TOR VERGATA
UNIVERSITÀ DEGLI STUDI DI ROMA

EPITAXIAL GROWTH OF 2D MATERIALS

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2D MATERIALS

Crystalline solids constituted by a single layer of atoms (or molecules)

- ❑ single element → suffix –ene
- ❑ compounds of two or more materials → suffix –ane or –ide

WHY ARE THEY INTERESTING AND FASCINATING?

- ❑ Enhanced quantum confinement
- ❑ High surface-to-volume ratios

Structural, thermal, chemical, optical,
magnetic, electrical and mechanical properties

absent in their 3D counterpart
&
otherwise unattainable

NOT ALWAYS EXISTS A BULK COUNTERPART

2D MATERIALS

LAYERED: 3D COUNTERPART EXISTS !

IN-PLANE **covalent or ionic bonding &** ***OUT-OF-PLANE*** **vdW or hydrogen bonding**

EASY TO EXFOLIATE

- Graphene, group V (phosphorene, arsenene, antimonene, bismuthene) semiconductors, TMDC (especially MoS_2, WS_2, $MoSe_2$, and WSe_2)
- h-BN, h-SiC, vanadium oxide and Sb_2Te_3, Bi_2Se_3, Bi_2Te_3
- Charged polyhedral layer sandwiched between hydroxide or halide layers by electrostatic forces: e.g. Perovskite type oxides

→ TOP-DOWN AND BOTTOM-UP FABRICATION APPROACHES

NON LAYERED: IN 3D ONLY CHEMICAL BONDS!

NEED OF STRATEGIES TO ARTIFICIALLY FABRICATE

- silicene, germanene, stanene, group III (borophene, gallenene) metals
- metal oxides
- some metal chalcogenides and dichalcogenides

→ BOTTOM-UP FABRICATION APPROACHES

ORGANICS: single crystalline sheets with molecular level thickness mostly based on small molecules (e.g. pentacene, rubrene, nucleic acid, etc.) & polymers such as poly(3-hexylthiophene), polypropylene, polystyrene, proteins.

→ BOTTOM-UP FABRICATION APPROACHES

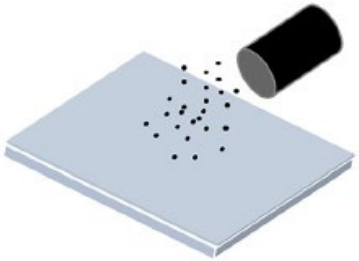
EPITAXIAL GROWTH of 2D MATERIALS

EPITAXY
- EPI «ABOVE»
- TAXIS «AN ORDERED MANNER»

Growth on a crystalline substrate of a crystalline layer following the structure of the substrate

The deposited layer is the epitaxial layer

Crystalline Substrate + Material to grow on



Epitaxial growth

Most used techniques :

- ❖ Molecular Beam Epitaxy (MBE) in ultra-high-vacuum (UHV)
- ❖ Electron beam deposition in ultra-high-vacuum
- ❖ Chemical Vapor Deposition (CVD)
- ❖ Metal Organic Chemical Vapor Deposition (MO-CVD)

WHY EPITAXIAL GROWTH?

In graphene case → high-quality material in X-ene case → it's necessary!

- SUBSTRATE → scaffold to support and stabilize the 2D materials grown on top

↓

construction of 2D materials
naturally non-existing or not stable (e.g. free-standing films)

- UV or UHV CONDITIONS → clean 2D material surfaces

↓

Fundamental to avoid contaminants and decorations
dramatically changing the 2D layer physical and chemical properties

- HIGH QUALITY EPITAXIALLY GROWN 2D MATERIAL + DEVELOPED/ING TRANSFER TECHNIQUES

↓

facilitate device fabrication

Potentially influencing the intrinsic properties of 2D materials and preventing a direct translation into manufactured devices

WHICH ARE the EPITAXIAL GROWTH DRIVING FORCES?

- ✓ THE SUBSTRATE CRYSTAL SURFACE NETWORK

- ✓ THE EFFECT OF THE SUBSTRATE ON THE INTRODUCTION OF STRAIN AND STRESS INTO THE RESULTING MATERIAL DURING THE EPITAXIAL GROWTH

- ✓ THE ATOMIC PROPERTIES OF THE SUBSTRATE
  - ➢ IS IT PRONE TO STRONG INTERACTIONS WITH THE OVERLAYER?
    - ❑ Change in the (expected) physical properties of the 2D material
    - ❑ Restriction in obtaining surface aggregation of atoms
  - ➢ OR ARE THE INTERACTIONS TOO WEAK?
    - ❑ Generation of three-dimensional islands

- ✓ THE PHASE DIAGRAM OF THE SUBSTRATE AND OVERLAYER ATOMIC ELEMENTS
  - ❑ $\frac{\Delta a}{a}$ < 15% gives rise to substitutional alloy
  - ❑ The smaller electronegativy difference, the higher solubility

THIS IS NOT ENOUGH !

- ✋ It neglects the higher surface reactivity than bulk
- ✋ The energy released by absorbed atoms which can be used to overcome energy barrier and interact with surface host atoms

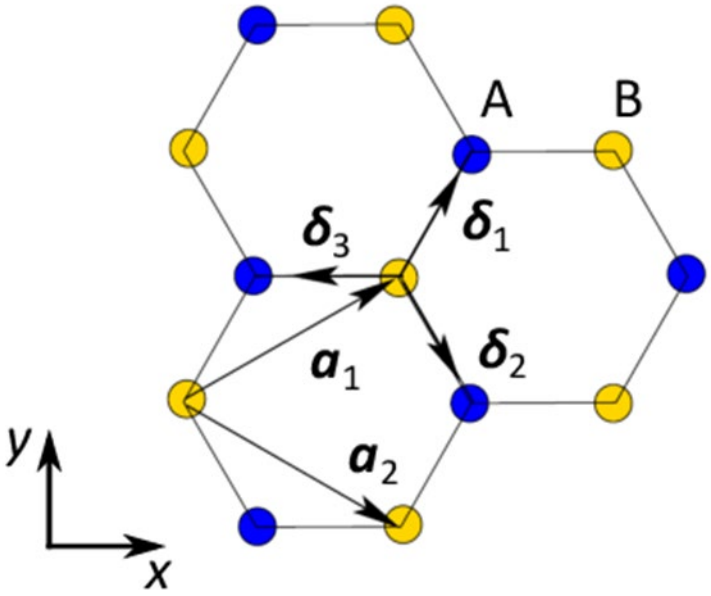
- ✓ THE SURFACE ENERGY OF THE AS-PREPARED MATERIAL WHICH MUST BE LOWER THAN THE SUBSTRATE ONE

GRAPHENE

sp^2 HYBRIDIZATION – PLANAR

OUT-of-PLANE π_z ORBITALS

DIRECT LATTICE NETWORK

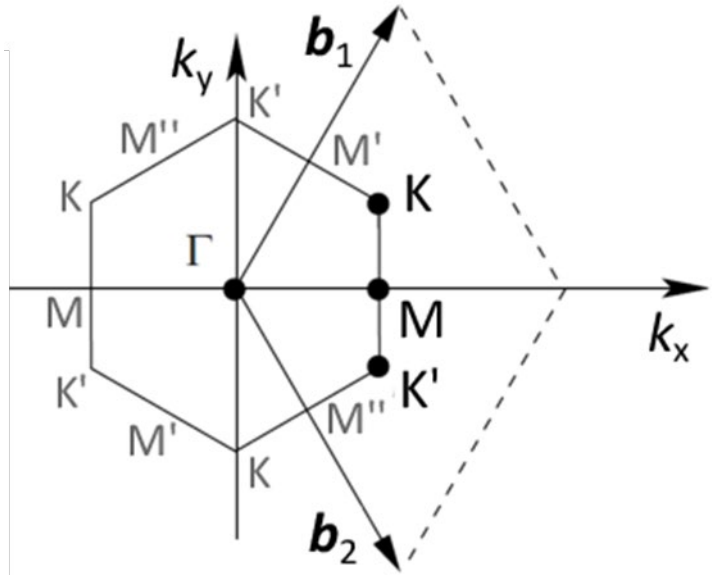


Honeycomb network

$a = |a_1| = |a_2| = 0.246$ nm

$|\delta_1| = |\delta_2| = |\delta_3| = 0.142$ nm

RECIPROCAL LATTICE & FIRST BRILLOUIN ZONE



$$\vec{a_i} \cdot \vec{b_j} = 2\pi\,\delta_{i,j}$$

$$\vec{b_1} = 2\pi/\Omega\,(\vec{a_2} \times \vec{a_3})$$

$$\vec{b_2} = 2\pi/\Omega\,(\vec{a_3} \times \vec{a_1})$$

$$\vec{b_3} = 2\pi/\Omega\,(\vec{a_1} \times \vec{a_2})$$

where $\Omega = \vec{a_1} \cdot (\vec{a_2} \times \vec{a_3})$

Any point of the cell is closer to the chosen lattice point ($b \equiv 0$, i.e. Γ point) than any other

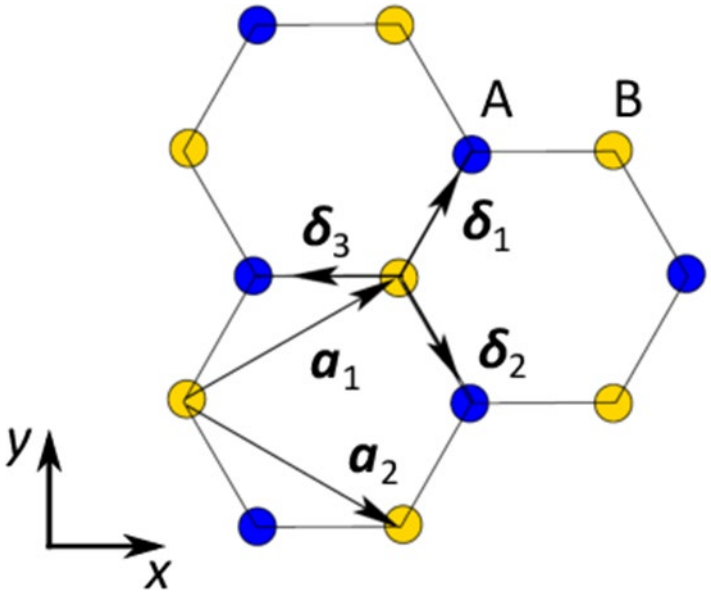
Obtained by bisecting with normal planes nearest neighboir reciprocal lattice vectors

GRAPHENE

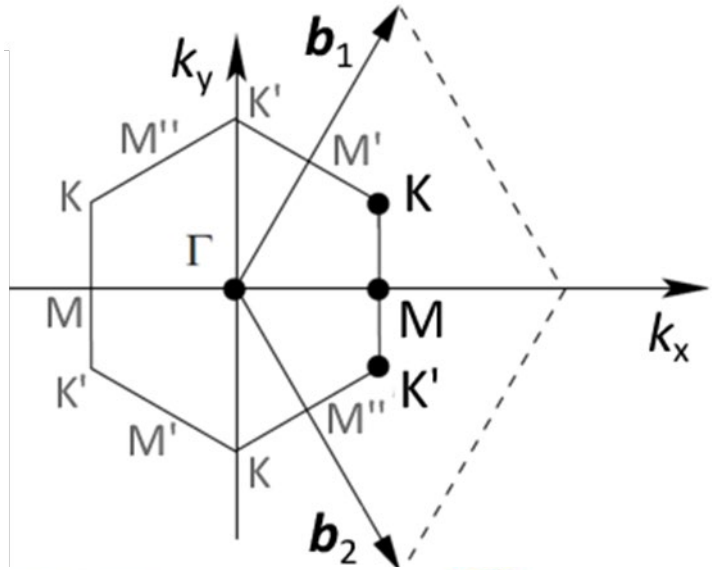
sp^2 HYBRIDIZATION – PLANAR

OUT-of-PLANE π_2 ORBITALS

DIRECT LATTICE NETWORK



RECIPROCAL LATTICE & FIRST BRILLOUIN ZONE



Honeycomb network

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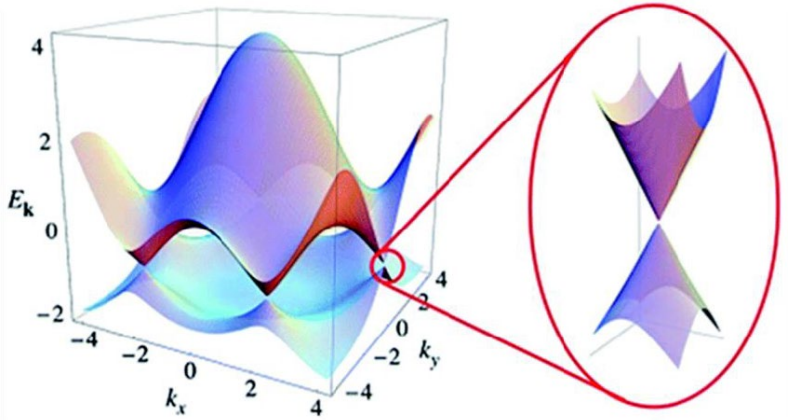


- Dirac cones formation , crossing at E_F
- semiconductor with Eg = 0
- high electron mobility 1.5 x10^5 $cm^2 \cdot V^{-1} \cdot s^{-1}$

HIGH QUALITY GRAPHENE EPITAXIALLY GROWN ON SEVERAL TYPES OF SUBSTRATES INCLUDING:

- ✓ TRANSITION METAL
- ✓ SEMICONDUCTING (E.G. SIC)
- ✓ LARGE BAND-GAP DIELECTRICS (E.G. H-BN) SUBSTRATES

Ru(0001), Ni(111), Pt(111) and Cu(111) →

[Kr]4d^{7}5s^1 [Ar]3d^{8}4s^2 [Xe]4f^{14}5d^{9}6s^1 [Ar]3d^{10}4s^1

- ❑ **Lattice misfit, $\frac{\Delta a}{a} < or > 1\%$**
- ❑ **Substrate-overlayer interactions**

H-SiC(0001) because of its importance in technology

MOST USED C SOURCES:

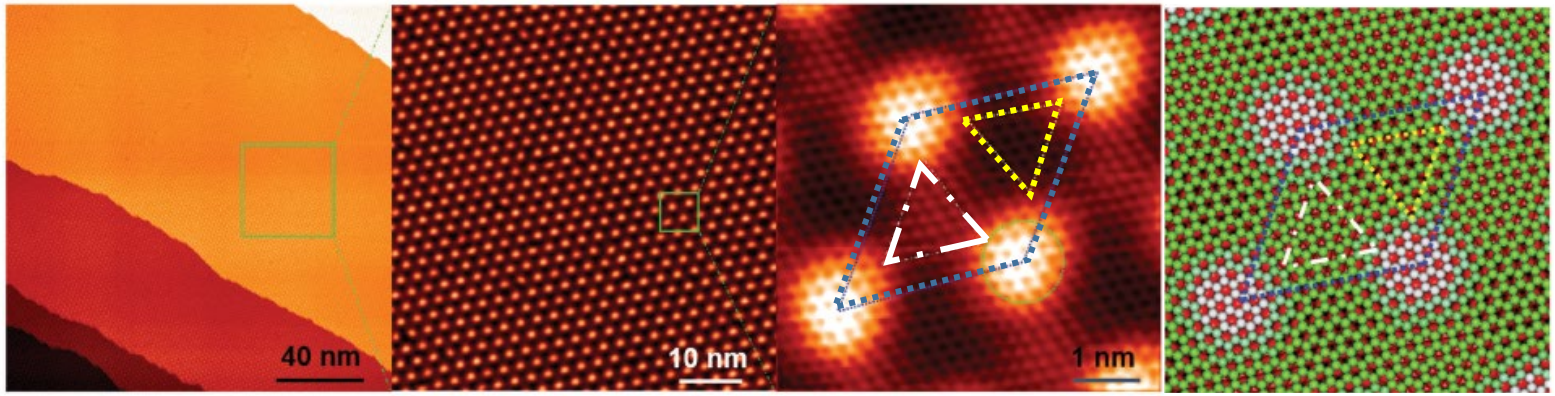
- ❖ **Hydrocarbon thermal decomposition on surface**
- ❖ **Segregation of C impurities from the bulk to the surface during the annealing and cooling stages.**
- ❖ **C-Si bonds decomposition via direct annealing in SiC**

SINGLE CRYSTAL EPITAXIAL GRAPHENE on Ru(0001) SUBSTRATE

Depending on the initial C concentration

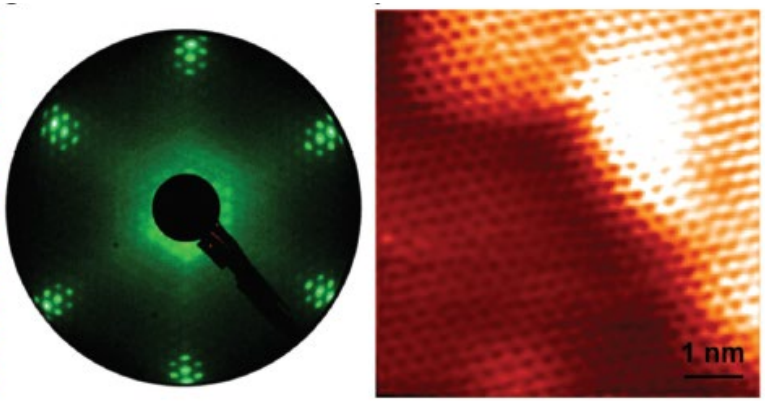
- ❖ **Direct annealing of Ru(0001) substrate at T > 1000°C , thus exploting the low % of C**
- ❖ **By annealing at high T (~ 800°C) Ru(0001) substrate during ethylene exposure**

MOIRÉ PATTERN



$$\frac{\Delta a}{a} \cong 9\ \%$$

different C atom absorbing sites on Ru(0001) surface



Graphene honeycomb and hcp arrangements

MEASURED DISTANCE Ru - GRAPHENE ~0.2 nm

Y. Pan et al., Adv. Mater., 21 (2009) 2777–2780.

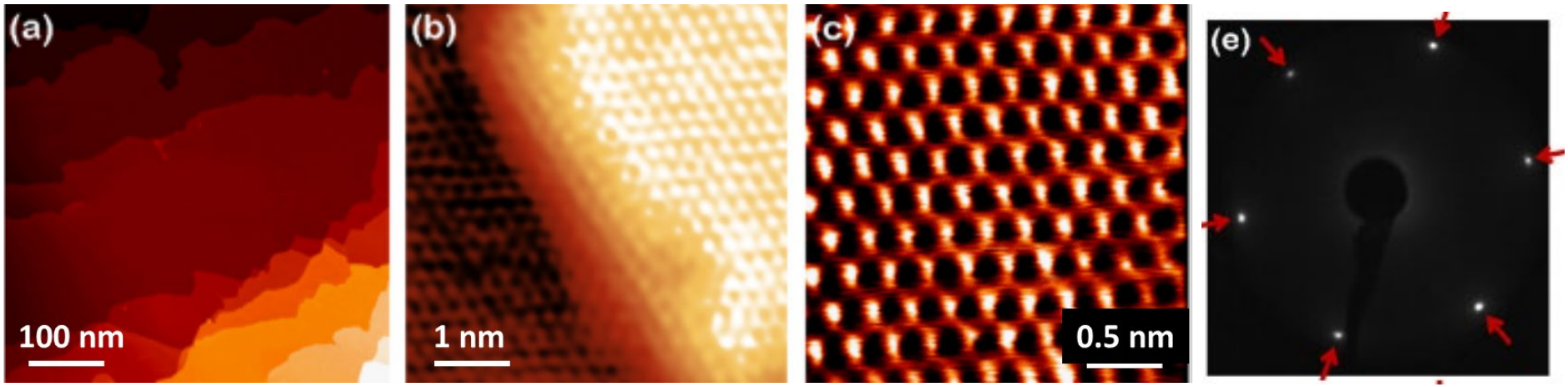
SINGLE CRYSTAL EPITAXIAL GRAPHENE on Ni(111) SUBSTRATE

By annealing at T (500°C ÷ 700°C) the Ni(111) substrate during ethylene (hydrocarbon gas) exposure

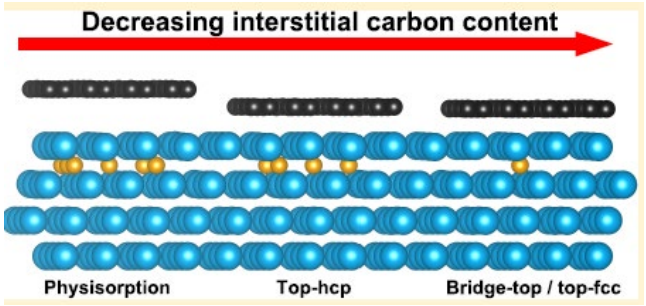
MEASURED DISTANCE Ni - GRAPHENE ~0.2 nm

$$\frac{\Delta a}{a} \cong 1.2\ \%$$

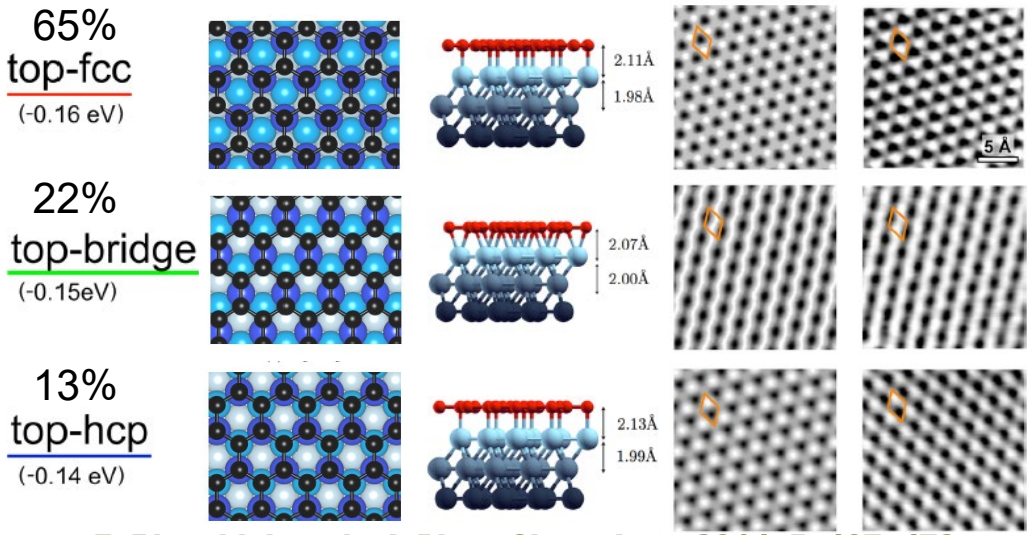
NO MOIRÉ PATTERN



F. Ronci et al., Carbon 158 (2020) 631-641



S. C. Matysik et al., J. Phys. Chem. C 2018, 122, 26105−26110

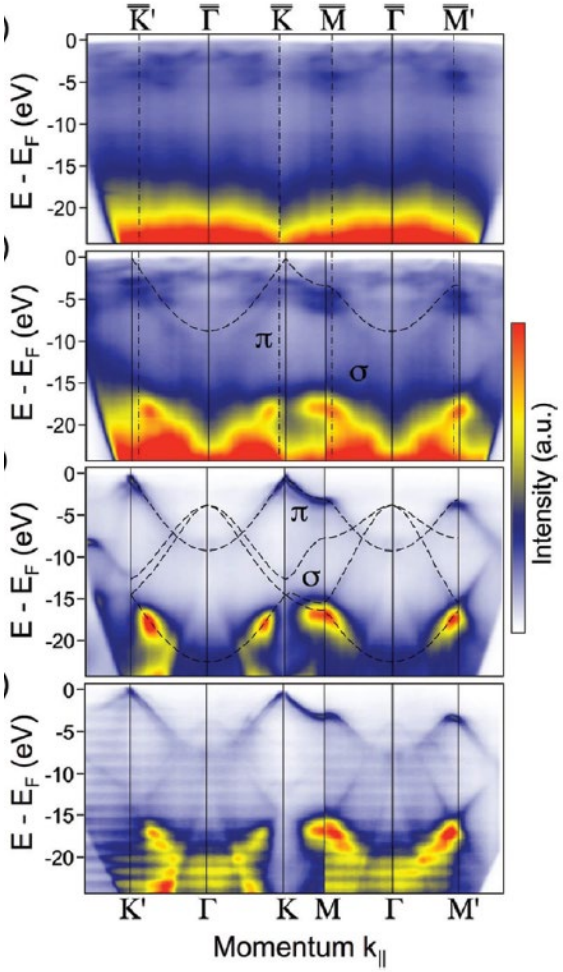


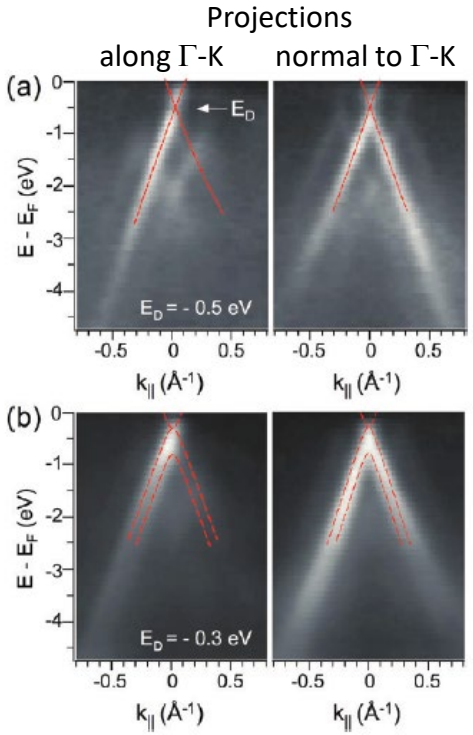
F. Bianchini et al., J. Phys. Chem. Lett. 2014, 5, 467−473

STRONG C ATOM INTERACTION WITH THE SUBSTRATE ATOMS → 1 ML GRAPHENE
NO LINEAR ENERGY DISPERSION

Gr/Ru(0001) and Gr/Ni(111)

A. Dahal et al. Nanoscale 6 (2014) 2548-2562.





P. Sutter et al., Nano Lett., Vol. 9, No. 7, 2009

2 ML graphene

- ❑ Dirac cones appear
- ❑ Dirac point not at E_F

Effect of the substrate atom charge transfer

By increasing graphene ML charge transfer to the Graphene overlayers decreases

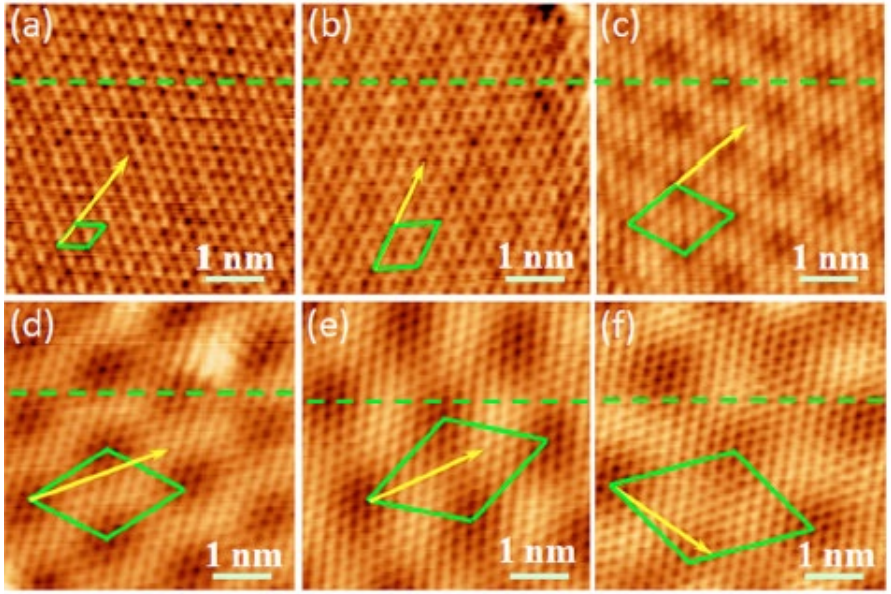
1st Graphene ML acts as a buffer layer, passivating the Ru d-states

POLYCRYSTALLINE GRAPHENE GROWTH on Pt(111) SUBSTRATE

$$\frac{\Delta a}{a} \cong 11\ \%$$

- ✓ Dirac cones
- ✓ Upshift of the Dirac point due to charge transfer from Gr to Pt

WEAK INTERACTIONS ➡ Multiple superstructures & orientations



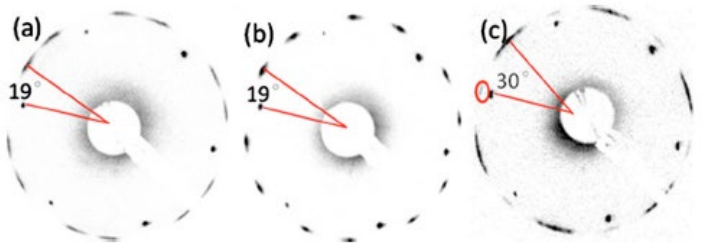


FIG. 1. (Color online) LEED pattern of EG on Pt (111) prepared by exposing to ethylene at different temperature, (a) 773, (b) 873, and (c) 973 K. The beam energy is 60 eV.

