STM study of nanorods formed by Ho deposition on the Ge(111) surface

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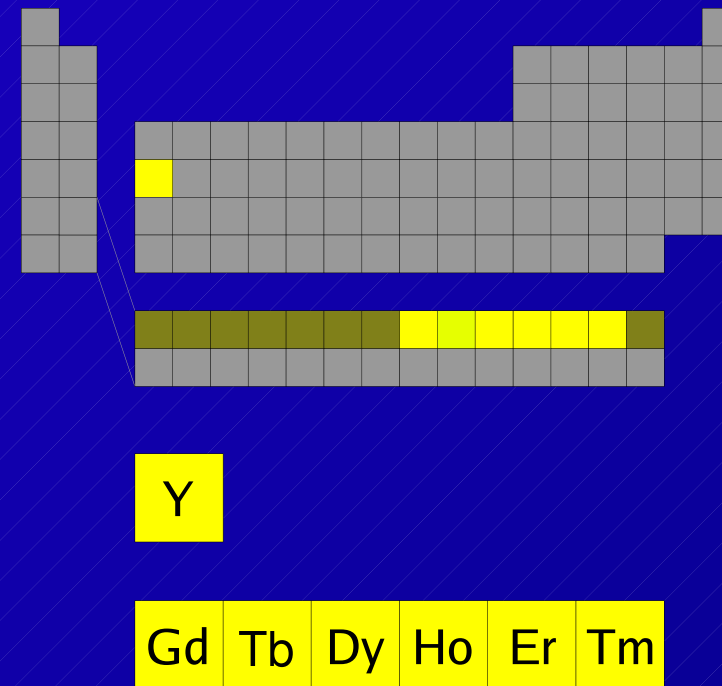
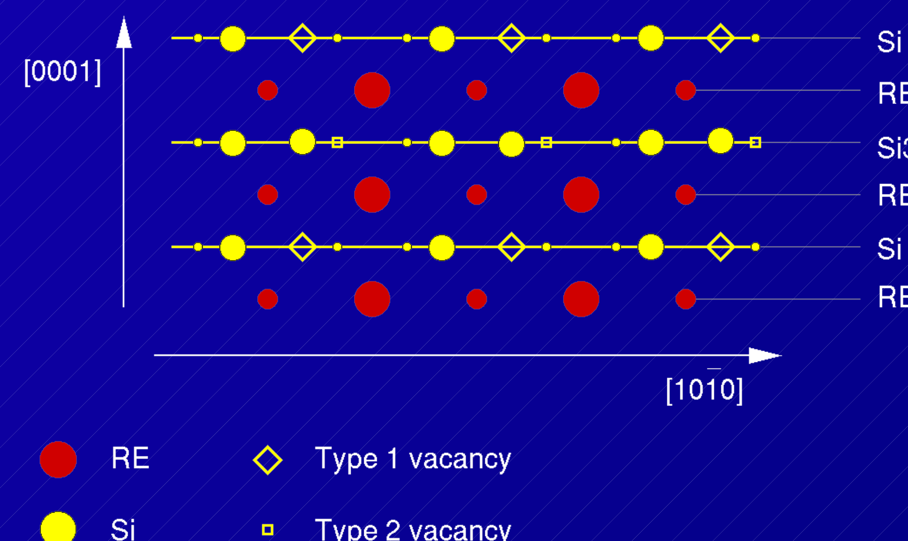
Overview

- Introduction to rare earth (RE) metals on Si & Ge.
  - Importance.
  - Bulk RE/Si and RE/Ge compounds.
  - Important structures formed on the surfaces of Si and Ge.
  - Differences in behaviour between (111) and (001) surfaces.
- STM experiments.
  - Low coverages of Ho — comparisons of Ge(111) with Si(111).
  - Nanorod formation.
  - Control of growth — local periodicity.
  - High-resolution STM.
- Models & comparison with *ab-initio* calculations.
  - Nanorod properties.
- Conclusions.

Introduction

- Great deal of interest in RE silicides [1].
- Form unusually low Schottky barriers on *n*-type Si.
- RE silicides $RESi_{2-x}$ have AlB_2 structure; generally good lattice match to Si(111).
- Nanowire growth on Si(001) due to lattice mismatch anisotropy.
- Interest in Ge due to improved carrier mobilities.
- $REGe_{2-x}$ structure similar.

