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Selective Self-Assembly of Semi-metal Straight and Branched Nanorods on Inert Substrates

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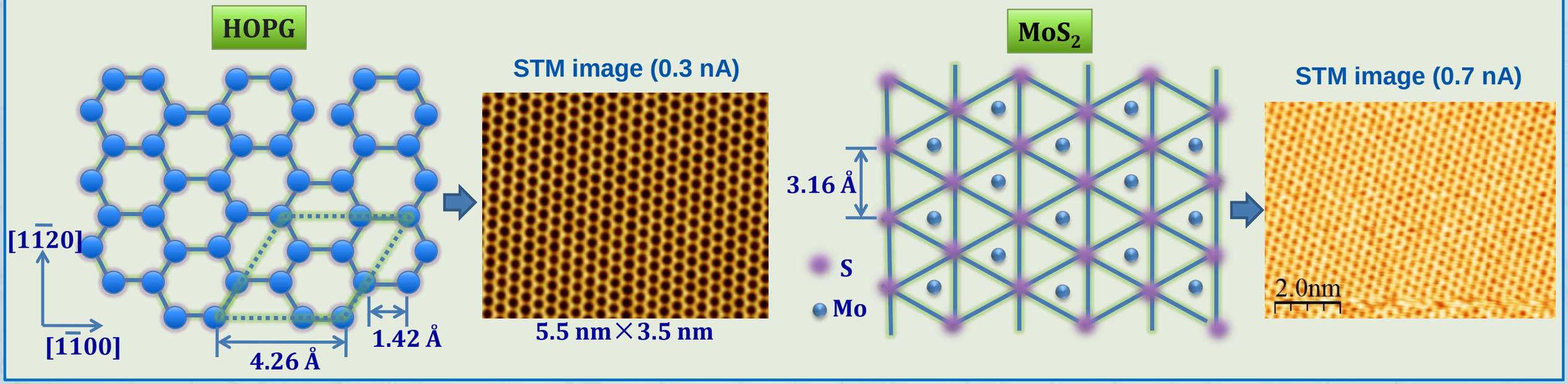
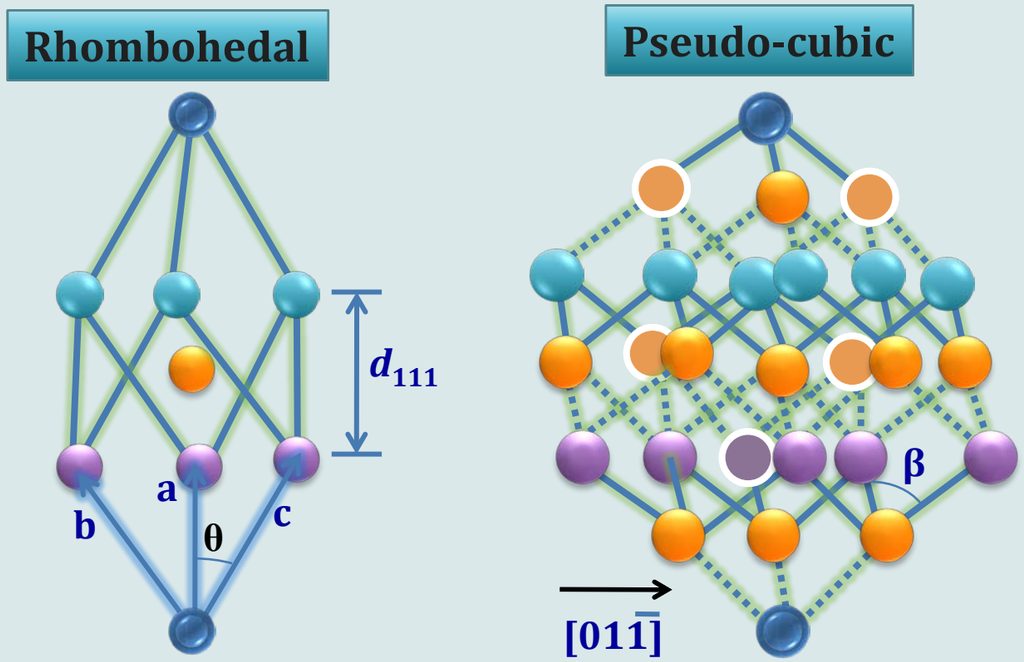
INTRODUCTION

HOPG (Highly Oriented Pyrolytic Graphite) and MoS_2 are layer-structured substrates. Surface energy are 0.16-0.20 J/m^2 and 0.26 J/m^2 respectively.

