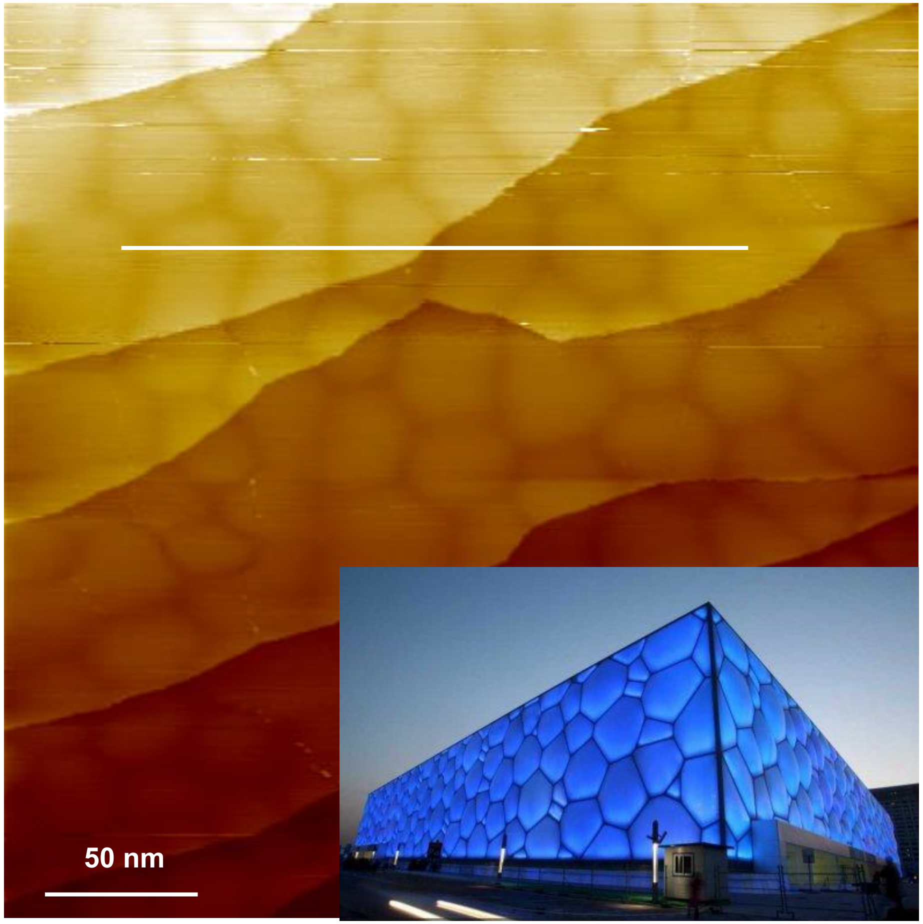


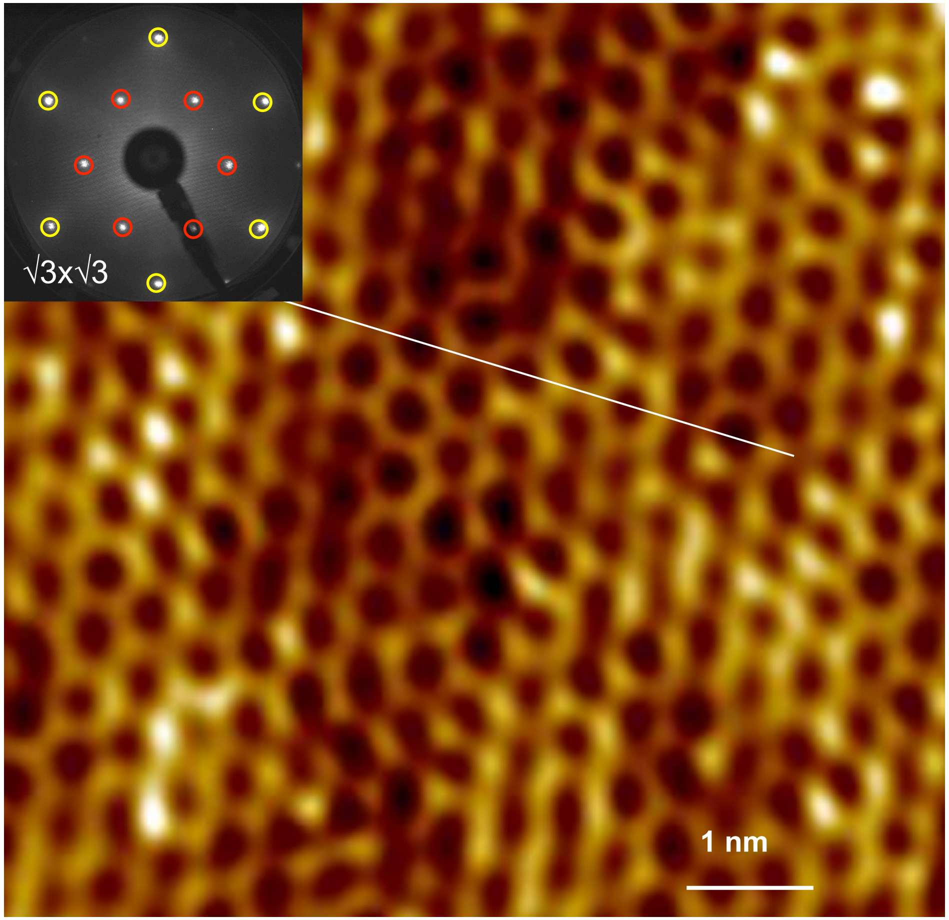
Large area epitaxial stanene on Ag(111)

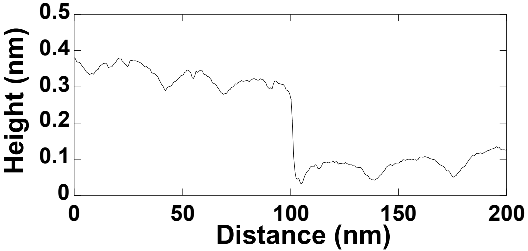
Yuhara *et al*., 2D Mater., 5, 025002 (2018)

N.B.: **Superconductivity in few-layer stanene Liao *et al*.**, Nature Physics 14, 344 (2018)

Plumbene: silicene's Heavyweight brother

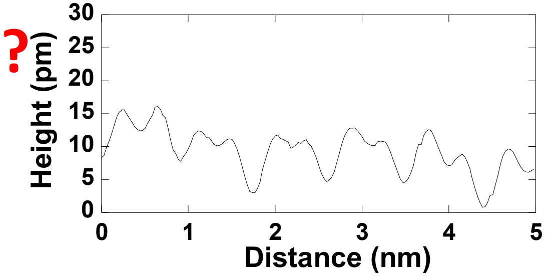






2D topological superconductor?

Discovery of a new quantum spin Hall phase in bilayer plumbene **Zhang *et al.*,**
Chem. Phys. Lett. 712 (2018) 78



Plumbene epitaxial growth on a "**Nano Water Cube**" : Pb/Pd(111)

Weaire-Phelan solution to the Kelvin conjecture

Yuhara *et al.*, submitted

Summary and outlook

Silicene (2012), PentaSilicene (2016), Kagome Silicene (2018),
Germanene (2014), Stanene (2017), Plumbene (2018)