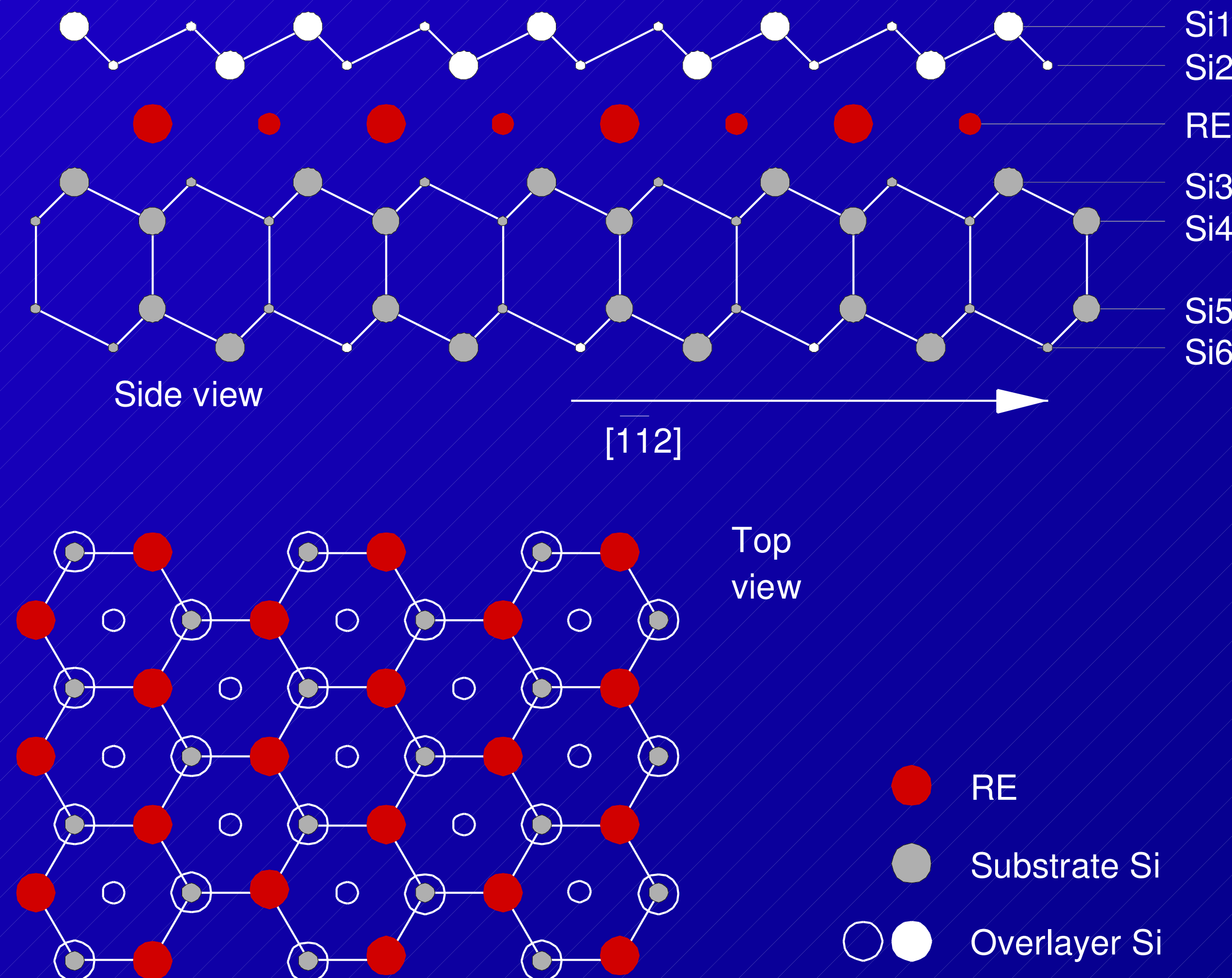




[1] F. P. Netzer, J. Phys. Condens. Matter, 7, 991-1022 (1995)

2D RE silicide/germanide structure

- Single monolayer of RE atoms sub-surface on T4 sites, covered by a B-type Si bilayer.
- Previously studied by AED, SEXAFS, SXRD [2], LEED *I-V*, MEIS.
- Grown in UHV: Clean Si or Ge surface, deposit 1 ML RE at room temperature, anneal 500 °C (or grow on hot surface).

