Different Functional Nanostructures Self-Assembled Selectively on Inert Substrates

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Nanostructural Self-assambly

- Nanostructures form themselves under thermodynamic/kinetic driving forces; parallel processes and no masks needed
- Metastable structures, hopefully with novel properties
- Examples: CNTs, nanowires, quantum dots, nanopatterns…
- The remaining problems: precise control of size, shape, type and location of nanostructures
- Understanding of growth mechanism: effects of kinetics, surfaces, thermodynamics and mechanics

Functional Nanostructural Materials

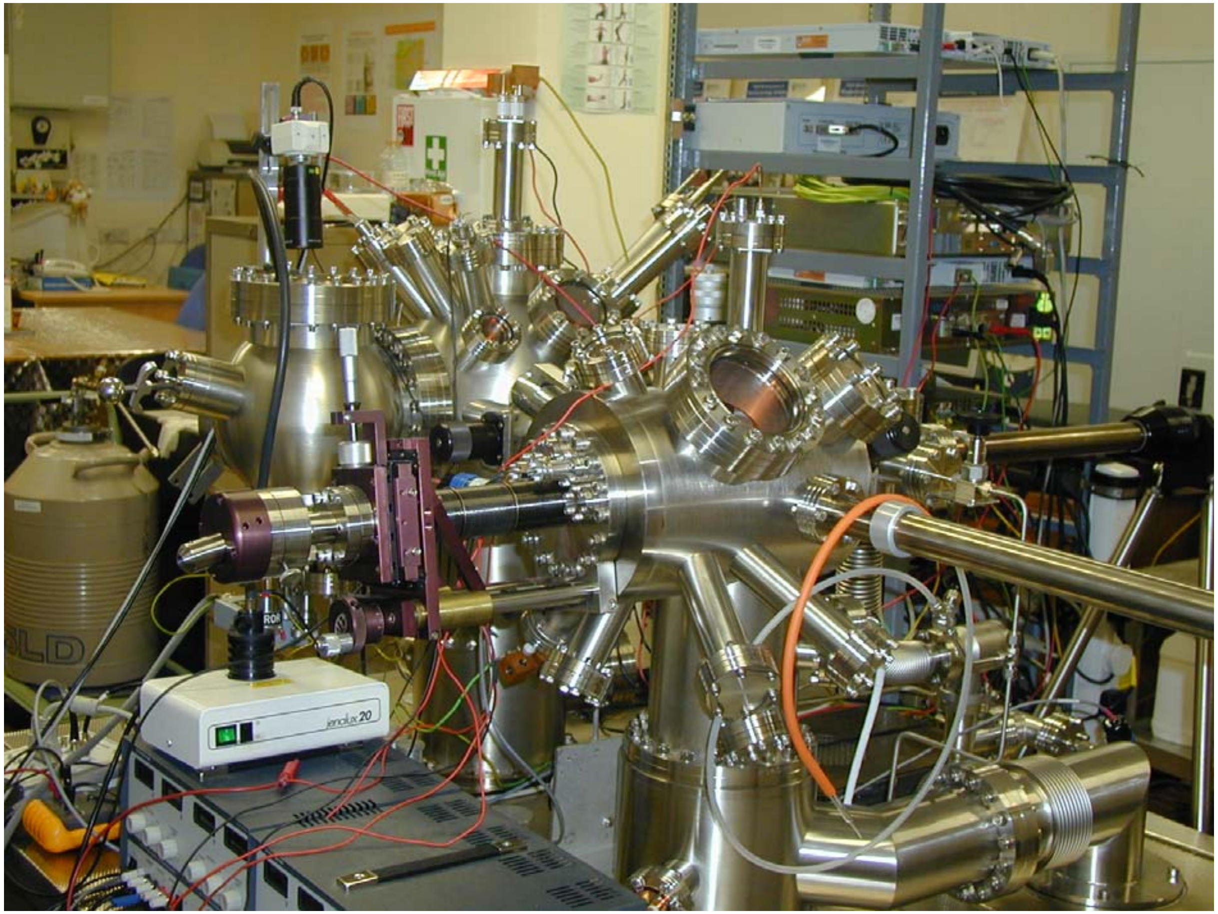
1. Semiconductor quantum dots, nanowires
2. Semimetal (Sb, Bi) nanostructures: thermoelectric
3. Magnetic/spintronic materials: Mn, MnSb,…
4. …

Inert Substrates

- HOPG (highly-oriented pyrolytic graphite): easy-to-prepare inert conductive substrate for growing nearly *free-standing* nanostructures, mostly clusters & compact crystallites, but 1D or quasi-1D nanostructures also form sometimes
- Si-based inert surfaces: dielectric layers (SiO_2, Si_3N_4, HfO_2, $SrTiO_3$) on Si, close to real applications

Experimental Facility

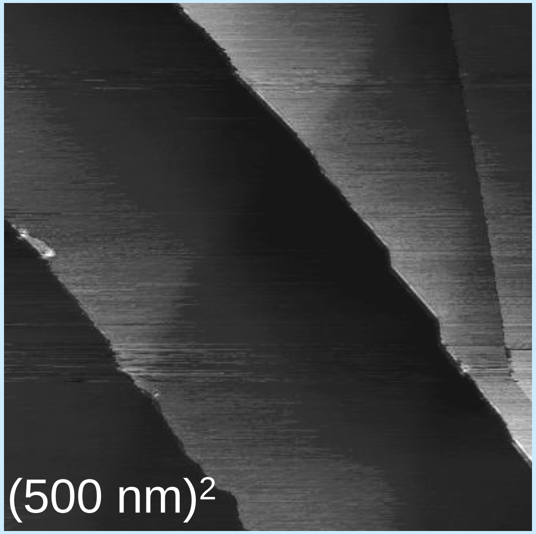
- Sb (mostly Sb_4) Bi, Mn, Al, Ge from thermal evaporators
- STM at RT
- Other ex situ measurement: XPS, AFM, SEM, VSM

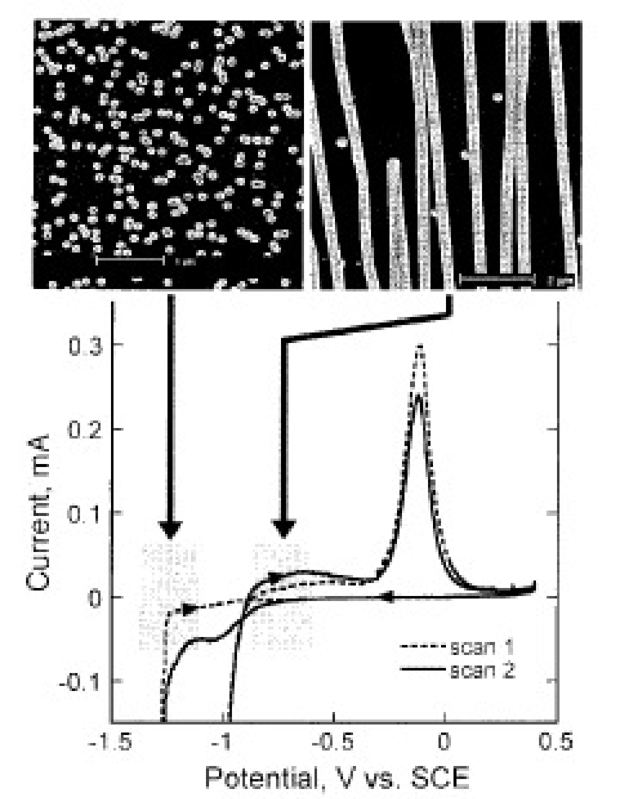


Omicron UHV STM system

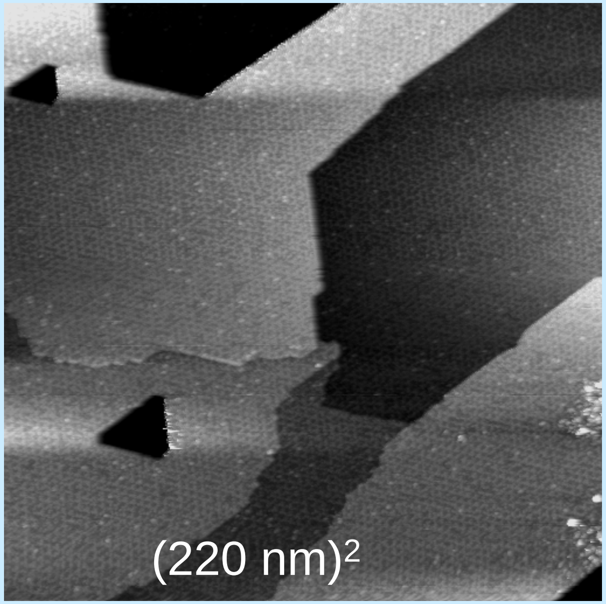
Substrate Preparation

HOPG: Cleave in air, quickly loaded into UHV chamber, degas at ~ 500 °C for hours





Mo particles and wires on HOPG by electrodeposition
(Penner, J. Phys. Chem. B 106 (2002) 3339)

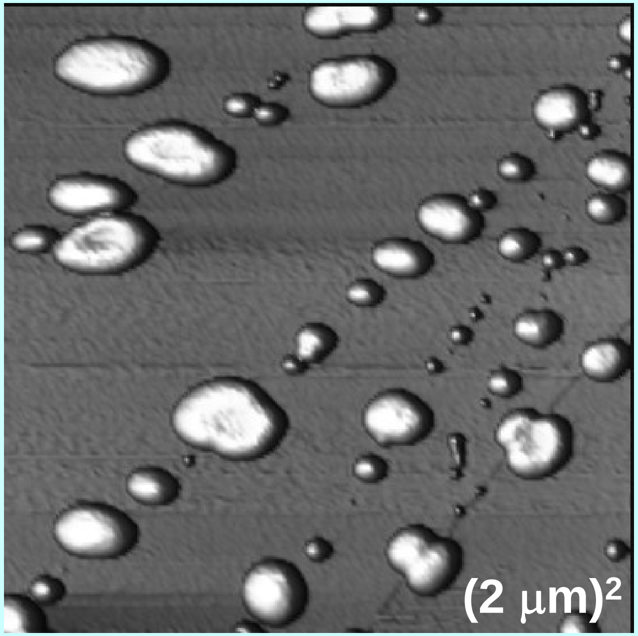


SiN$_x$ on Si(111): obtained by nitridation of Si(111) at ~ 900 °C using NH_3 or NO