SIMILAR ENERGY OF SUPERSTRUCTURES

Figure	Moiré superstructure with respect to graphene	Moiré periodicity (nm)	The rotation angle between graphene and Pt lattices (°)
Figure 3(a)	2×2	0.5	30
Figure 3(b)	3×3	0.738	19
Figure 3(c)	4×4	1	14
Figure 3(d)	(√37× √37) R21°	1.5	6
Figure 3(e)	(√61× √61) R26°	1.87	3
Figure 3(f)	(√67× √67) R12°	2.1	2

MEASURED DISTANCE Pt - GRAPHENE ~ 0.31 nm

Growth depends on

- ➢ C atom density at surface
- ➢ substrate T

➡ Balance between low density of nucleation sites & low growth rate

LOW AMOUNT OF GRAPHENE DEFECTS

LARGE GRAPHENE DOMAINS

Gao et al., Appl. Phys. Lett. 98, 033101 2011

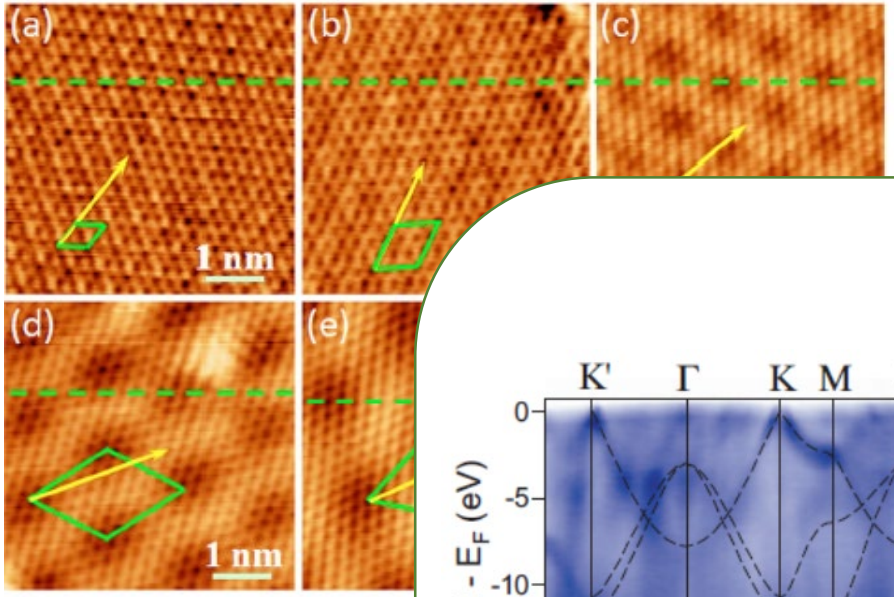
POLYCRYSTALLINE GRAPHENE GROWTH on Pt(111) SUBSTRATE

$\frac{\Delta a}{a} \cong 11\ \%$

- ✓ Dirac cones
- ✓ Upshift of the Dirac point due to charge transfer from Gr to Pt

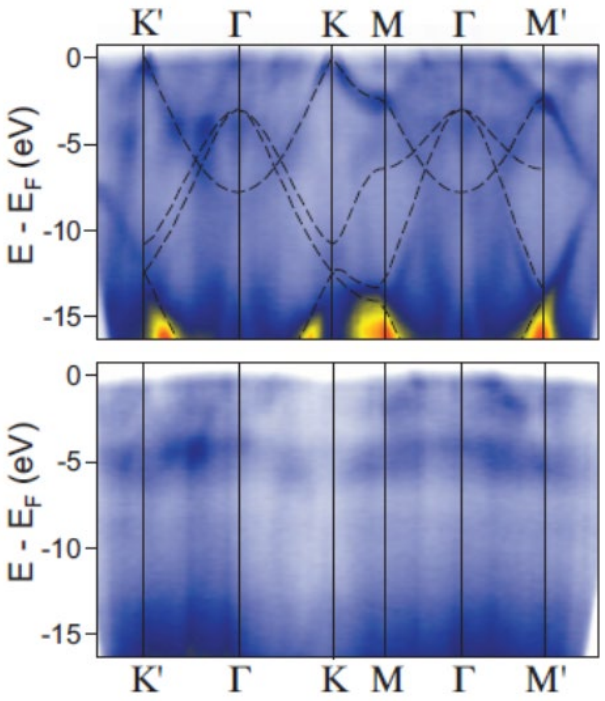
WEAK INTERACTIONS ➡

Multiple superstructures & orientations



Growth depends o

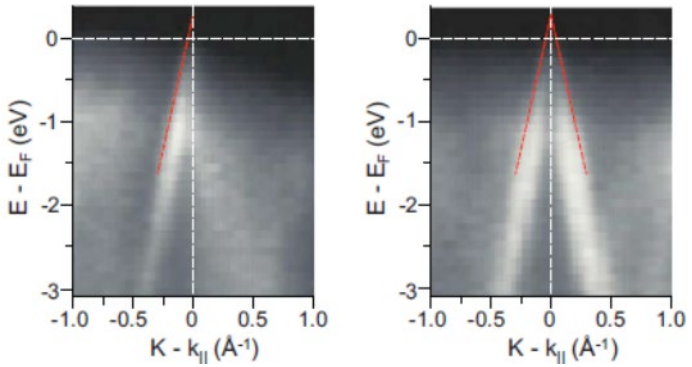
- ➢ C atom density
- ➢ substrate T



Projections

along Γ-K

normal to Γ-K



No significant hybridization between graphene π states and Pt metal d

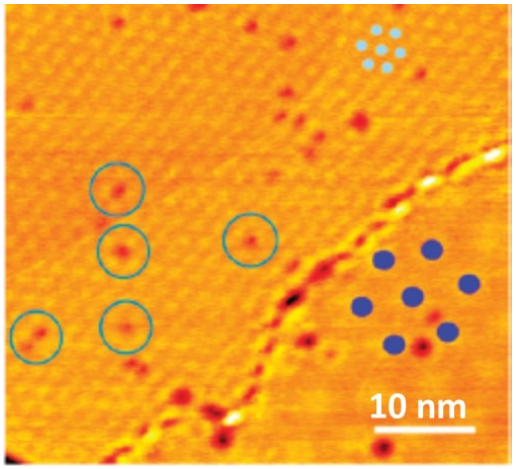
Upshift of Dirac point of ~ 0.3 eV

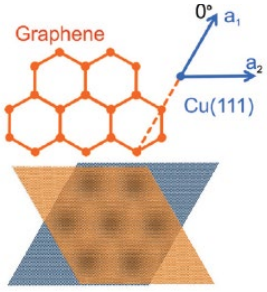
P. Sutter et al., PHYSICAL REVIEW B 80, 245411 2009

Gao et al., Appl. Phys. Lett. 98, 033

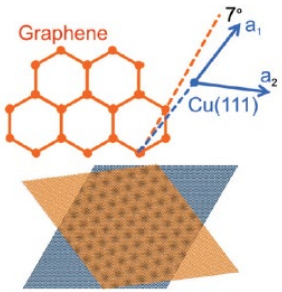
POLYCRYSTALLINE GRAPHENE GROWTH on Cu(111) SUBSTRATE

L. Gao et al., Nano Lett. 2010, 10, 3512–3516





~ 6 nm

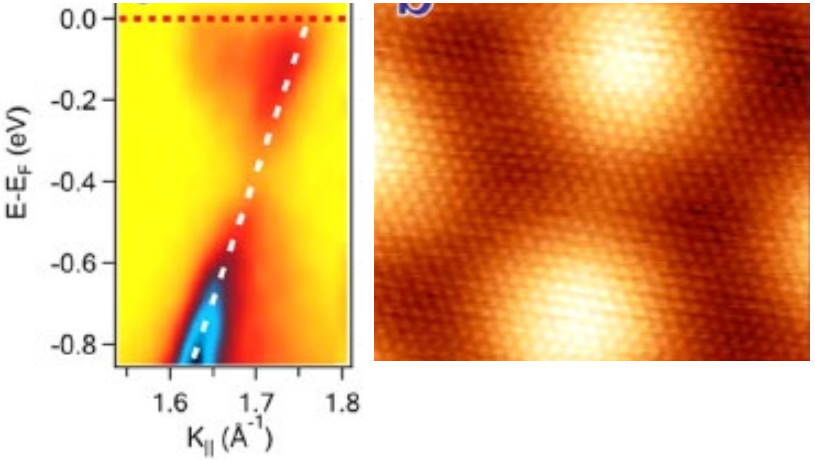


~ 2 nm

$$\frac{\Delta a}{a} \cong 3.5\ \%$$

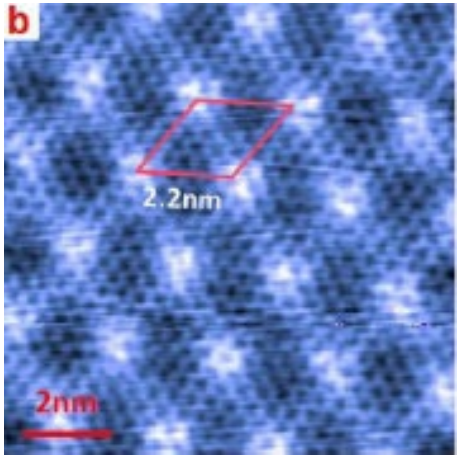
Weak interaction due to Cu full 3d orbitals

S. Gottardi et al., Nano Lett. 2015, 15, 917−922



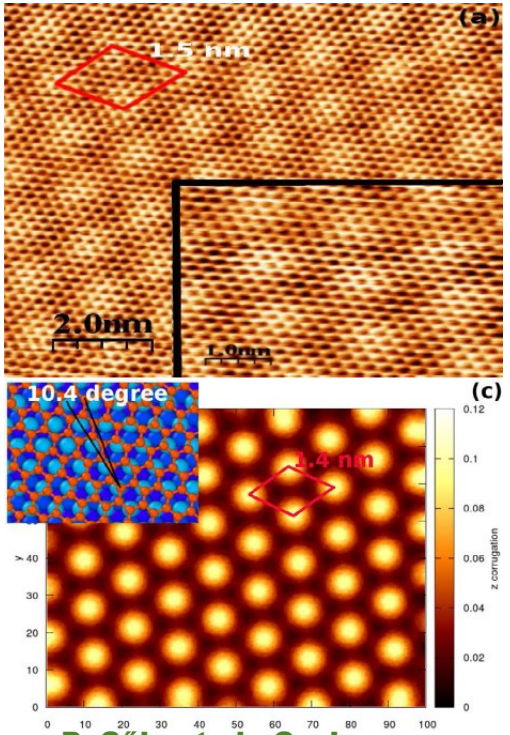
Dirac cone , Dirac point downshifted with respect to E_F

Charge transfer from Cu to graphene



T. Niu et al., J. Am. Chem. Soc. 2013, 135, 8409−8414

Small height corrugation 0.025 nm



P. Súle et al., Carbon 77(2014)1082–1089

GRAPHENE GROWTH on SiC(0001) SUBSTRATE

→ No transfer problems
→ Substrates as large as 6 inches availability
→ SiC provides epitaxial conditions
→ Commercially available as semiconducting (n- or p-type) and semi-insulating

GROWTH TECHNIQUES :

- Sublimation methods at high T in UHV or in Ar overpressure environment to improve uniformity

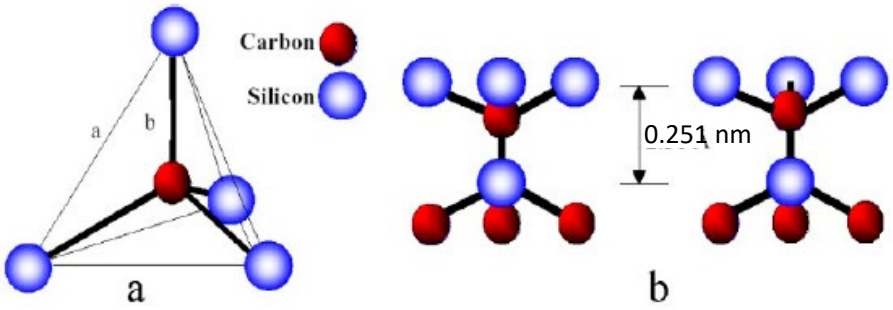
  Exploting the higher vapor pressure of Si than C atoms in the SiC substrate, Si atoms desorb and leave C atoms behind, allowing a C-rich surface to emerge and order and clean in graphene layer

- Controlled sublimation methods, providing Si background vapour in a confined cavity during Si sublimates from SiC. It needs T higher than 300°C.

  It provides controlled and constant silicon vapor density over the surface and near-thermodynamic equilibrium, which is essential for uniform and high quality graphene growth

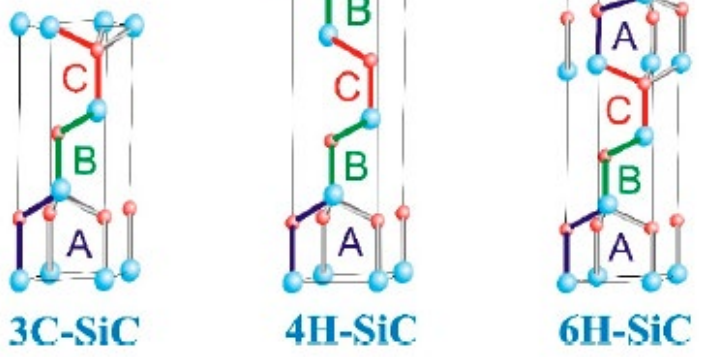
- Using hydrocarbon gases in a CVD furnace. It allows to use lower T than by using sublimation methods.

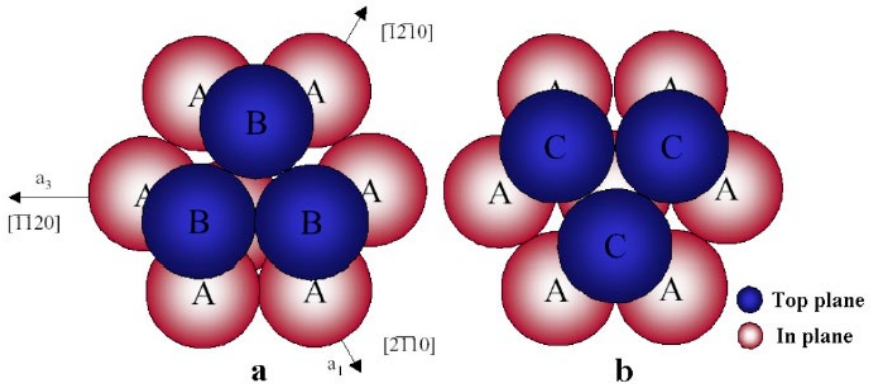
SiC POLYTYPE STRUCTURES



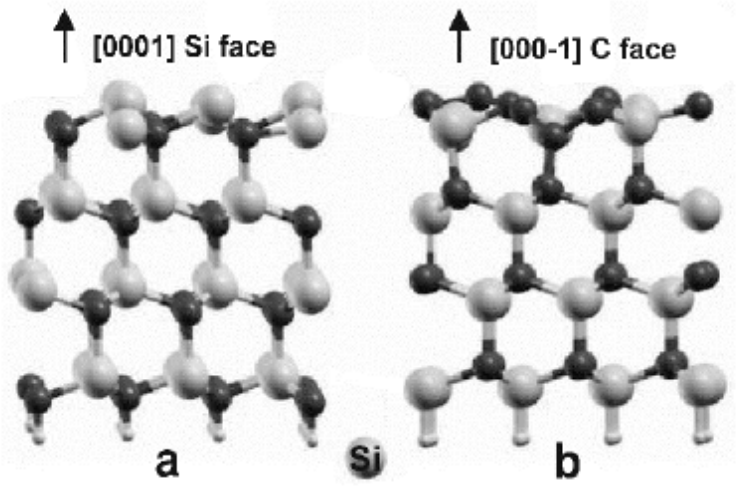
Two possible configurations one rotated with respect to the other of 180°

Si-Si or C-C : ~ 0.308 nm
C-Si ~ 0.189 nm



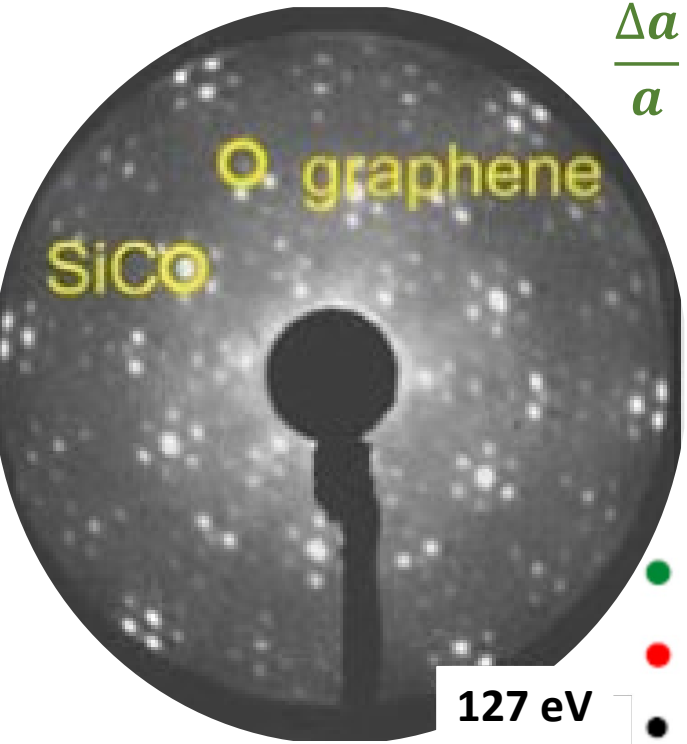


All the three polytypes have polar axes, due to microscopic presence of all aligned dipoles along those axes.

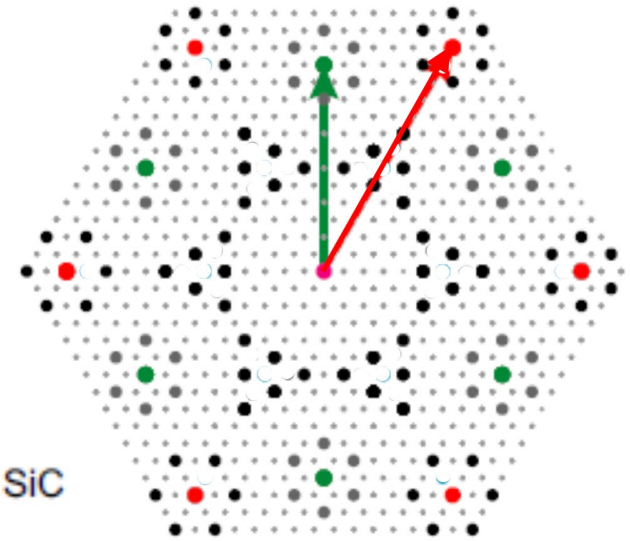


Si-TERMINATED 4H-SiC(0001) & 6H-SiC(0001)

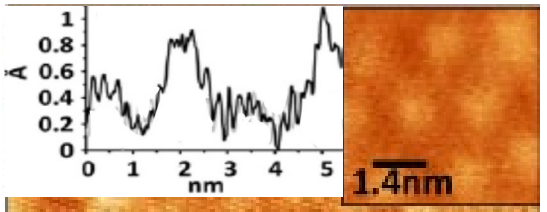
S. Goler et al., Carbon 51 (2013) 249-254

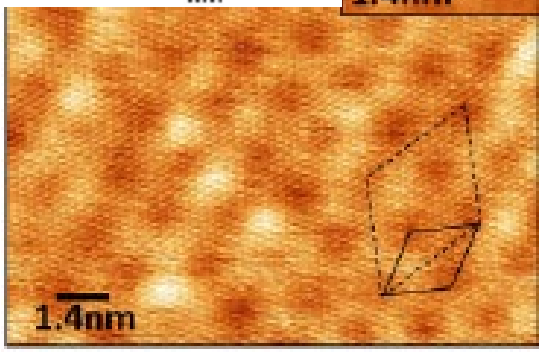


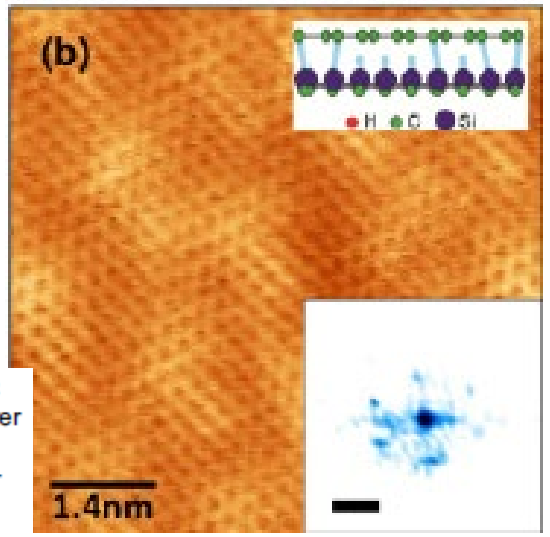
$$\frac{\Delta a}{a} \cong 2\ \%$$



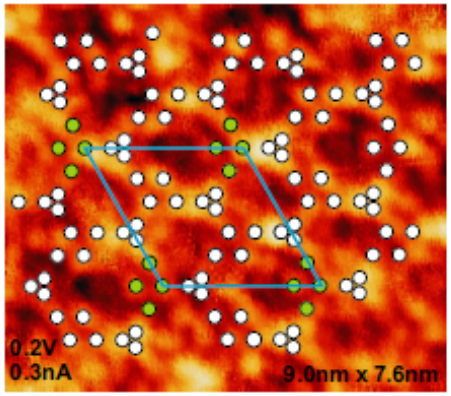
- SiC
- graphene
- visible spots on 6√3 grid
- visible spots on (6x6) grid
- positions of 6√3 grid

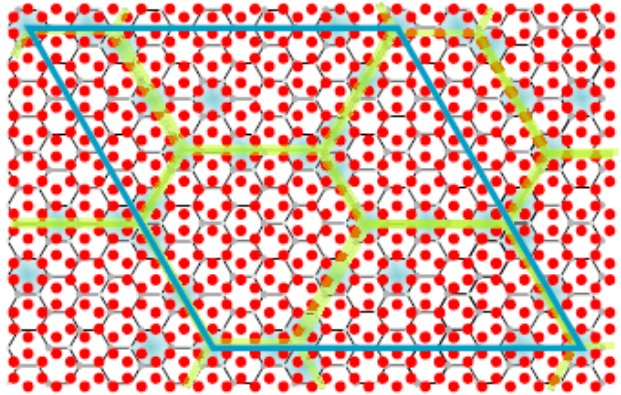


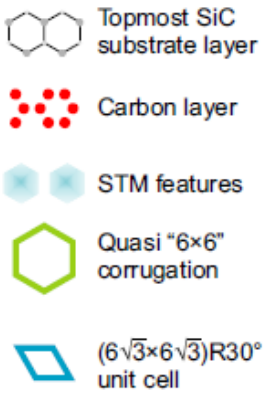




C. Riedl et al., J. Phys. D: Appl. Phys. 43 (2010) 374009
C. Riedl et al., PRL 103, 246804 (2009)





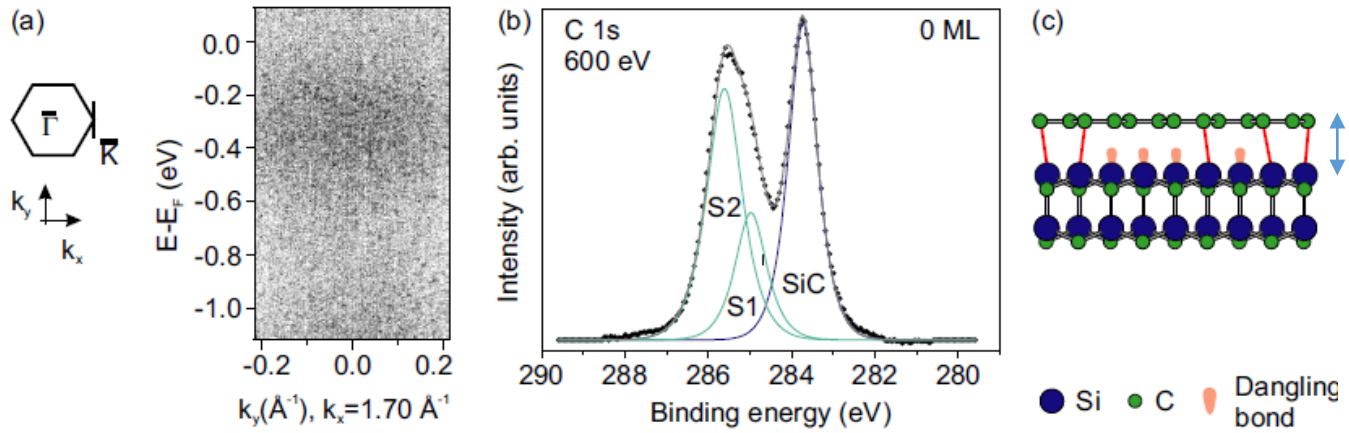


Height corrugation ~ 0.1 nm

F. Varchon et al., Phys. Rev. B 77, 235412 (2008)

Si-TERMINATED 4H-SiC(0001) & 6H-SiC(0001)

