ATOMISTIC MODELLING OF SPUTTERING AND CONTROL OF DEFECTS IN THIN FILM GROWTH

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Overview

- Background
- Introduction to the methodology
- Applications:

  sputtering of Au...*high energy impacts on surfaces*

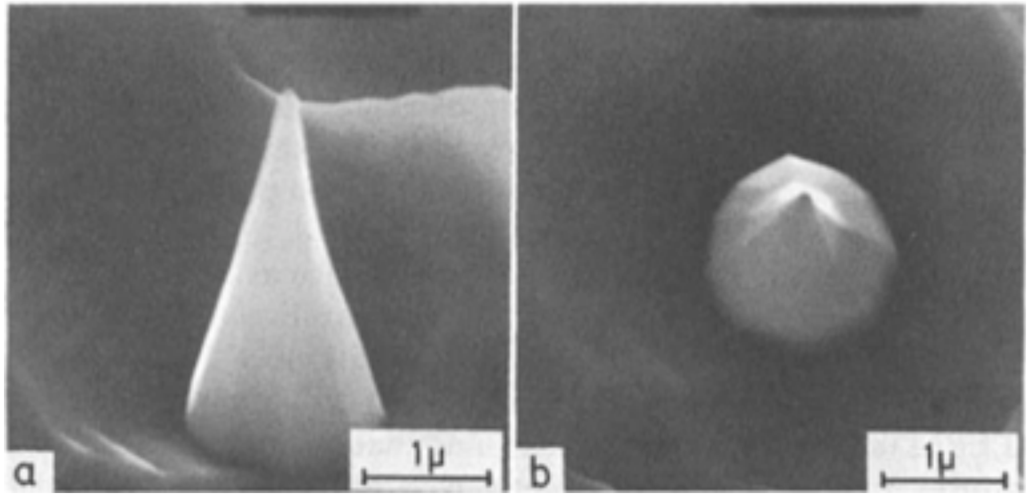
  thin film growth of Ag, Al and ZnO..*low energy impacts on surfaces*

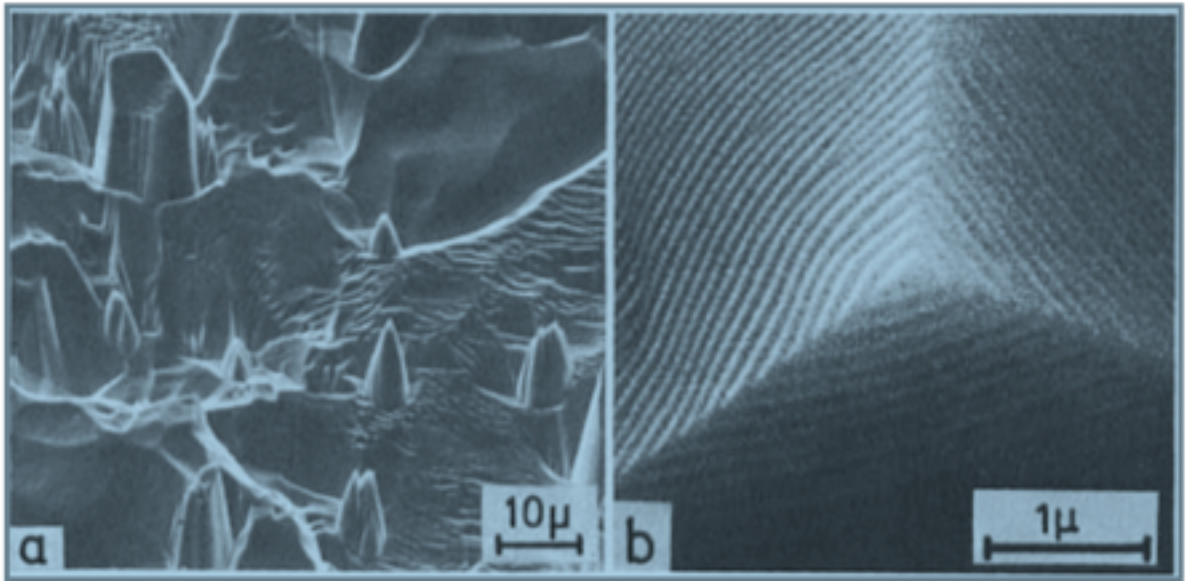
Background- sputtering

- Discovered in 1842 by Grove

- Sputtering is used for depth profiling in surface analysis, thin film deposition...lots of applications

- During the sputtering process the surfaces roughen, topography and subsurface defects are formed.





continuum theory
Smith & Walls Surface
Science 1979

Background- thin films

- Thin films can be grown in many different ways, e.g.
  - Evaporation… deposition energies < 1 eV
  - Evaporation with ion assist (energies up to ~100 eV)
  - RF sputtering… deposition energies up to 100 eV, depending on substrate bias
  - HIPIMS, deposition energies of 6-8 eV in short intense pulses
  - Sputtering..same process but higher energies, here 500 eV

- Stoichiometric mix and deposition rates are also variables. Films can also be post annealed… lots of parameters.