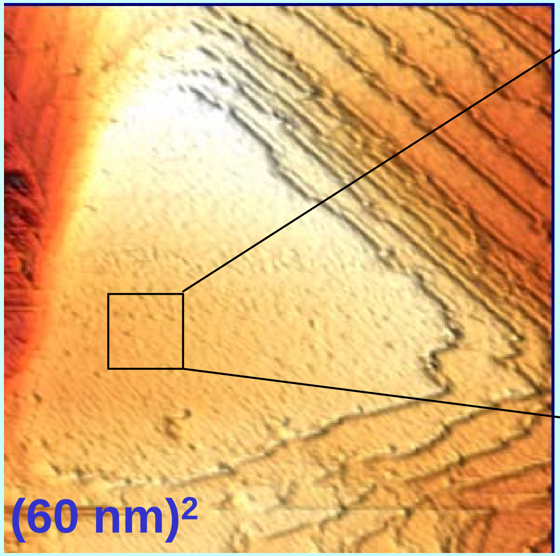
Crystalline SiN$_x$ of thickness 1-2 nm

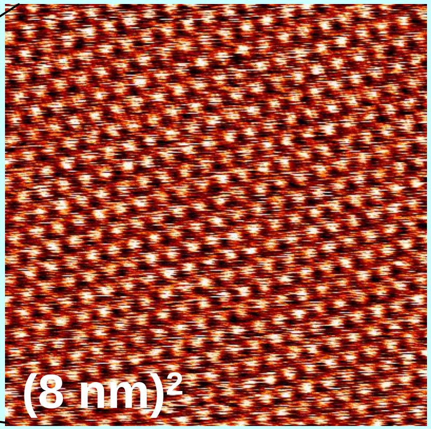
(Wang et al., Surf. Sci. 494 (2001) 83)

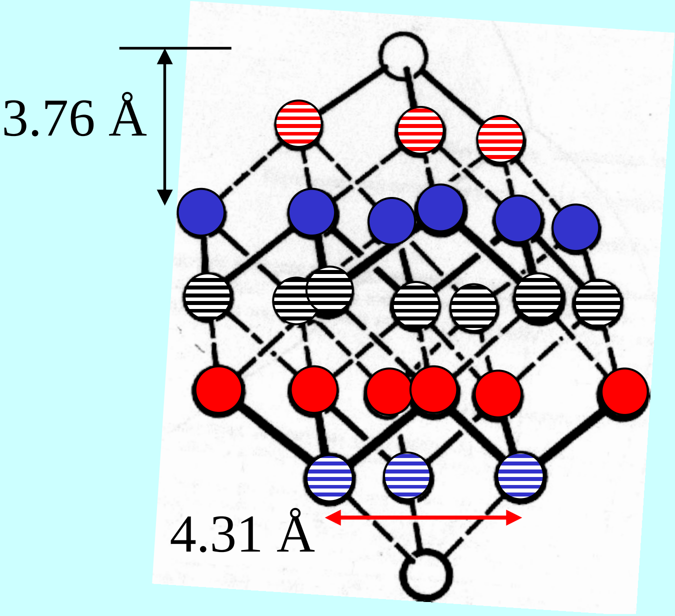
3D Sb Islands on HOPG



- Formed after deposition at RT
- Mostly found along HOPG steps
- Extremely easy coarsening
- Round surface even at large volume
- (111) Facets on top of large islands, hexagonal period 4.24±0.08 Å

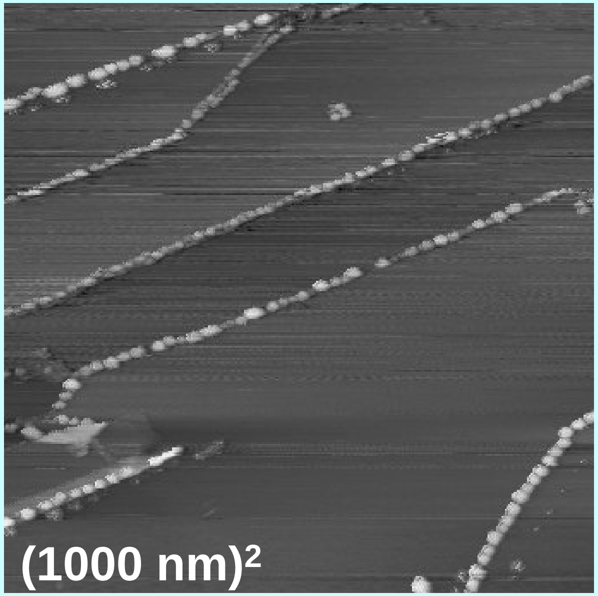






Rhombohedral Sb

Al on HOPG: Clusters → crystallite chains → film

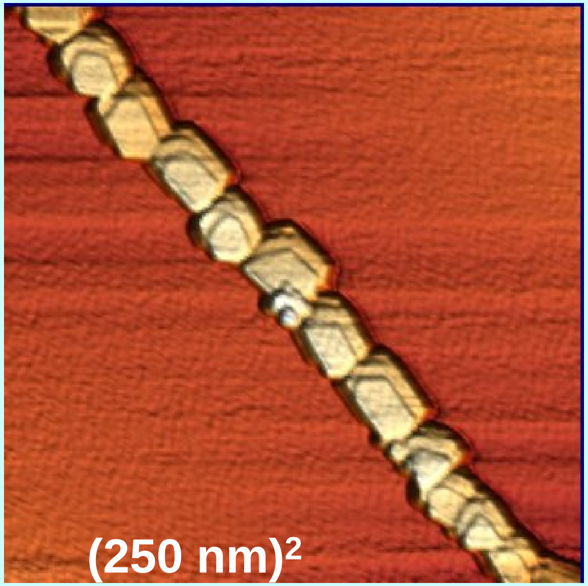


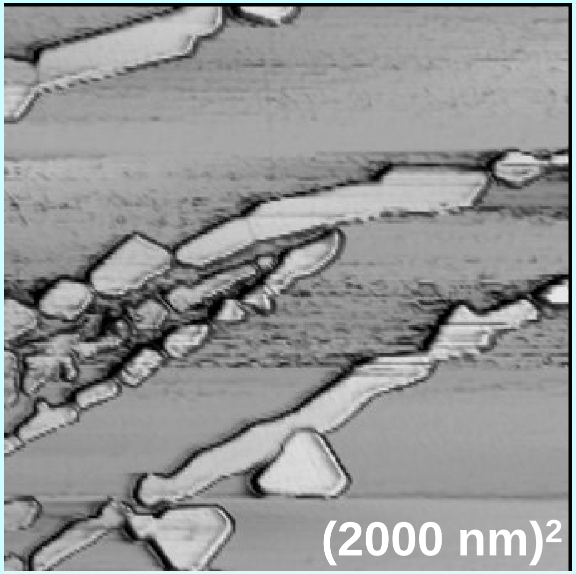
3 Å deposited at RT

Spherical clusters (h ~ 4 - 8 nm) mostly found at HOPG steps

After 8 Å deposition

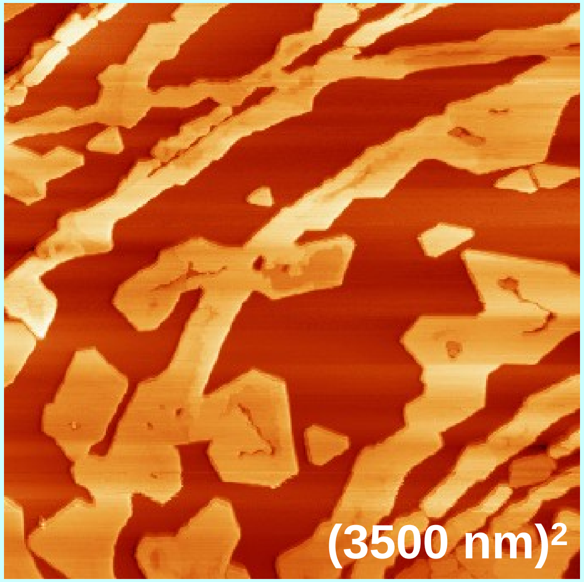
Flat crystallites (h ~ 3 - 5.5 nm)



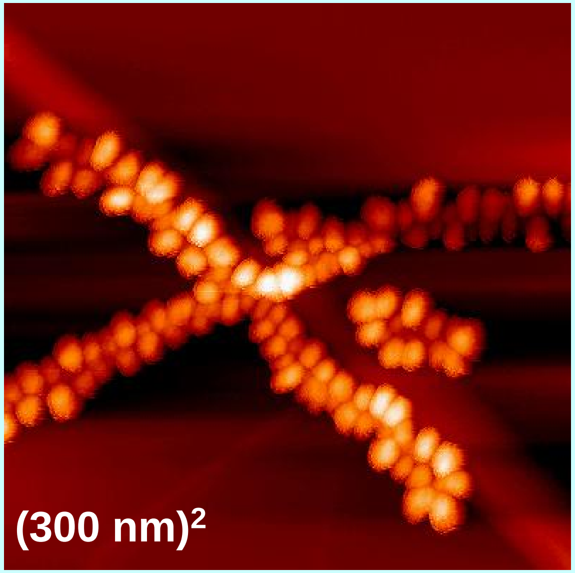


Easy coalescence of Al crystallites

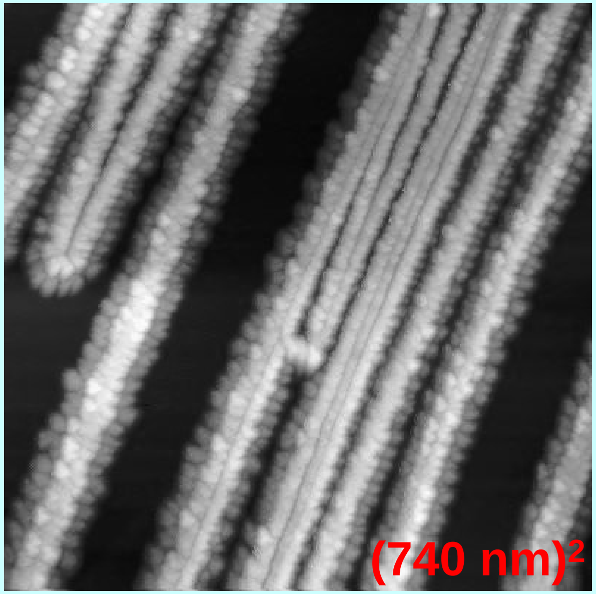
further deposition gradually leads to a continuous film of thickness ≤ 30 nm