C. Riedl et al., J. Phys. D: Appl. Phys. 43 (2010) 374009



$d_{BL-Si} \sim 0.2 \div 0.25$ nm

About 30% of C atoms covalently bound to SiC substrate Si outermost atoms

No Dirac cones measured by ARPES

No Graphene features at 284.6 eV in the C 1s XPS spectrum

Formation of the so-called Buffer or Zero- layer

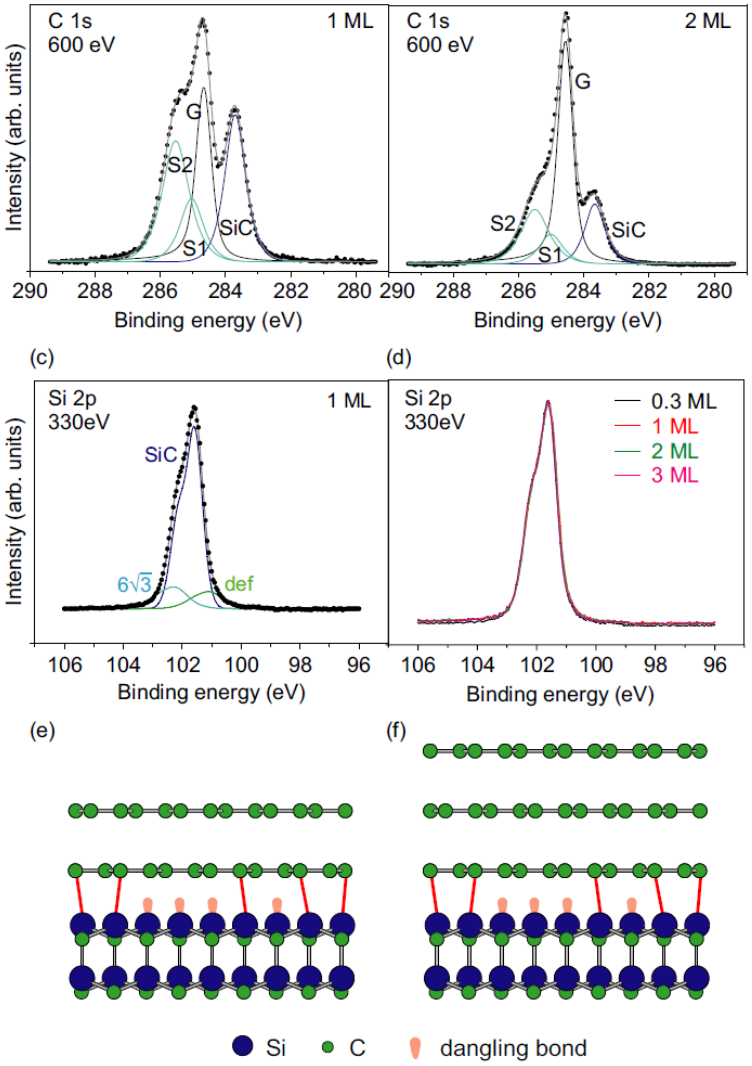
Upon longer time process →

One or more graphene layers obtained by

- further bulk SiC outermost layers Si atoms desorption
- formation of a new buffer layer with consequent raising of the prexistent one as graphene

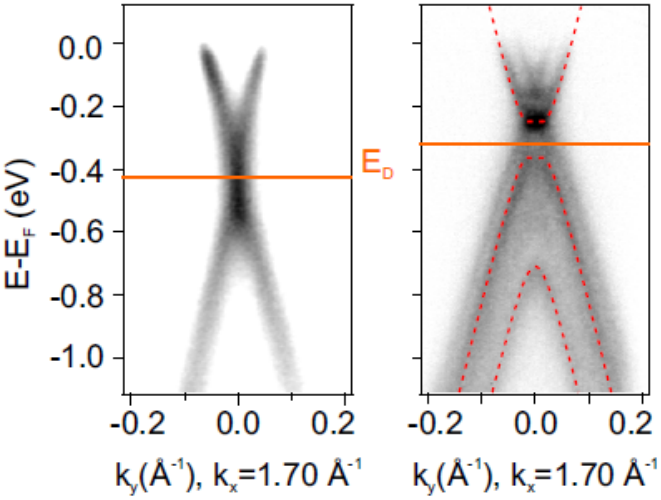
Graphene stacking keeps the 30° rotation with respect to bulk SiC

Si-TERMINATED 4H-SiC(0001) & 6H-SiC(0001)



C. Riedl et al., J. Phys. D: Appl. Phys. 43 (2010) 374009

GRAPHENE DOPING



For 1 ML

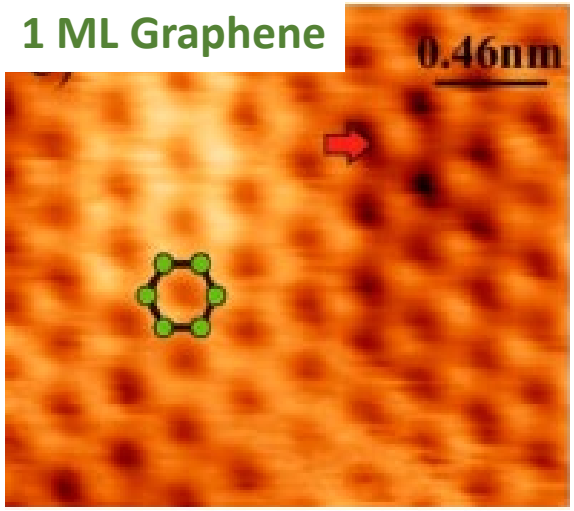
~ -420 meV

$n \sim 1 \times 10^{13}$ cm^{-1}

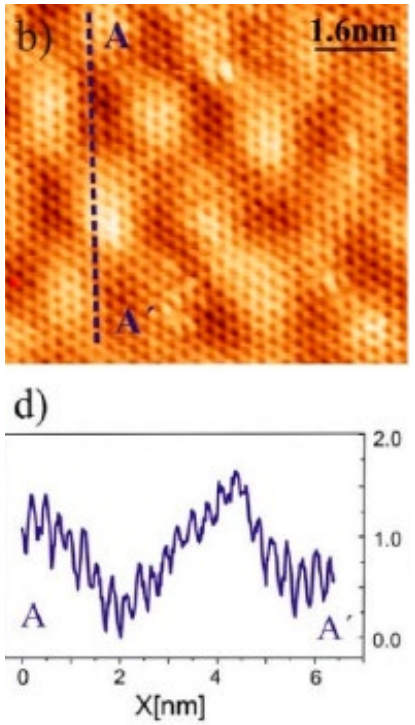
Independent on

- ❑ preparation procedure
- ❑ polytype
- ❑ substrate doping level

1 ML Graphene



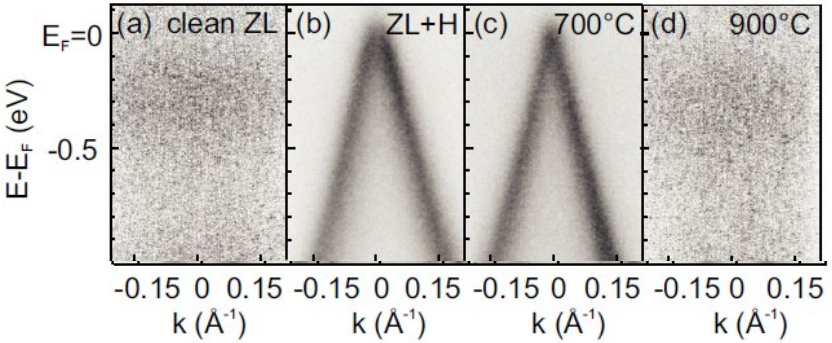
C. Virojanadara et al., Surf. Sci. 2009, 603, L87–L90.

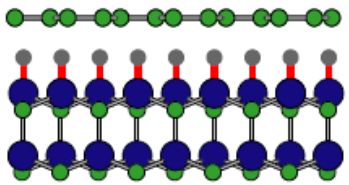


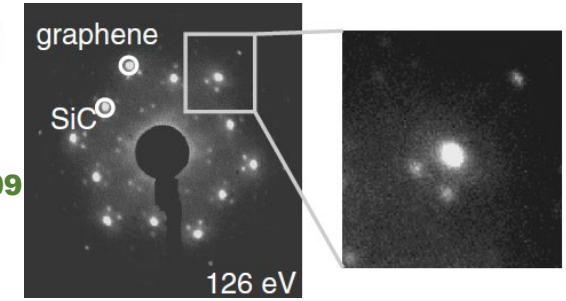
Si-TERMINATED SiC(0001): H INTERCALATION

Two routes:

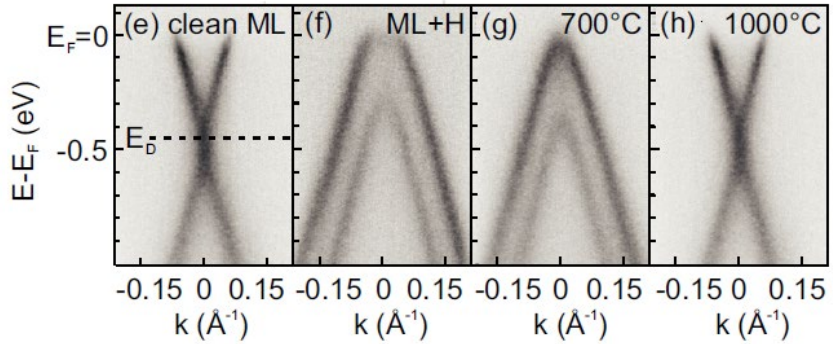
- **Annealing of BF or 1ML Gr/SiC(0001) substrate upon H_2 exposure at T between 600 and 1000°C.**
- **CVD using a hydrocarbon gas (i.e. propane) and the H_2 (or H_2 /Ar mixtures) carrier gas @ T between 1550 and 1650 °C**

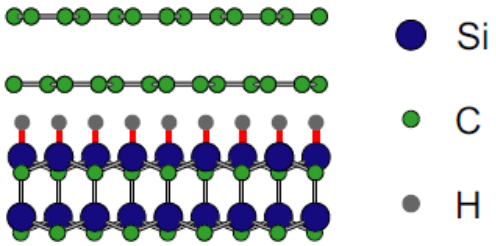


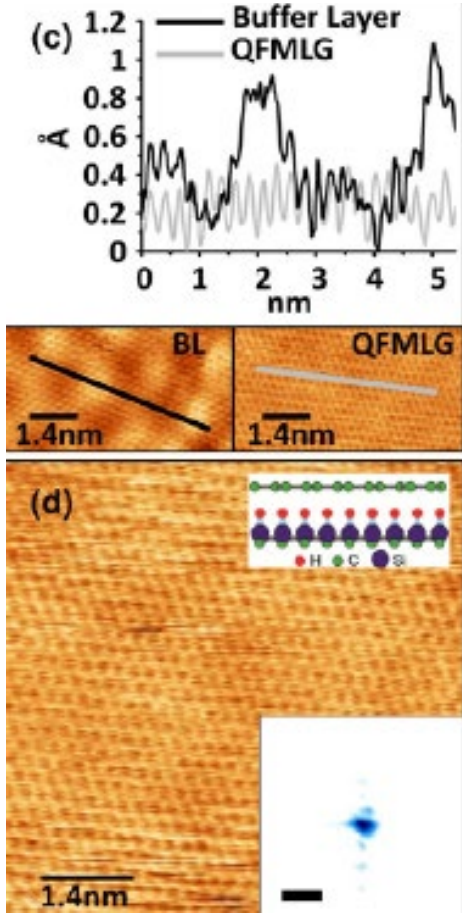




C. Riedl et al., J. Phys. D: Appl. Phys. 43 (2010) 374009
C. Riedl et al., PRL 103, 246804 (2009)



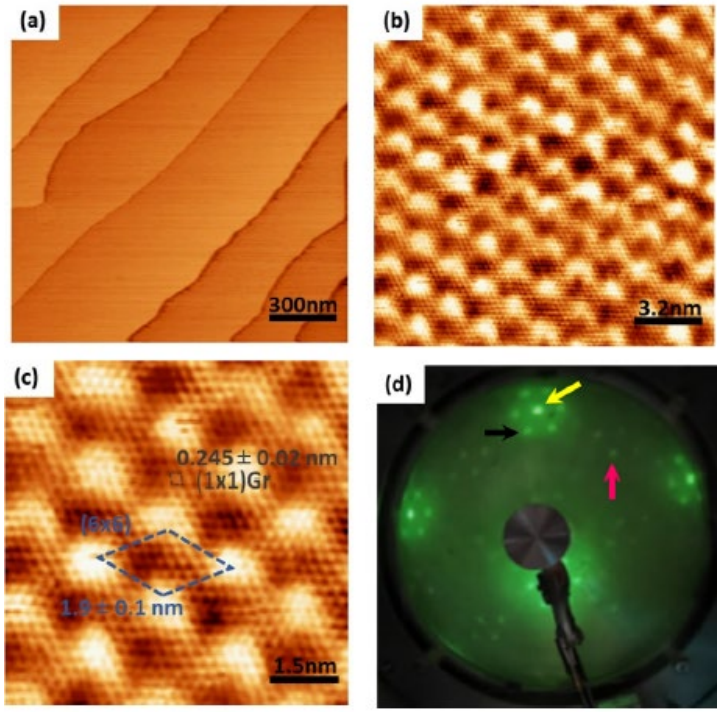




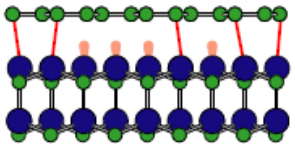
S. Goler et al., Carbon 51 (2013) 249-254

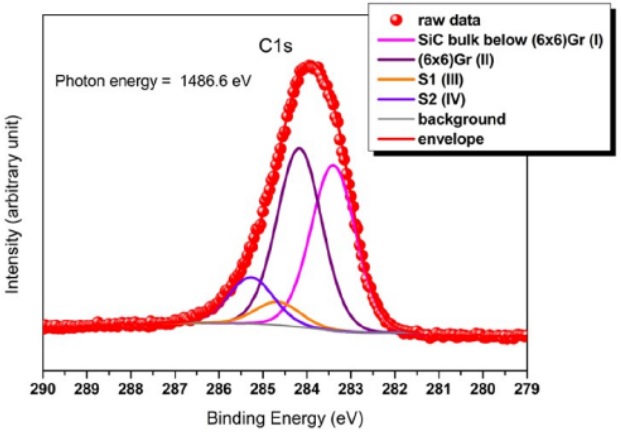
Si-TERMINATED SiC(0001): H INTERCALATION

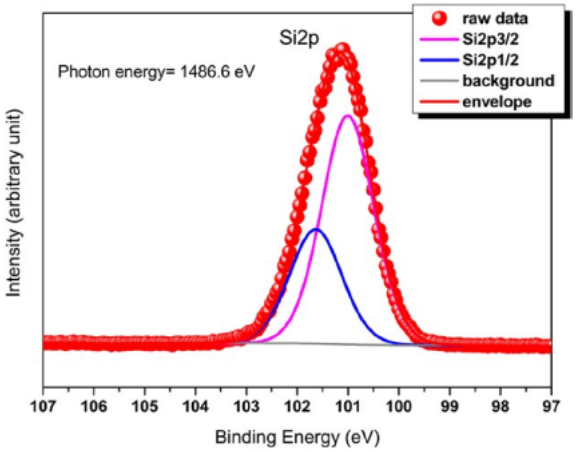
CVD using a hydrocarbon gas (i.e. propane) and the H_2 (or H_2/Ar mixtures) carrier gas @ T between 1550 and 1650 °C (during the T ramp heating/cooling no propane was introduced)

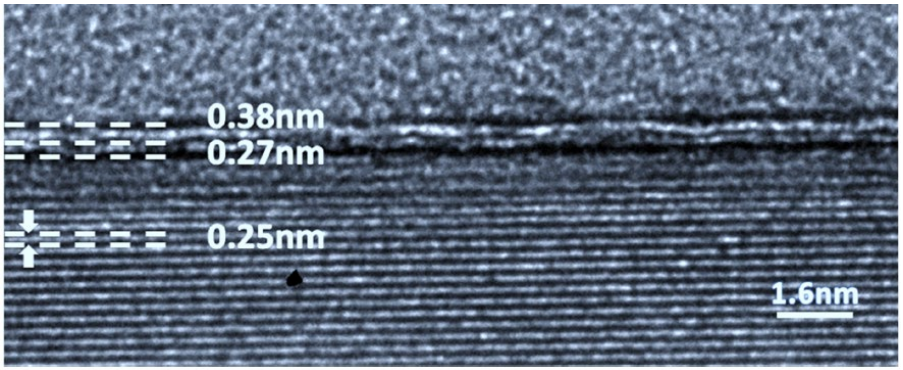


H_2/Ar = 9 %





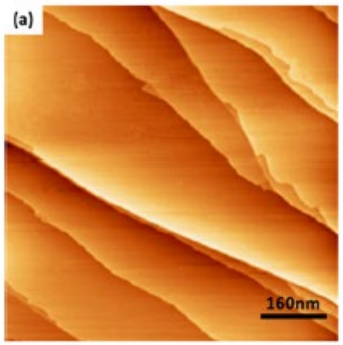


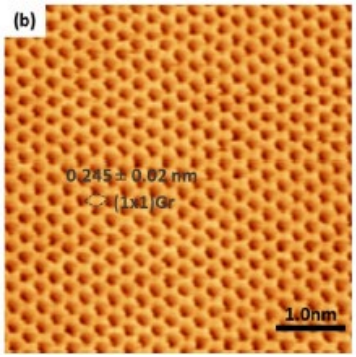


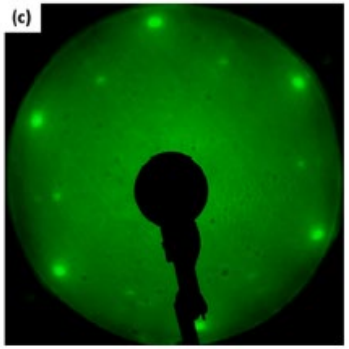
Z. Ben Jabra et al., ACS Appl. Nano Mater. 2021, 4, 4462−4473

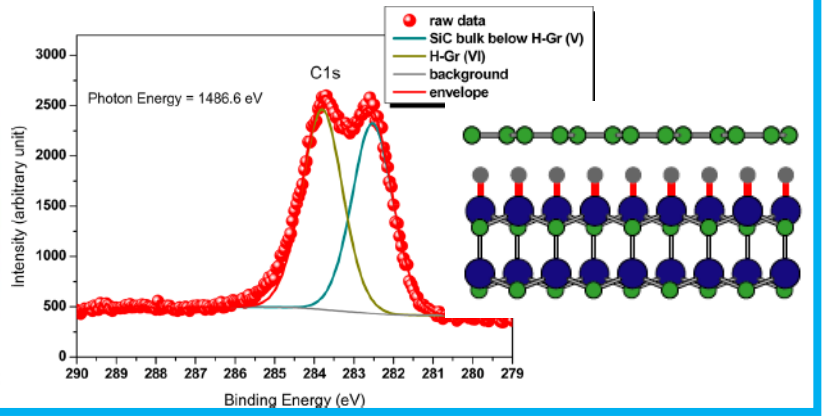
Si-TERMINATED SiC(0001): H INTERCALATION

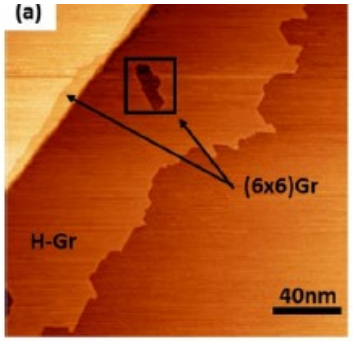
CVD using propane and H_2 /Ar = 42 % 1 ML Graphene

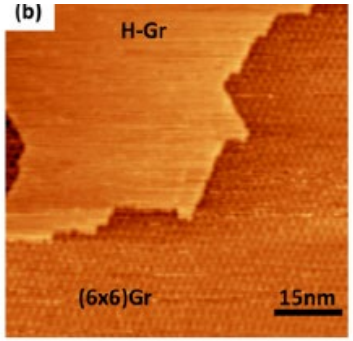


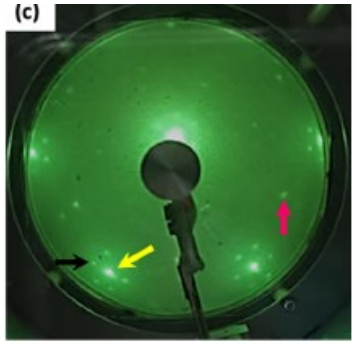


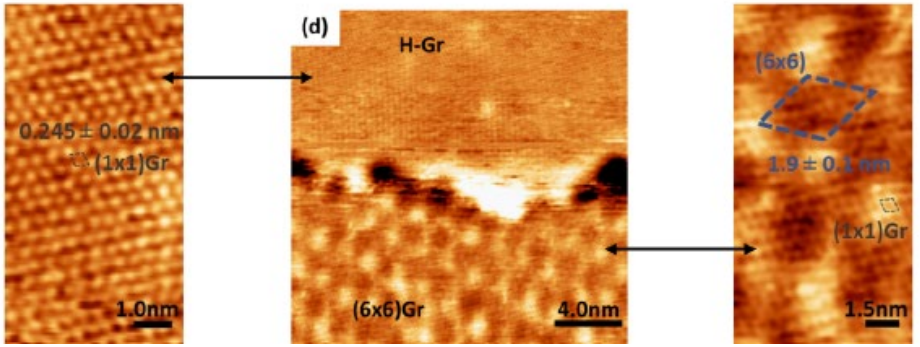




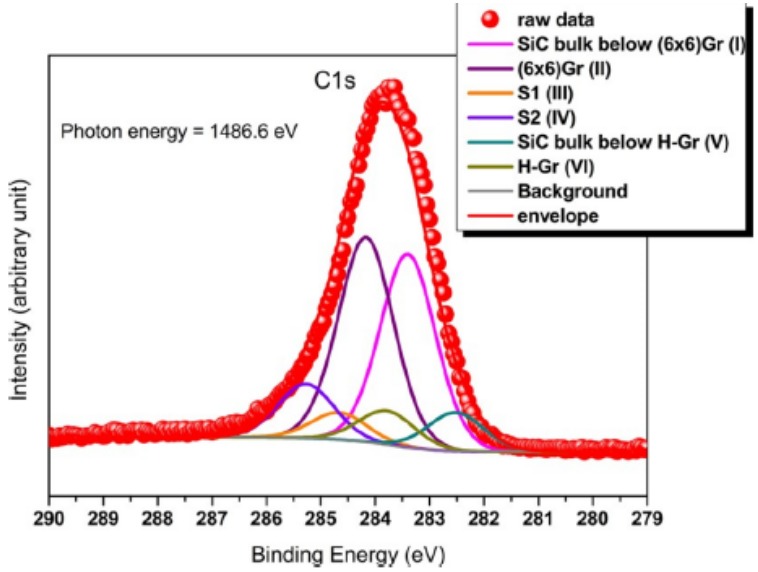








H_2 /Ar = 33 %

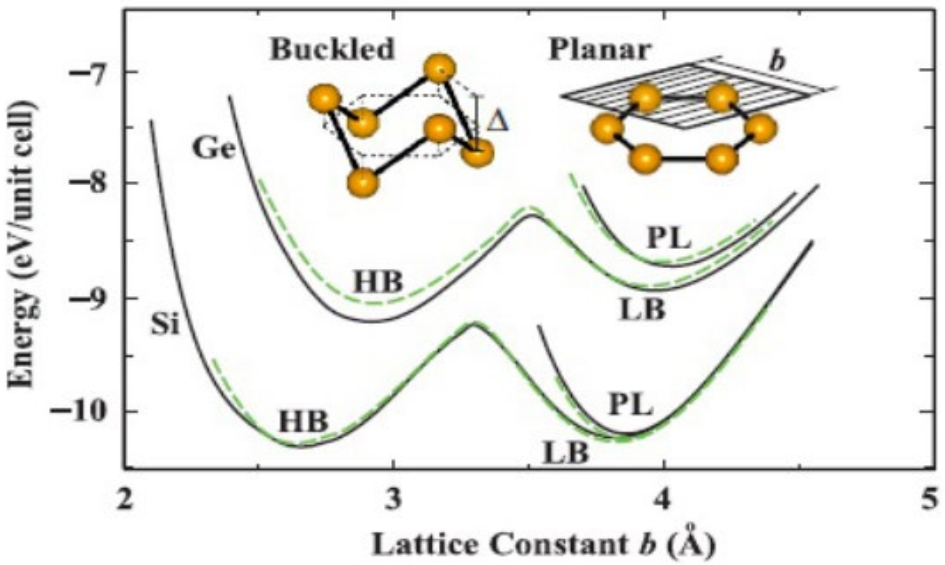


Z. Ben Jabra et al., ACS Appl. Nano Mater. 2021, 4, 4462−4473

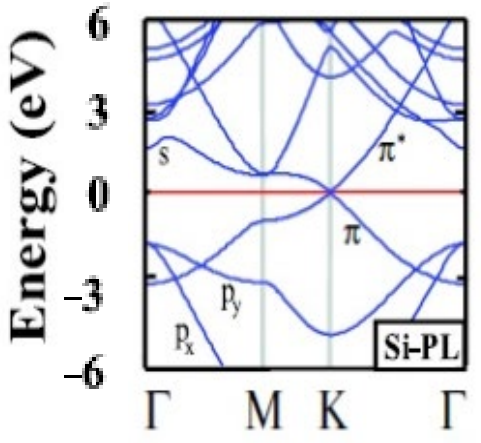
FREE-STANDING SILICENE THEORETICAL PREDICTIONS

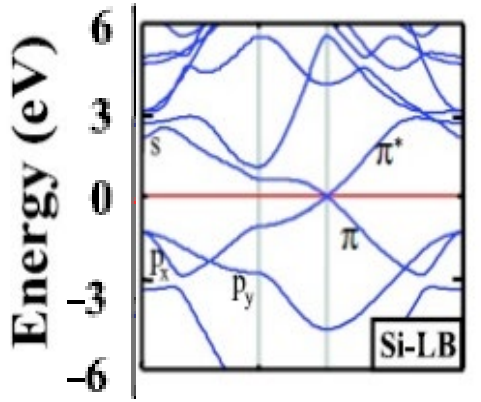
HB: Highly Buckled $\Delta = 0.21$ nm
LB: Low Buckled $\Delta = 0.044$ nm
PL: Planar