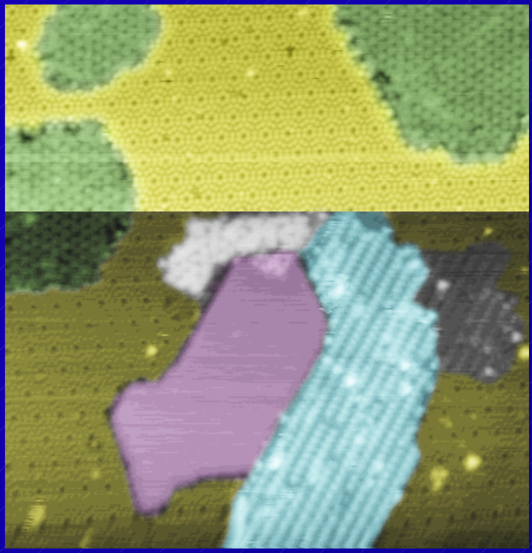


- Series of chemically similar RE elements from Gd to Tm which all form 2D silicides; Er, Dy, Ho (and possibly others) form 2D germanides.

*[2] M. Lohmeier et al. PRB **54**, 2004 (1996)*

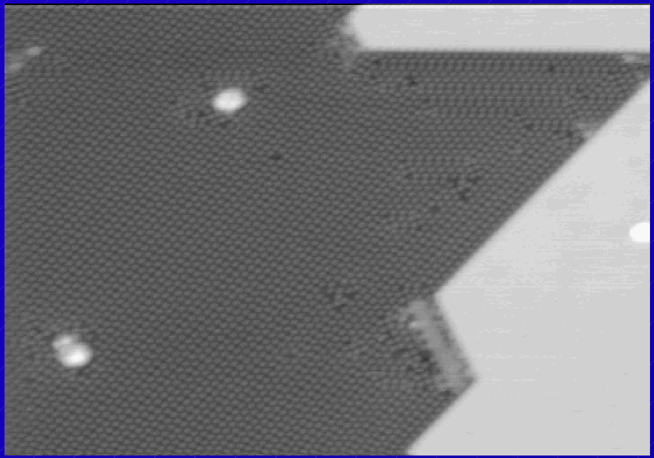
Compare Ho/Ge(111) with Ho/Si(111)

- On the Si surface...
  - Areas of clean Si(111)7×7.
  - The 2D silicide Si(111)1×1-Ho.
  - Si(111)(2√3×2√3)R30°-Ho and Si(111)5×2-Ho.
- On the Ge surface...
  - Areas of clean Ge(111)c(2×8).
  - The 2D germanide Ge(111)1×1-Ho.

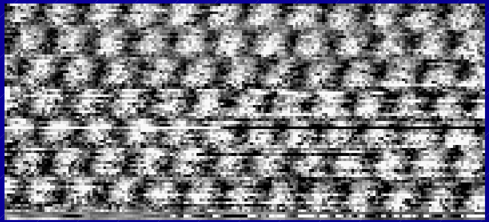


Ho/Si(111) 0.22 ML Ho
RDE ~550 °C; 15 min anneal
2 V, 2 nA, 57.0 × 57.0 nm

E.W. Perkins, I.M. Scott, S.P. Tear, Surf. Sci. 578 80-87 (2005).