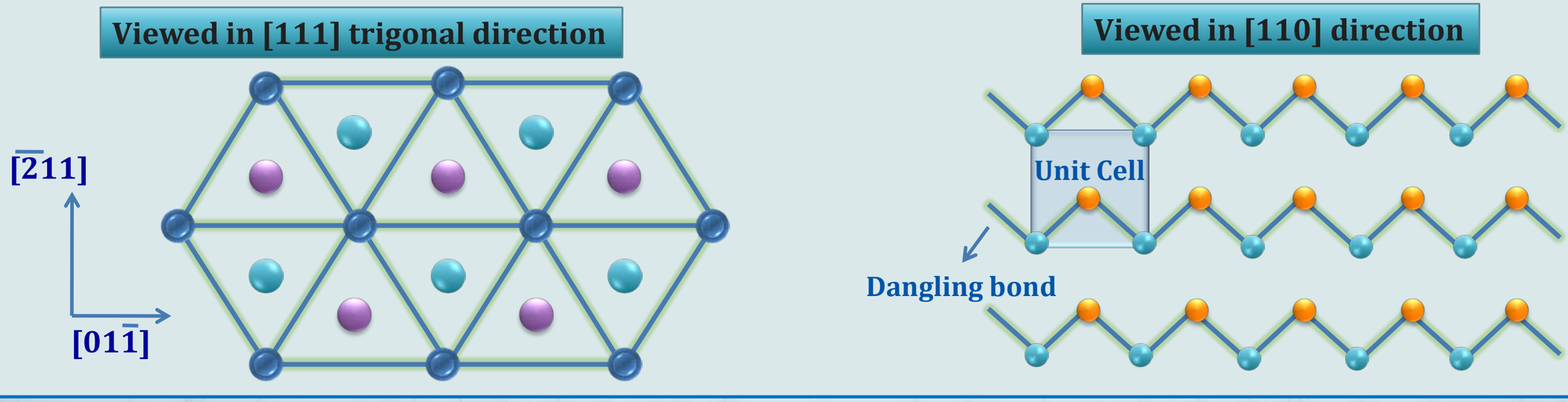


Antimony and bismuth, group-V elements, take Rhombohedral lattice structure with the surface energies 0.5-0.6 J/m^2.