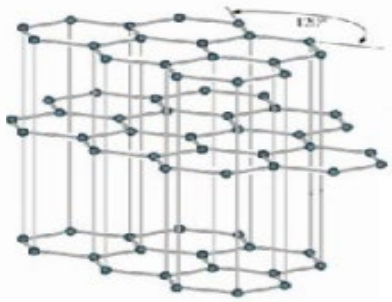
→ **Mixed sp^2 -sp^3**



S. Cahangirov, et al., Physical Review Letters 102, 236804 (2009)







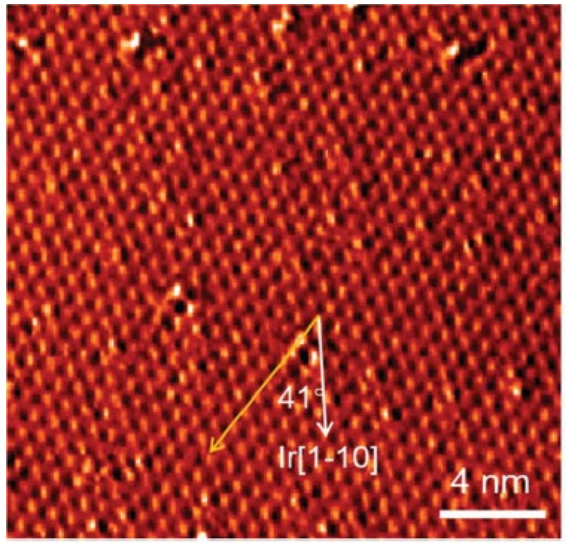
π and π* bands :

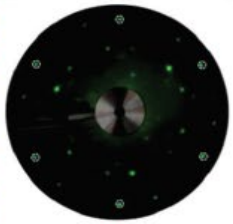
- **cross at K and K' points at E_F → semimetallic**
- **are linear close to K and K' point**
- **massless Dirac fermion character to charge carriers**

SILICENE on Ir(111)

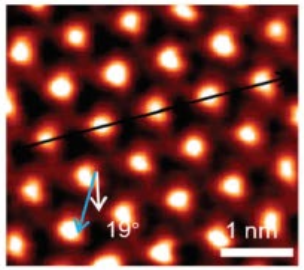
L. Meng et al., Nano Lett. 2013, 13, 685−690

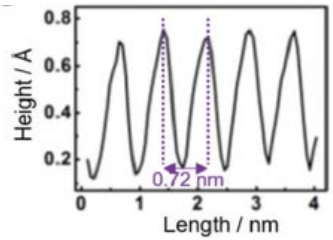
Si DEPOSITION (UNKNOWN AMOUNT) @ RT + ANNEALING @400 °C FOR 30 '

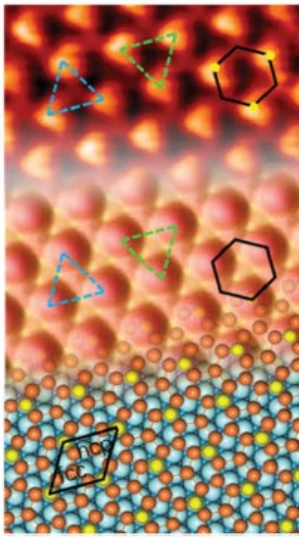




√7 x √7







DFT : Si atoms

- 2 different heights
- located on top (yellow), hollow (fcc and hcp) and bridge Ir sites
- strongly bonded and hybridized to Ir

XPS and LEED study vs Si DEPOSITED (0.1-1.5 ML) & GROWTH AND ANNEALING T:

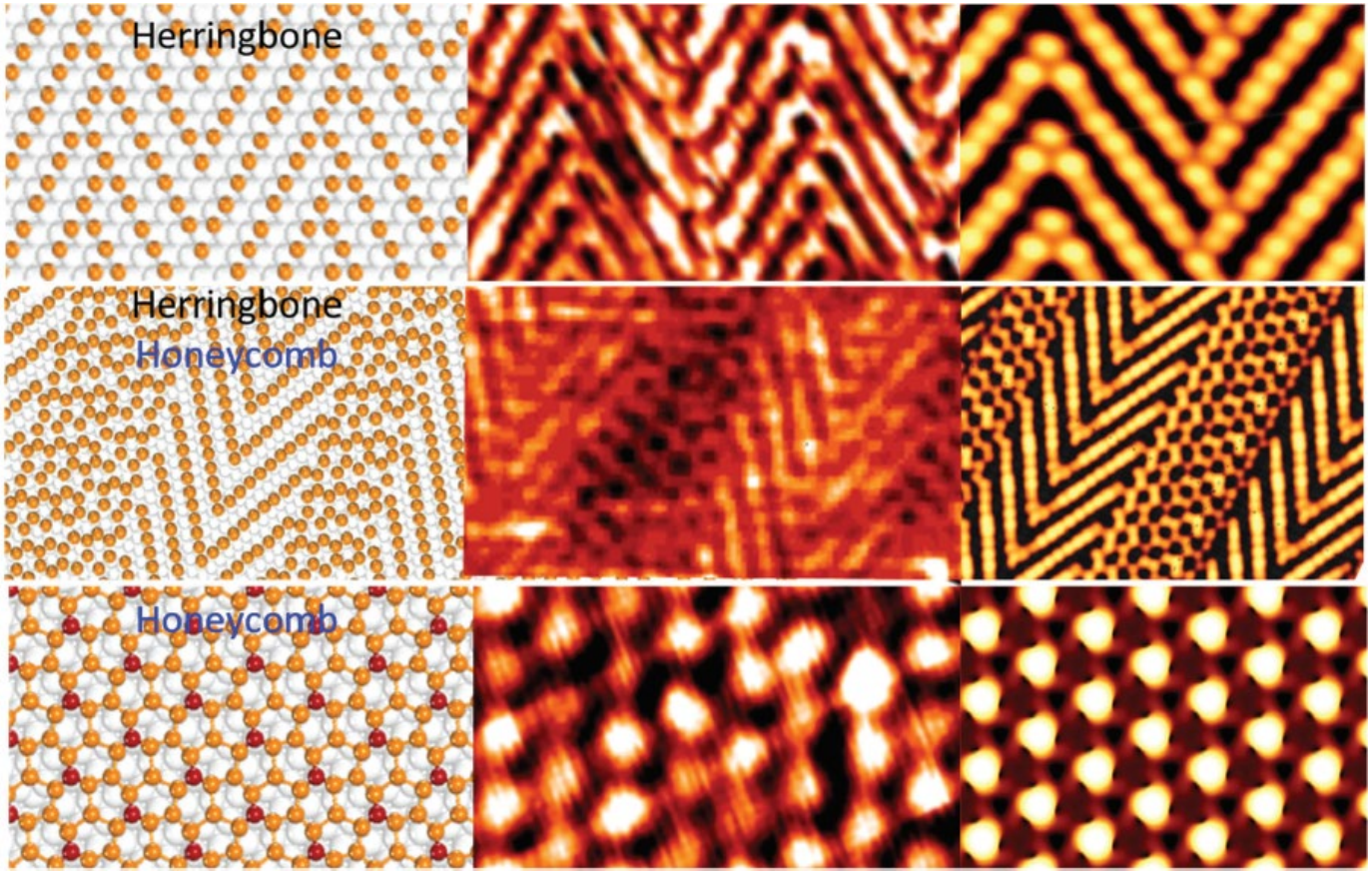
- Si ≤ 0.5 ML Si prevalently absorb at hollow Ir sites and Si penetrates Ir first layer. LEED shows √19 x √19 R 23.4°
- Si > 0.5 up to 1.5 ML Si, LEED exhibits √19 x √19 R 23.4° + a shorter rang[illegible]r 2x2 increasing in intensity with Si amount. Si atoms disorder on I[illegible]d the first Ir layers are strongly perturbed whatever depositing [illegible]g T. No observation of √7 x √7 .
- No indication of full Si-Ir alloy, Si complete penet[illegible]n Ir substrate probably prevented from the high Ir coesive energy

NO SILICENE FORMATION

M. Satta et al., Nanoscale. 2018, 10, 7085-7094

SILICENE on Ru(0001)

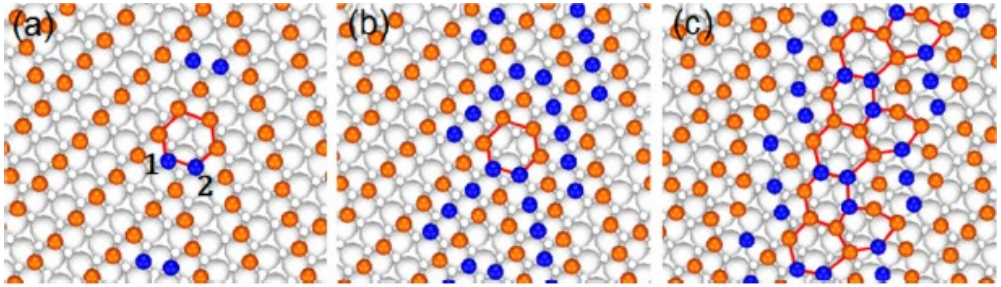
Si DEPOSITION @ RT and ANNEALING @500 °C



Low Si coverage
3-fold hollow sites

Medium coverage
Honeycomb lattice
close to the elbow up
to form Si nanoribbons

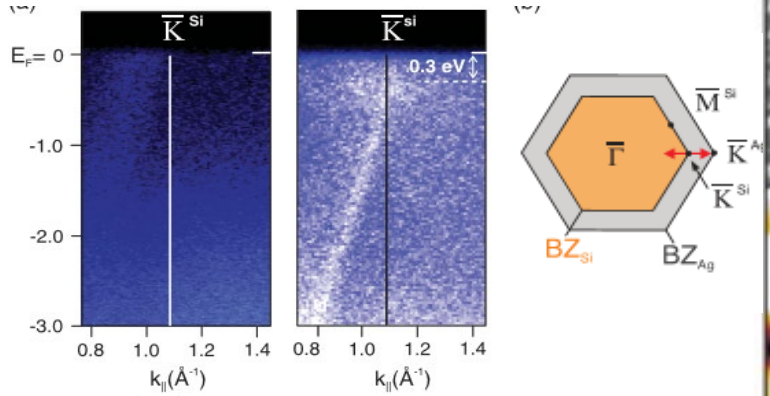
High coverage
Si nanoribbons
extend to all the
surface → $\sqrt{7} \times \sqrt{7}$



No Dirac cones in the
calculated band structure
due to a high charge density
between Si and Ru

L. Huang et al., Nano Lett. 2017, 17, 1161−1166

SILICENE on Ag(111)



FORMATION OF SILICENE ?

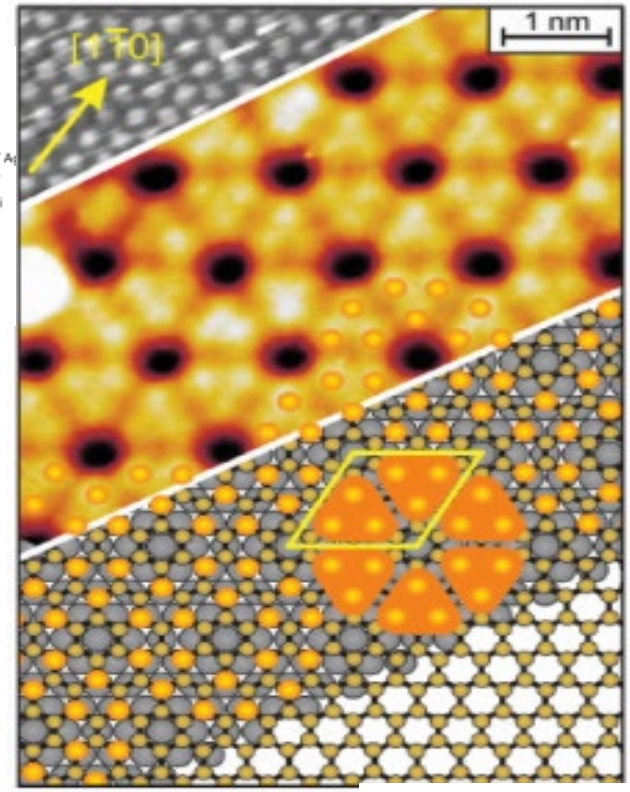
- Identified to originate from Ag s-p band. Dirac cones do not survive due to the strong interaction with Ag atoms

Lin et al., PRL 110, 076801 (2013)

- 6 pairs of Dirac cones at the edges of the 1° BZ of Ag(111) → originating through the interaction of silicene with Ag which generates a new state

Feng et al., PNAS 113, 14656–14661, 2016

Si on AG(111) @ 250 °C



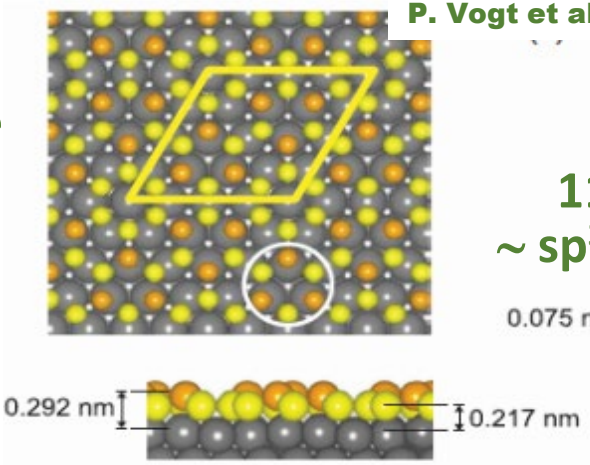
(3x3) Silicene unit cells on (4x4) Ag(111) ones

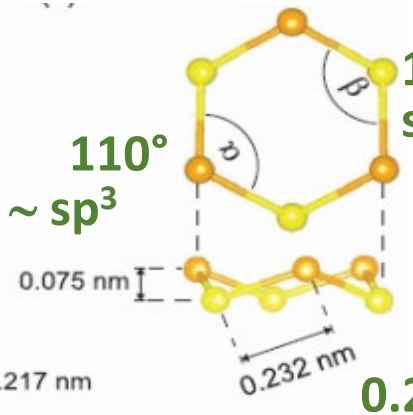
Si on top of a Ag atom

Si between Ag atoms

Ag atom

P. Vogt et al., Phys. Rev. Lett. 108, 155501 (2012)





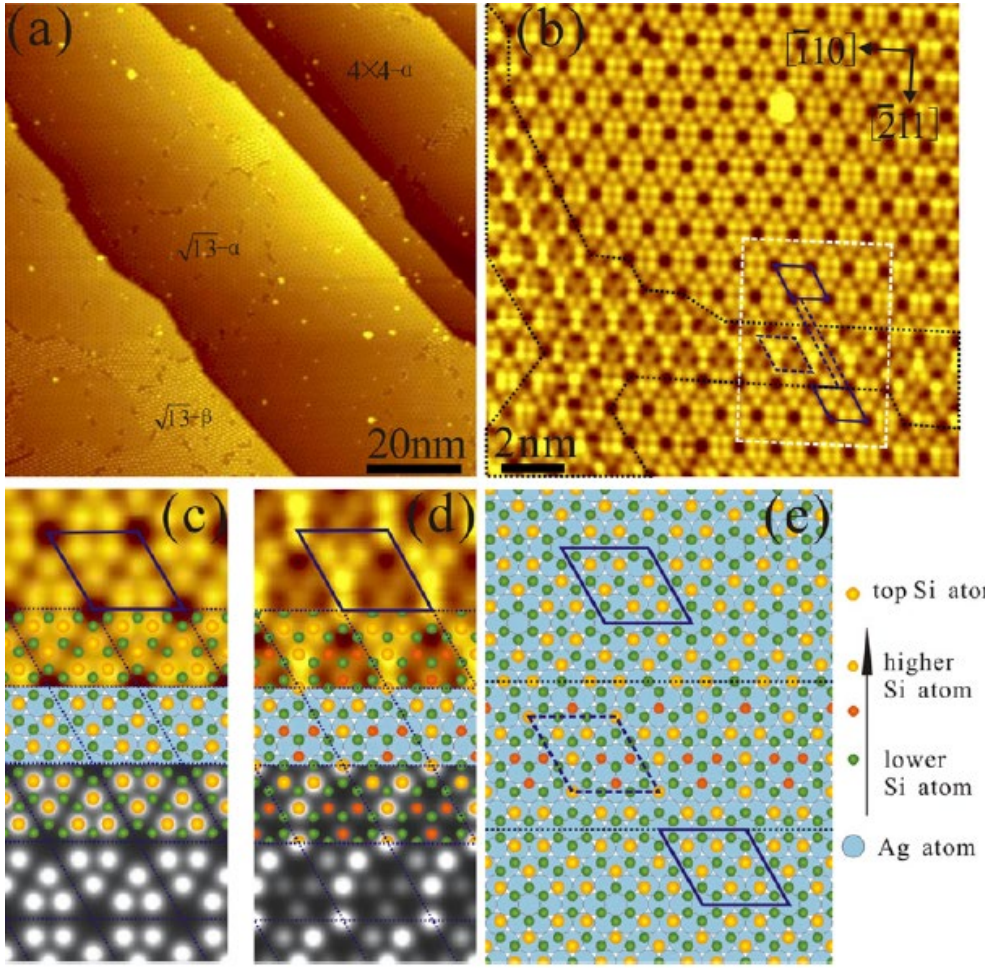
110°
~ sp^3

112°-118°
sp^2-sp^3

0.22 ± 0.01 nm

SILICENE on Ag(111)

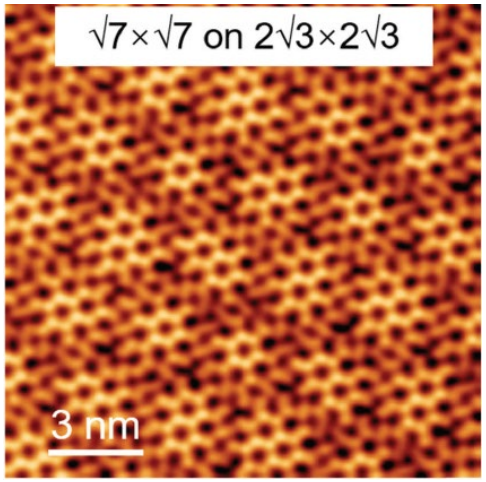
not only (4x4) but also other superstructures!



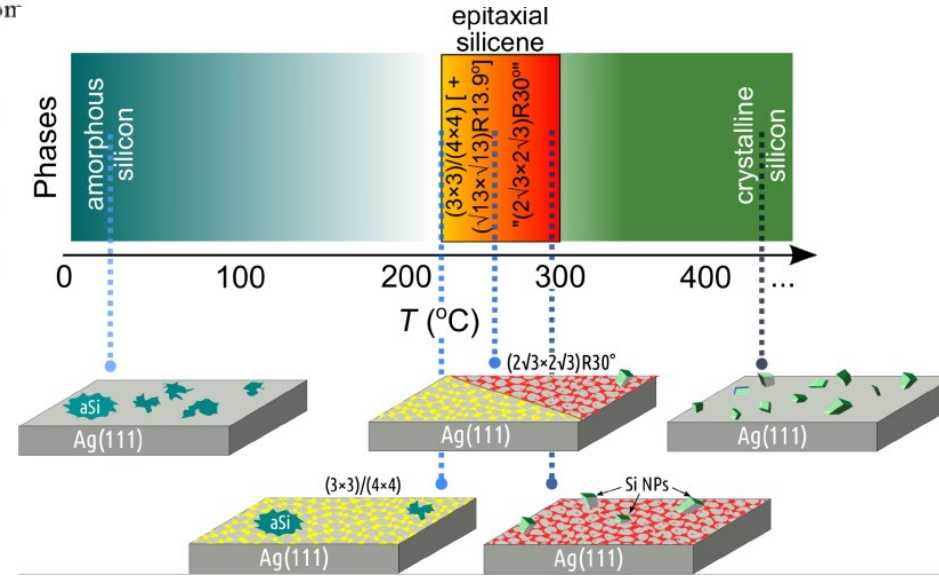
Silicene (√7x√7)R ± 19.1° lattice cells on (√13x√13)R ± 13.9° Ag(111) ones

Z.L. Liu et al., New Journal of Physics 16 (2014) 075006

B. J. Feng et al., Nano Lett., 2012, 12, 3507–3511



For silicene > 1 ML



D. Solonenko et al., *Beilstein J. Nanotechnol.* 2017, *8,* 1357–1365.

SILICENE on Ag(111), are we sure?

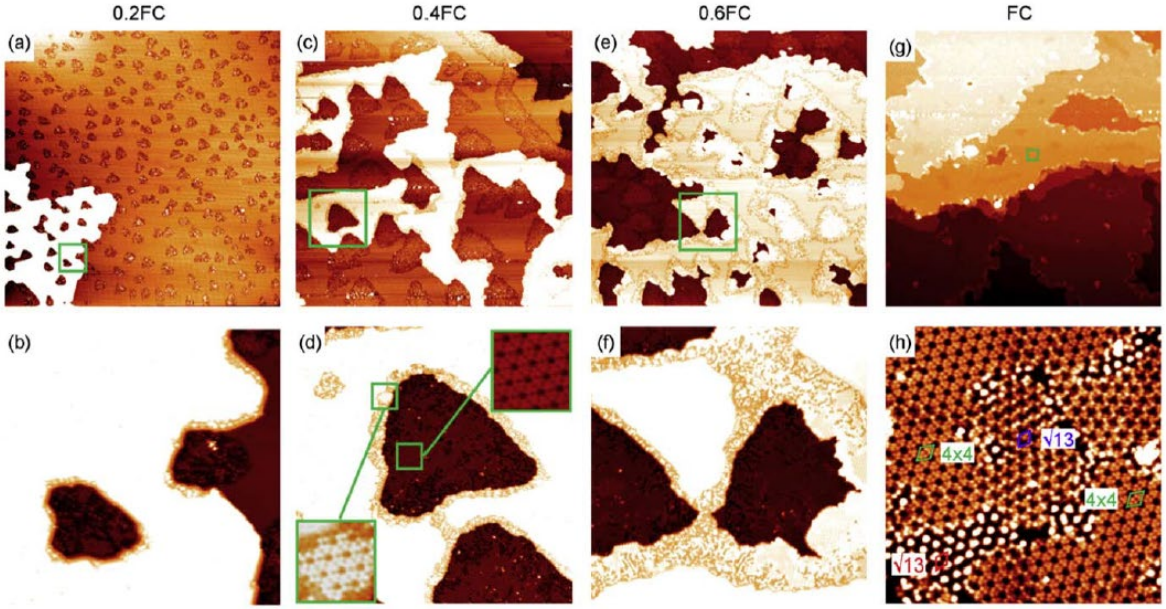
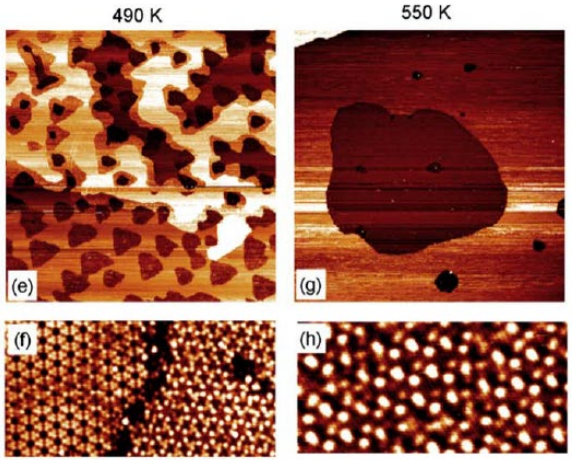


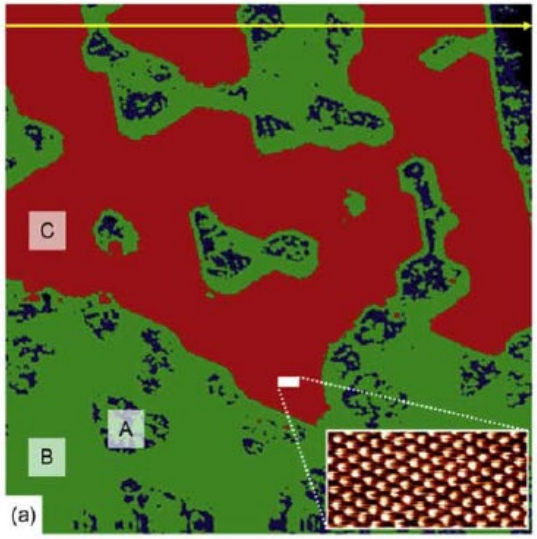
Figure 10. Constant current STM images ($V_S = +2$ V, $I_T = 2$ nA, $T = 80$ K) of Si/Ag(111) samples grown at $T = 490$ K as a function of increasing silicon coverage. (a) 0.2 FC, 500 × 500 nm^2. (b) 0.2 FC, 50 × 50 nm^2. (c) 0.4 FC, 500 × 500 nm^2. (d) 0.4 FC, 100 × 100 nm^2. (e 0.6 FC, 500 × 500 nm^2. (f) 0.6 FC, 100 × 100 nm^2. (g) FC, 500 × 500 nm^2. (h) FC, 20 × 20 nm^2.