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

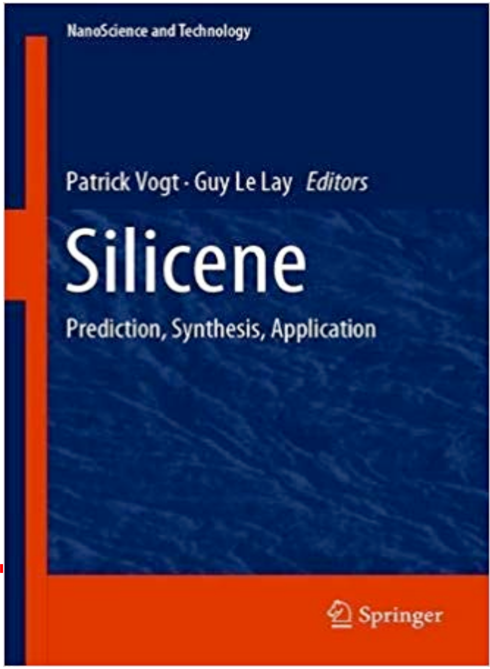
Prototypical 2D Topological Insulators with a sizeable band gap.

Evidence of layered silicene, germanene and stanene

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

Prospects **Interfacing with superconductors!**

The Holy Grail **Majorana's, anyons…**



NanoScience and Technology

Patrick Vogt · Guy Le Lay *Editors*

Silicene

Prediction, Synthesis, Application

Springer

IMPORTANT DATES

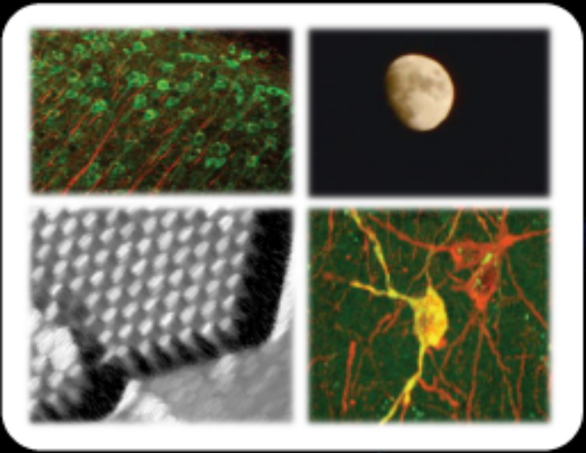
Abstract deadline (oral or poster presentation)
March 31, 2019

Author submission acceptance notification
April 12, 2019

Early bird registration fee
May 31, 2019

CONFERENCE SITE

Campus du Pharo, Aix-Marseille Université,
Jardin du Pharo 58, bd Charles Livon, 13007 Marseille



From the NanoWorld to StarDust

NW2SD

International conference

July 17-19 2019, Marseille, France

Palais du Pharo

https://nw2sd.sciencesconf.org/

SCOPE

The multi-disciplinary theme of the conference, commemorating the 50th anniversary of the first step of Neil Amstrong on The Moon, will cover space observations and spectroscopic signatures of molecules and nanostructures (in the environments of comets, exoplanets, cosmic dusts etc.) to experimental simulations of their formations in the laboratory. Typically, such studies associate in a synergetic way plasma and molecular physics, surface science, nanosciences, quantum chemistry, laboratory astrophysics and astronomy. Furthermore, sessions will be devoted to neurosciences and molecular biology, since nanosciences play a key role in the development of these disciplines.
The conference will be attended both by nanoscience experts and by astronomers.

PLENARY SPEAKERS

Prof. Bernard Bigot, Director-General, ITER Organization, Cadarache, France
Prof. Yves Coppens, discoverer of Lucy, the first Australopithecus Afarensis, in 1974, Collège de France *(to be confirmed)*
Prof. Ewine van Dishoek, Kavli price Laureate in Astrophysics (2018), Leiden Univ., The Netherlands *(to be confirmed)*
Dr Pedro Duque, Astronaut, Spain's Minister of Science, Innovation and Universities *(to be confirmed)*
Prof. Albert Fert, Nobel Laureate in Physics (2007), Univ. Paris-Sud, France
Prof. Christoph Gerber, Kavli Prize Laureate in Nanosciences (2016), Univ. of Basel, Switzerland
Prof. Michel Mayor, Wolf Prize Laureate 2017, discoverer of the first exoplanet 51 Peg b at the OHP in 1995, Univ. de Genève, Switzerland
Prof. Francisco Mojica, Albany Medical Center Prize (2017), pioneer of CRISPR (molecular biology), Univ. of Alicante, Spain
Prof. Christine Petit, Kavli Prize Laureate in Neurosciences (2018), Institut Pasteur, Paris, France

Credit: Jianping Guo


Credit: Jianping Guo

CONTACT

nw2sd@sciencesconf.org
https://nw2sd.sciencesconf.org/

REGISTRATION FEES

See the web site, https://nw2sd.sciencesconf.org/

CONFERENCE CHAIR

Prof. Guy Le Lay (Aix-Marseille Univ.)