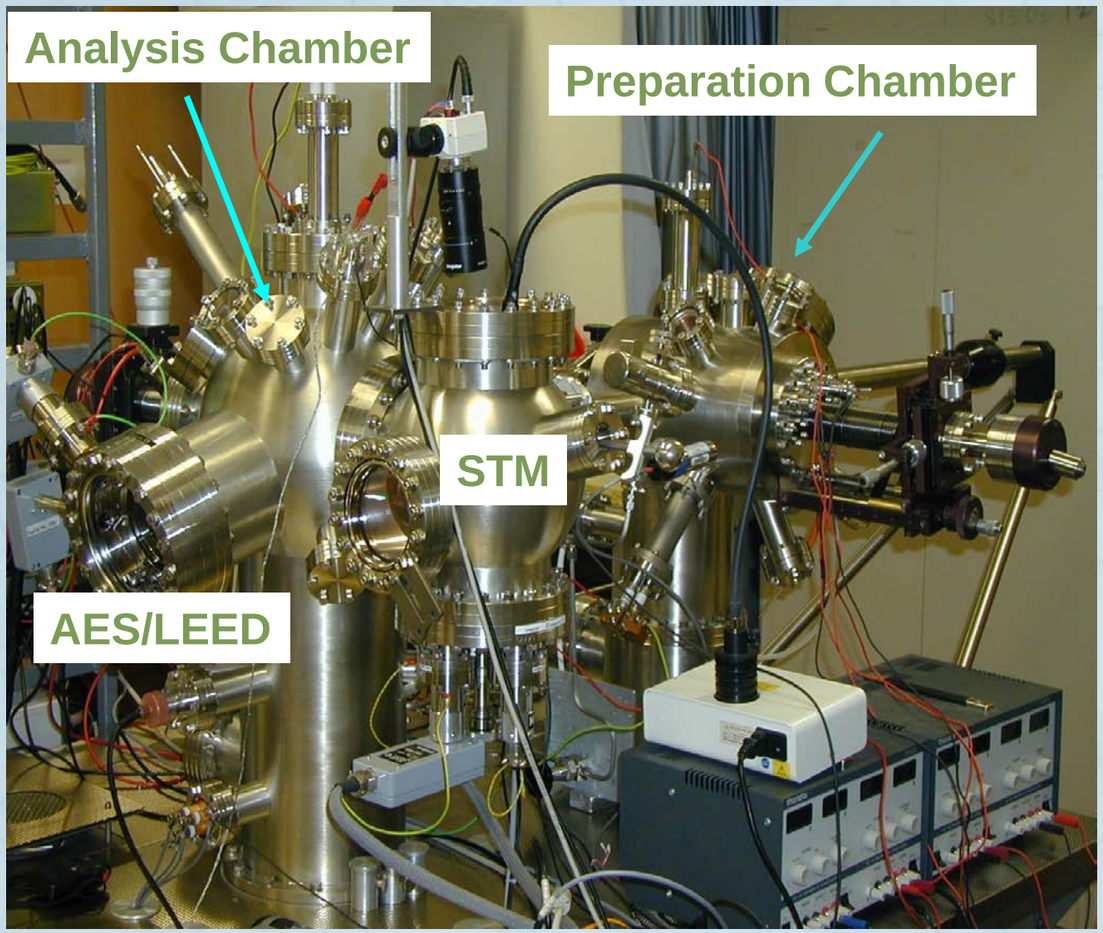


Lattice, surface, and elastic parameters of normal Bi and Sb crystals

Parameters	Bi	Sb
Rhombus base vector angle θ	57.23°	57.1°
Rhombus base vector length	4.75 Å	4.51 Å
Covalent bond angle β	95.5°	95.6°
Covalent bond length	3.065 Å	2.905 Å
Period in (111) plane, a_{111}	4.545 Å	4.31 Å
Period in (110) plane	4.745×4.545 Å	4.54×4.31 Å
(110) Layer spacing	3.28 Å	3.11 Å



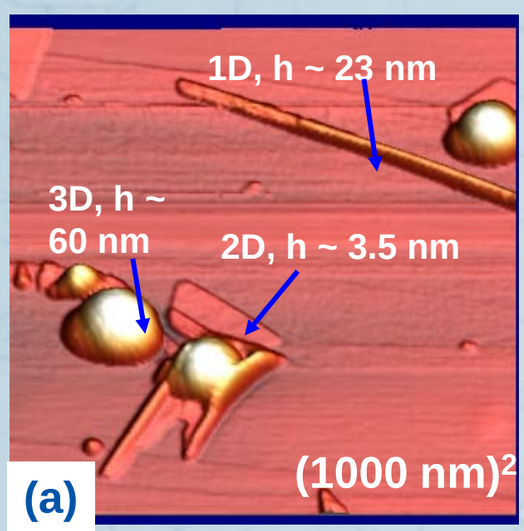
Experimental Facility

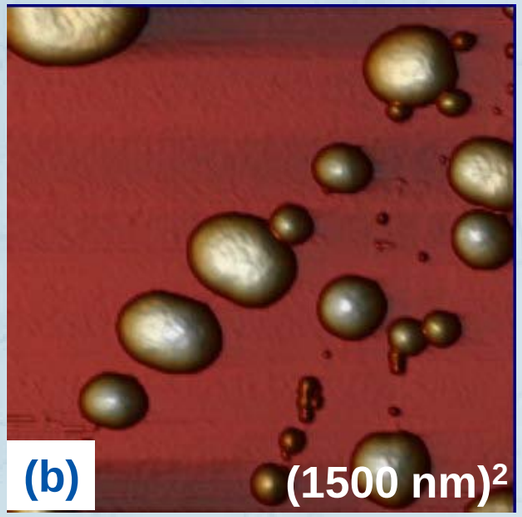


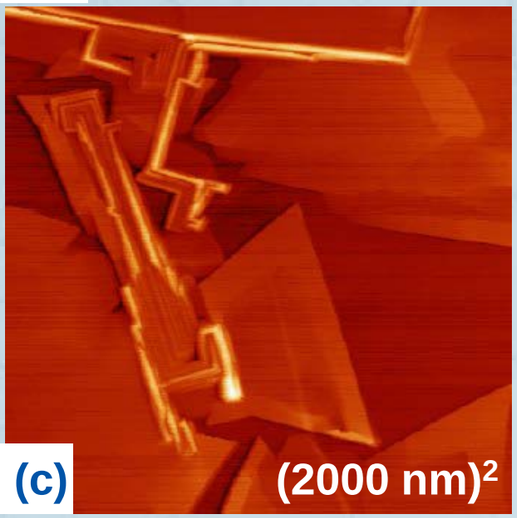
Omicron UHV STM System

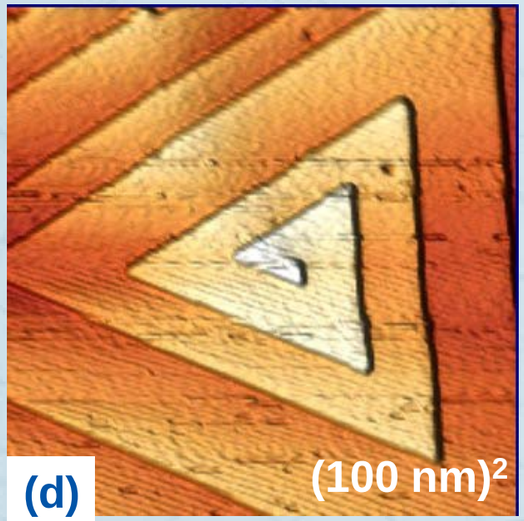
- Base Pressure < 1×10^{-10} mbar;
- HOPG and MoS_2 was cleaved in the air, degassed at 200-500^{o}C for several hours;
- High purity Sb was evaporated in a Ta-boat at 340-380^{o}C range; the flux mostly consisted of Sb_4.
- High purity Bi was evaporated in a Ta-boat at 410^{o}C;
- STM images taken at RT
- Flux calibrated by measuring AES peak ratio and the island volume in STM images;