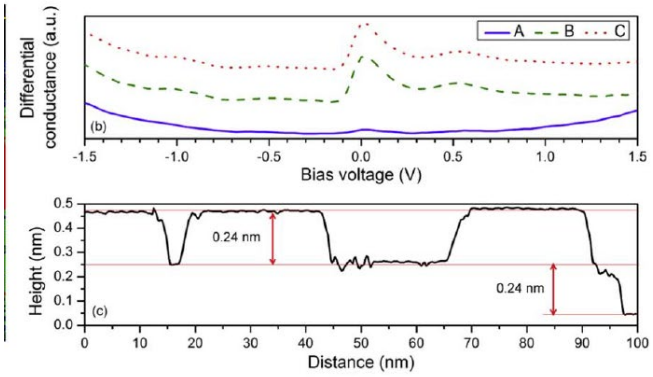
Higher diffusivity of Ag atoms at 250°C→ accumulation at terraces edge and no new terrace formation



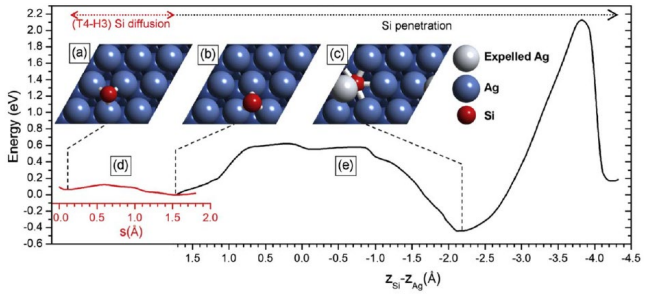
(√13x√13)R13.9°, 4x4 (√3x√3)

0.25 Full Coverage





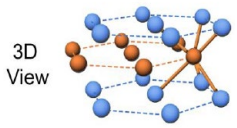
ENERGY RELASED OF THE Si ADATOM ABSORPTION PROCESS

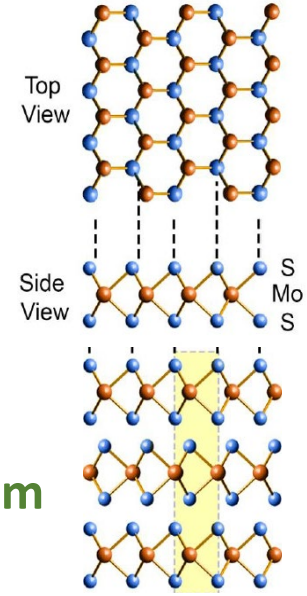


S. Colonna et al., Nanotechnology 32 (2021) 152001

SILICENE on NON-METALLIC & NON INTERACTING SUBSTRATE: LAYERED HEXAGONAL MoS_2

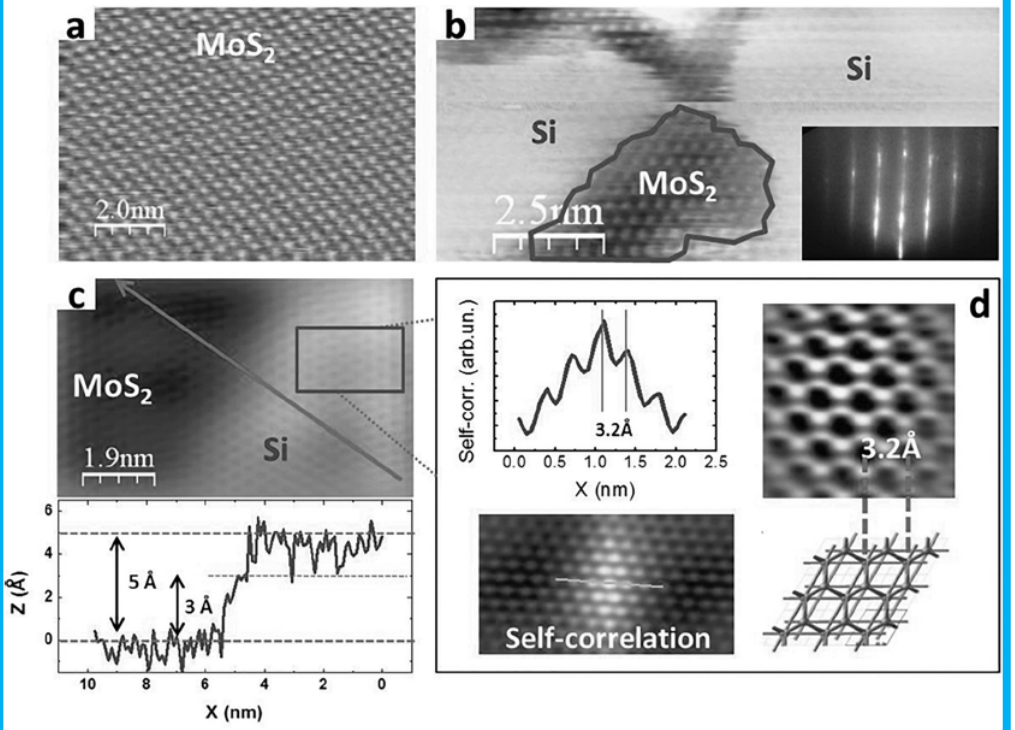
$\frac{\Delta a}{a} \cong 20\ \%$





MoS_2 lattice parameter: 0.316 nm

MBE growth @ 200°C



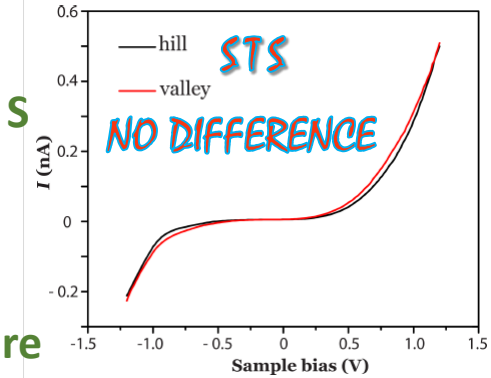
DFT calculations gave a high buckled silicene 0.2 nm, due to silicene lattice shrinking induced by the high lattice mismatch

Chiappe et al., Adv. Mater. 26, 2096 (2014).

Si atoms intercalation under the outermost MoS_2 layer, probably close to MoS_2 defects, vacancies and step edges

XPS analysis:

- no interaction between Si and S or Mo
- 5% Si resists at the oxidation after air exposure
- Upon sputtering Si increases, S decreases

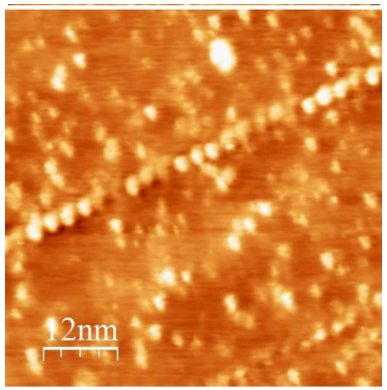


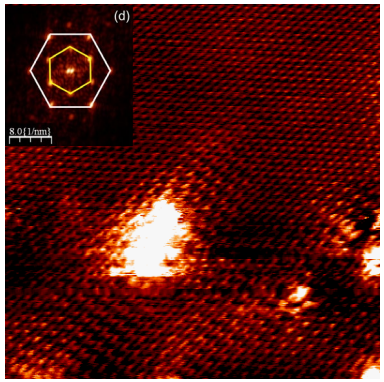
Beilstein J. Nanotechnol. 2017, 8, 1952–1960

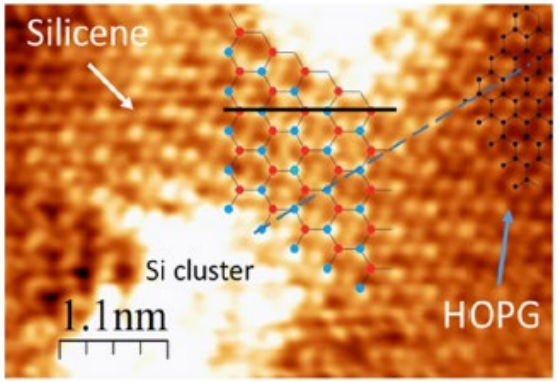
SILICON on HOPG @ RT

$\frac{\Delta a}{a} \cong 54\ \%$

Honeycomb, a= 0.246 nm

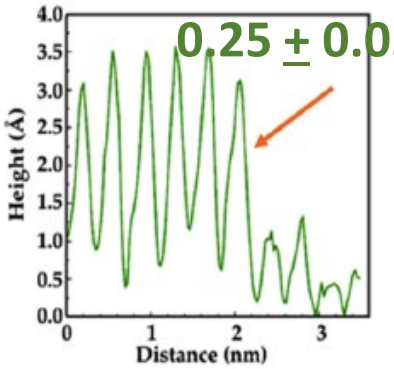






0.38 ± 0.03 nm

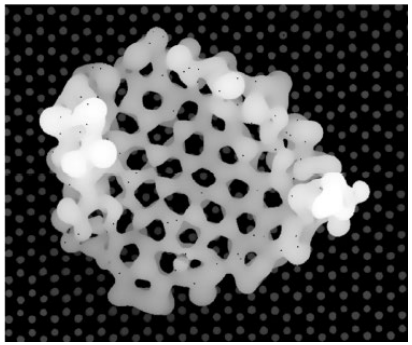
0.25 ± 0.05 nm

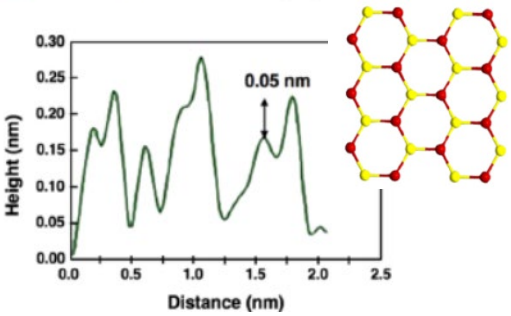


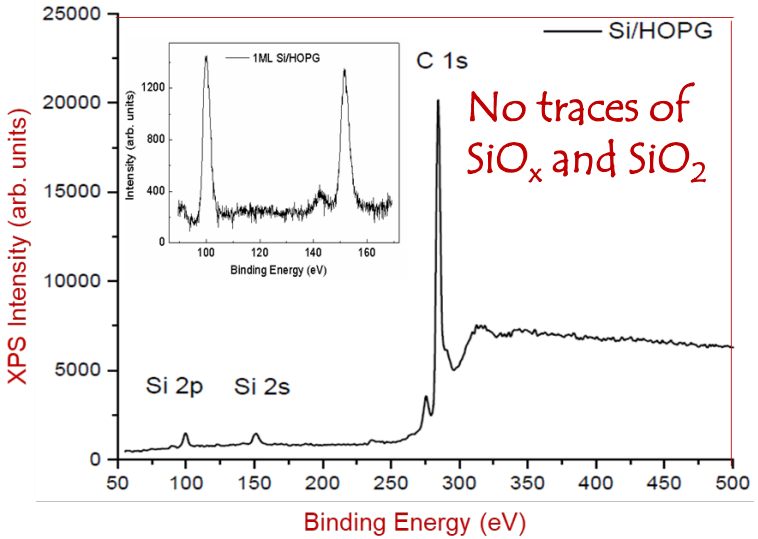
From 2D-FFT:

0.41 ± 0.02 nm (√3x√3)R30°

0.25 ± 0.02 nm







Charge modulations resulting from the quantum interferences guide the incoming Si atoms to positions above the graphite substrate that correspond to a template given by those charges

And after they reach a size of few nm, nanoislands will reorganize in 3D clusters

DeCrescenzi et al., ACS Nano 10, 11163 (2016)

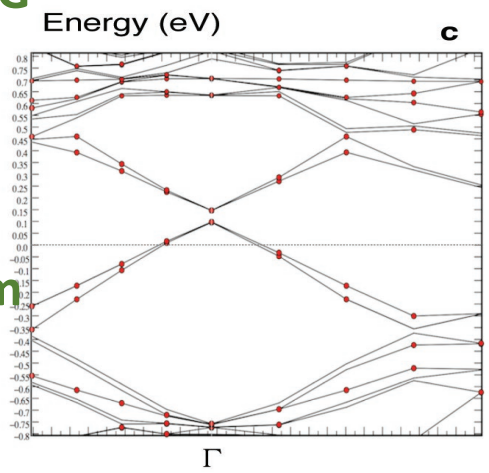
F. Jardali et al., Nano Res. 2020, 13(9): 2378–2383

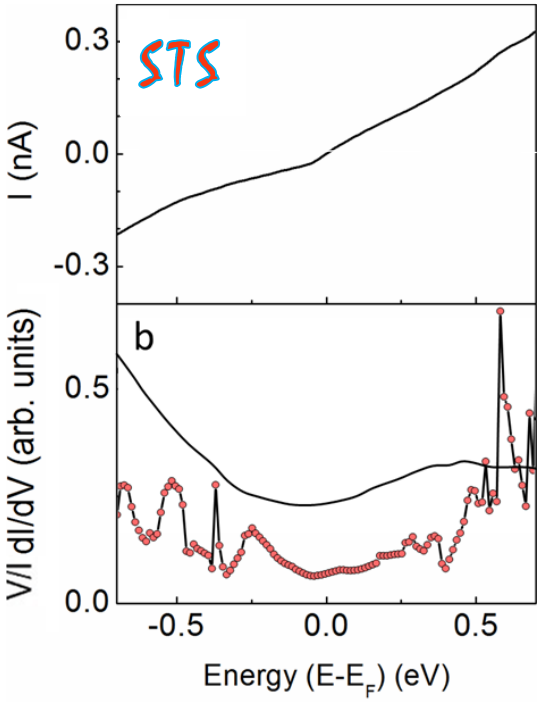
SILICON on HOPG @ RT

DFT CALCULATIONS

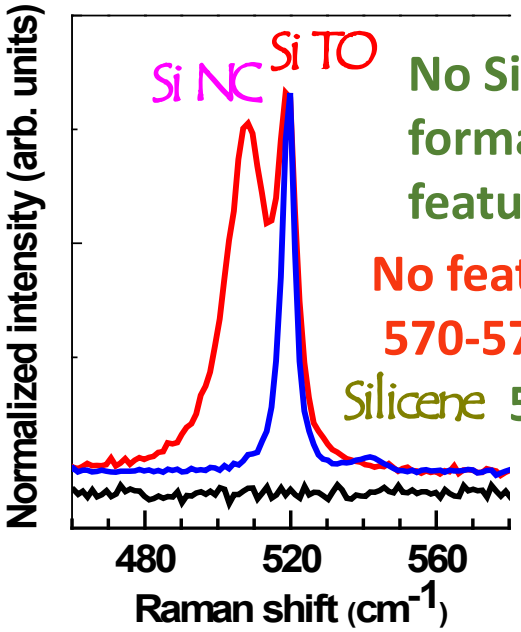
Silicene R30° with respect to HOPG
Metal character, Eg = 48 meV
No Si-C bond formation

Buckling :0.051 nm
Silicene -HOPG distance: 0.333 nm
Lattice parameter : 0.379 nm





DeCrescenzi et al., *ACS Nano 10, 11163 (2016)*



No SiC formation feature!

No feature @ 570-575cm^{-1}

Silicene 542 cm^{-1}

Calculations indicate that for Silicene Nanosheets with side length of 1.3-1.5 nm

Such Raman shift is reasonable!

Si-Si distance: 0.228 nm
due to the removal of periodic constrain with respect to the interface
→ a_{Sil} = 0.395 nm
→ Buckling: 0.052-0.053 nm

Castrucci et al. Nano Res. (2018), 11(11), 5879-5889

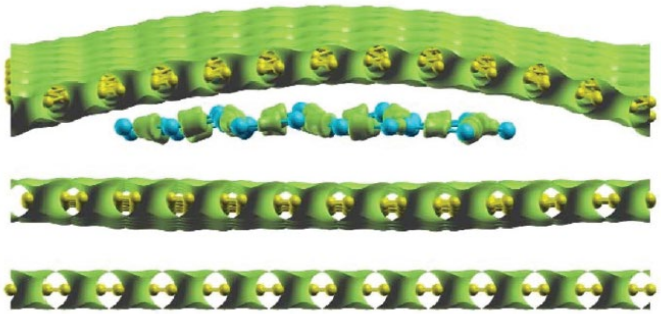
les

th a height of 0.2-0.3 nm

nost flat on top

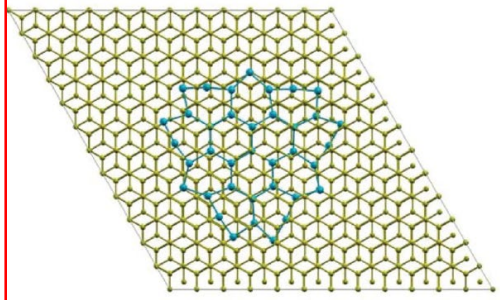
th the graphene atomic

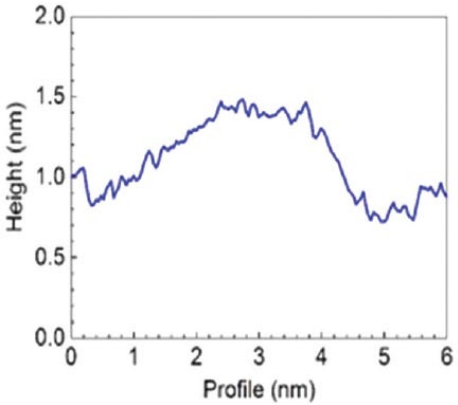
riodicity



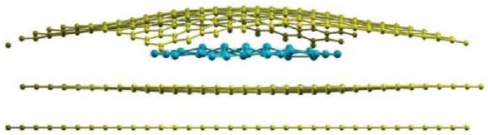
Charge density calculations

No bonds are present between Si and C atoms

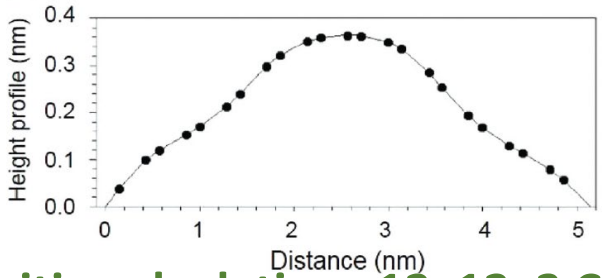




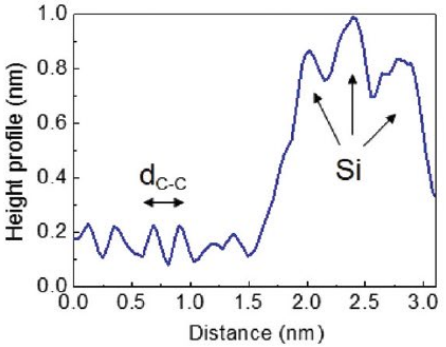
(b)

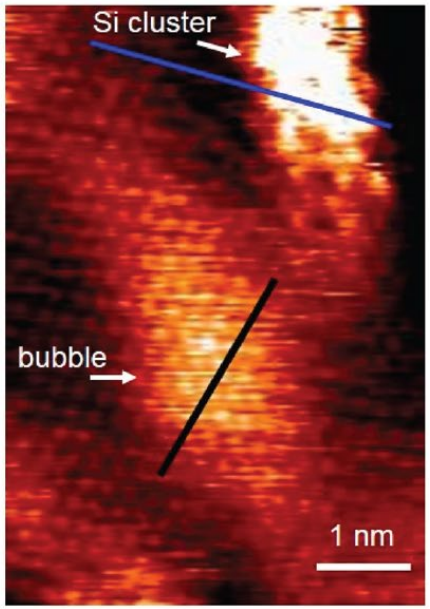


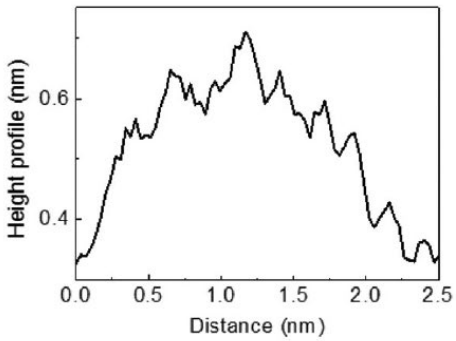
(c)



Ab-initio calculations 12x12x3 C slab + 37 Si atoms inserted under the outmost carbon layer

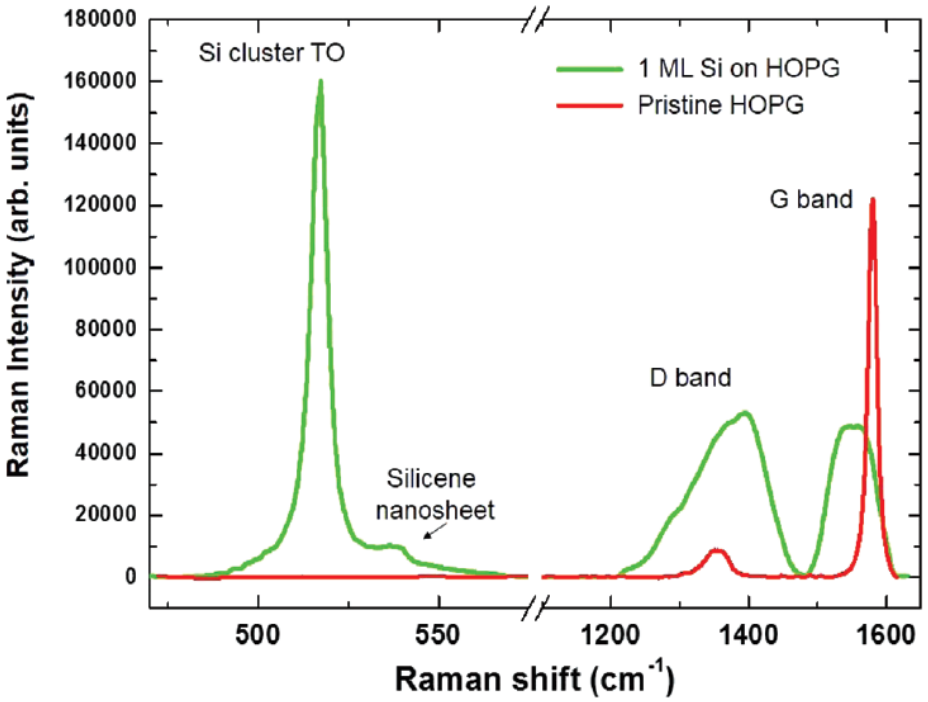


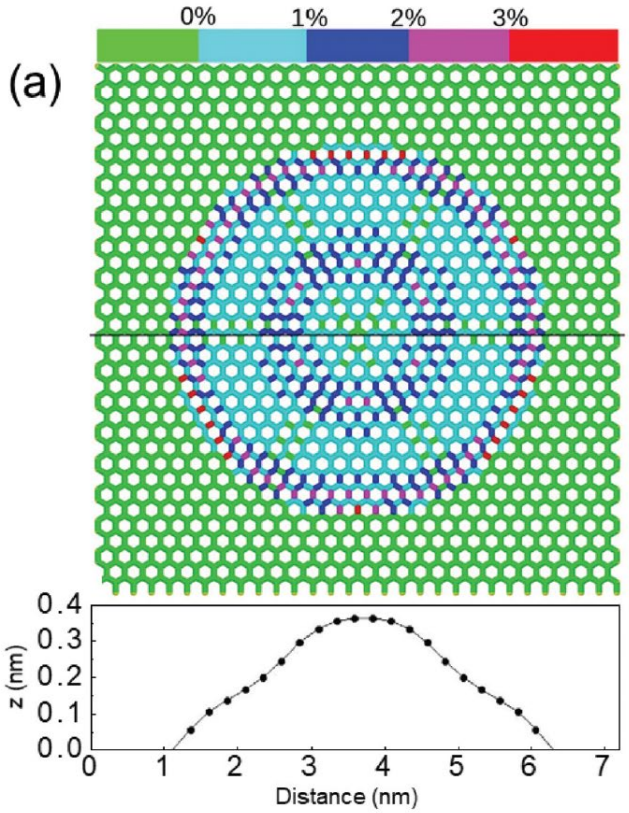




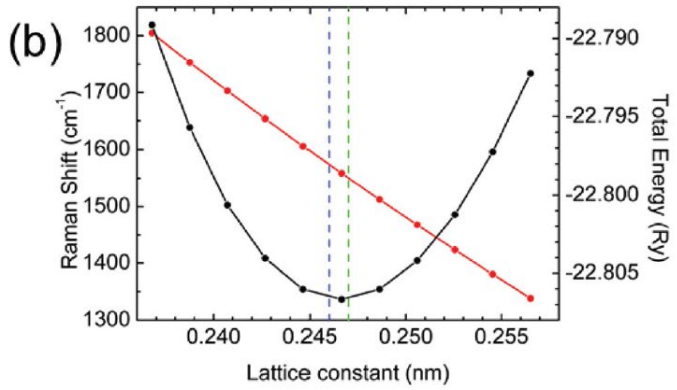
I.Kupchak et al., Nanoscale, 11 (2019) 6145 - 6152

RAMAN MEASUREMENTS & CALCULATIONS



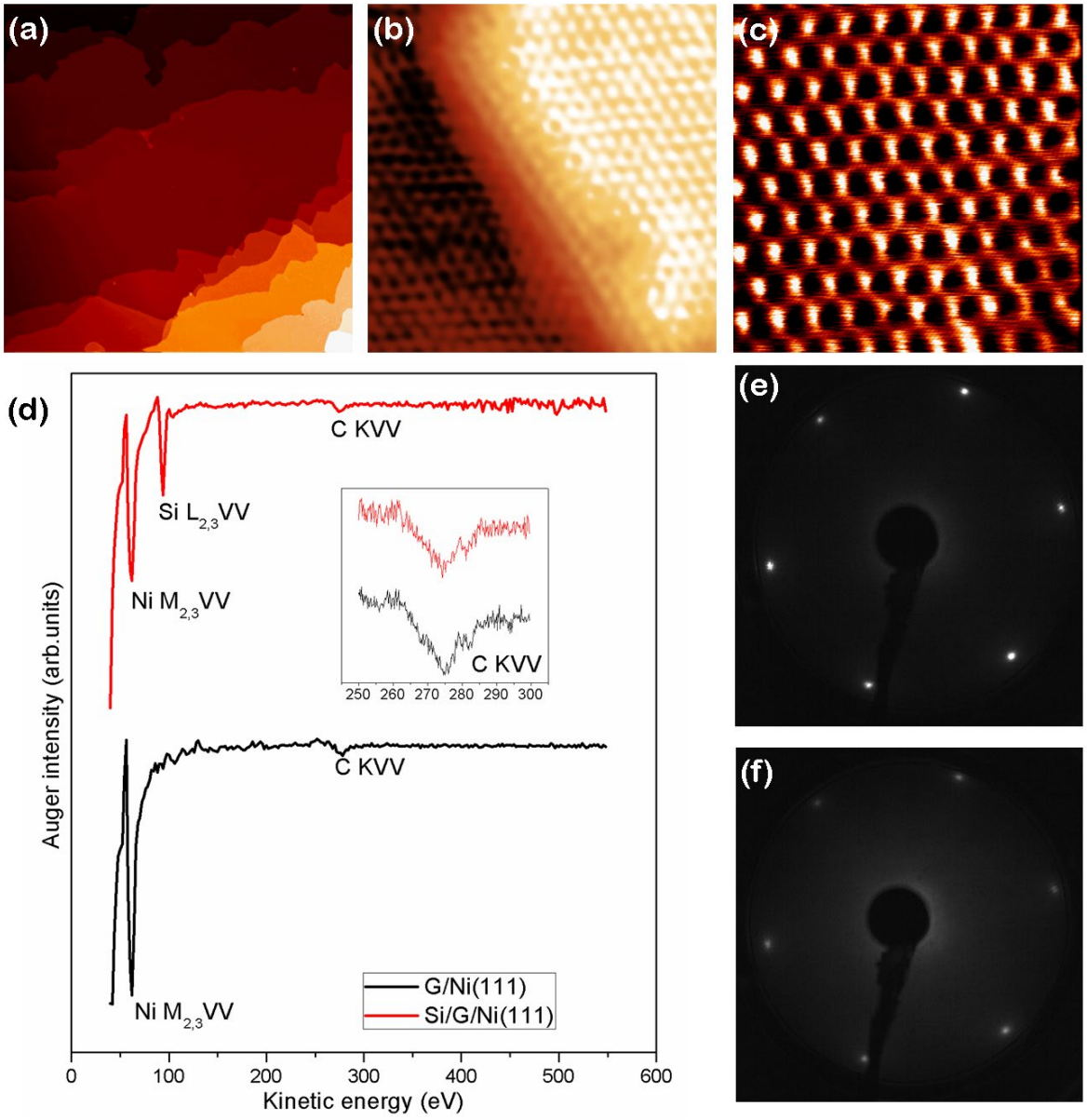


There is strain due to intercalated silicene nanosheets, shifting towards lower wavenumber the graphene G band. Calculations made under density functional perturbation theory.



