Self-assembled Shape-controlled growth of crystalline Sb on Graphite

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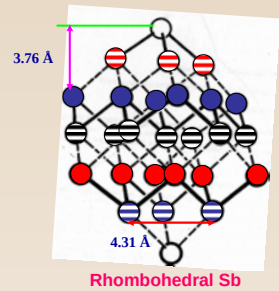
We have investigated the growth of three-dimension (3D) spherical, 2D thin film and 1D nanorods of antimony on highly oriented pyrolytic graphite (HOPG) in ultra-high vacuum (UHV) using in situ scanning tunneling microscopy (STM). The shape and size of islands depend on a variety of growth parameters, i.e. flux, substrate temperature, deposition time, and layer thickness. Nucleation and growth of spherical 3D islands are dominant at low flux and room temperature. With a moderate flux, all three types of structures grow initially, but further deposition leads to mostly 2D and 1D crystalline islands at room temperature. The 3D and 2D structures of Sb on graphite have same bulk crystalline rhombohedral structure, but the 1D structure shows different crystalline structure from the bulk Sb lattice. At elevated temperature and higher flux, only the crystalline 2D and 1D islands were observed.

Experimental Details

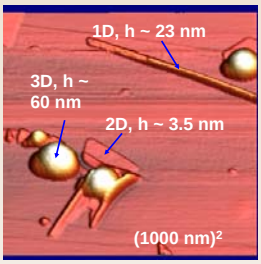
- Cleave HOPG in atmosphere and degassed thoroughly at 700 K for 10 hours in UHV.
- Deposit Sb (mostly Sb_4) on HOPG from W-boat evaporator at various conditions such as at different flux and substrate temperature.
- In-situ STM imaging of Sb deposited HOPG in constant current mode at room temperature (RT) in UHV.



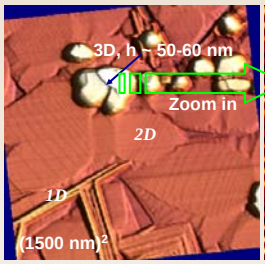
Rhombohedral Sb

Results and Discussion

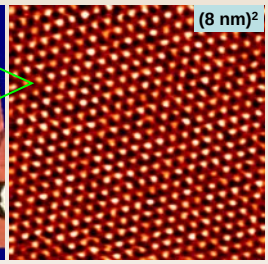
Three types of Sb structures on HOPG: 3D, 2D and 1D islands



Sb deposited at ~ 4 Å/min for 3 min at RT
3D, 2D & 1D islands formed in early stage

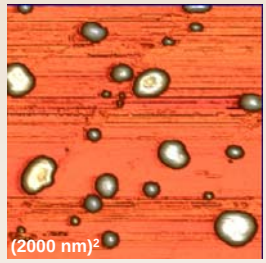


100 Å Sb deposition at ~4 Å/min & RT
Facets formed on 3D islands

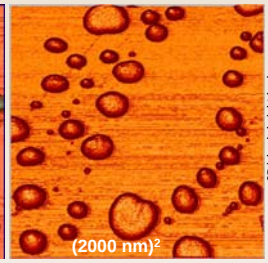


High resolution image on top of 3D island
Lateral period 4.28±0.05 Å

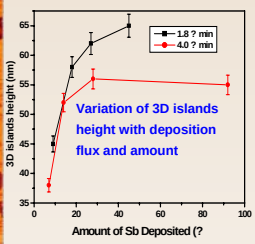
At low flux and at RT: Exclusively 3D islands