Sb nano-structures on HOPG



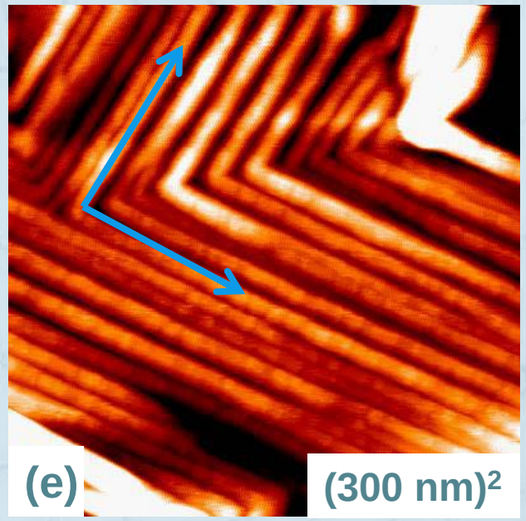


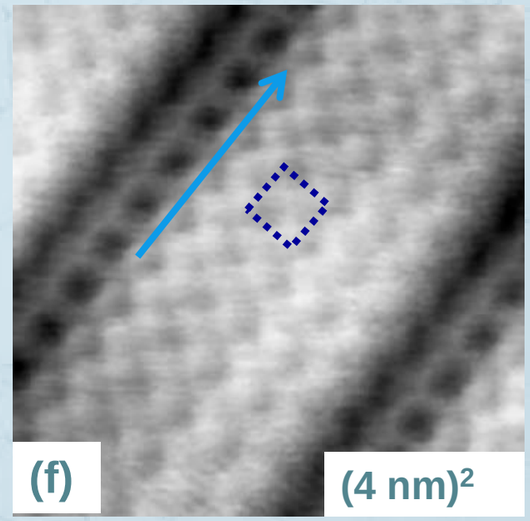


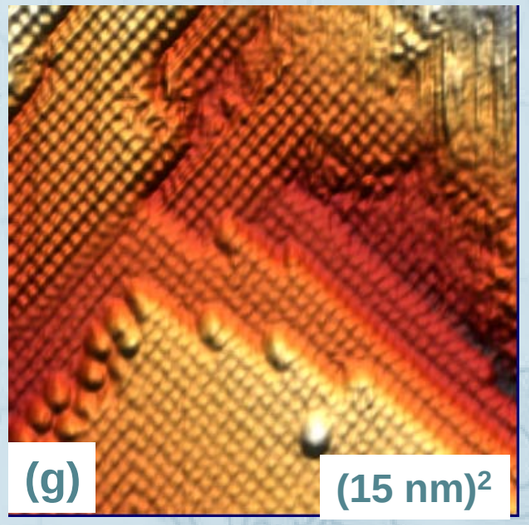


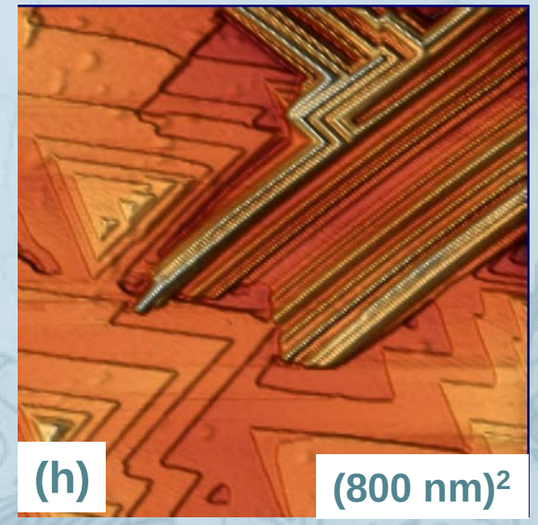
- (a) Three types of Sb structures on HOPG. (moderate flux, RT)
- (b) Only 3D islands observed under lower flux and small amount of deposition, RT.
- (c) Only 2D and 1D structures under higher flux and 100°C substrate temperature.
- (d) 2D island with a screw dislocation and steps running in three equivalent directions.

Sb Nanorods on HOPG and MoS_2









- (e) Nanorods in perpendicular directions on HOPG.
- (f) Atomic structure away from the 90° intersection with a rectangular cell-(3.93±0.06 **Å**)×(4.40±0.06 **Å**).
- (g) Atomic structure at the right-angle intersection showing simple cubic lattice-4.18±0.06 **Å**.
- (h) Sb nanorods and 2D wetting layer grown on MoS_2 at 100°C

Self-assembly and lattice contraction mechanisms of straight Sb nanorods and Bi nanobelts

Surface stress of nanostructures induces additional large **Laplace pressure** (ΔP), which is inversely proportional to a characteristic size of an object.