I.Kupchak et al., Nanoscale, 11 (2019) 6145 - 6152

Si-GRAPHENE-Ni(111) SYSTEM



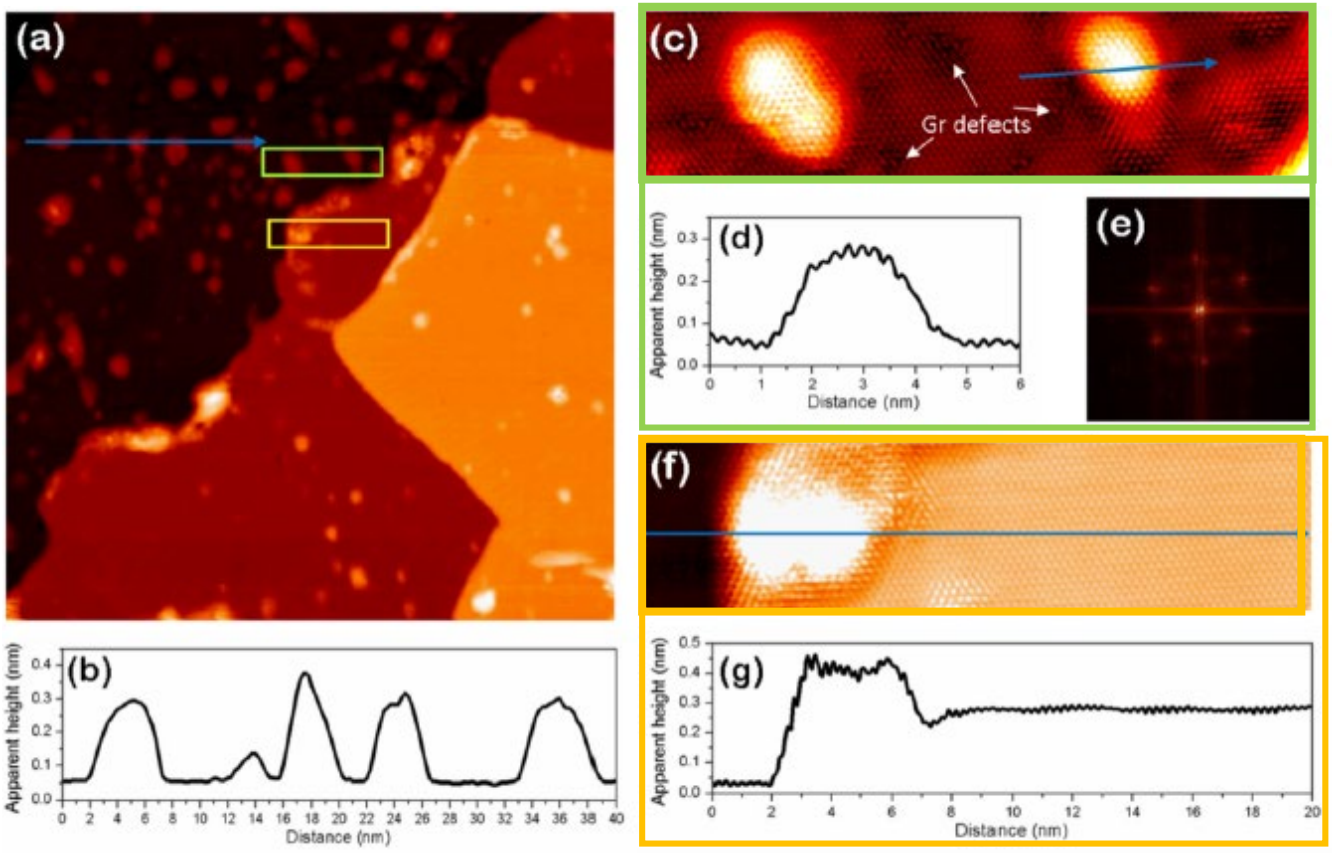
Graphene on Ni(111)

Graphene on Ni(111)
+ Si deposition at RT

F. Ronci et al., Carbon 158 (2020) 631-641

Bubbles randomly distributed on the Graphene terraces and edges

- with a height of 0.2-0.3 nm
- almost flat on top
- with the graphene atomic periodicity
- Only graphene lattice spots in the 2D-FFT → disordered atom arrangement underneath



Si intercalation under the graphene layer at RT?

Si intercalation through the graphene layer has been reported for Si deposition or post-growth annealing at T > 600K

F. Ronci et al., Carbon 158 (2020) 631-641

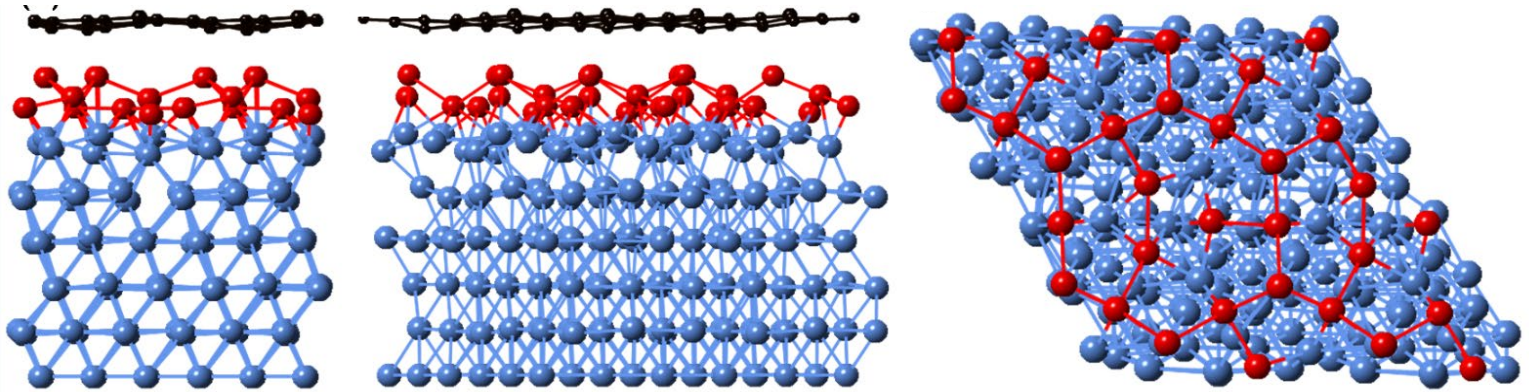
DOES SI FORM A LOW INTERACTING SILICENE LAYER BETWEEN GR AND NI(111)?

A perfect nickel/silicene/graphene sandwich has been modelled and optimized with *ab initio* molecular dynamics (AIMD) approach :

After 8ps:

0.44 nm

Gr-Ni surface distance : 0.20 nm



Height difference between silicon atom intercalated areas and pure Gr/Ni(111) ones : 0.24 nm

No intermixing between Si and Ni atoms is observed during this simulation time at 300K.

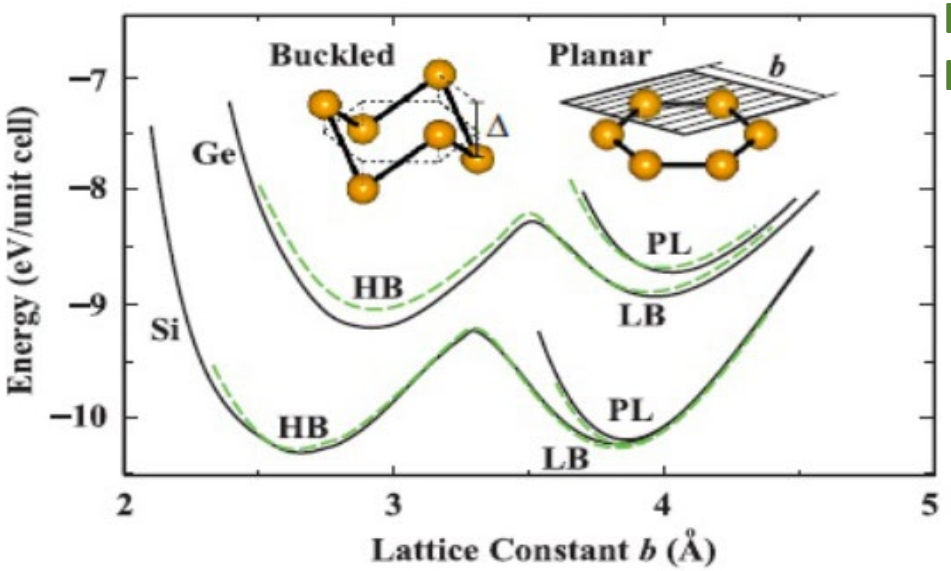
In order to observe intermixing (alloy formation), within the small time period of 8 ps, the sample temperature must be increased at least to 475K according to our AIMD simulations.

F. Ronci et al., Carbon 158 (2020) 631-64

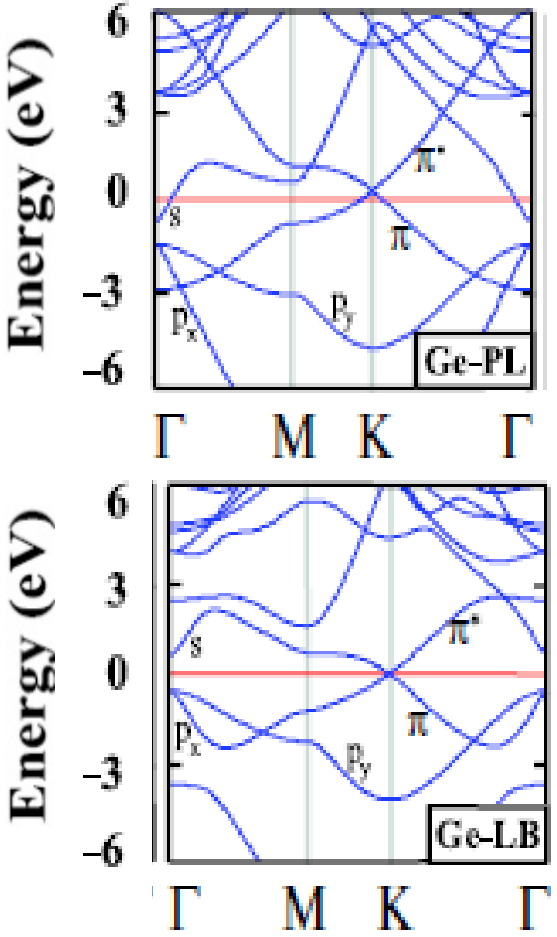
FREE-STANDING GERMANENE THEORETICAL PREDICTIONS

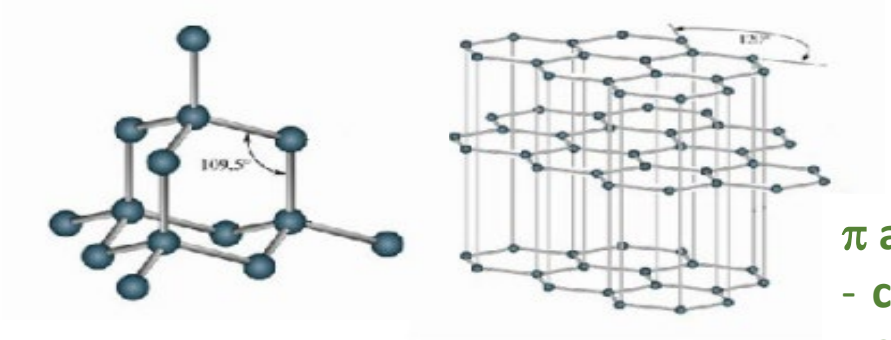
HB: Highly Buckled $\Delta = 0.22$ nm
LB: Low Buckled $\Delta = 0.064$ nm
PL: Planar

⇨ **Mixed sp^2 -sp^3**



S. Cahangirov, et al., Physical Review Letters 102, 236804 (2009)

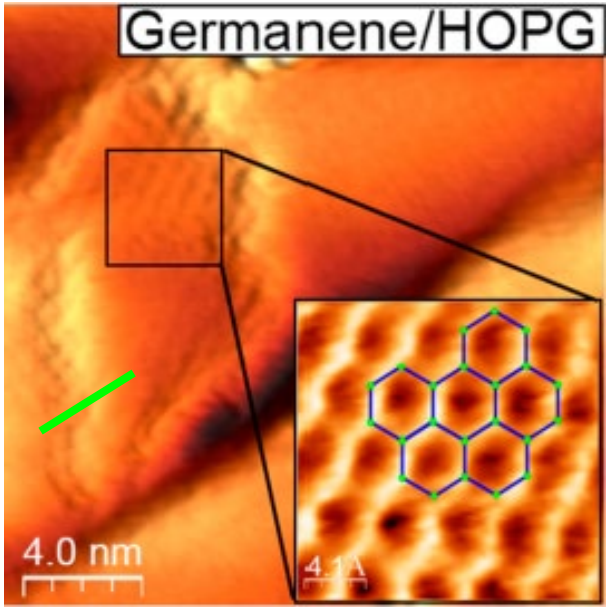




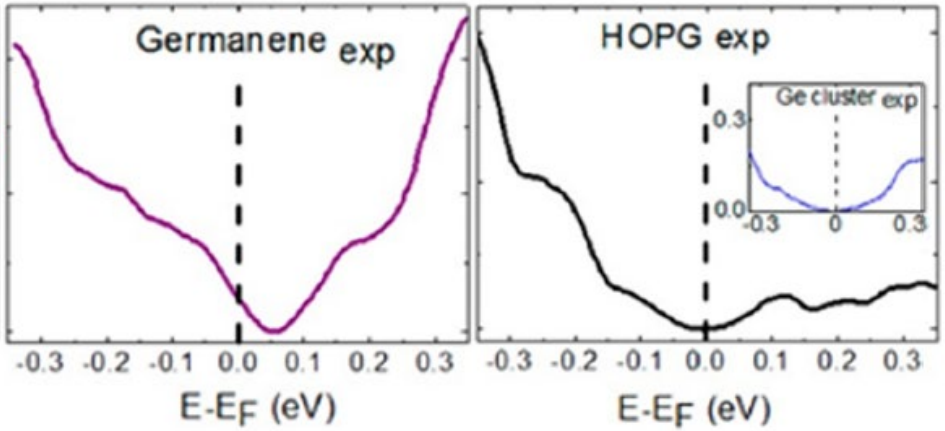
π and π* bands :

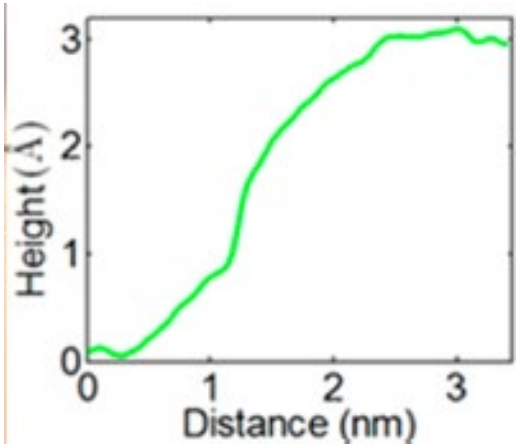
- **cross at K and K' points at E_F → semimetallic**
- **are linear close to K and K' point**
- **massless Dirac fermion character to charge carriers**

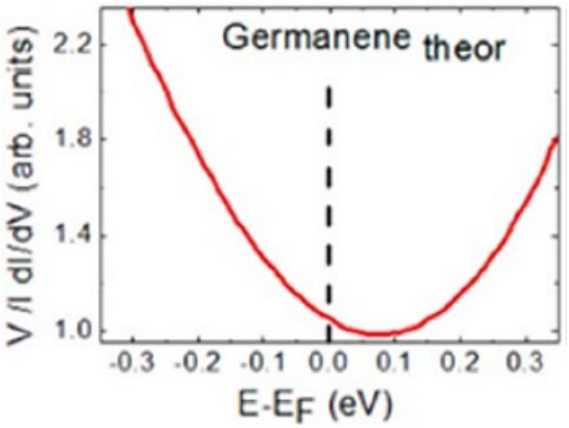
GERMANENE on HOPG

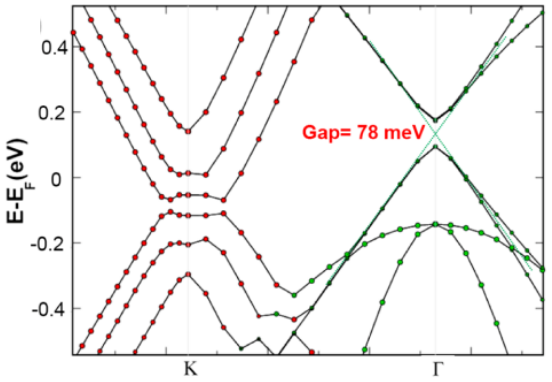


0.42 ± 0.03 nm and 0.07nm , values that closely match those theoretically predicted for free-standing germanene, that is 0.397 nm and 0.064 nm, respectively





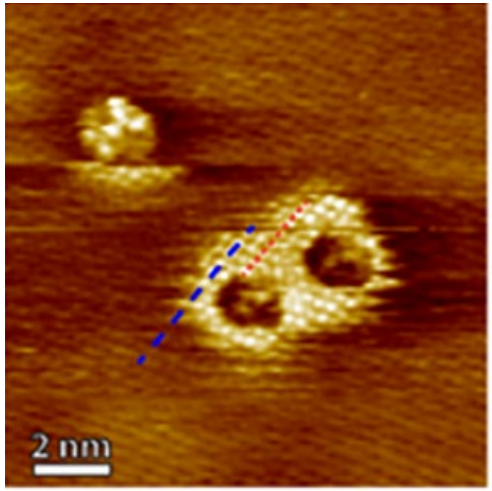


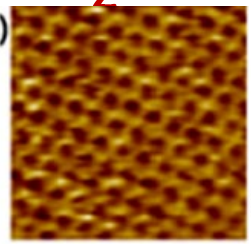


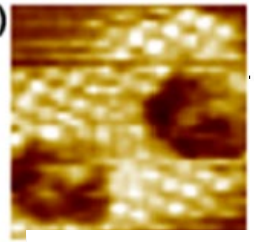
A value compatible with Ge-HoPG out-of-plane distance

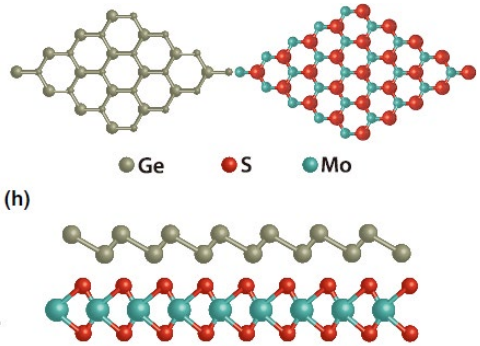
L. Persichetti et al., J. Phys. Chem. Lett. 7, 3246 (2016).

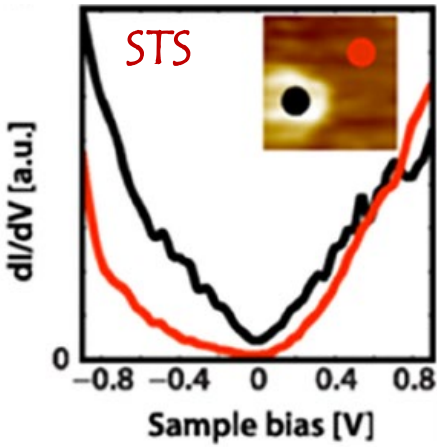
GERMANENE on MoS_2

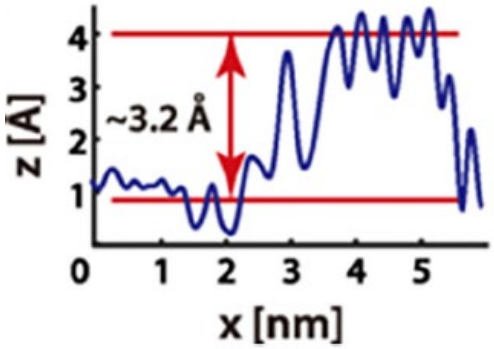


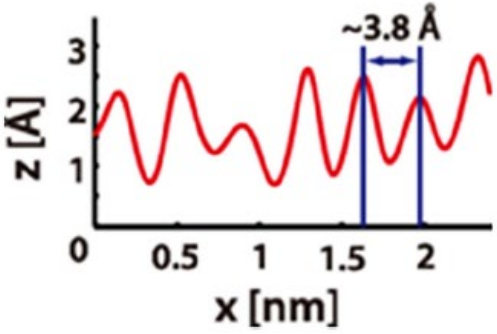






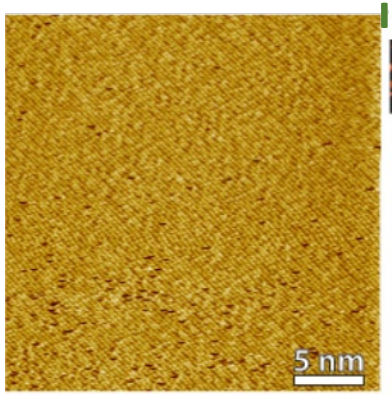


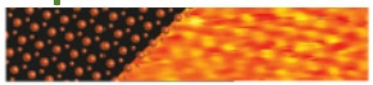


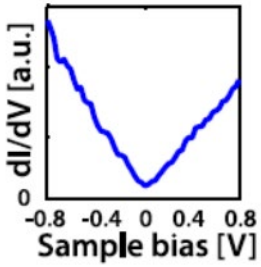


Metal character, no doping
Dirac point at E_f contrary to the DFT calculations, showing an electron transfer from MoS_2 to Germanene upshifting E_f of 0.3eV (n-type).
Experimentally not observed probably because of acceptor impurities or unsaturated defects

At low coverage, different shapes and sizes all showing a hexagonal hole.
Ge lattice parameter, contracted of about 5% to that for free-standing germanene (0.38 nm and 0.397 nm, respectively)





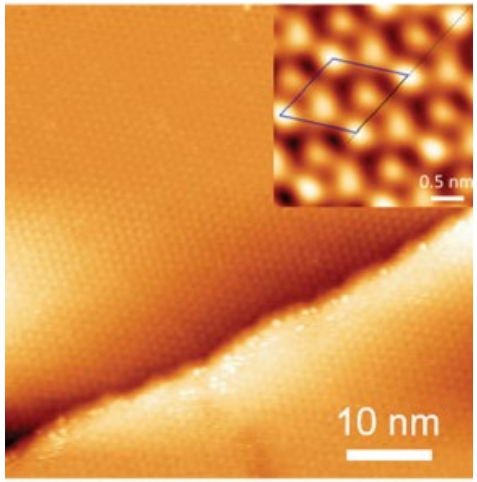


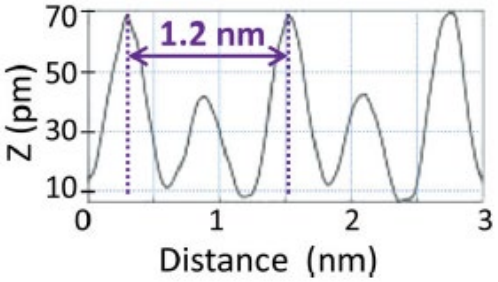
At higher coverage hexagonal network with Germanene lattice periodicity

Zhang et al., Phys. Rev. Lett. 116, 256804 (2016).

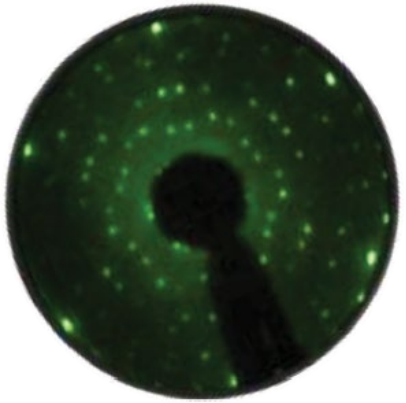
GERMANENE on Pt(111)

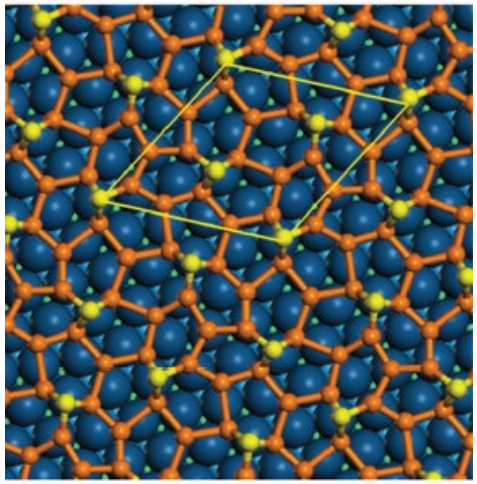
Ge/Pt(111) ANNEALED @300-350 °C



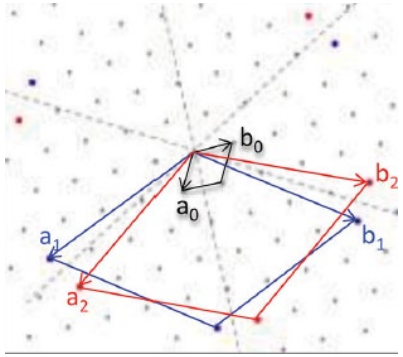


(3x3) Germanene on
(√19 x√19) Pt(111)





Theoretical calculations
Ge-Ge strong covalent bonding!



R23.4° or R36.6°

L. Li et al., Adv. Mater. 2014, *26*, 4820–4824

Ge/Pt(111) ANNEALED @700 °C

Pt-Ge alloy with √19 x√19 superstructures

XPD analysis: Ge substitutional atom in Pt sites

C.-S. Ho et al. / Surface Science 603 (2009) 1161-1167

GERMANENE on Pt(111), Au(111), Al(111), Ag(111), Ge_2Pt

2D MATERIAL EPITAXIAL GROWTH

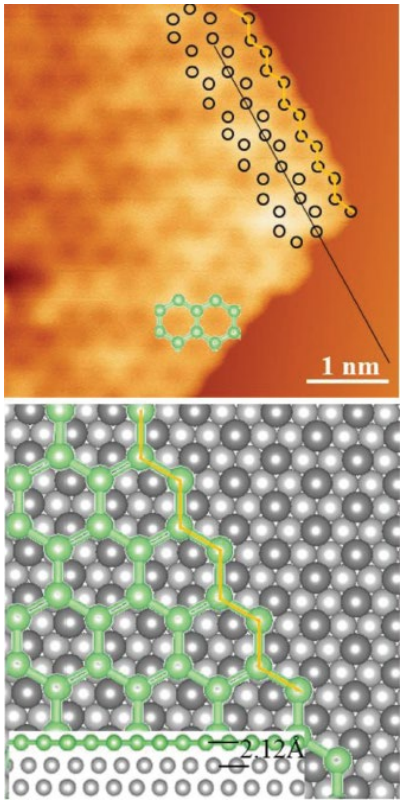
- It is always a Ge layer ?
- Strong interaction between the substrate and Ge atoms
- Strong modifications of Dirac cones or disappearence

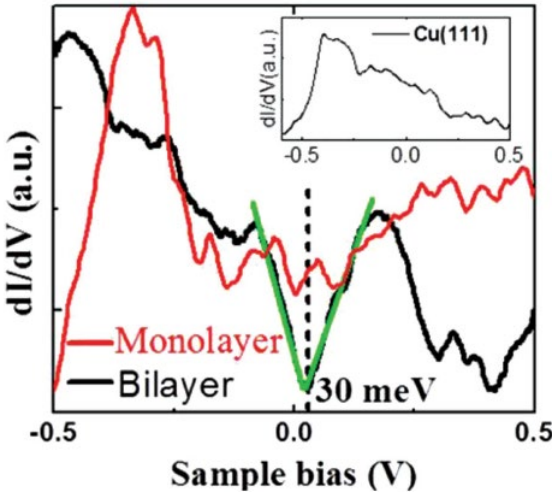
HOW CAN WE OBTAIN GERMANENE?

