Exotic forms of low-dimensional epitaxial silicon and Xenes

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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 nm²)
Large area stanene on Ag(111)V3xV3
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
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
Experimental synthesis and characterization of 2D Topological Insulators remain a major challenge at present, offering outstanding opportunities for innovation and breakthrough. 


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?

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”


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

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

Only 18 citations until Dec. 31, 2011!

Nobody believed that sp²-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)

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

\[ \Delta Si = 0.44 \text{ Å} \quad \Delta Ge = 0.64 \text{ Å} \]
\[ \Delta_{Si(111)} = 0.78 \text{ Å} \]

\[ a_{Si} = 3.9 \text{ Å} \quad d_{Si-Si} = 2.25 \text{ Å} \]

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.


Silicene/Germanene/Stanene ↔ Graphene

Buckled

2D Topological insulators

QSHE at 15 K / ~RT / > RT

too low T

S. Cahangirov et al., PRL 102, 236804 (2009)
Few predicted properties

Electrically tunable band gap

Electric field controlled topological phase transition

![Graph showing band structure transition](image)

Predicted mobilities at 300K ($10^5$ cm$^2$/V.s)
along the zig-zag and armchair directions

<table>
<thead>
<tr>
<th>Material</th>
<th>$\mu_e$</th>
<th>$\mu_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Germanene</td>
<td>6.09</td>
<td>6.39</td>
</tr>
<tr>
<td>Silicene</td>
<td>6.24</td>
<td>6.54</td>
</tr>
<tr>
<td>Graphene</td>
<td>2.58</td>
<td>2.23</td>
</tr>
<tr>
<td></td>
<td>2.57</td>
<td>2.22</td>
</tr>
<tr>
<td></td>
<td>3.39</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>3.51</td>
</tr>
</tbody>
</table>

Extremely high mobilities
X.-S. Ye et al., RSC Adv., 4, 21216 (2014)

Phonon mediated superconductivity
Silicene

4x4 LEED pattern

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

27 eV

STM image at RT

The “flower pattern”

Non Contact AFM image at 77 K (2013)


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

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

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

\[ \Theta = \frac{18}{16} = 1.125 \]

Nothing looking like a honeycomb structure!

INSPIRATION: a hidden underlying honeycomb structure


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 $\Rightarrow \theta = 1.125$.

- 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 Graphene-like 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 Germanium
   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** 3x3 reconstructed (yellow cell, while the primitive 1x1 is in black) matching a 4x4 Ag(111) supercell 9 nm x 9 nm tunnel current 0.55 nA, sample bias -520 mV

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

Filled states STM image; **after hydrogenation the 3x3 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 x 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)**
**Pentasilicene**


**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


and by Photoelectron Diffraction

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

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**Si nanoribbons and nanodots**

**Single strand & Double strand SiNRs**

(a) 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)

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

(a) Scheme of the lift off of a SiNR with an STM tip. (b) Conductance trace measured as a function of tip vertical position \(Z\). \(G_0\) is the conductance quantum \((7.75 \, \text{Å} \sim 10^{-5} \, \text{S})\). The feedback is turned off at \(V_S = 100 \, \text{mV}\) and \(I_t = 20 \, \text{pA}\) and the conductance is measured at \(V_S = 100 \, \text{mV}\). 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 \((2.6 \, \text{Å} \sim 10^{-6} \, G_0)\) taken for \(V_S = 100 \, \text{mV}\) and \(I_t = 20 \, \text{pA}\). (c) Histogram of \(Z_{\text{gap_max}}\), 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).

R. Hiraoka et al., Beilstein J. Nanotechnol. 2017, 8, 1699
Zero Dimension: Symmetric, \textit{benzene-like (?)} nanodots on Ag\textit{(110)}

DFT-GGA with vdw, SIESTA-GREEN package

\textit{Symmetric Si} nanodots

F. Ronci, S. Colonna, A. Cricenti, P. De Padova, C. Ottaviani, C. Quaresima, B. Aufray, and Guy Le Lay, 

(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. Stawińska, G. Le Lay, A. C. Marele, J. M. Gómez-Rodríguez, and M. E. Dávila, 
\textit{Nature Comm., 7, 13076 (2016)}

\textit{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)
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) ↔ ???

The “other side” of the Schottky barrier formation process: Si 3×3 overlays 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 overlays on Al(111). The overlays 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)
3x3 LEED pattern and STM image of Si deposited onto Al(111) at RT

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

Y. Sassa \textit{et al.}, in preparation
2D Si weird structure epitaxially formed on Al(111) at RT in a single orientation

Y. Sassa \textit{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 \( hv = 136 \text{ eV} \) acceptance 4°

Si is on top!
Narrow Al 2p core-levels with their phonon replicas ($h\nu = 136$ eV)
Extremely narrow Si 2p CLs fitted with 3 components + 3 phonon replicas

$hv = 136$ eV
Normal emission

$hv = 136$ eV
60° emission
Kagome Silicene
in fact 1x1 Kagome silicene / Al(111)$\sqrt{3}\times\sqrt{3}$ !!!

For clarity only the last Al plane is displayed in the left figure.
Kagome Silicene further stabilized by **dumbbells**

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

\[ \Theta = \frac{10}{9} = 1.11 \]

**STM image** 11 nm x 11 nm

\[ V_{\text{GAP}} = -10 \text{ mV} \text{ (filled states)}, \quad I_T = 150 \text{ pA} \]

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

Germanene on Au(111)

VASP, DFT-GGA


In plane $d_{\text{Ge-Ge}} = 2.55$ Å

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

Weak corrugation $\sim 0.2$ Å

Atomic model: $\sqrt{3}\times\sqrt{3}$ germanene on $\sqrt{7}\times\sqrt{7}$ Au

DFT calculations

<table>
<thead>
<tr>
<th>Structure</th>
<th>Energy per Ge atom (eV/atom)</th>
<th>$N_{\text{Ge}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure 01</td>
<td>-3.641</td>
<td>8</td>
</tr>
<tr>
<td>Structure 02</td>
<td>-3.628</td>
<td>8</td>
</tr>
<tr>
<td>Structure 03</td>
<td><strong>-3.744</strong></td>
<td>6</td>
</tr>
<tr>
<td>Diamond Ge (bulk)</td>
<td>-3.727</td>
<td>-</td>
</tr>
</tbody>
</table>

**TABLE I**: Absorption energy for different germanene structures on Au (111) surface.
STM image: germanane by segregation through a thin Ag(111) film grown on Ge(111)

Single phase: $3\sqrt{21} \times 3\sqrt{21}$ germanane matching a $7\sqrt{7} \times 7\sqrt{7} R\pm 19^\circ$ Ag(111) supercell Yuhara et al., ACS Nano, in press

(J. Yuhara et al. ACS Nano (2018))
Large area epitaxial stanene on Ag(111)

Yuhara et al.,
2D Mater., 5, 025002 (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…