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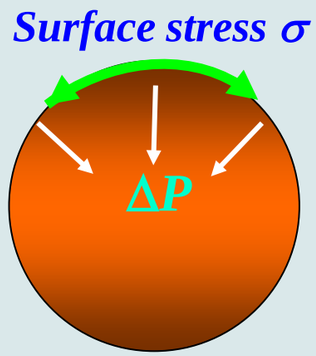
For sphere of radius r, Laplace pressure:



$\Delta P = 2\sigma/r$, *where* σ *is surface stress*

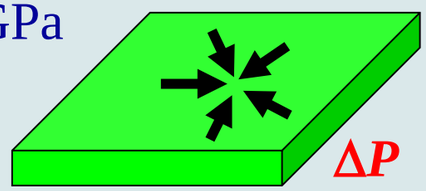
For $\sigma \sim 1$ N/m, $r \sim 1$ nm, $\Delta P \sim 2$ GPa

Nanostructures can be in a strongly compressive state intrinsically, especially in nucleation stage.

In-plane pressure in Sb or Bi 2D wetting layer

(Free-standing, thickness t) $\Delta P \sim 2\sigma/t$

For $\sigma \sim 1$ N/m, $t \sim 1$-2 nm, $\Delta P \sim$ GPa



Mostly σ ~ 1N/m for low index metal surfaces

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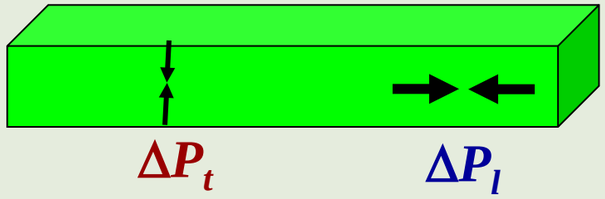
Laplace pressure in Sb and Bi NWs

Pressure along axis: $\Delta P_l = 4\sigma/d$

Transverse pressure: $\Delta P_t = 2\sigma/d$

Length *L* >> *width d*



Taking account of the Poisson ratio $v \approx 0.28$ for Sb and treating the NWs as a homogenous isotropic linear elastic object, the strains are:

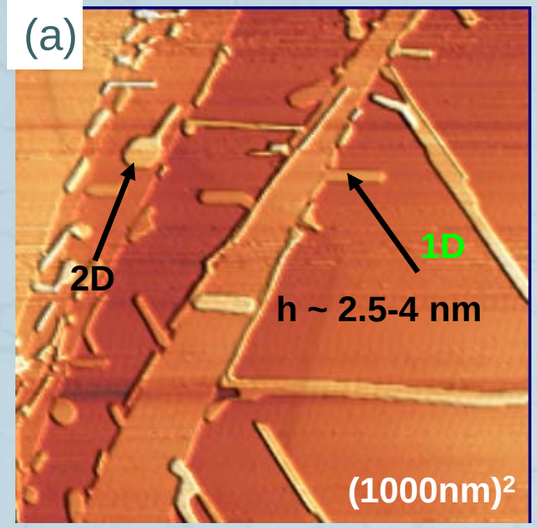
$$\varepsilon_t = -[(1- v)\Delta P_t - v\,\Delta P_t]/Y \approx -0.3\sigma/(Yd)$$

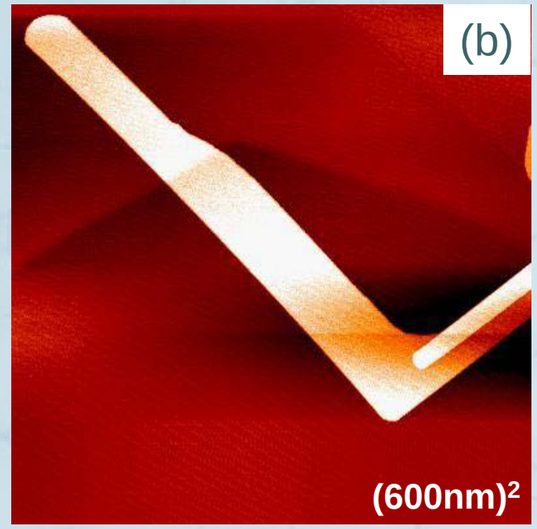
$$\varepsilon_l = -[\Delta P_l - 2v\,\Delta P_t]/Y \approx -2.9\sigma/(Yd)$$

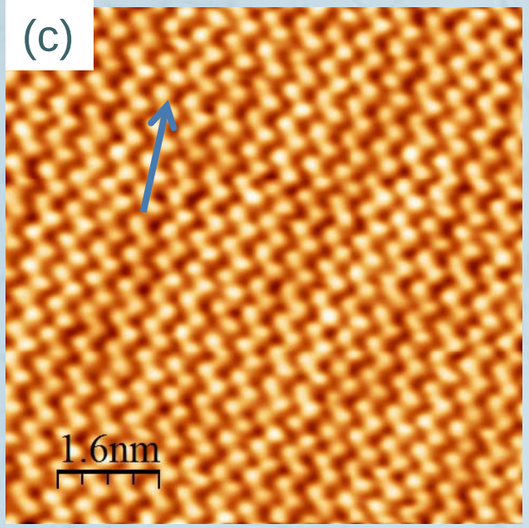
For Bi nanobelts, the Poisson ratio and Young's modulus are 0.33 and 34 GPa. For a 1 nm thick nanobelts, the contractive strain are:

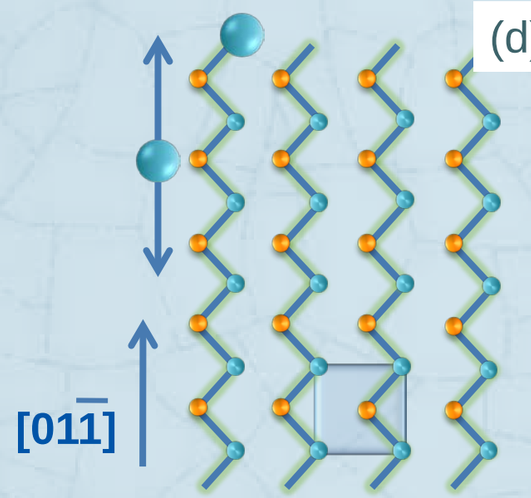
Along the axis: 3.8%; transverse strain: 0

Bi Nanobelts on HOPG and MoS_2





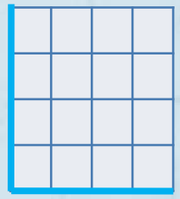




- (a) Bismuth nanobelts and 2D islands on MoS2(0001)
- (b) A 90°-branched Bi nanobelt grow on HOPG at RT
- (c) Zoom-in STM image taken on the (110) surface of a Bi belt with axis along the arrow
- (d) Schematic atomic bonding on Bi(110) showing the rectangular surface unit cell, dangling bonds at the nanobelt ends and fast migration direction of deposited atoms.

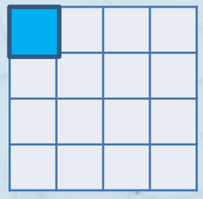
Nucleation and growth of straight nanorods or nanobelts

Simple Cubic Phase

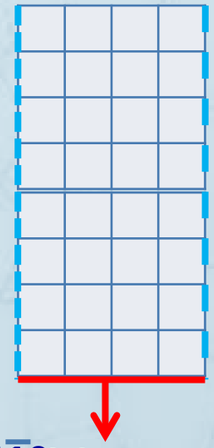


$\{100\}_{SC}$ facets (equal to $\{110\}_{RHL}$) has a low surface energy for Sb and Bi