L. Li er al., *Adv. Mater.* 2014, *26*, 4820.
M. E. Dávila et al., *New J. Phys.* 2014, *16*, 095002.
M. Derivaz et al., *Nano Lett.* 2015, *15*, 2510.
Y. Fukaya et al., *2D Mater.* 2016, *3*, 035019.
L. Zhang et al., *Appl. Phys. Lett.* 2015, *107*, 111605.
P. Bampoulis et al., *J. Phys. Condens. Matter* 2014, *26*, 442001

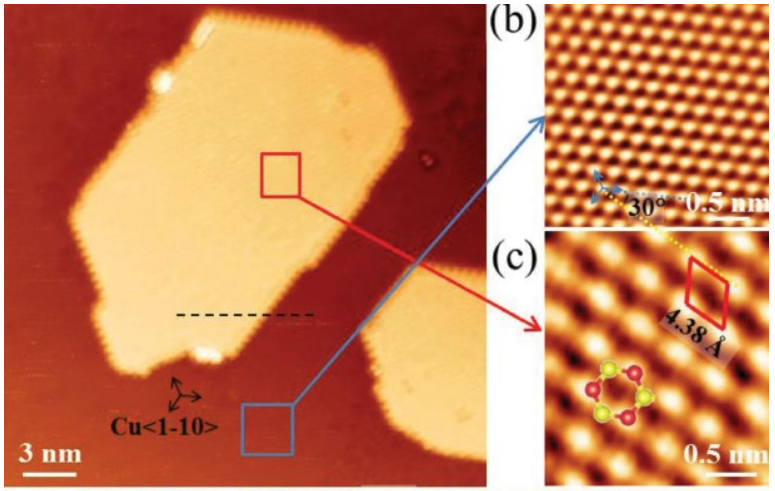
GERMANENE on Cu(111) → use of a BUFFER LAYER

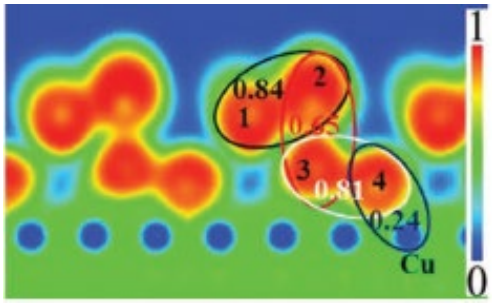
1 Ge ML → honeycomb

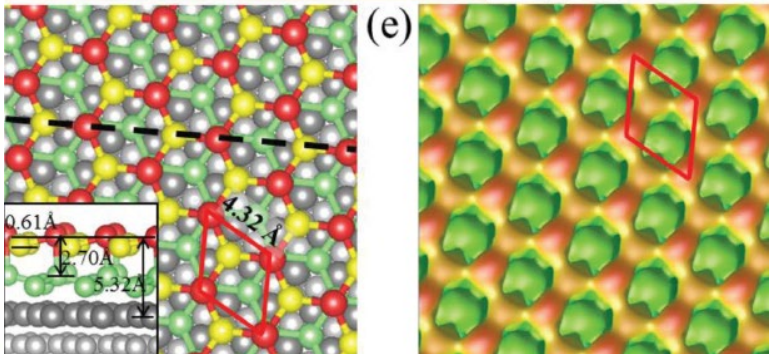




2 Ge ML → (√3x√3)R30°







Ge-Ge distance: 0.254 nm (instead of 0.238 nm). Partial misfit strain relief giving rise to a quasi-planar Ge layer?

ELF calculations : values < 0.5 → electrostatic interactions

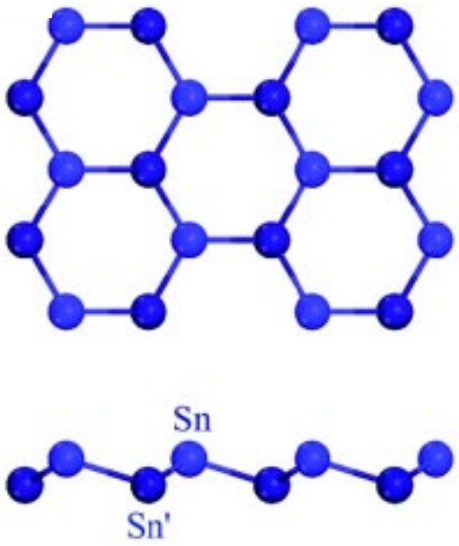
- Electrons from ½ Ge atoms of the first ML to Cu atoms

→ Hole doping of Germanene 2nd layer → 30 meV downshift of the Dirac point

- ½ Ge atoms of the first and the second layer covalently bound

Z. Qin et al., Adv. Mater. 2017, 1606046

FREE-STANDING STANENE THEORETICAL PREDICTIONS

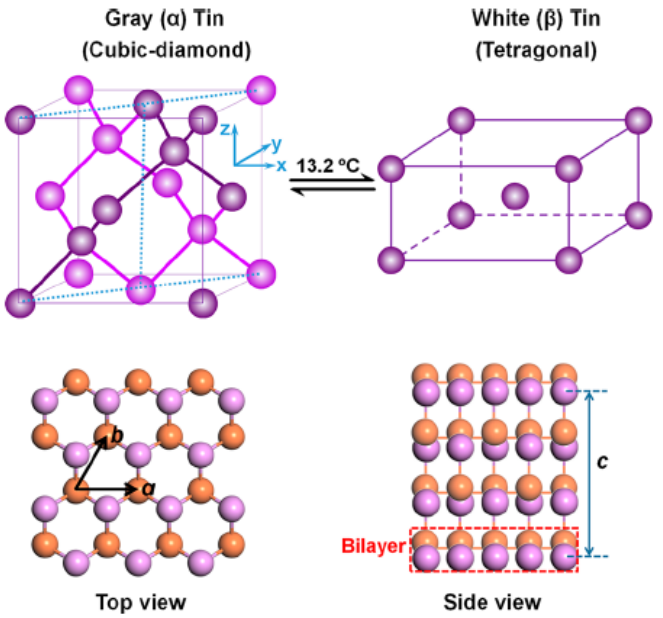


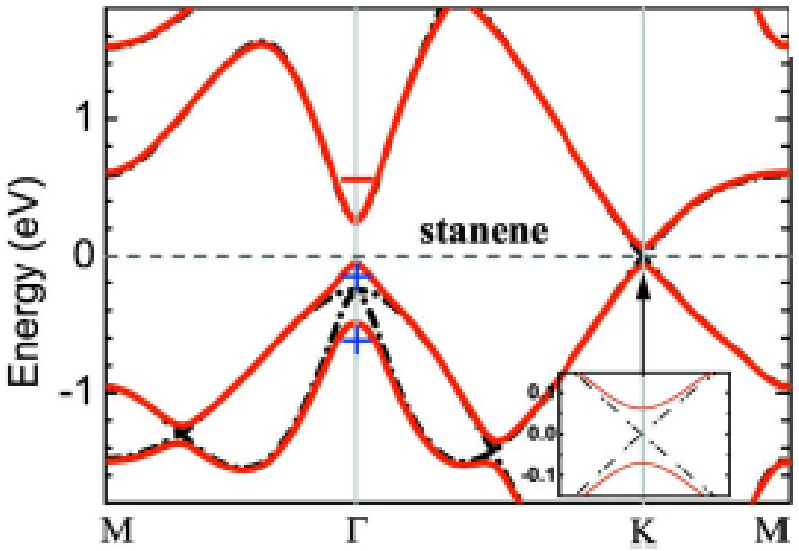
Low-buckling due to the weak π-π^* interactions

a = 0.462 nm

Δ = 0.085 nm

STABLE Sn 3D STRUCTURES





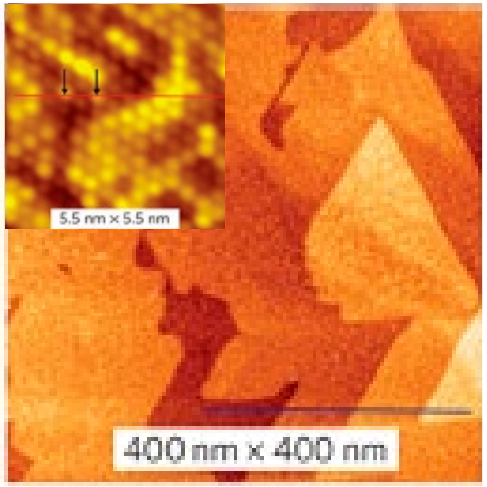
Dirac cones that without accounting for spin-orbit-coupling crosses at E_F at K

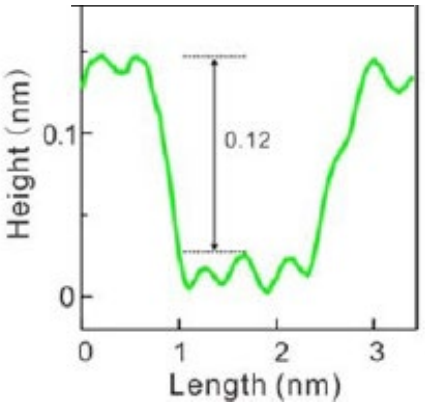
SOC opening of a gap 0.1 eV at K

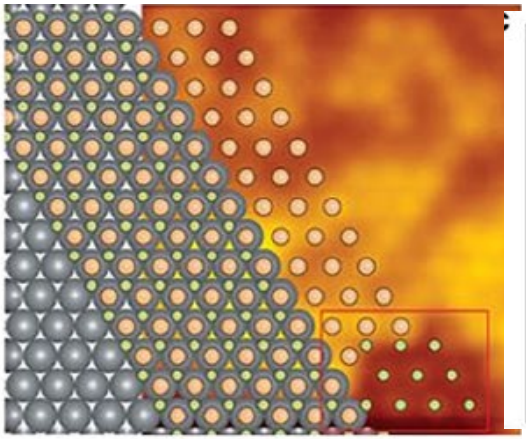
Xu et al. PRL 111, 136804 (2013)

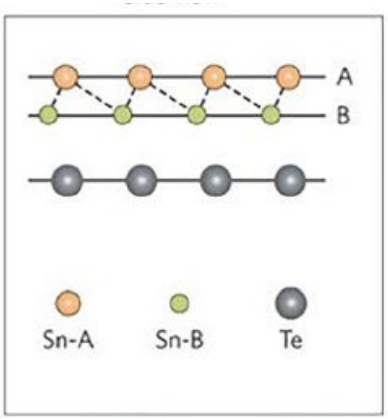
Sn on Bi_2Te_3 SUBSTRATE or FILM on Si(111)

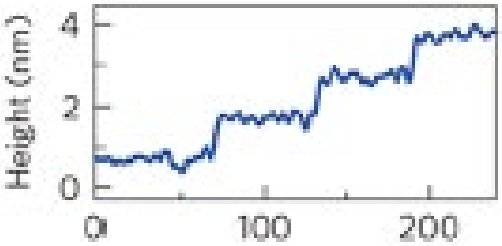
Sn MBE DEPOSITED @RT





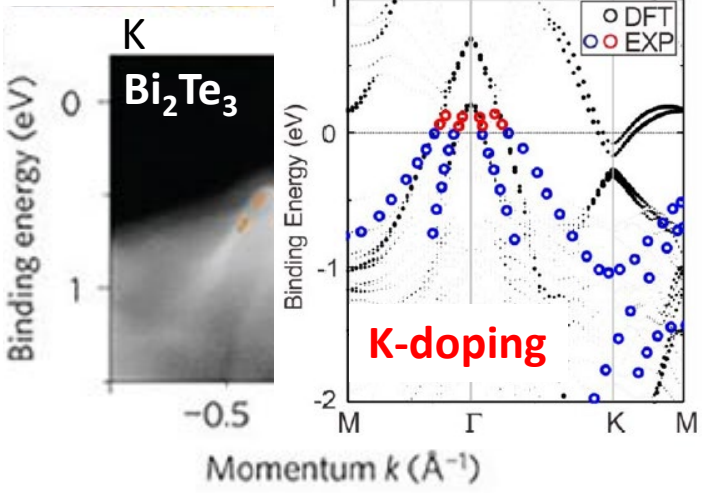


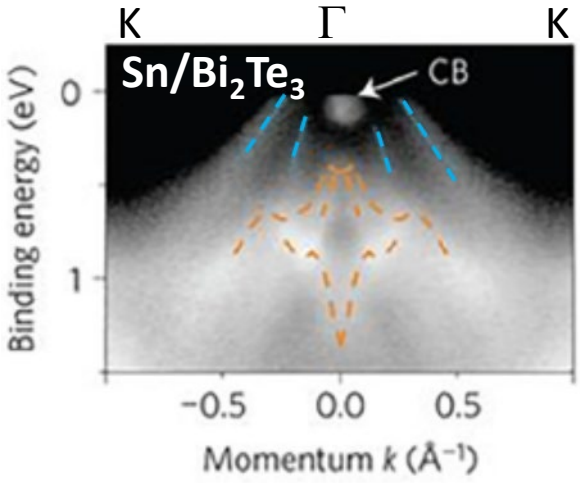




a_{Bi2Te3} = 0.438 nm , $a_{Stanene}$ = 0.462 nm

DFT calculations: compressive strain on stanene → an increase in the buckling from 0.085 to 0.109 nm





Bi_2Te_3 becomes metal

Electron transfer from stanene to Bi_2Te_3

Stanene hole bands appear

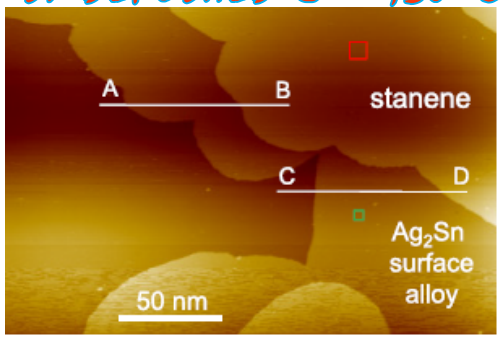
F. Zhu et al., Nature Materials 14, 1020–1025 (2015)

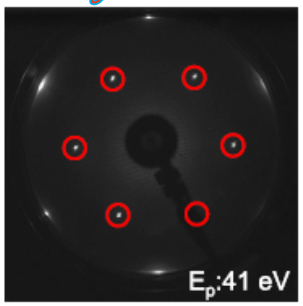
Sn on Ag(111) SUBSTRATE

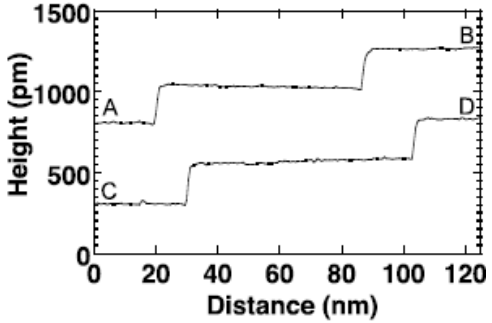
J. Yuhara et al., 2D Mater. 5 (2018) 025002

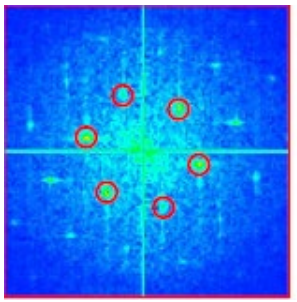
Sn DEPOSITED @ ~ 150 °C on Ag(111)

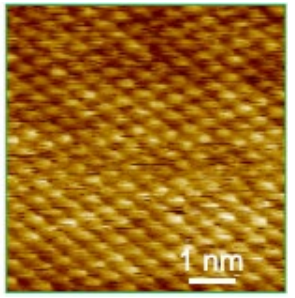
√3 x√3 Ag_2Sn

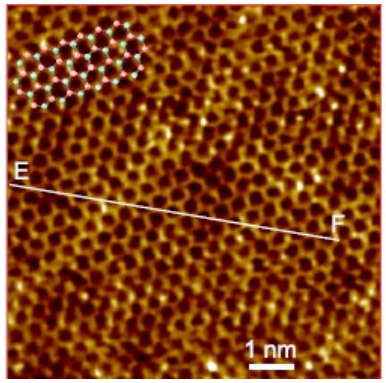


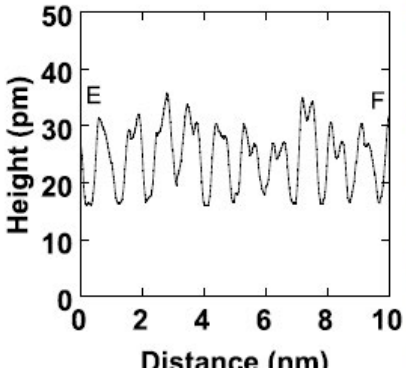


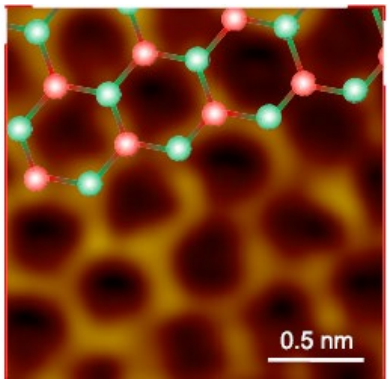


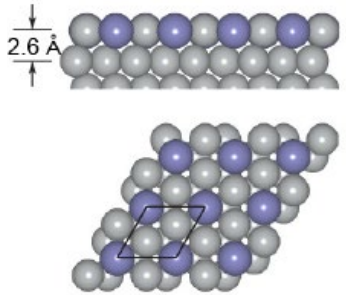


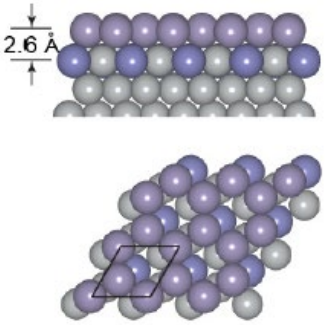


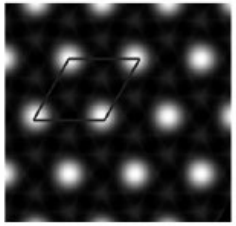


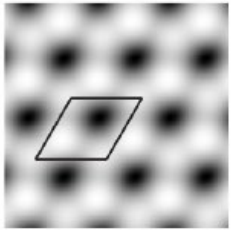




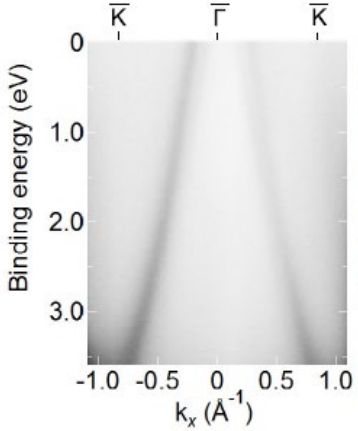


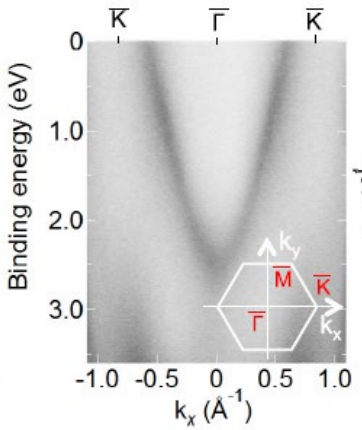


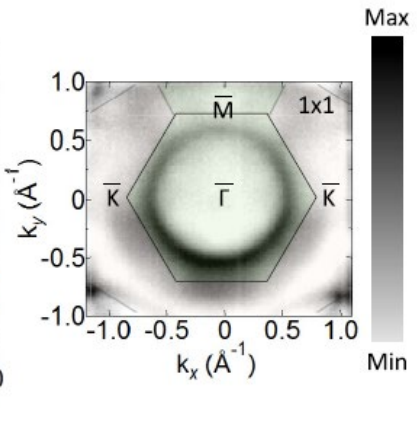




Low buckling (~ 0.012 nm) due to low mismatch





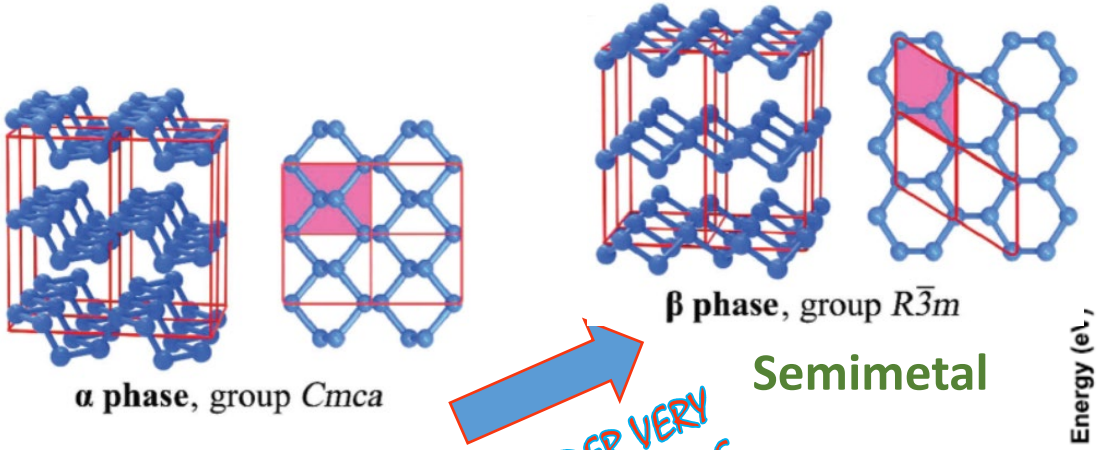


Strong interaction with the Ag_2Sn layer underneath

No Dirac cone in stanene

FREE-STANDING PHOSPHORENE THEORETICAL PREDICTIONS

PHOSPHORUS ALLOTROPES:
RED, WHITE AND BLACK.
NO ONE AVAILABLE IN NATURE.



@ UNDER VERY HIGH PRESSURE (SCP4)

Semimetal

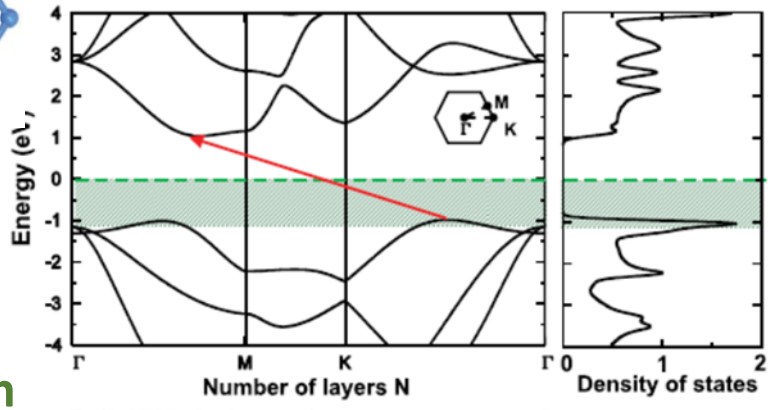
Black P

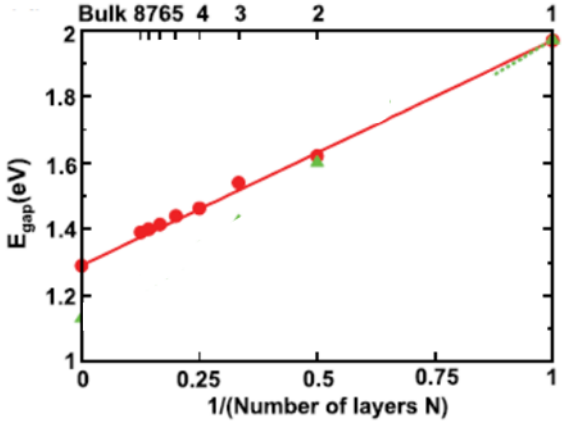
Most thermodinamical stable @ ambient conditions

- Semiconductor, Eg=0.3eV
- high $\mu \sim 10^3$ cm^2 V^{-1} s^{-1}
- Eg increases with N of layers decreasing

a = 0.333 nm

Blue P





~ 2 eV indirect gap

CHARGE INTERACTIONS INTERLAYER BONDING TYPE

Z. Zhu et al., PRL 112, 176802 (2014)

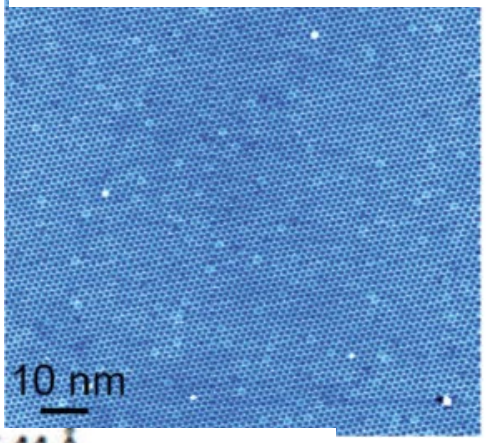
BLUE P or PHOSPORENE on Au(111)

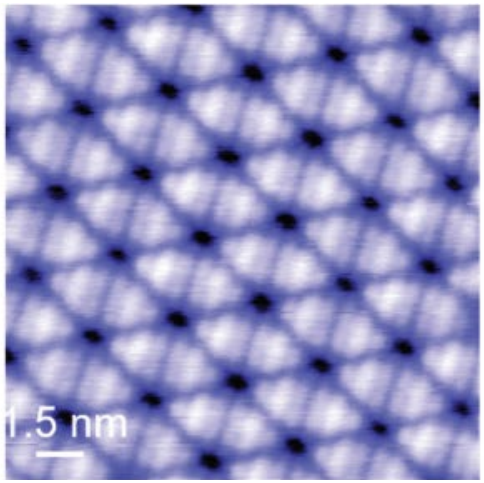
(√19 x√19) BlueP on (5x5) Au(111)