- Objective : *understand the atomistic mechanisms and optimise the parameters computationally to produce the best grown films and model sputtering more accurately.*

Old Methodology

- Use Molecular Dynamics (MD) with empirical potentials to describe the interatomic forces.

- BUT : consider a small system with 200 atoms in the surface layer. If we grow 1 monolayer per second a particle arrives every 5 x 10^{-3} s. A typical integration time step in an MD simulation is 10^{-15} s. So we need 5×10^{12} steps to deposit 2 particles !
- AND a lot of surface diffusion can occur in 5 x 10^{-3} s
- The past solution was to run MD until the surface atoms settle into position (a few ps) and then run a new particle impact, i.e. unrealistically high deposition rates BUT this ignores diffusion between impact events

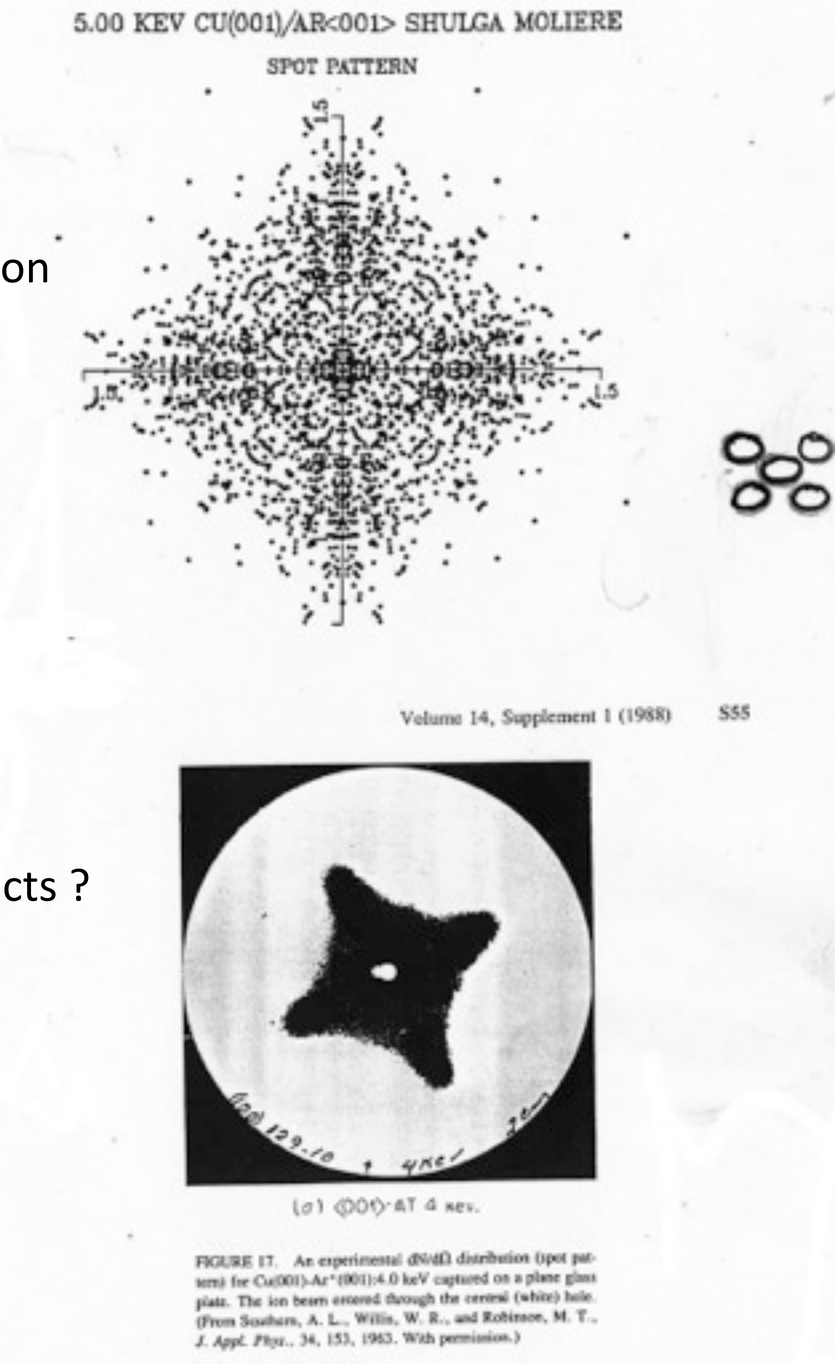
Landmarks in classical MD computer simulation

- 1782 A. L. Lavoisier postulated that classical theory could be used to model chemical phenomena
- 1957 First MD simulations using hard spheres by Alder and Wainwright
- 1960 MD simulations of radiation damage by Vineyard's group at Brookhaven
- 1960 MD simulations of sputtering by Don Harrison
- 2012 Standard packages such as DLPOLY and LAMMPS are available for use.