Laplace Pressure decrease

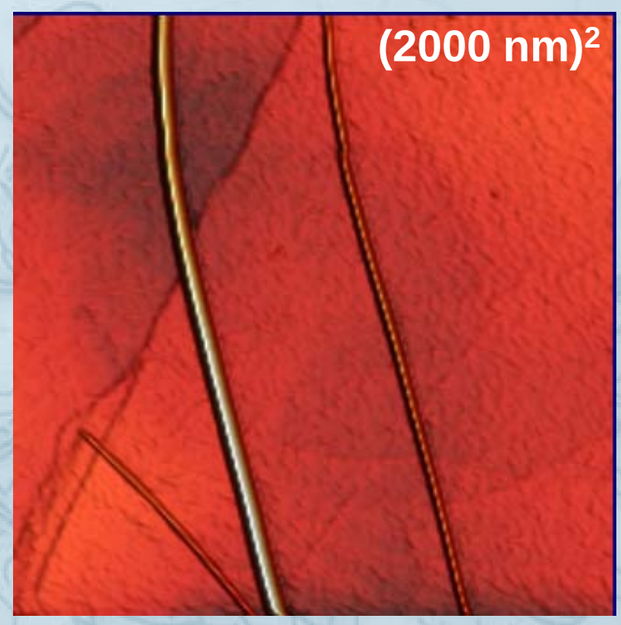


Relax towards RHL lattice



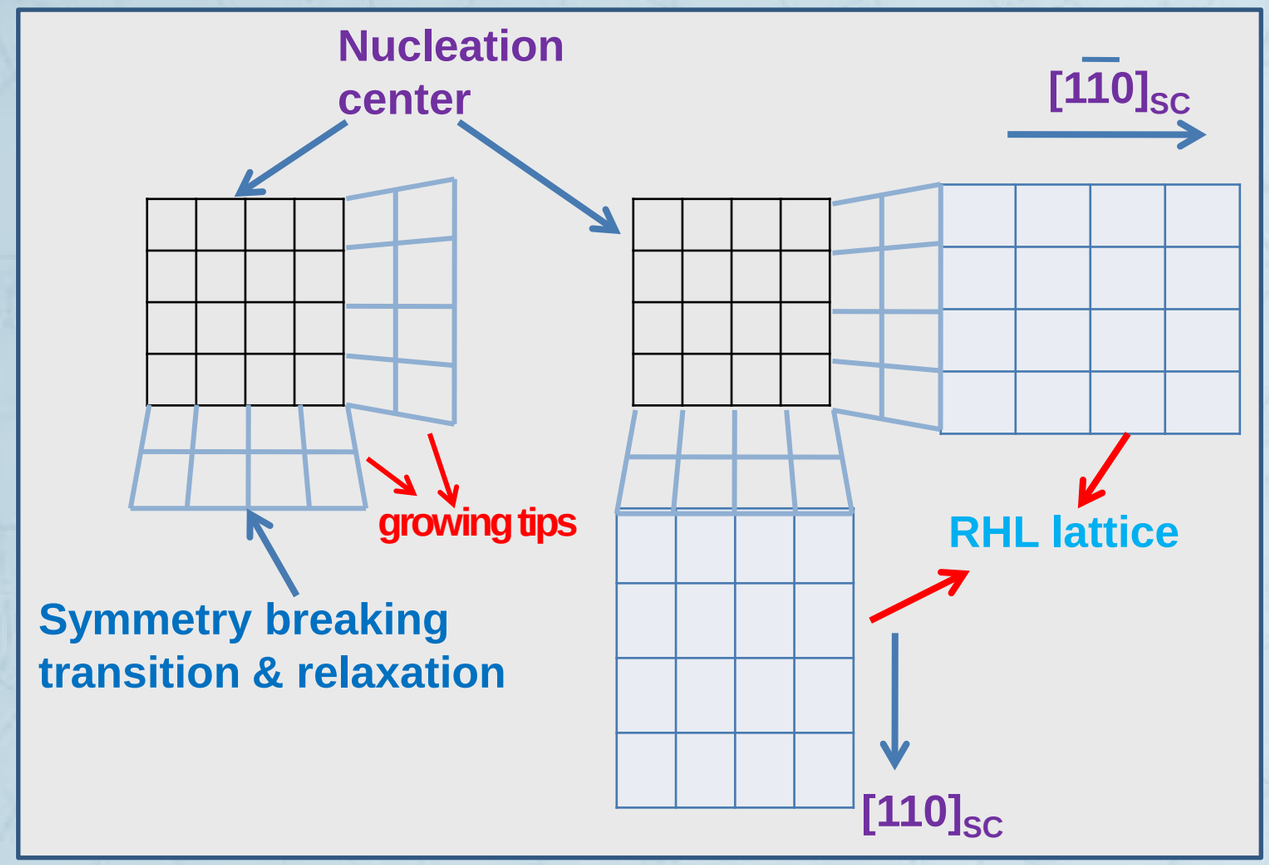
$\{1\bar{1}0\}$ facets with dangling bonds

Highly anisotropic growth kinetics results in straight rods

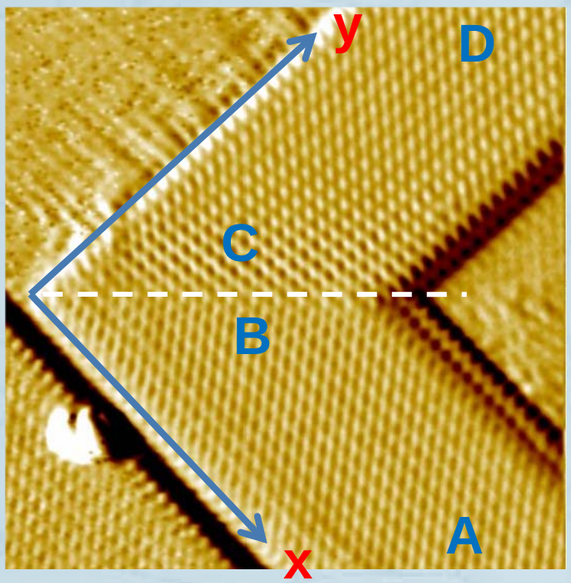


STM image shows dominance of nanorod growth after 1.5 nm Sb deposited with a flux of 3 Å/min on HOPG at 100°C