Ho/Ge(111) 0.5 ML Ho
RDE ≈450 °C
50.0 × 35.0 nm
2 V, 2 nA



Ge(111)1×1-Ho
4.5 nm × 2.0 nm
2 V, 1 nA

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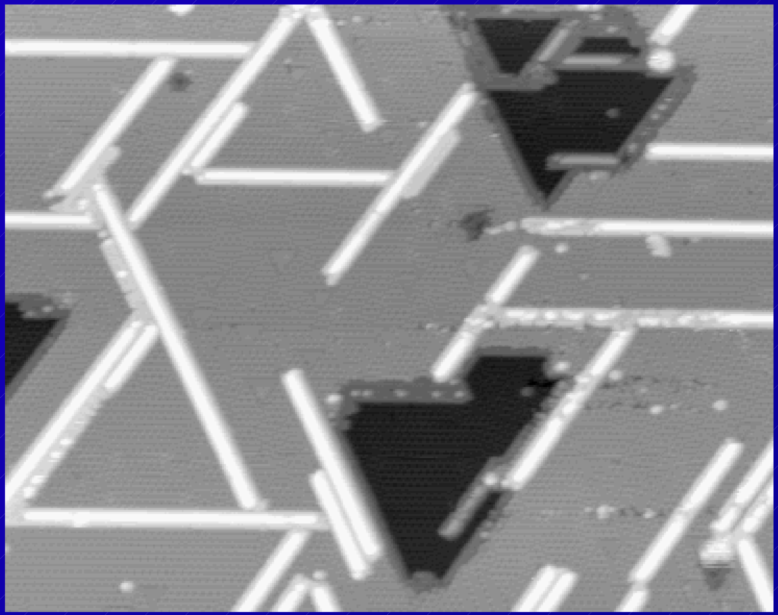
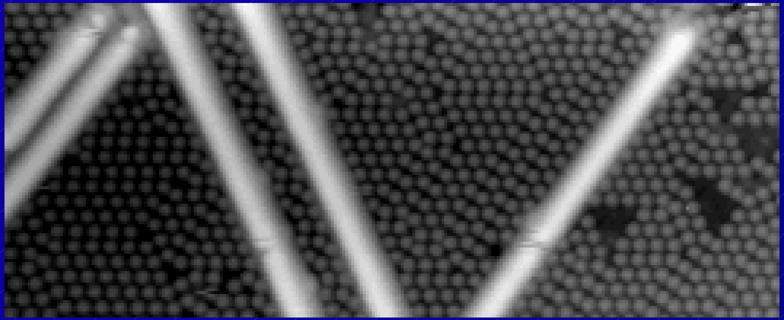
Ho/Ge(111) nanorods: STM overview

- Deposition of 0.1 ML Ho onto clean Ge(111) surface at 250 °C.
- Isolated nanorods form which align themselves along substrate ⟨110⟩ directions. Apparent uniform width ≈1.5 nm, lengths ~40 nm.
- Can still see c(2×8) in LEED pattern – consistent with STM overview that shows large areas of clean Ge surface between nanorods.



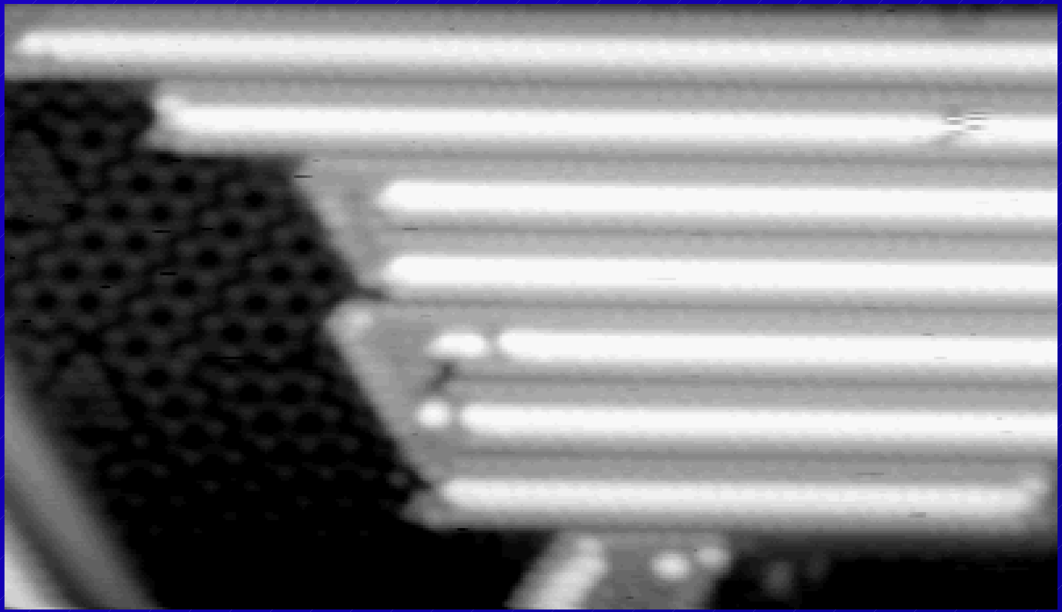
−2 V, 2 nA, 75.0 nm × 59.3 nm



2 V, 2 nA, 33.3 × 13.5 nm

Periodic arrays of nanorods

- Coverage 0.25 ML.
- Start to see domains form in which nanorods stack parallel to each other with specific separation between rods.