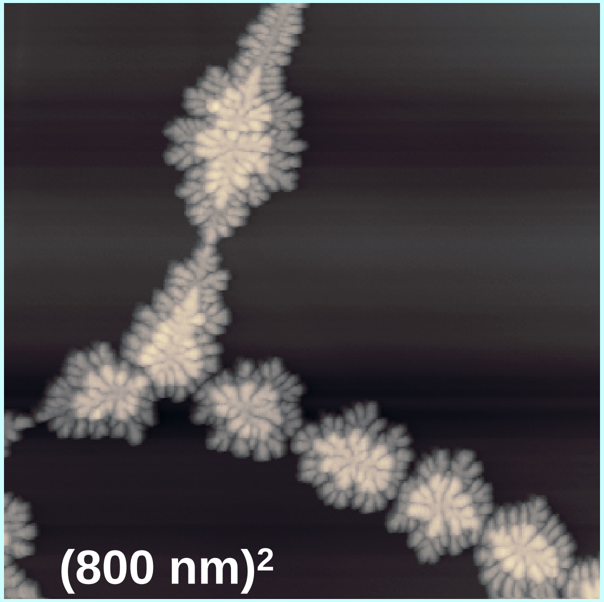
Ge on HOPG: clusters chains & islands



1) Ge cluster at steps and defects, height ~ 9 nm

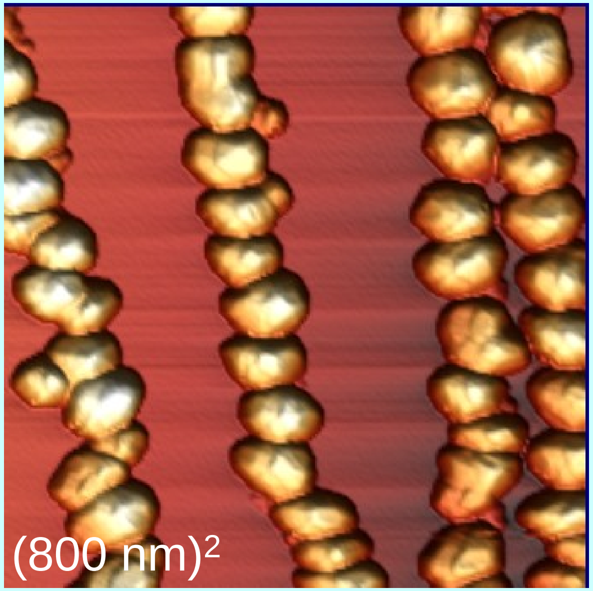


2) Double-layer cluster chains, not necessarily along HOPG steps

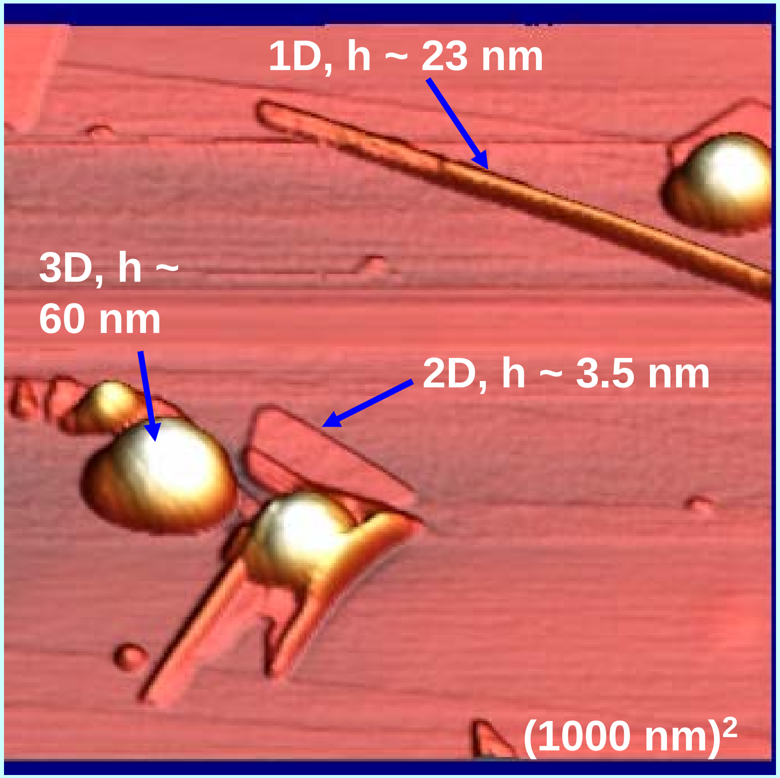


3) Double-layer fractals islands formed at defects & sub-surface steps

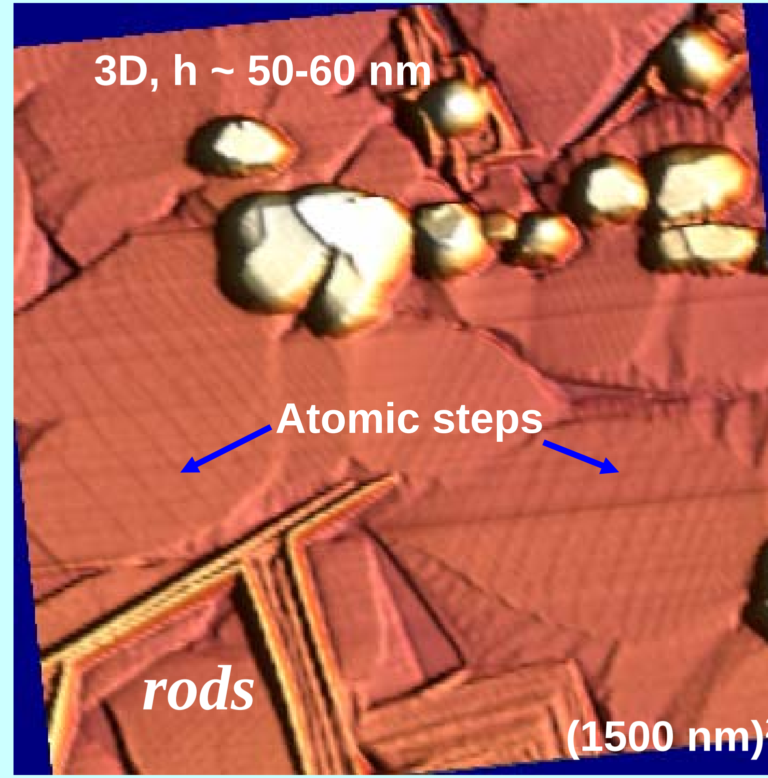
5 nm Ge deposited at 450 K, Crystallites of h ~ 45 nm



2D & 1D Sb Nanostructures on HOPG



Sb_4, F = 4 Å/min, 12 Å deposited at RT. 3D, 2D & 1D islands formed in early stage



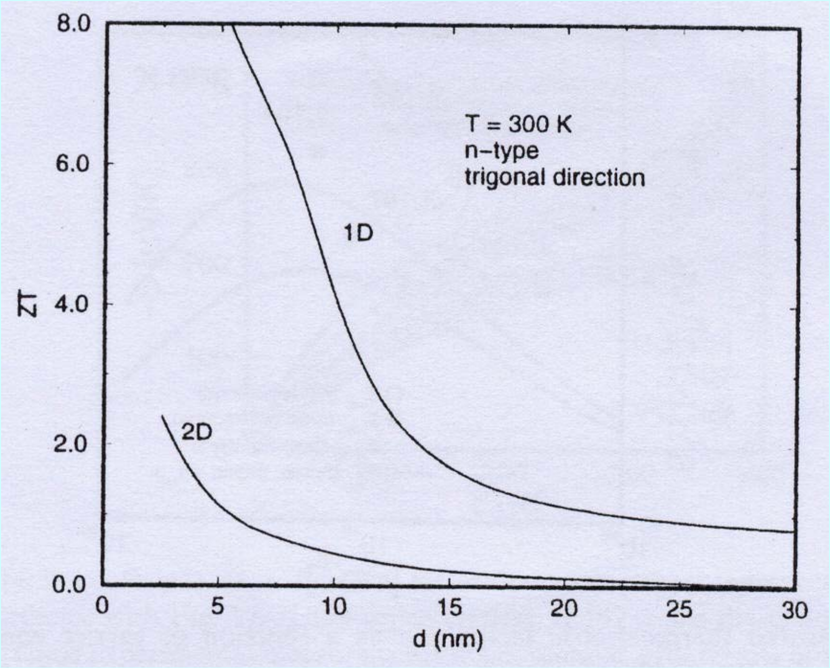
Sb_4, F = 4 Å/min, 100 Å deposited at RT. 3D islands “crystallize”, 2D film grows dominantly in later stage

Semimetal (Sb, Bi) Nanostructures

- **Bulk Sb & Bi:** low carrier density (~ 10^{-5} of metal), low carrier effective mass, high mobility, long electron de Broglie wavelength (~ 40 nm), highly effective phonon scattering by heavy ions

- ***Low-D* Sb & Bi:** easy to show quantum confinement effect, semimetal-to-semiconductor transition

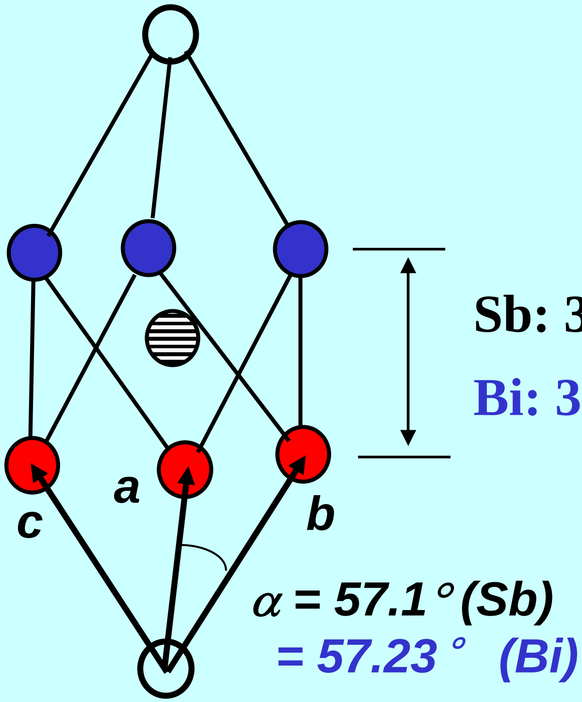
- Thermoelectric application of *low-D* Bi & $Bi_{1-x}Sb_x$: high efficiency thermoelectric materials



Calculated thermoelectric figure of merit *ZT* for low-D Bi

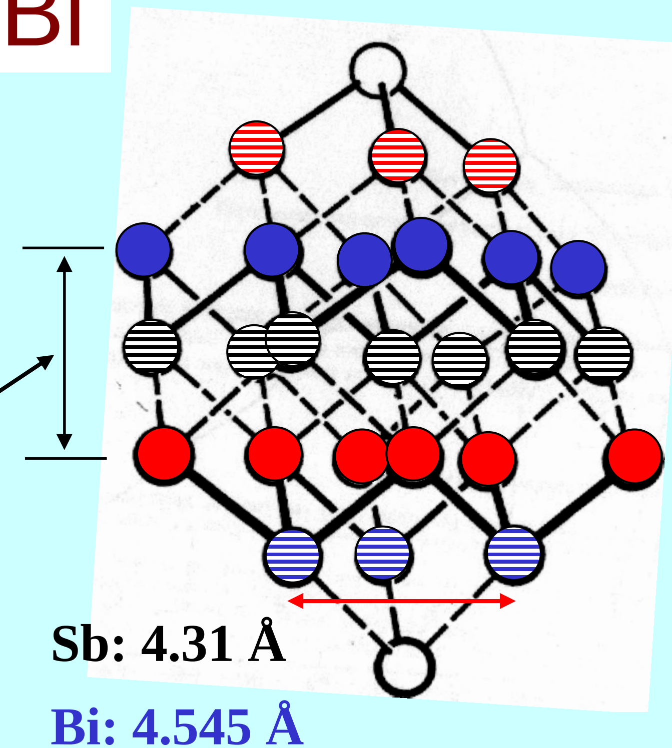
(see: MS Dresselhaus et al, 2001; JP Heremans et al, PRL, 2002; TE Humphrey et al, PRL, 2005)