Nucleation and growth of branched nanorods or nanobelts

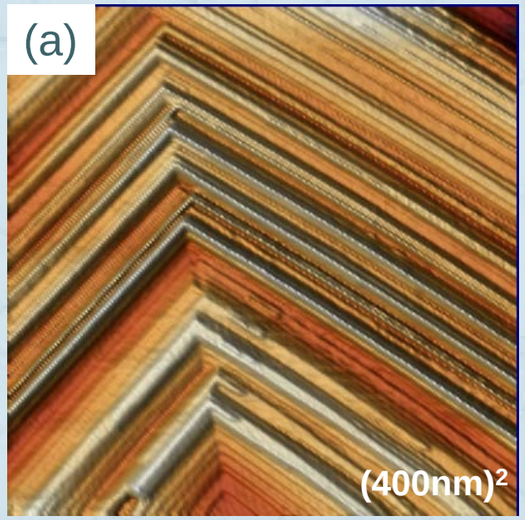


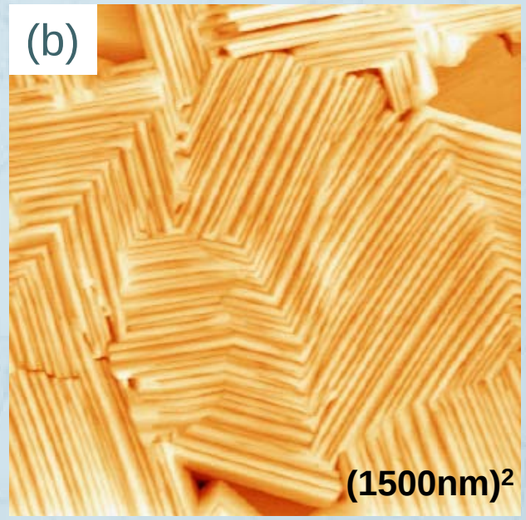
Lattice transition in branched Bi nanobelts

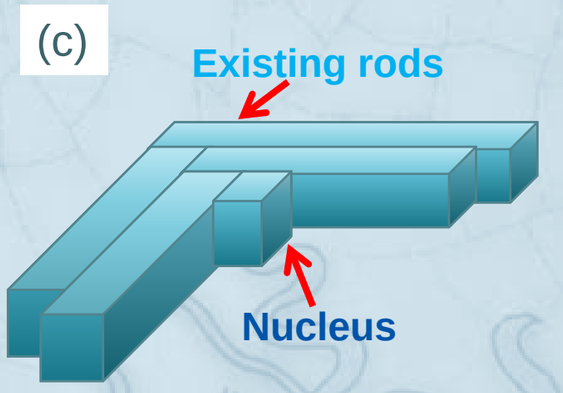


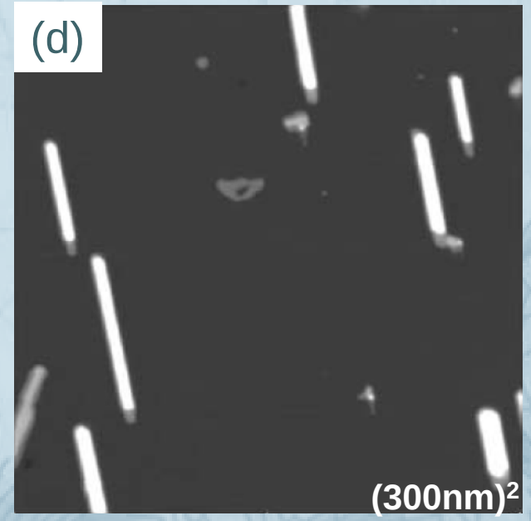
Along x direction			
A	B	C	D
4.47 Å	4.49 Å	4.73 Å	4.88 Å
Along y direction			
A	B	C	D
4.85 Å	4.76 Å	4.47 Å	4.34 Å

Controlling the type and alignment of nanorods and nanobelts









- (a) and (b): 12-nm Sb deposited on $MoS_2(0001)$ with a low flux and RT to retard the SC-to-RHL transition, leaving more time for the tip formation on a few facets.
- (c) Schematic diagram showing the trapping of a nucleus by existing branched nanorods to form aligned bundles of nanorods or nanobelts.
- (d) Aligned Bi nanobelts self-assembled at RT on the Bi(110) wetting layer (anisotropic surface lattice) formed on Ag(111).

Comments on the growth of branched II-VI compound nanorods

- II-VI compound semiconductors, including CdSe, CdS, ZnO and ZnS form bipods, tripods and tetrapods, besides straight rods, in self-assembly processes.
- The growth model of formation of II-VI branched rods is wurtzite-phase (WZ) branches grow on four equivalent {111} facets of a zinc-blende-phase (ZB) core which possesses a higher symmetry than the WZ lattice of the branches, so the ZB-to-WZ phase transition is also a symmetry breaking process.
- The mechanisms of formation of Sb and Bi nanorods and nanobelts can be used to explain and control the self-assembly of II-VI semiconductor straight rods and tetrapods.

Summary

- We demonstrate the self-assembly of Sb rods and Bi belts (including straight and branched) on HOPG and MoS_2 (0001) by vapor deposition in vacuum without using any nano-template, catalyst or surfactant.
- STM images, with careful scale calibration and drift correction, reveal that the Sb nanorods and Bi nanobelts start as compressed highly isotropic SC-phase nuclei.
- In a later growth stage, the nuclei undergo a symmetry-braking phase transition to RHL lattice as strain relaxation occurs, then the highly anisotropic growth yields nanorods or nanobelts.
- The stochastic growth and strain relaxation processes lead to the formation of either straight or branched nanorods.
- At a relatively high temperature with a low deposition flux, straight nanorods grow exclusively, whereas at a low temperature and a high flux, branched nanorods can be dominant.

Reference

1. X.-S. Wang, S.S. Kushvaha, Z. Yang and W. Xiao, Appl. Phys. Lett. 88 (2006) 233105
2. Z. Yan, S.S. Kushvaha, W. Xiao and X.-S. Wang, Appl. Phys. A 88 (2007) 299.