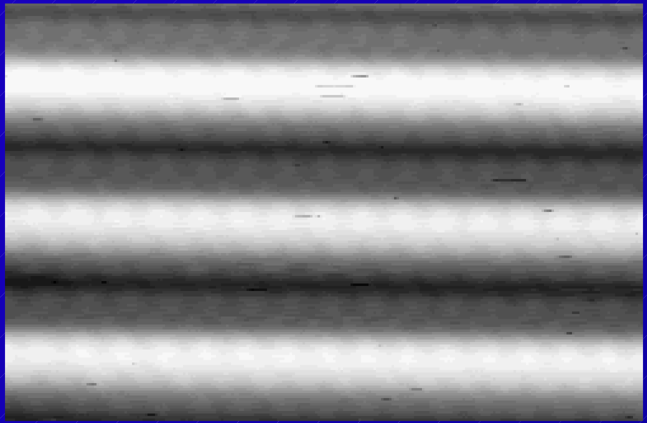


−2 V, 2 nA, 20.0 nm × 11.5 nm

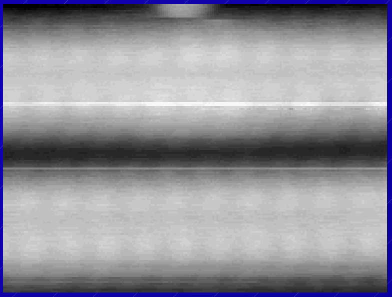
- Locally the nanorod structure is periodic and has a 5×1 unit cell wrt. the substrate. Nanorod width 1.7 nm.
- If coverage is increased to try and cover whole surface with nanorod arrays, this structure is no longer stable. Applying e.g. quantitative LEED problematic but can look at *ab-initio* calculations.

High resolution STM images

- Peak of nanorod is 3.9 Å above rest atoms; 3.1 Å above adatoms of nearby Ge(111)c(2×8).
- Filled states images suggest atoms occupy two distinct levels.
- Lower level 2.1 Å above Ge rest atoms.
- Medium-energy ion scattering experiment: no sub-surface Ho.
- Conclude that the top layer consists of Ho.