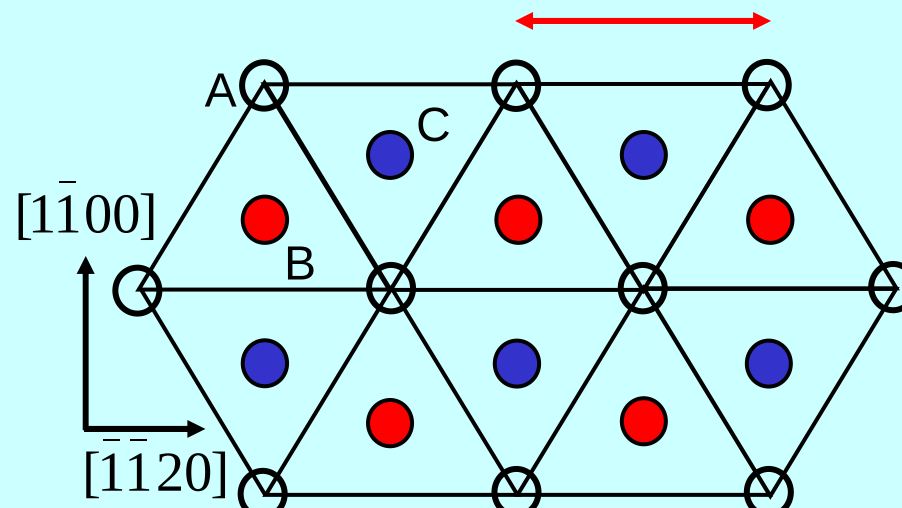
Lattice Structure of Sb & Bi



Sb: 3.76 Å

Bi: 3.95 Å

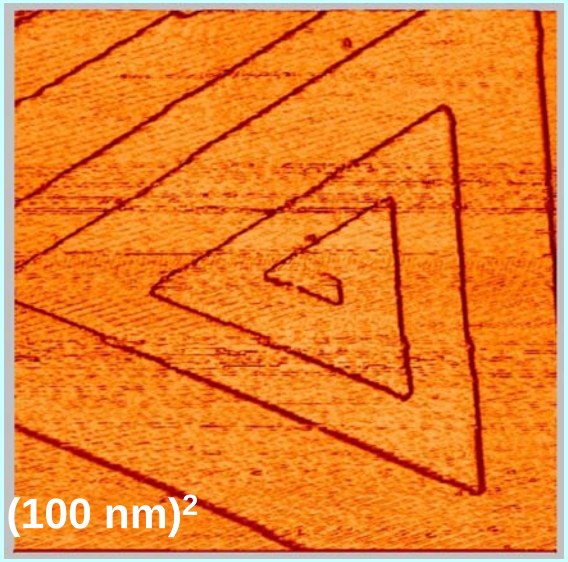


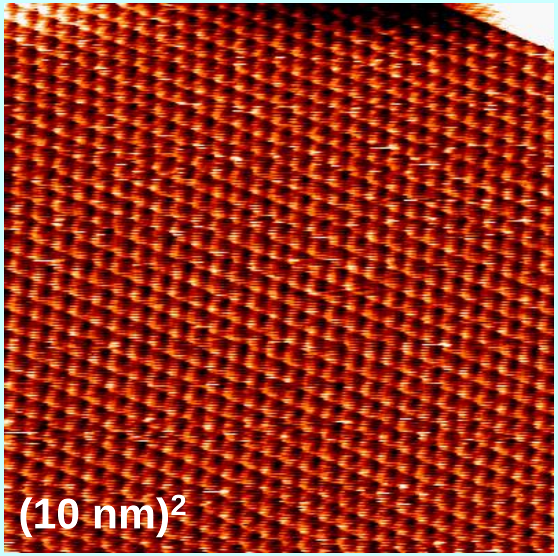


Rhombohedral lattice:

A distorted cubic lattice

Sb wetting film on graphite





Steps straight

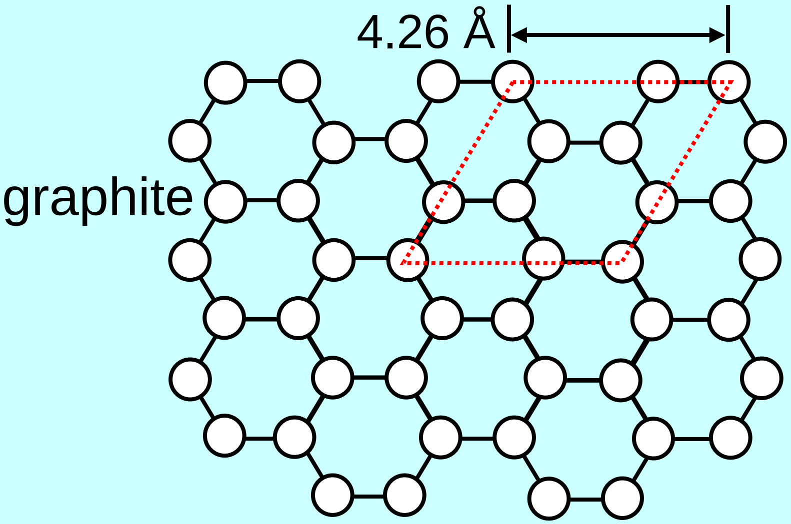
Unit-layer step height:
h = 3.96±0.20 Å

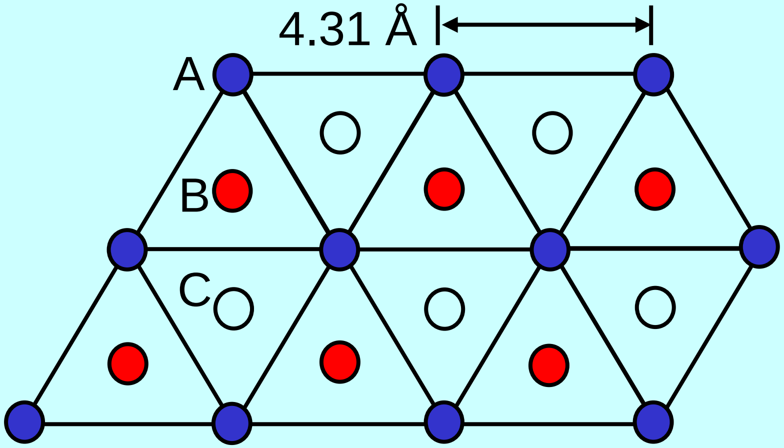
Lateral period:

a = 4.17±0.06 Å

Shrinking film

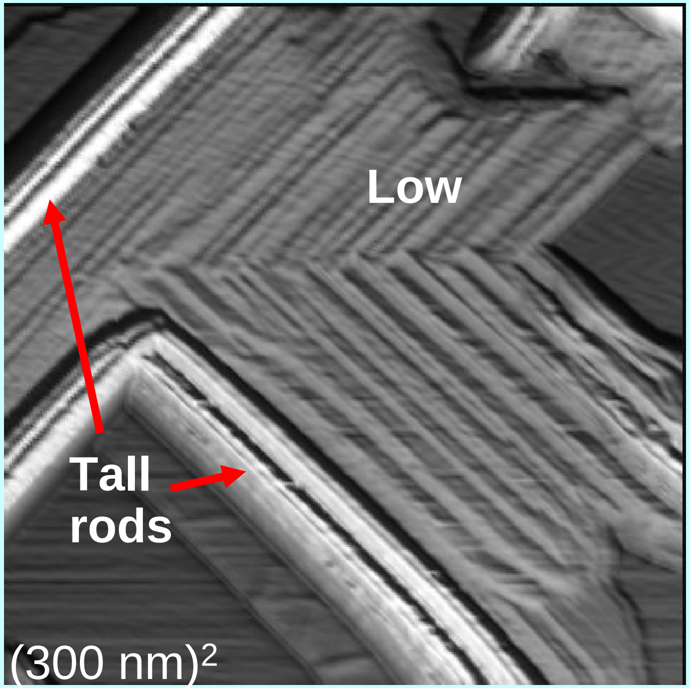
Sb crystalline 2D films wet graphite, but not perfectly epitaxial



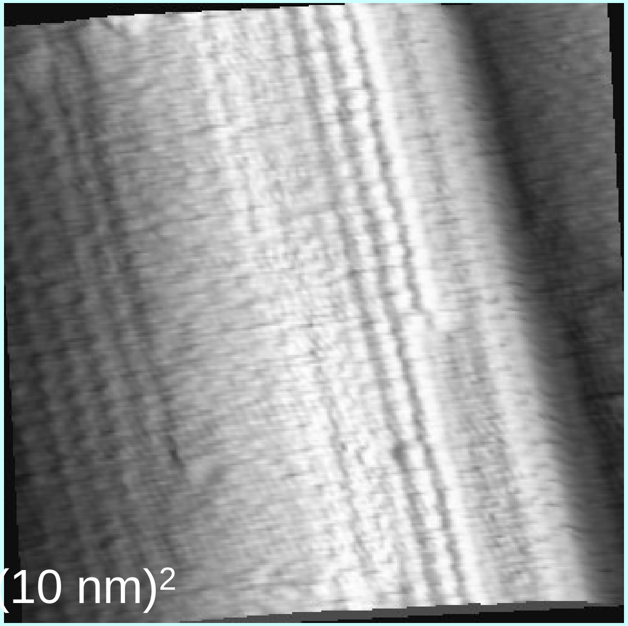


Bulk Sb α-phase (RHL):
layer spacing h = 3.8 Å,
lateral period a = 4.31 Å

Sb Nanowires on HOPG



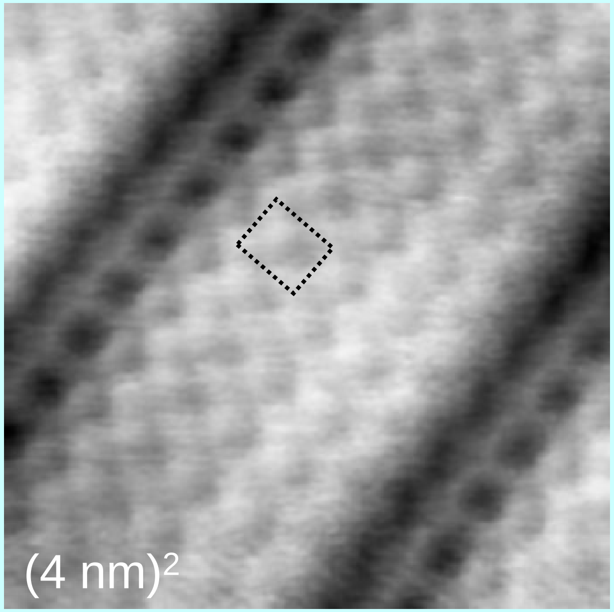
Tall (≥ 20 nm) & Low (≤ 15 nm) NWs, some in "L" shape