INTERNATIONAL ADVISORY COMMITTEE

Chair, Prof. Patrick Soukiassian, Univ. Paris-Sud & CEA, France
Members :
Prof. Masakazu Aono, NIMS, Tsukuba, Japan
Dr Catherine Cesarsky, CEA, Saclay, France
Dr Athanasios Dimoulas, Demokritos, Athens, Greece
Prof. Vladimir Fal'ko, Univ. of Manchester, GB
Prof. Fernando Flores, Univ. Autonoma, Madrid, Spain
Dr José Angel Martin Gago, ICMM-CSIC, Madrid, Spain
Prof. James Gimzewski, Univ. of Calif., Los Angeles, USA
Prof. Shuji Hasagawa, Tokyo Univ., Japan
Prof. Jinfeng Jia, Jiaotong Univ., Shanghai, China
Prof. Ulf Karlsson, Linköping Univ., Sweden
Dr Roger Malina, Univ. of Texas, Dallas, USA
Prof. Nils Martensson, Uppsala Univ., Sweden
Prof. Enrique Ortega, San Sebastian Univ., Spain
Prof. Angel Rubio, Univ. of Hamburg, Germany
Prof. Lok Lew Yan Voon, Univ. of West Georgia, USA
Prof. Andree Wee, National Univ., Singapore
Prof. Paul Weiss, Univ. of Calif., Los Angeles, USA
Prof. Kehui Wu, Acad. Sciences, Beijing, China
Prof. Qi-Kun Xue, Tsinghua Univ., Beijing, China

ORGANIZING COMMITTEE

Chair, Prof. Jean-Marc Layet, Aix-Marseille Univ., France
Members :
Prof. Thierry Angot, Aix-Marseille Univ., France
Dr. Aurélie Bétourné, Aix-Marseille Univ., France
Nathalie Bonifay, Aix-Marseille Univ., France
Dr Annette Calisti, Aix-Marseille Univ., France
Prof. Magali Deleuil, Aix-Marseille Univ., France
Dr Christian Grisolia, CEA Cadarache, France
Prof. Francois Roman, *Aix-Marseille* Univ., France
Dr Eric Salomon, Aix-Marseille Univ., France
Dr Auguste Le Van Suu, OHP, Saint Michel l'Observatoire, France

ABOUT NW2SD

The incursion of science into the nano-world and into the world of low dimensionality for several decades has led to a new vision of the properties of matter with extraordinary repercussions in a large number of scientific fields. The multi and interdisciplinary themes presented in this conference cover broad fields of current science ranging from observations of the spectroscopic signatures of molecules and nanostructures in space environments (stellar dusts, comets, exoplanets, ...) to the experimental simulations of their laboratory formation. This type of study is carried out in synergy with atomic, molecular and plasma physics, nanosciences, quantum physicochemistry and astrophysics and laboratory astrochemistry. In addition, sessions will present recent results of the contribution of nanoscience in the development of neuroscience and biology.

TOPICS

- Artificial low-dimensional materials, 2D topological insulators and superconductors
- Nanostructures for spintronics, quantum computing, neuromorphic computation
- Ion-ice interactions and carbon-based nanomaterials beyond Earth
- Nanobiology and Neurosciences
- Formation of cosmic dusts and related physico-chemical processes
- Spectroscopy and chemistry on (exo)planets, comets, and dust clouds
- Dusty plasmas in tokamaks

Credit: Jianping Guo