−2 V, 2 nA, 6.3 nm × 4.1 nm

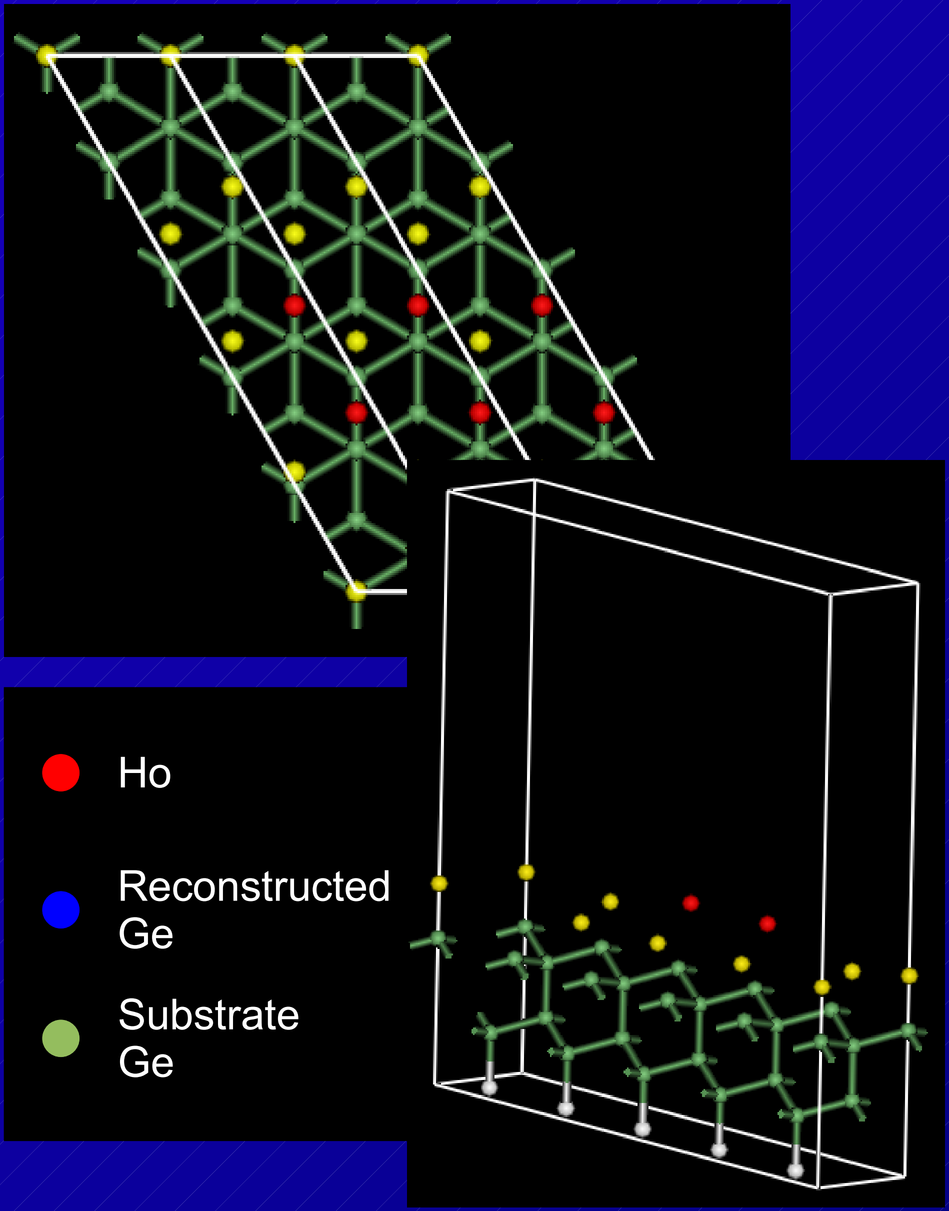


2 V, 2 nA
4.0 nm × 3.0 nm

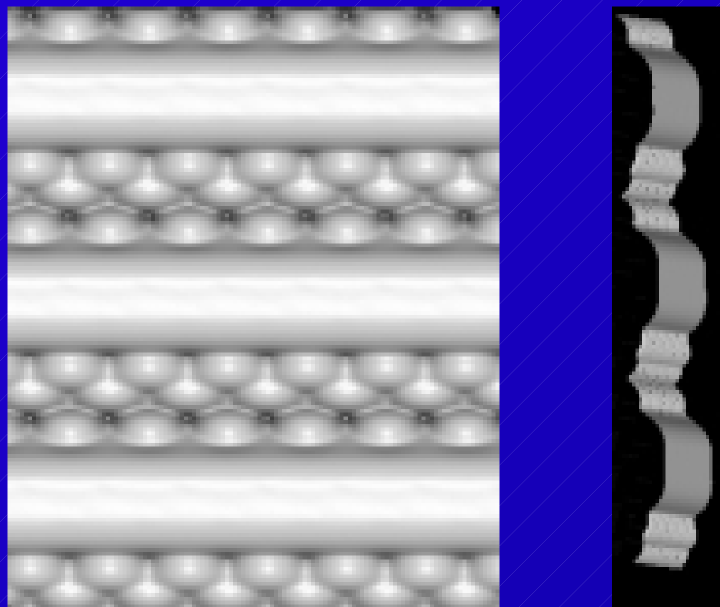
- Atoms on lower level too low to be full Ge bilayer step (3.27 Å) and too high to be simple adatom layer (e.g. 0.66 Å).
- Lower level likely to be single Ge monolayer.