Row structures on tall NWs

Row spacing: 4.5 ± 0.2 Å

Period along row: 3.70 ± 0.15 Å

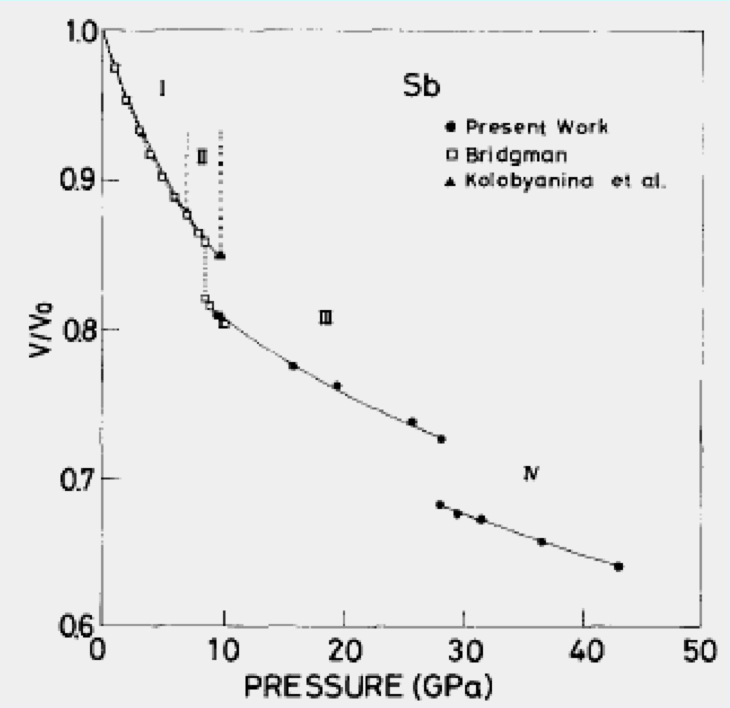


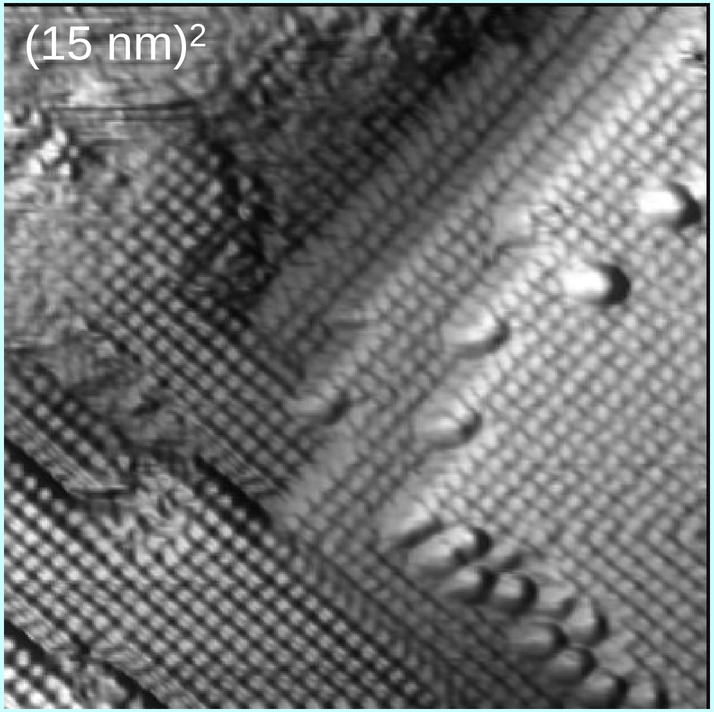
Lower NWs away from corner

Rectangular cell: (4.40±0.15 Å) × (3.93± 0.15 Å)

Sb NWs: Simple cubic Sb in compressed state

Sb under increasing pressure:
RHL → SC → dis. bcc → bcc
(Aoki *et al.*, Solid State Comm. (1983))





Lower Sb NWs at corner: Square cell of period 4.18 ± 0.15 Å

Sb in SC phase (at ~ 7.5 GPa)

Atomic volume $V \approx 0.85V_0 = 25.7$ Å^3

Atomic spacing in SC: 2.95 Å

Period of $\sqrt{2}\times\sqrt{2}$ supercell on Sb(100): 4.17 Å

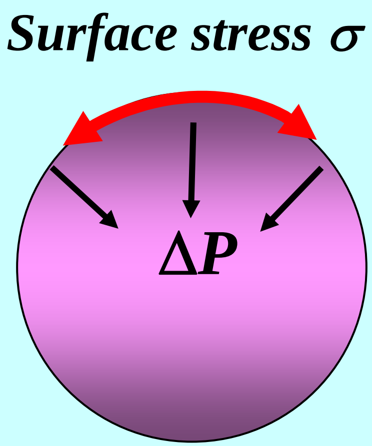
Why are Sb NWs & films in compressive state?

Surface stress on nanostructures induces *large* Laplace pressure (Cammarata et al, 2000)

In a sphere of radius *r*, Laplace pressure:

$$\Delta P = 2\sigma/r$$

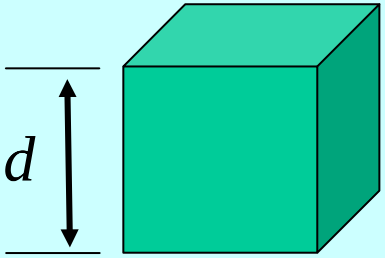
For $\sigma \sim 1$ N/m, $r \sim 1$ nm, $\Delta P \sim 2$ GPa



A nanostructure can be in a strongly compressive state intrinsically, especially in nucleation stage

Laplace pressure in a cube

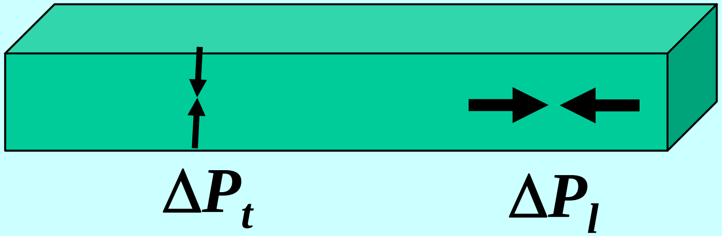
$$\Delta P = 4\sigma/d$$



Laplace pressure in Sb NWs

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

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



In NW, internal longitudinal P_{Lap} is twice of transverse P_{Lap}

Strain in Sb NW

(Poisson ratio $\nu \approx 0.3$)

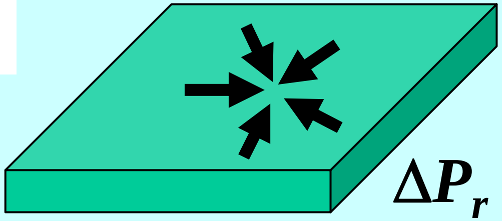
Along NW axis: $\varepsilon_l = -[\Delta P_l - 2\nu\Delta P_t]/Y = -2.8\sigma/(Yd)$

Transverse to axis: $\varepsilon_t = -[(1-\nu)\Delta P_t - \nu\Delta P_l]/Y \approx -0.2\sigma/(Yd)$

In-plane pressure in Sb weting layer

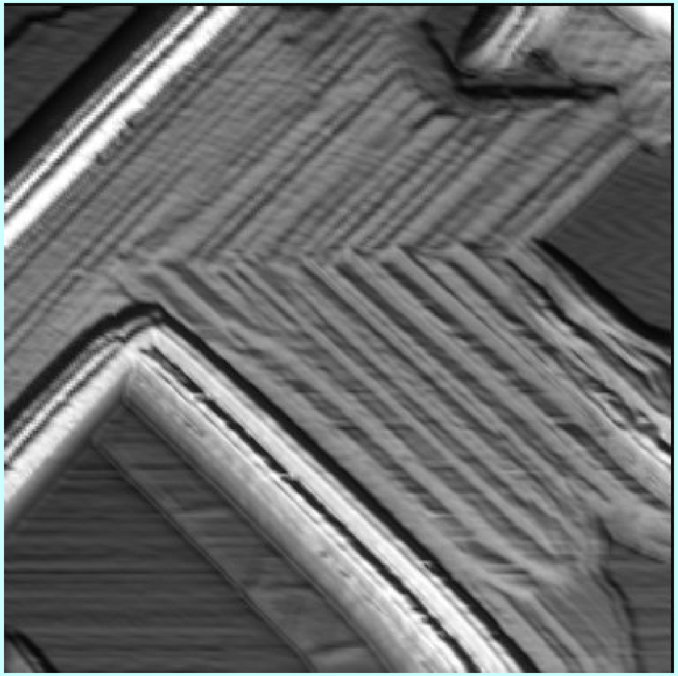
(Free-standing, thickness t)