Modelling Sputtering- old version

- For low energy (~20 keV or less) bombardment ballistic sputtering occurs in the first few ps after impact
- Use MD to impact ions over an irreducible symmetry zone on a crystal surface, typically several hundred for good statistics.
- Amass statistics such as sputtering yields and distributions, KE and angular distributions of sputtered particles
- Successive particle impacts not considered

MD simulation; Ar on
Cu(010)


5.00 KEV CU(001)/AR<001> SHULGA MOLIERE

SPOT PATTERN

Volume 14, Supplement 1 (1988) S55

FIGURE 17. An experimental dN/dΩ distribution (spot pattern) for Cu(001)-Ar^+⟨001⟩:4.0 keV captured on a plane glass plate. The ion beam entered through the central (white) hole. (From Southern, A. L., Willis, W. R., and Robinson, M. T., *J. Appl. Phys.*, 34, 153, 1963. With permission.)

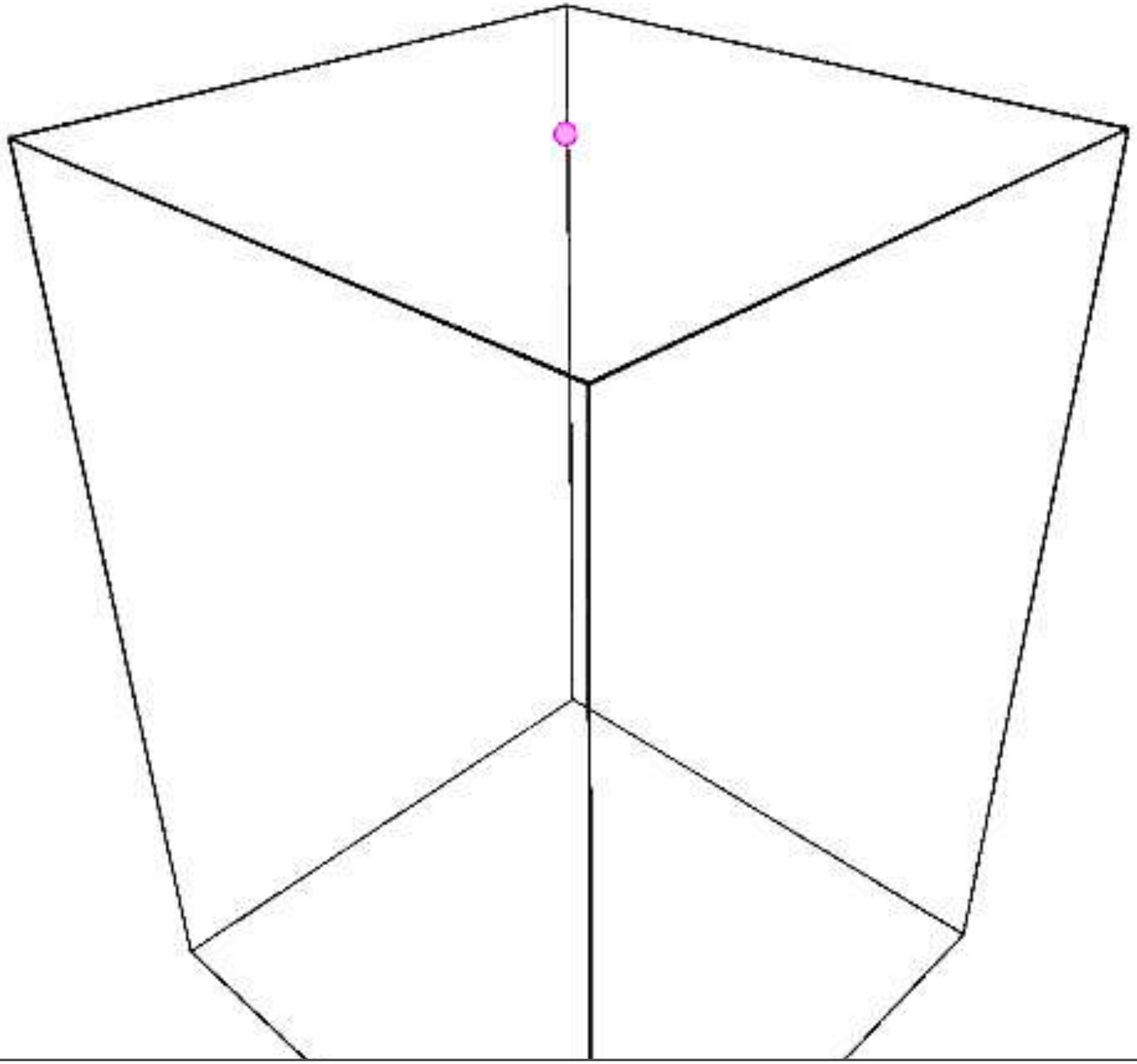
What about dose effects ?