Growth of Sb at low flux ~1.8 Å/min for 5 min at RT

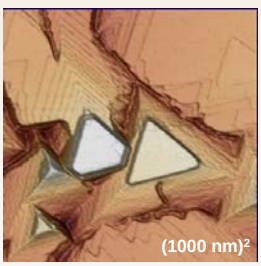


Sb deposition at flux ~ 1.8 Å/min at RT for 10 min

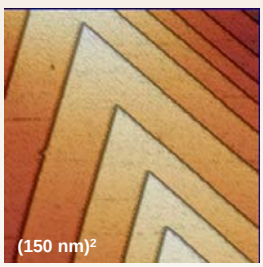


Heights of 3D islands saturate at 60±5 nm

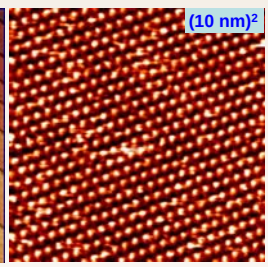
2D crystalline Sb structure



40 nm Sb deposited at ~ 20 Å/min at RT

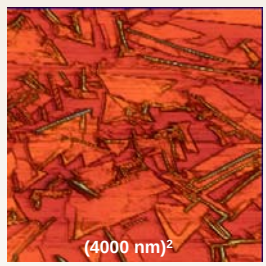


Step height 3.85±0.35 Å



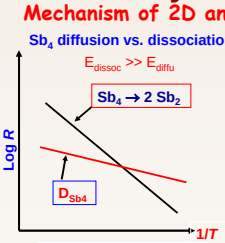
Lateral period: 4.22±0.16 Å

At high flux and at 100 ° C: Only 2D & 1D



At high flux ~ 18 Å/min for 3 min at 100 ° C

Mechanism of 2D and 1D structures formation



On Si(001): E_{dissoc} = 0.7 eV (Mo, PRB 48 (1993) 17233)

Sb_4 on HOPG, assuming:
E_{dif} ~ 0.1 eV
E_{dissoc} ~ 0.9 eV

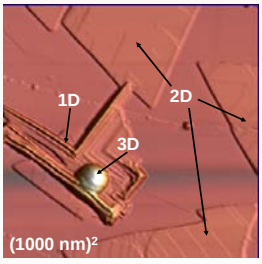
$$\frac{R_{chemisorb}}{R_{diffusion}} \propto \exp\frac{(E_c - E_d)}{kT}$$

$R_{chemisorb}/R_{diffusion}$ at 100 °C is 310 times higher than that at RT.

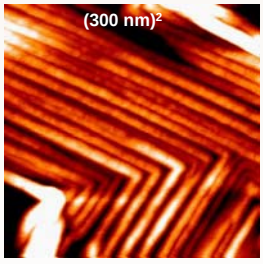
Channel 1: physisorbed Sb_4 to 3D islands; dominant at RT and low flux

Channel 2: chemisorbed Sb_2 forms 1D & 2D structures; dominant at elevated T and high flux

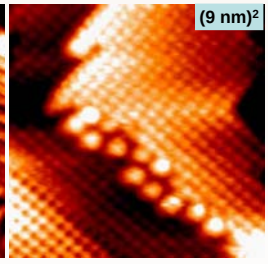
1D crystalline Sb Nanorods



After ~3 nm Sb deposition at RT



45 Å Sb at RT, Bundles of nanorods
Width of rods:15 ± 4 nm, Height of rods: 13 – 25 nm



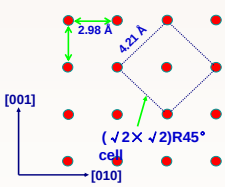
Square lattice structure on top of rods
Lateral period ~4.15±0.11Å

Summary of Crystal Structures of 3D, 2D and 1D

Structure	Crystal Structure	Lateral period	Step height
Bulk Sb	Rhombohedral	4.31 Å	3.76 Å
3D	Rhombohedral	4.28±0.05 Å	-
2D	Rhombohedral	4.22±0.16 Å	3.85±0.35 Å
1D	Simple Cubic	4.15±0.11 Å	2.97±0.31 Å

Atomic volume of rhombohedral Sb at normal pressure & RT V_0 = 30.21 Å^3, whereas in our case, volume of simple cubic structure is V = 26.46 Å^3. So we have V/V_0= 0.88

Proposed model for 1D Structure



Predicted ratio in compressed SC phase: V/ V0 ~ 0.86

(K.J. Chang, M.L. Cohen, Phys. Rev. B 33 (1986) 7371)

Summary

- Spherical 3D, 2D thin film as well as 1D crystalline nanorods of Sb were observed on HOPG at different stages at RT.
- At $T \approx 100$ ° C and a high flux, only 2D and 1D Sb islands were formed, whereas only 3D islands were obtained initially at low flux and at RT.
- The crystalline structures of 3D and 2D structures of Sb reveal same bulk crystalline structure, but the 1D nanorods shows simple cubic structure.