$\Delta P_r \sim 2\sigma/t$

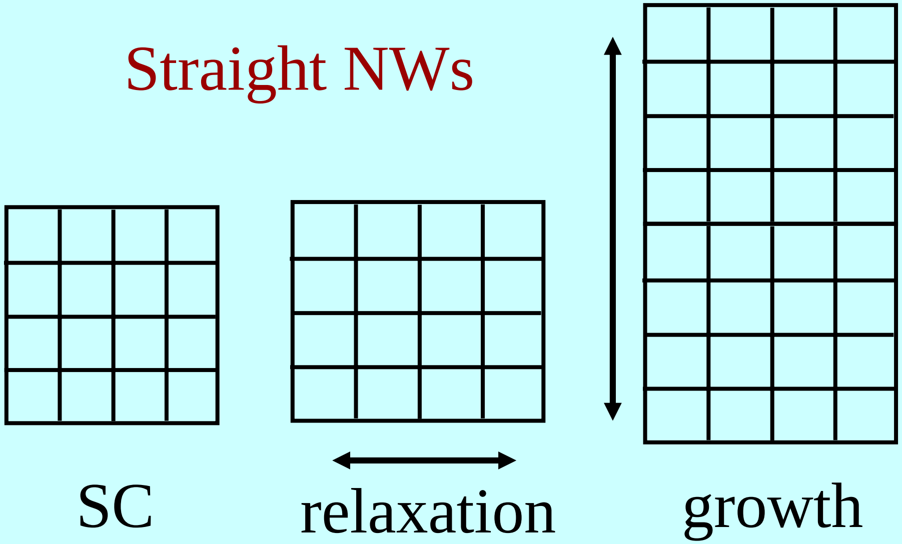


Sb NW Growth

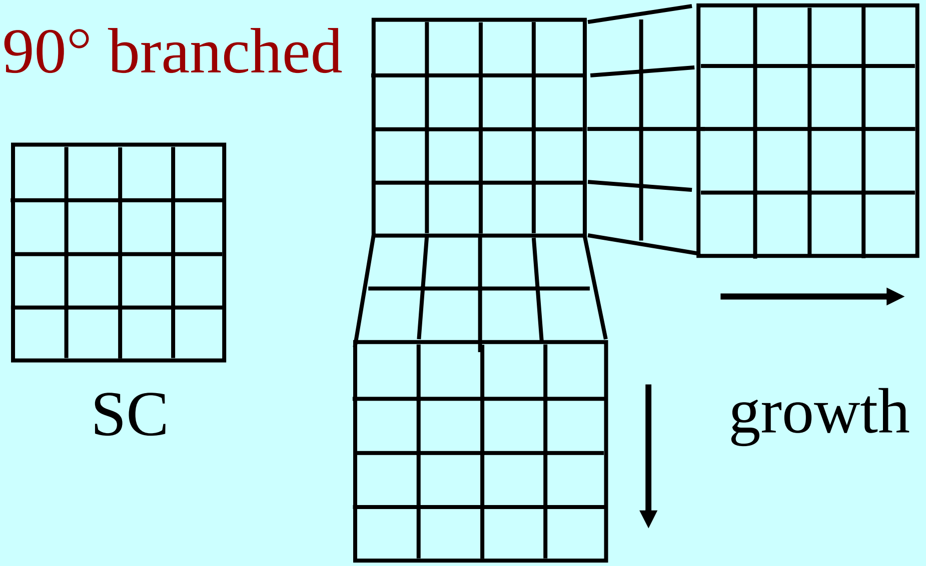
symmetry breaking



Straight NWs

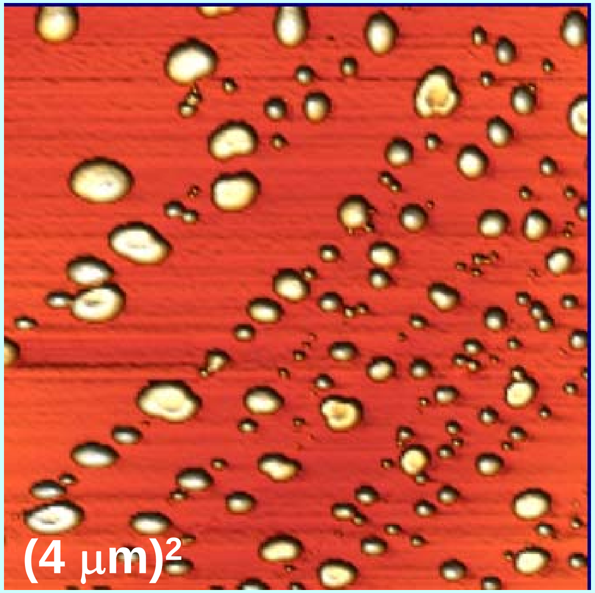


90° branched



Strain energy is reduced effectively even with stress relief in one direction (Tersoff & Tromp, PRL **1993**).

Selective fabrication of Sb Nanostructures

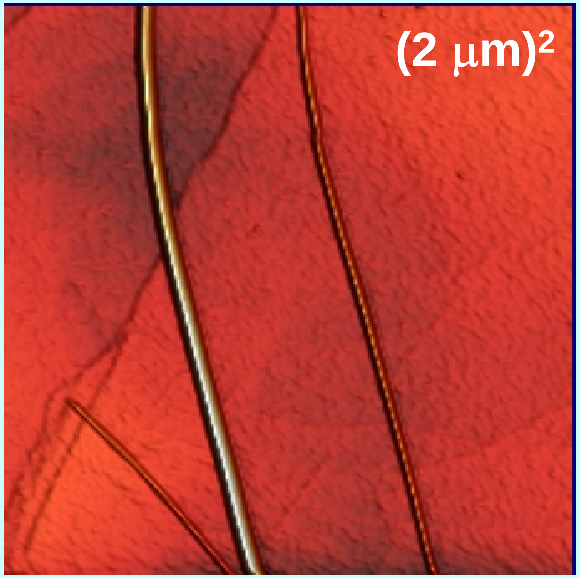


Low flux (1.8 Å/min) at RT

Little Sb_4 dissociation

3D islands exclusively

High flux (18 Å/min)



Low flux (3 Å/min)

at 100 °C

More Sb_4 dissociation

3D islands suppressed

Diffusion vs dissociation of Sb_4: play with the rates

Selective fabrication: Play with the rates of Diffusion & dissociation of Sb_4 on HOPG

$E_{\text{diffu}}(\text{Sb}_4) \leq 0.1$ eV

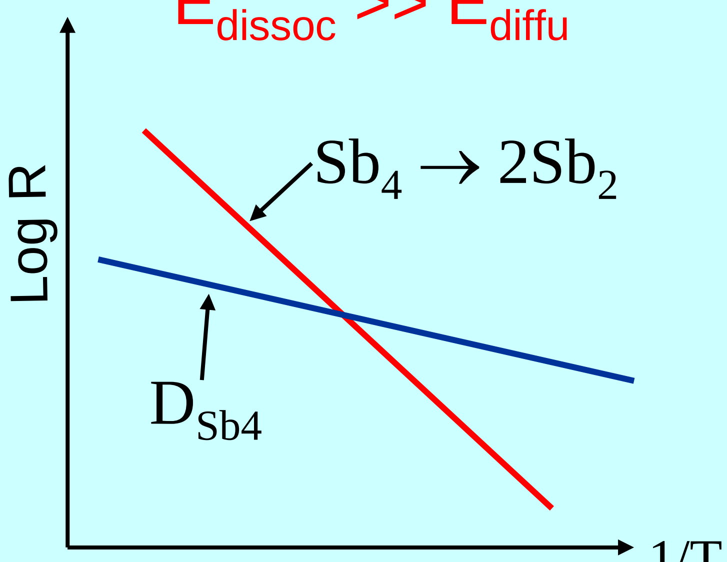
On Si(001): $E_{\text{dissoc}} = 0.7$ eV
(Mo, PRB 1993)

On HOPG: $E_{\text{dissoc}} \sim 1$ eV

Ratio of dissociation vs diffusion rates:

$$\frac{R_{\text{chemisorb}}}{R_{\text{diffusion}}} \propto \exp\left(-\frac{E_c - E_d}{kT}\right)$$

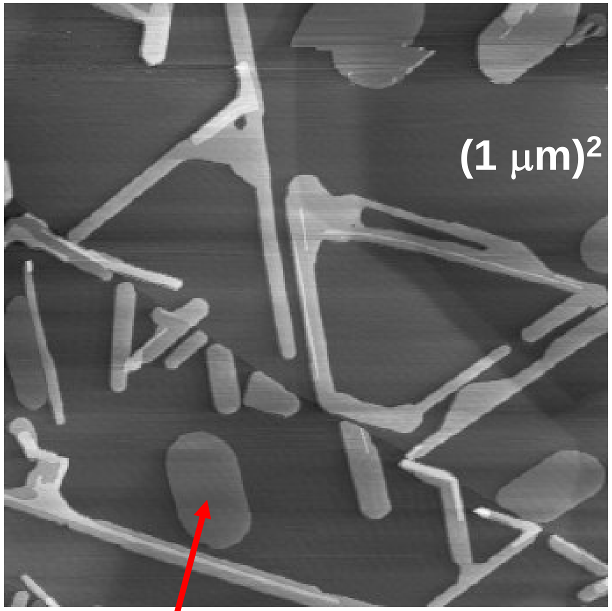
$E_{\text{dissoc}} >> E_{\text{diffu}}$



This ratio increases by a factor of $\geqslant 300$ as T changes from 30°C to 100°C

Formation of quasi-1D Bi Nanostructures

(Bi evaporator only generates Bi_1 & Bi_2, so no 3D islands form initially)

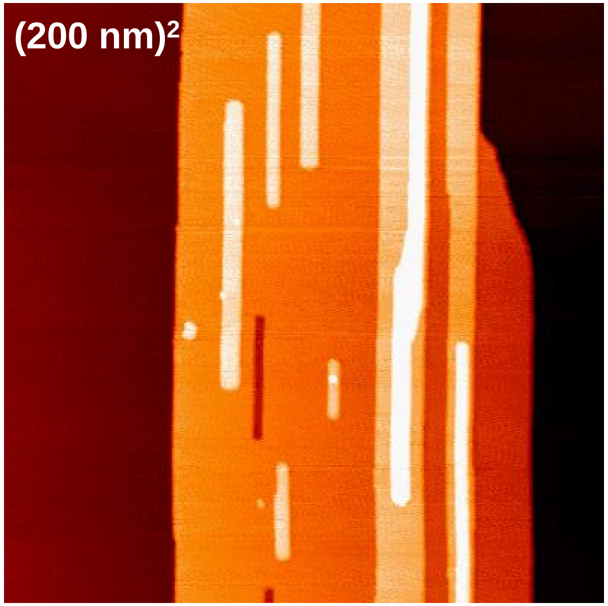


2D islands, height ~ 1 nm

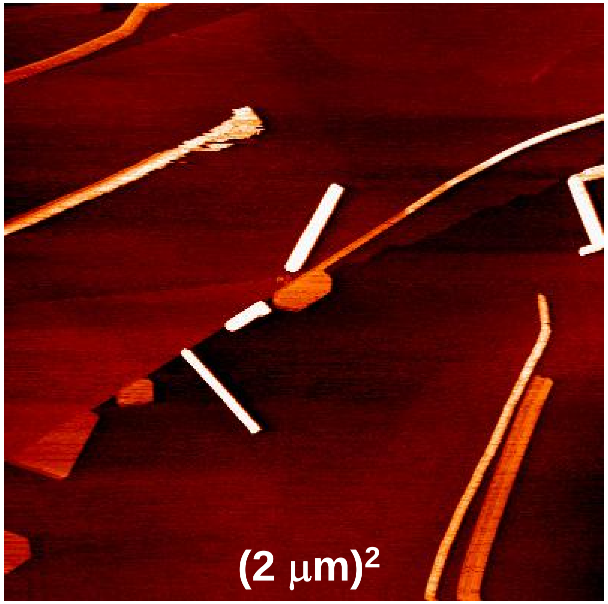
Hexagonal (111) lattice of period:

4.31 ± 0.06 Å (4.55 Å in bulk)

Strongly compressed in-plane



Stripes with rectangular lattice:
4.34 Å × 4.67 Å
on bulk Bi(110):
4.55 Å × 4.75 Å