Model of the nanorod & *ab-initio* calculations

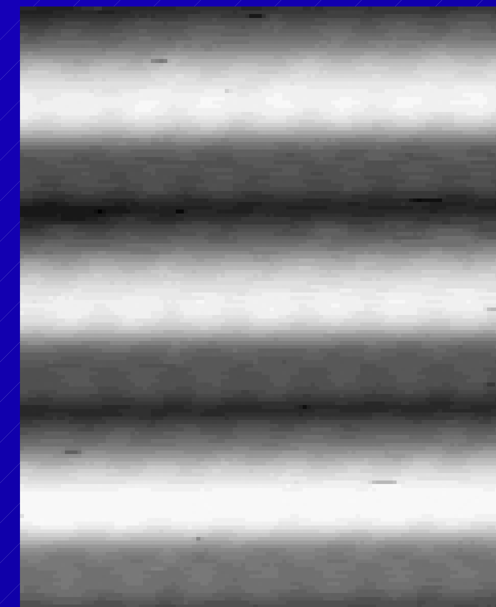
- Model constructed based on Ho atoms atop a single reconstructed Ge layer above a bulk-like termination of the Ge(111) surface.
- Starting points for height and registrations from STM images.
- Model refined by geometry optimisation with *ab-initio* DFT using the CASTEP code.



Comparison with *ab-initio* calculation (1)



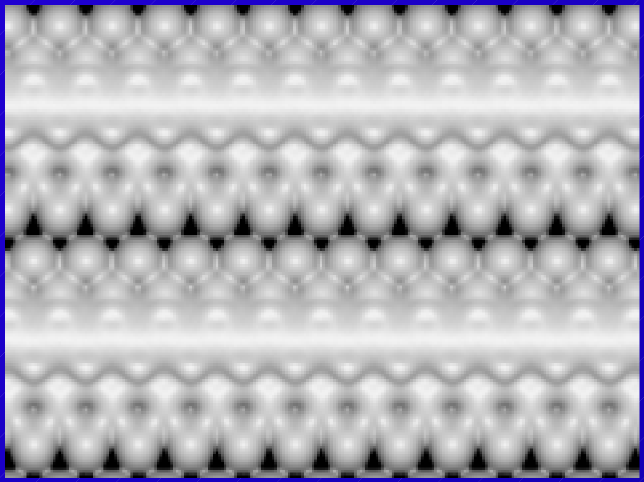
Calculation (filled states)
Tersoff-Hamann 2 V



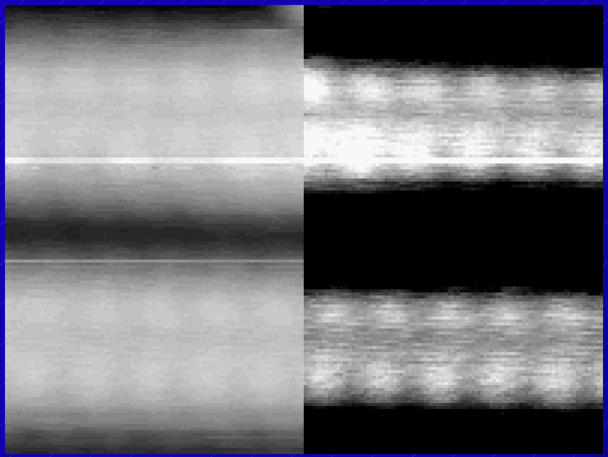
Experiment (filled states)
2 V, 2 nA
3.0 nm × 4.1 nm

- Simulated STM image based on *ab-initio* calculation shows strong corrugation corresponding to nanorod (particularly obvious in side-view).
- Very favourable comparison to experiment.

Comparison with *ab-initio* calculation (2)



Calculation (empty states)
Tersoff-Hamann 1.3 V



Experiment (empty states)
1.3 V, 2 nA

- STM image from *ab-initio* calculation shows more resolution in empty states.
- Central bright ridge centred over Ho atoms, as in experiment.

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Conclusions

- Novel nanorod structure found to form on low-coverage Ho deposition on Ge(111) with low *T* annealing.
  - Very different to behaviour on Si(111).
  - No patterning of substrate of exploitation of lattice mismatch anisotropy required.
- Increasing coverage very slightly favours formation of stacked arrays of nanorods that are locally periodic.
  - Valuable since this offers the opportunity for *ab-initio* calculations.
- Nanorod structure proposed and validated with *ab-initio* calculation : very favourable comparisons between calculated/experimental STM images.
  - Calculation indicates metallic structure : these are nanowires.
  - It has been possible to determine the structure of a nanowire.

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