Solid source epitaxy from BlackP: via P_4 and P_2 clusters

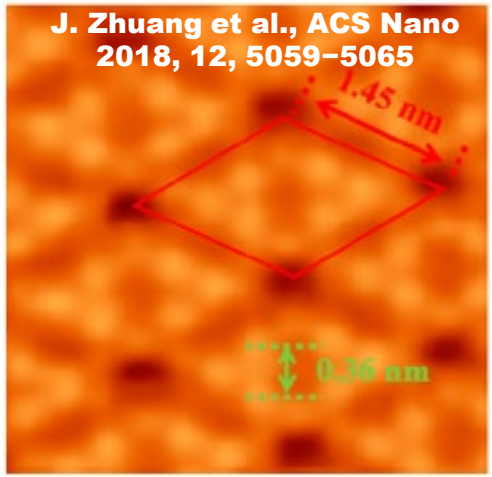
Annealing @ 170-200°C

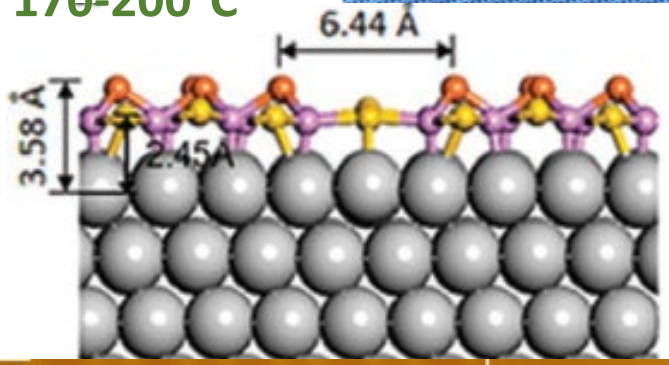
J. L. Zhang et al., Nano Lett. 2016, 16, 4903−4908



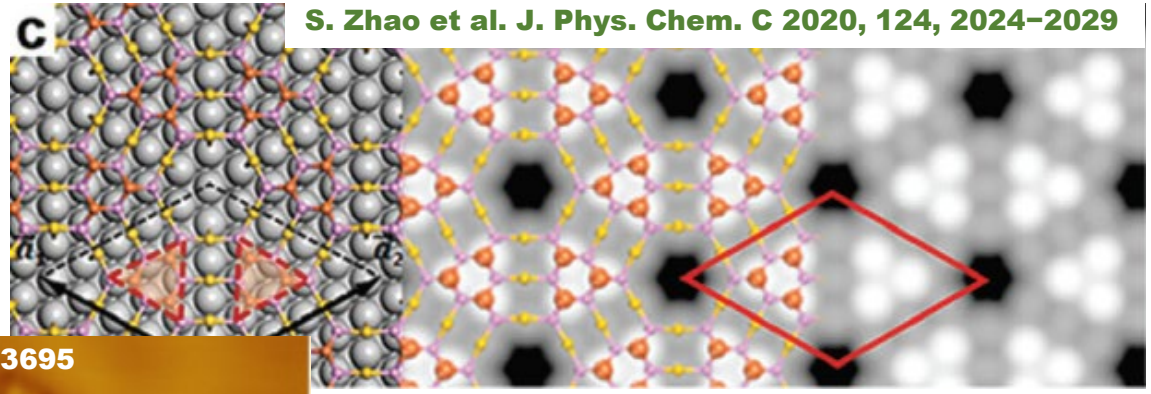


J. Zhuang et al., ACS Nano 2018, 12, 5059−5065

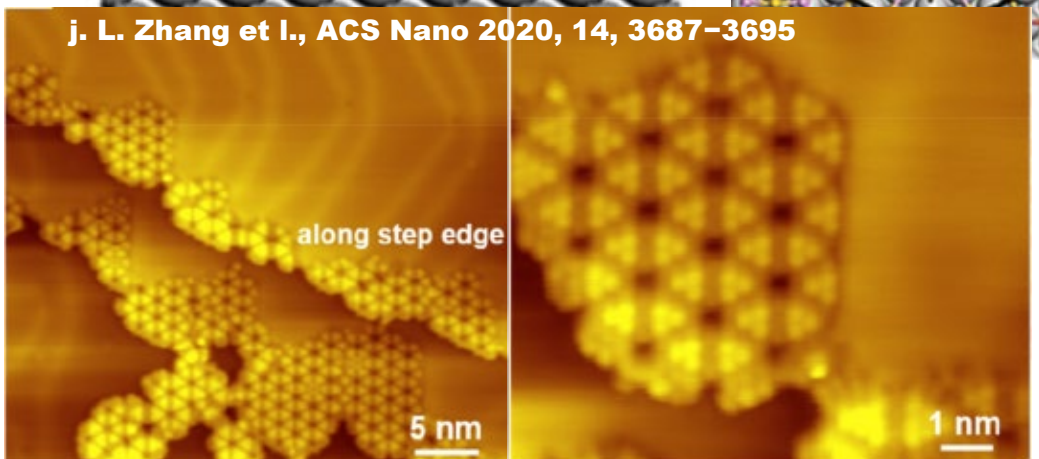




S. Zhao et al. J. Phys. Chem. C 2020, 124, 2024−2029



j. L. Zhang et l., ACS Nano 2020, 14, 3687−3695

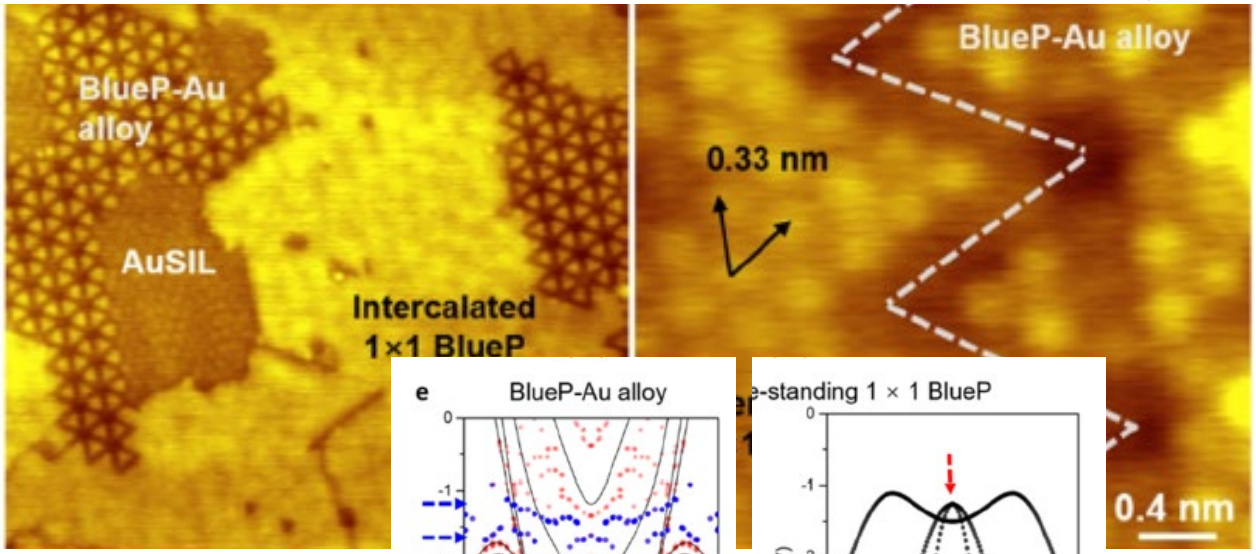


Strong interactions with substrate → P clusters break but P atoms remain confined and no stabilization in an extended P layer (also in Pt(111) & Cu(111))

Au atoms diffuse from the edges and interact with P atom fragments.

DECOUPLING P AND Au SUBSTRATE by Si INTERCALATION

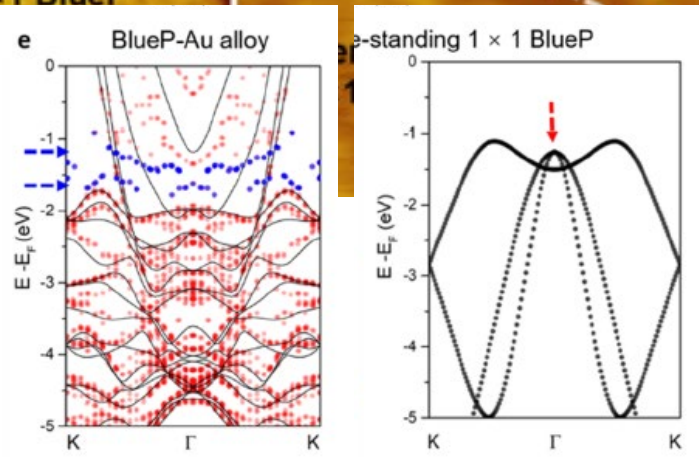
j. L. Zhang et al., ACS Nano 2020, 14, 3687−3695



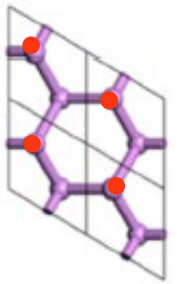
Si deposited on FC P/Au(111) substrate kept @ 250°C

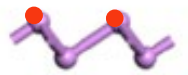
BlueP-Au alloy lower than (1x1) BlueP of ~ 0.05 nm

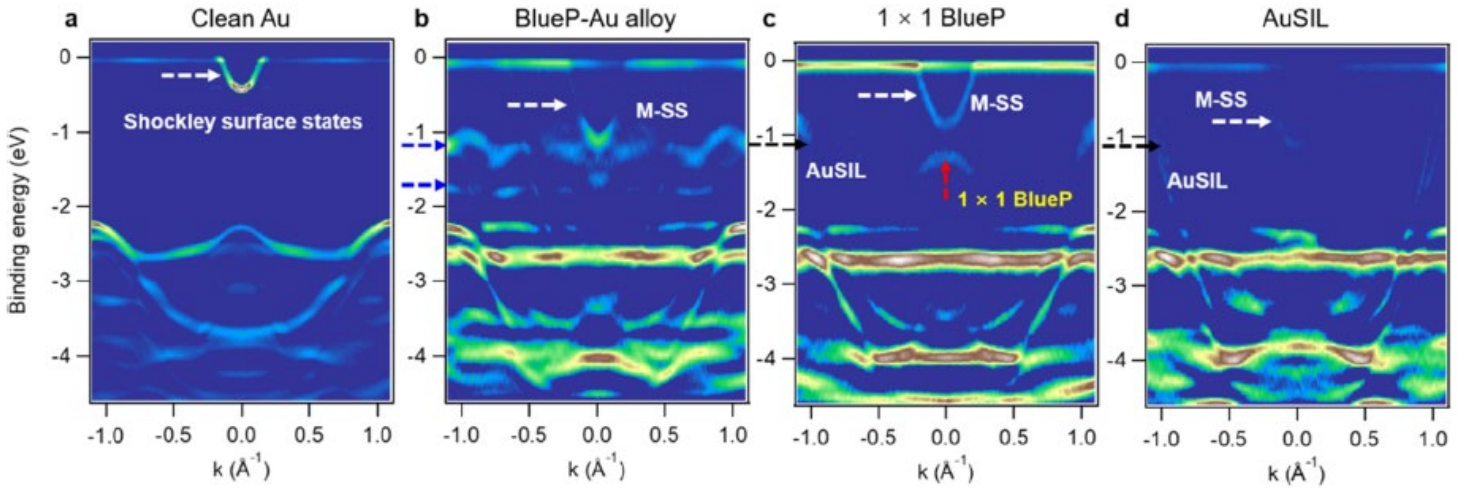
DFT CALCULATIONS



0.33 nm ≈ *a* of FS BlueP network

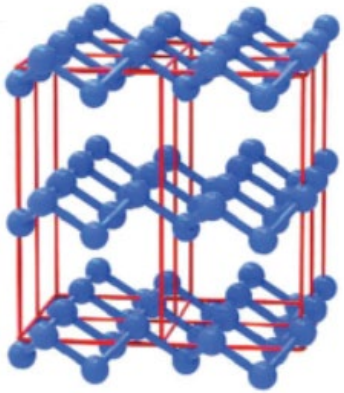






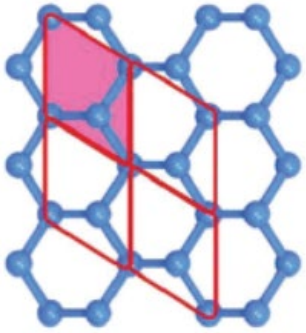
ARPES MEASUREMENTS

FREE-STANDING BISMUTHENE THEORETICAL PREDICTIONS



β phase, group $R\bar{3}m$

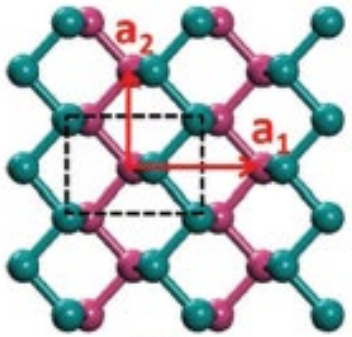
CHARGE INTERACTIONS
INTERLAYER BONDING TYPE



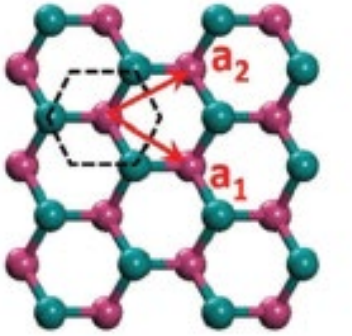
Metal

a_1 = 0.515 nm
a_2 = 0.451 nm
Bi-Bi = 0.310 nm

a = 0.438 nm
Δ = 0.174 nm
Bi-Bi = 0.307 nm



α-VAene



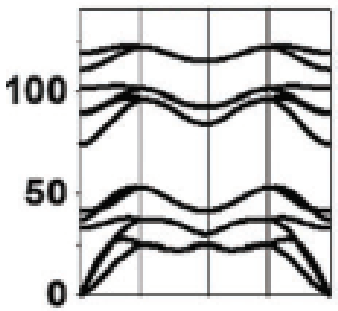
β-VAene

Eg ~ 0.16 eV
(indirect) gap

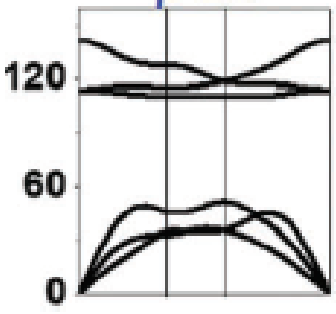
Eg ~ 0.6 eV
(indirect) gap

ENERGETICALLY QUASI – EQUIVALENT PHASES

α–Bi



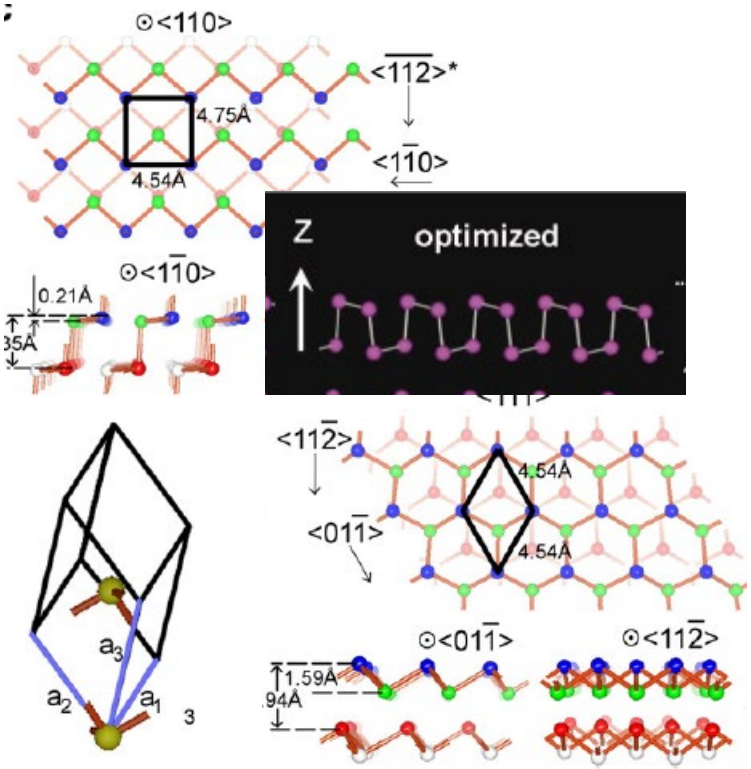
β-Bi



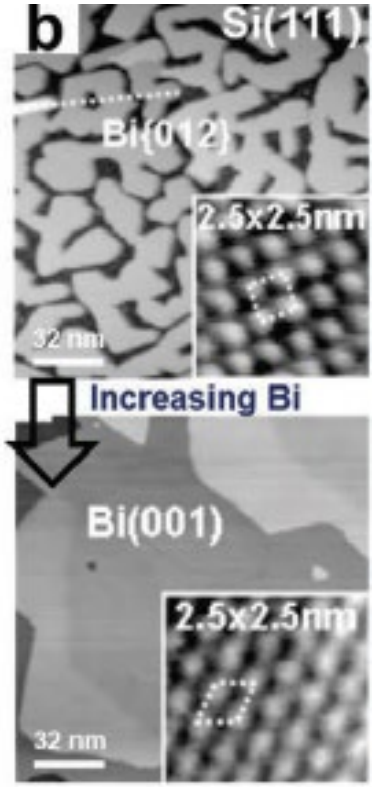
E. Akturk et al., Phys. Rev. B 94, 014115 (2016)

BISMUTHENE on Si(111)7X7 RECONSTRUCTED

Bi DEPOSITION @ RT



T. Nagao et al., PRL 93 (2004) 105501



Disordered wetting layer formation @RT, which orders in a $\sqrt{3} \times \sqrt{3}$ phase upon annealing.

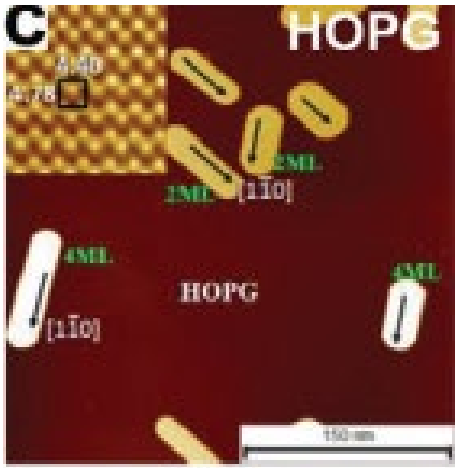
Bi(110) oriented layers grow, stable with an even number of layers: i.e. stable when p_z dangling bonds are filled = Black P-like Bismuthene?

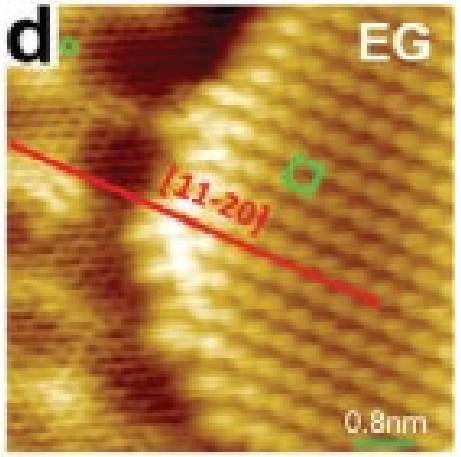
After Bi 4 ML, the BlackP-like Bi structure

BlueP-like Bismuthene

2 ML and 4 ML Bi short ribbons or flat island formation also observed for HOPG and Gr/SiC(0001) substrate, evidence of BlackP-like network with no Bi intercalation evidence.

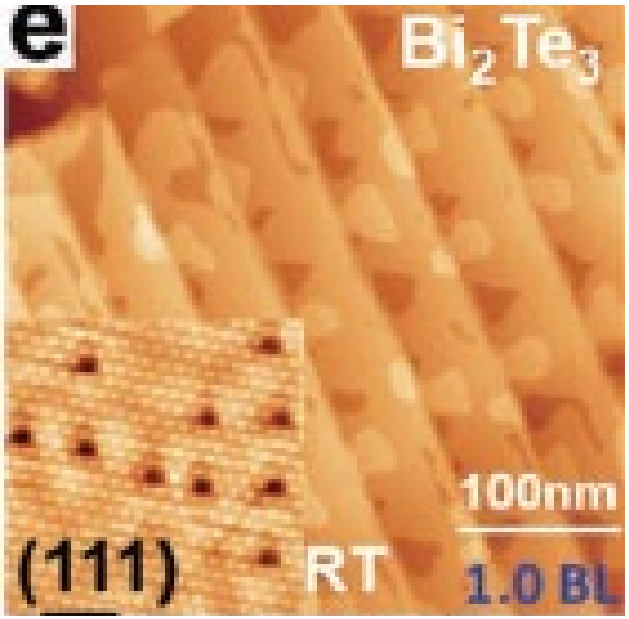
Y. Lu et al., Nano Lett. 2015, *15*, 80.
H. Huang et al., *J. Phys. Chem. C* 2014, *118*, 24995.

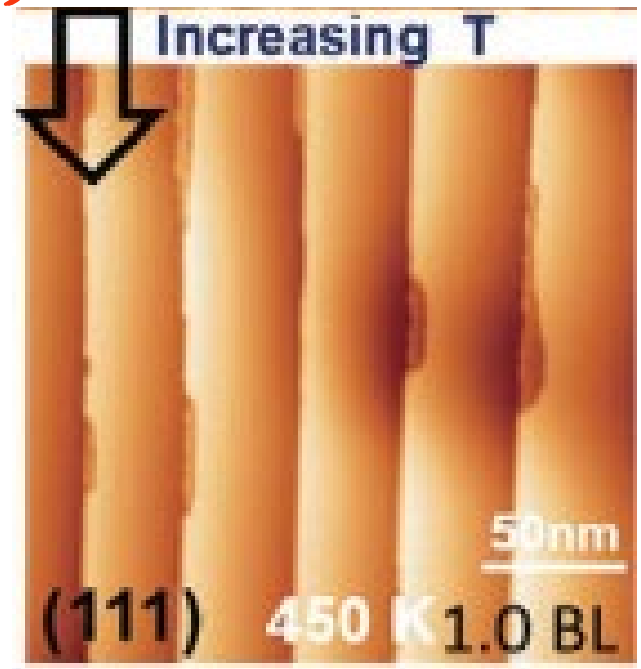




BISMUTHENE on Bi_2Te_3

RT DEPOSITION FAVORS BLUE-P-like Bi





M. Chen et al., Appl. Phys. Lett. 2012, 101, 081603.

At higher substrate T, higher surface mobility and longer diffusion length of Bi atoms which expand all over the TI terraces

Sharp interfaces ! vdW substrate!!!

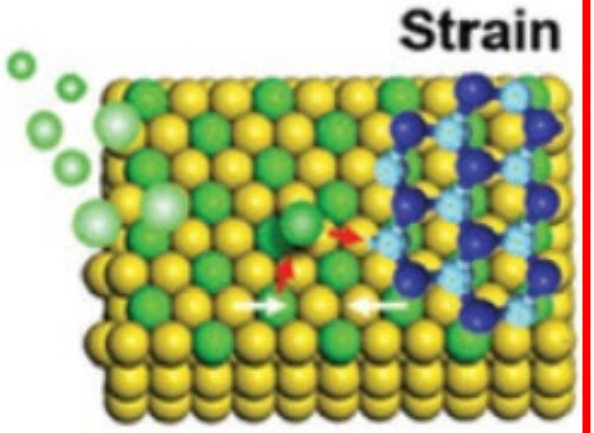
However in some cases (e.g. $NbSe_2$) behaviour is like Si(111) and graphene

F. Yang et al., Phy. Rev. Lett. 2012, 109, 016801.

On Au, Ag and Cu substrate

- No alloy on Au → after 60 ML BlueP-like network
- On Ag and Cu, complex alloying-dealloying process depending on the coverage

Beyond a certain coverage, strain on the alloy induced by the substrate produces a Bi segregation on the surface



To Summerize
It is not easy to obtain X-ene epitaxial growth

- ✓ CHOOSE of a SUITABLE SUBSTRATE CRYSTAL SURFACE NETWORK and LATTICE MISFIT

- ✓ THE ATOMIC PROPERTIES OF THE SUBSTRATE
  - ➢ IS IT PRONE TO STRONG INTERACTIONS WITH THE OVERLAYER?
    - ❑ Change in the (expected) physical properties of the X-ene
    - ❑ Restriction in obtaining surface aggregation of atoms
  - ➢ OR ARE THE INTERACTION TOO WEAK?
    - ❑ Generation of three-dimensional islands

NEW MATERIALS with UNUSUAL ELECTRONIC PROPERTIES

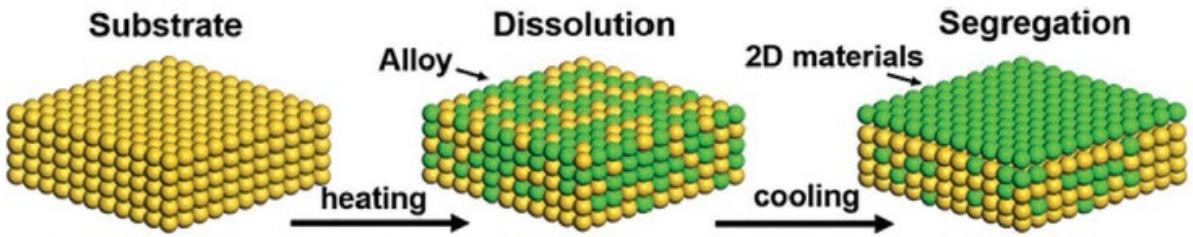
- ✓ THE PHASE DIAGRAM OF THE SUBSTRATE AND OVERLAYER ATOMIC ELEMENTS
  - ❑ $\frac{\Delta a}{a}$ < 15% gives rise to substitutional alloy
  - ❑ The smaller electronegativy difference, the higher solubility

- ✋ the higher surface reactivity than bulk
- ✋ The energy released by absorbed atoms which can be used to overcome energy barrier and interact with surface host atoms

- ✓ THE SURFACE ENERGY OF THE AS-PREPARED MATERIAL WHICH MUST BE LOWER THAN THE SUBSTRATE ONE

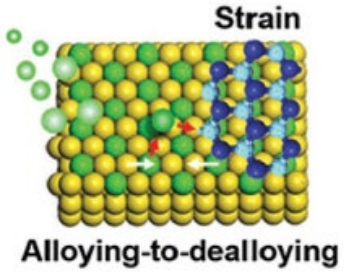
- ✓ DEFECTS AND TERRACE EDGES CAN PLAY A ROLE

ELEMENTS WITH HIGH SOLUBILITY IN THE SUPPORTED SUBSTRATES CAN DIFFUSE DEEPLY TO FORM A BULK-LIKE ALLOY



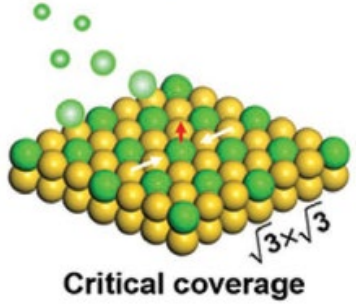
e.g. graphene/Ni, germanene/Ag(111)

ALLOYING-TO-DEALLOYING



e.g. Bi on Cu(111) and Ag(111); stanene on Au(111)

FORMATION of a WELL-DEFINED SURFACE ALLOY



✓ during the growth:
e.g. Bi on Si(111), HOPG and Gr/SiC; C on SiC

✓ through intercalation processes
e.g. H-Gr-SiC; P-Si-Au(111)

THANK YOU FOR YOUR ATTENTION

cnrs GDR CNRS Pulse SORBONNE UNIVERSITÉ insp Im2np LPS ORSAY C2N