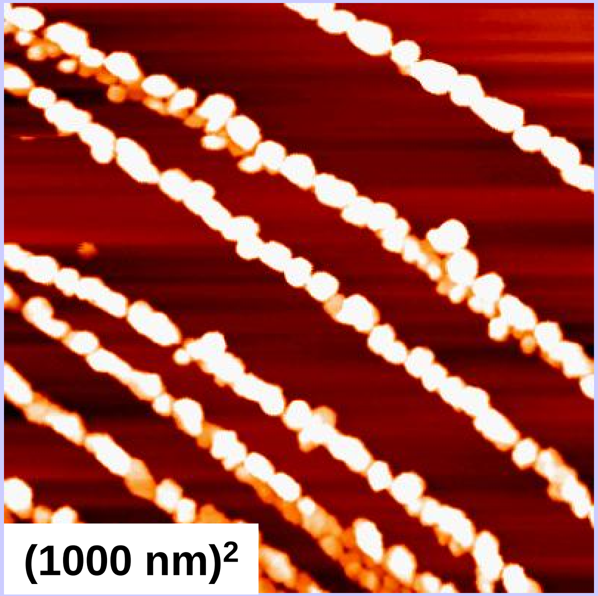


Bi nano-ribbons

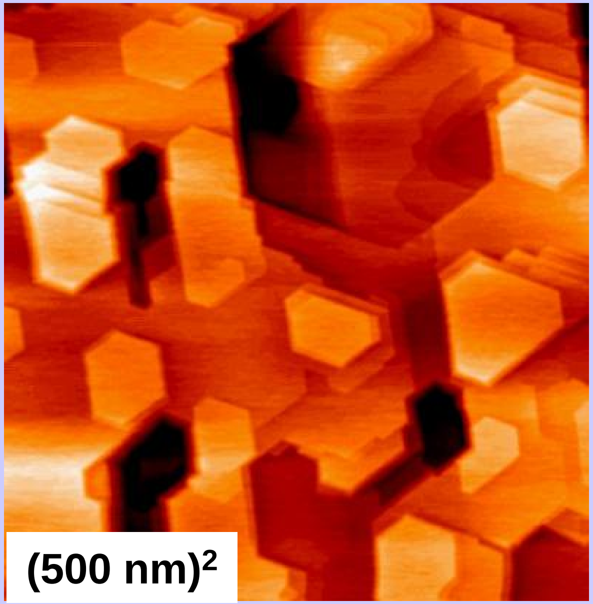
Height ~ 3-25 nm

Width ~ 25-70 nm

MnSb growth on HOPG

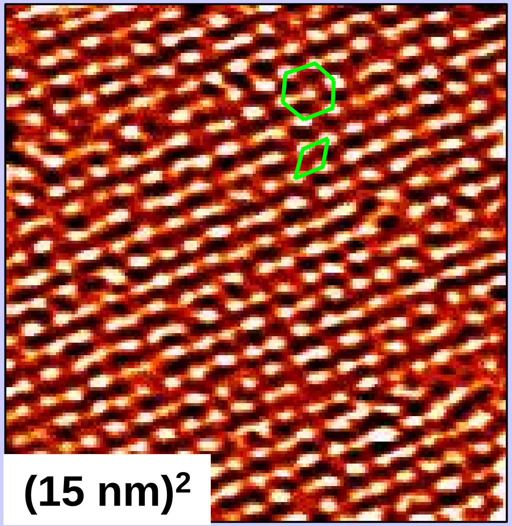


Co-evaporating Mn & Sb at 150° C, MnSb cluster chains along the steps initially, average cluster height ~ 20 nm, lateral size ~ 50nm.



Mostly hexagonal-shaped atomically flat MnSb(0001) terraces, minimum step height 5.8 $\pm$0.2 Å

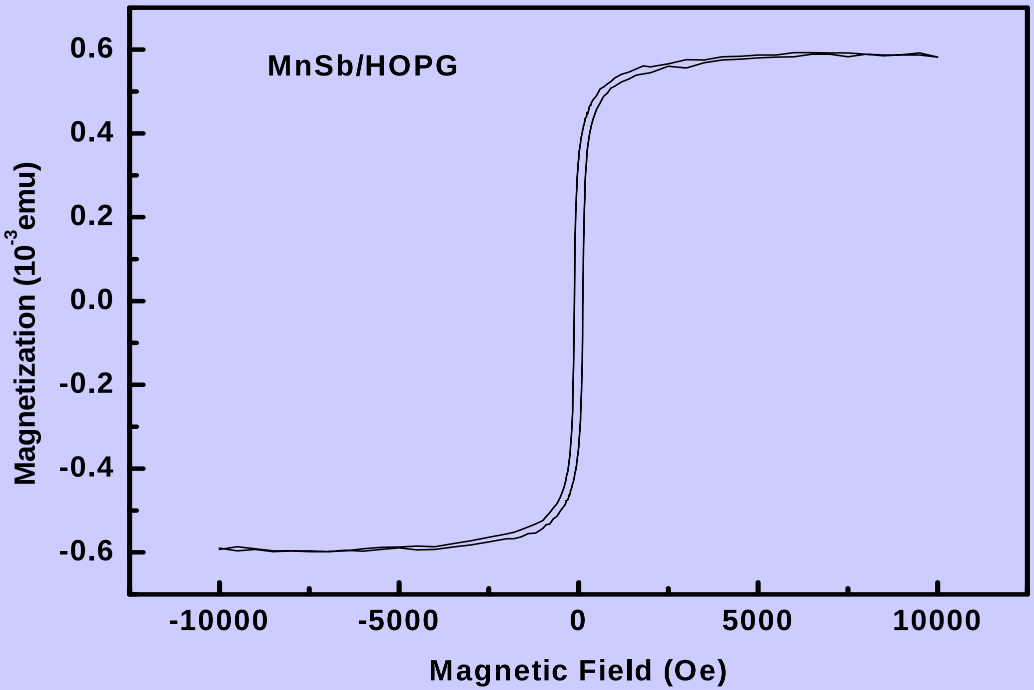
100 nm film



Periodicities 8.3 Å, MnSb(0001)-2×2. Grown in Sb-rich conditions & annealed in Sb flux, surface likely Sb-terminated.

MnSb: ferromagnetic (T_c 590 K), nearly half-metallic

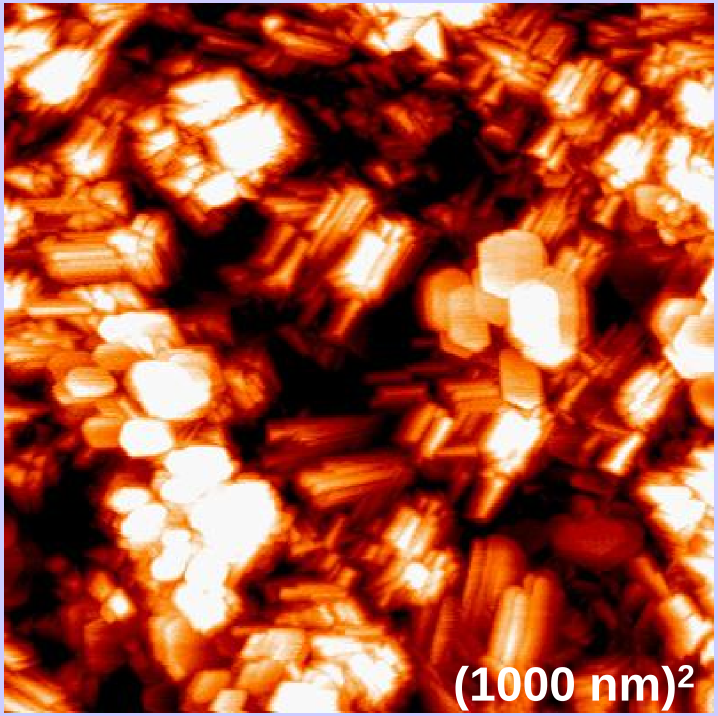
Magnetic measurement using VSM

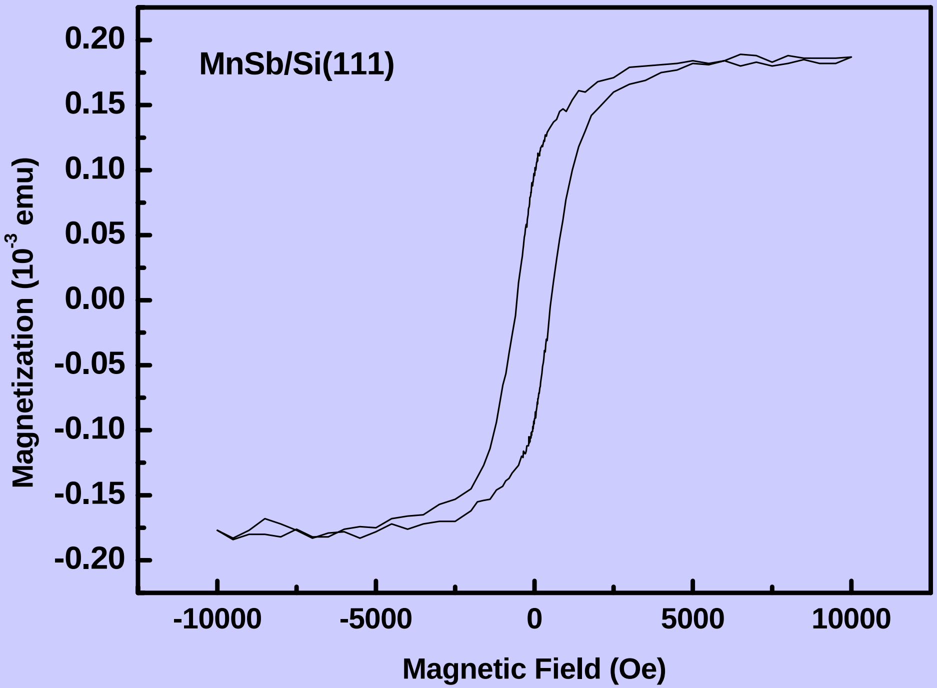


Hysteresis loop for 100-nm MnSb film on HOPG

measured at RT with H parallel to film plane.

MnSb growth on Si(111)



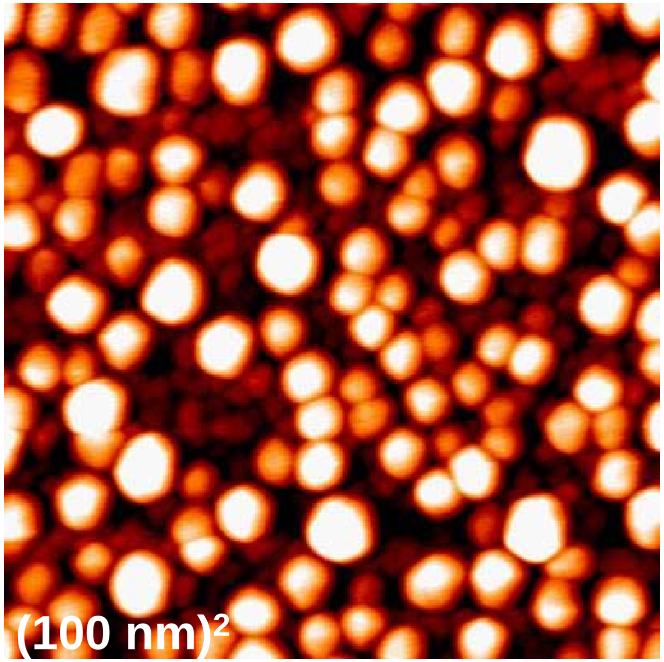


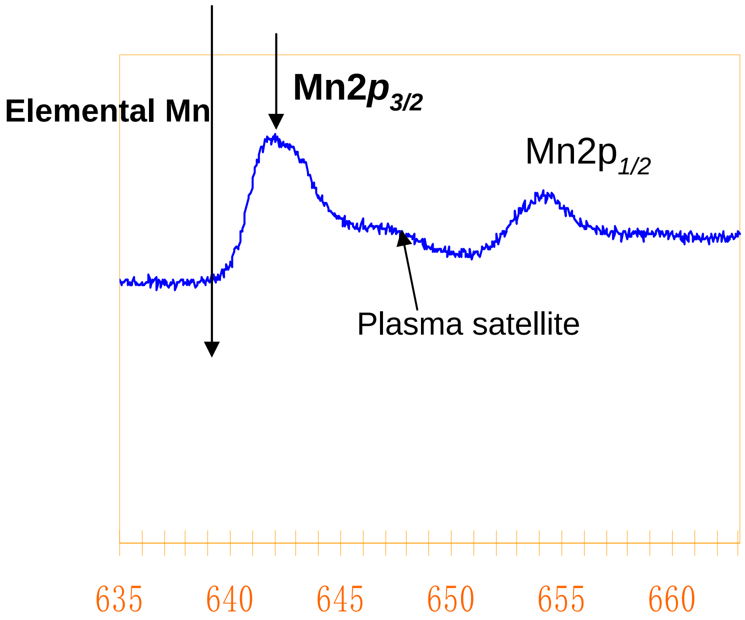
VSM at RT, H in film plane

MnSb (~ 30nm) grown on Si(111) at 300° C

Some islands in (0001), but other orientations also exist

MnSb growth on SiN_x/Si(111)





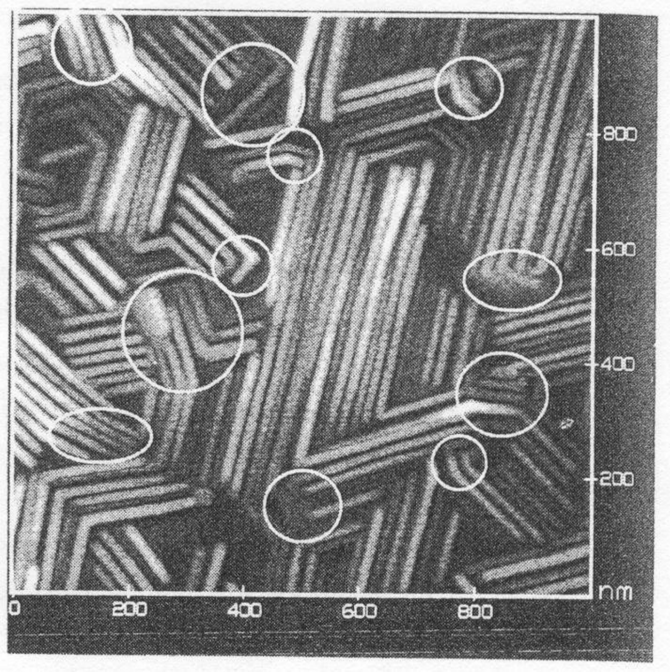
Mn2p XPS, shift ~ 2.5 eV to higher binding E, indicating MnSb compound

Grown at 250° C, MnSb nanodots with average diameter of 10nm, hard to grow further to show facets

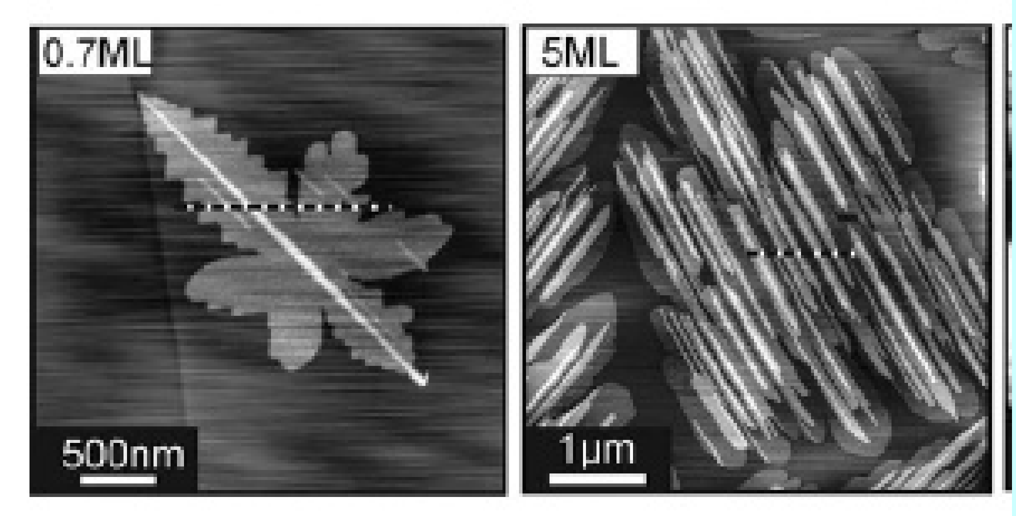
Summary

- Self-assembled cluster chains of Ge, Al & Mn on HOPG
- 3 types of Sb & Bi nanostructures form on HOPG. 3D & 2D close to RHL, 1D NWs highly compressed.
- Sb & Bi NWs start in a compressive state, due to $P_{Laplace}$ induced by surface stress on a nanoscale object
- Certain growth selectivity of Sb growth is realized: play with Sb_4 diffusion & dissociation rates
- Ferromagnetic MnSb: more oriented growth on HOPG than on Si(111) or SiN_x/Si(111)
- Bonding nature of Sb, Bi, MnSb on HOPG?

Bi nanostructures on HOPG



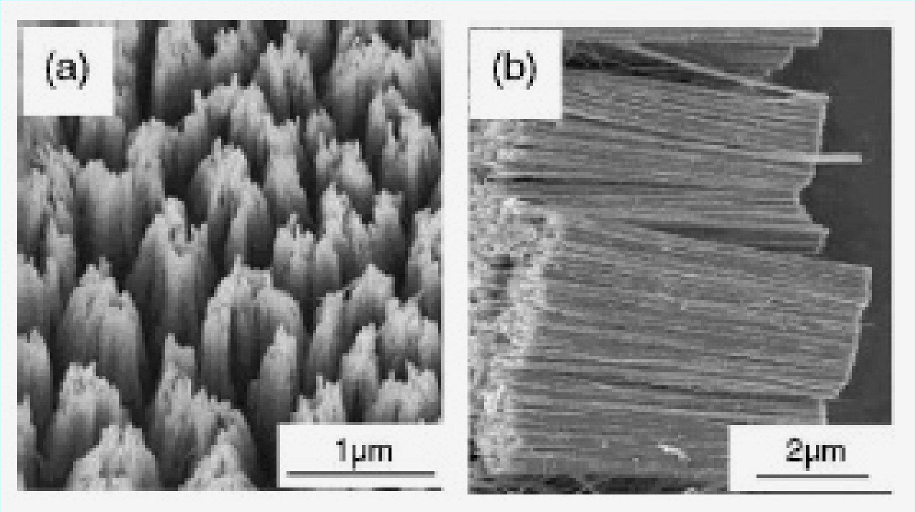
(H. Wang et al, 1993)



(S.A. Scott et al, 2005)

Bi NW array grown in AAM

(L. Li et al, 2005)

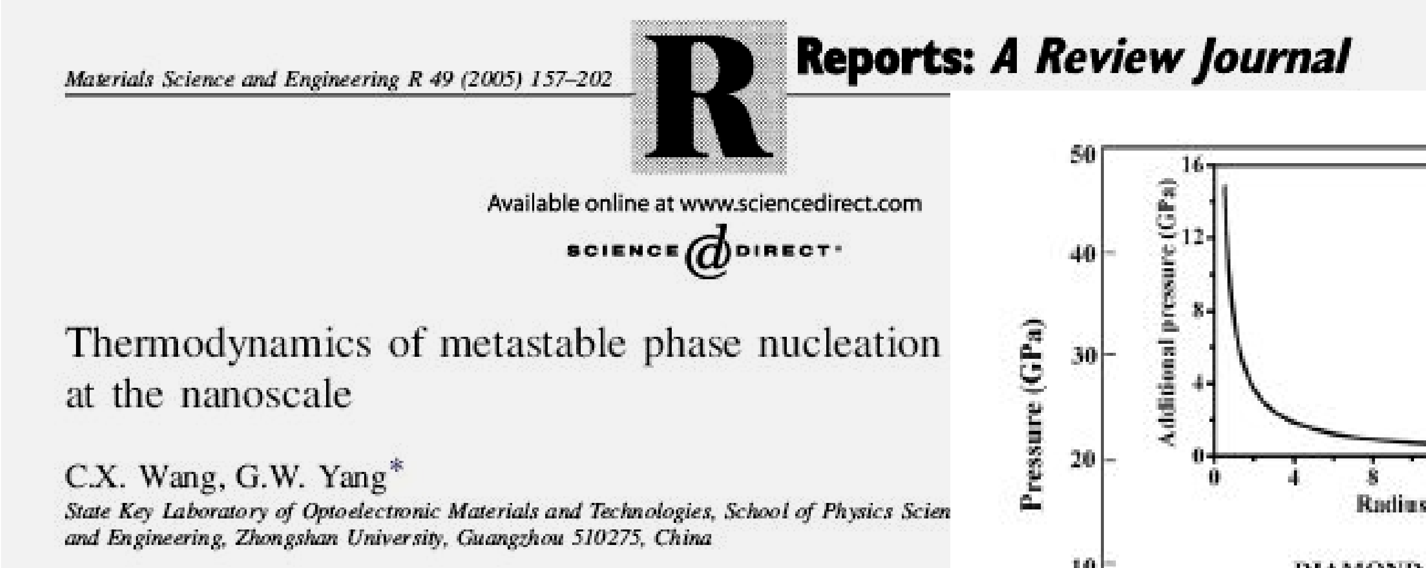


Different Sb Nanostructures on HOPG

3D island	Rhombohedral (111) Facet a= 4.27 $\pm$ 0.10 Å	Formed by diffusion & nucleation of Sb_4 at HOPG steps at low T & low F
2D film	RHL (small distortion) a = 4.17 $\pm$ 0.10 Å h = 3.96 $\pm$ 0.20 Å	Formed by chemisrption & dissociation of Sb_4 at high T & high F
1D rod	SC & distorted, V/V_0 $\approx$ 0.85, $\sqrt{2}\times\sqrt{2}$ supercell on Sb(100)	Formed by chemisrption & dissociation of Sb_4 at high T & high F

1D rods disappear @ 260° C anneal

2D & 3D islands are stable against annealing to 300° C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Thermodynamics of metastable phase nucleation at the nanoscale

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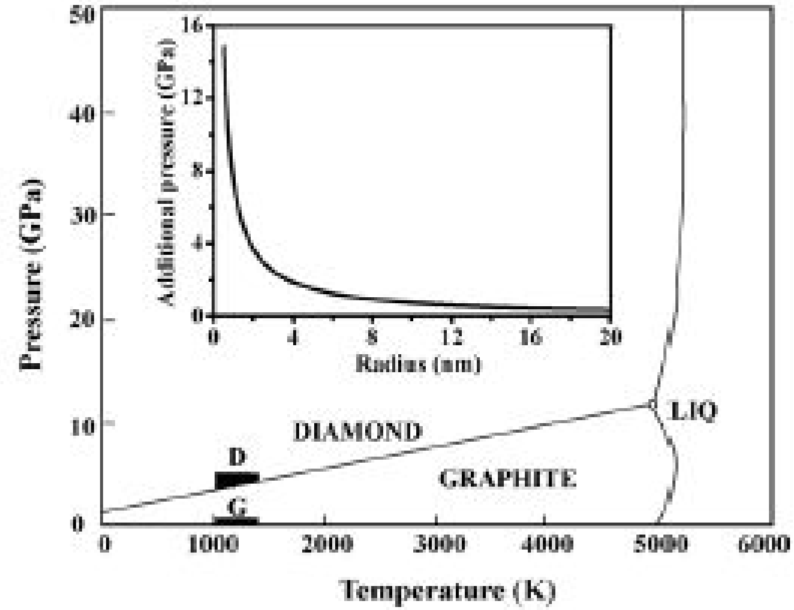

Deformation of Ni particle in CNT growth

(S. Helveg et al., Nature 427 (2004) 426)