MD simulation 2 keV Ar on Ni(100)

Key
red spheres Ni above the surface
purple sphere - Ar
green spheres - vacancies
cyan spheres - interstitials

Simulation duration : 10 ps
EAM potential

MD simulation 2 keV Ar on Ni(100)



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Example of MD : 1 eV O atom interaction with O-rich TiO_2 surface- variable charge potential

Red spheres O atoms
White spheres Ti

The ballistic-chemical etching event is over in 1.5 ps

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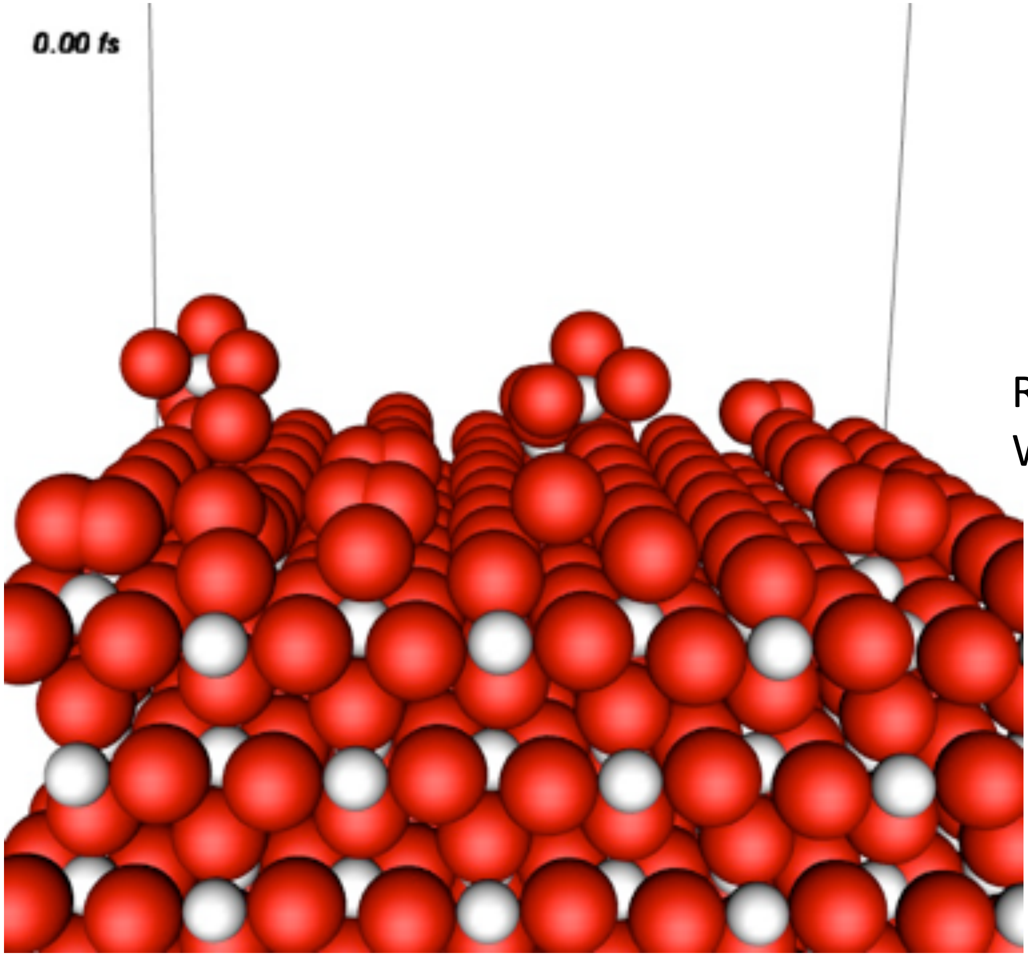

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The ballistic-chemical etching event is over in 1.5 ps

Example of MD : 1 eV O atom interaction with O-rich TiO_2 surface- variable charge potential

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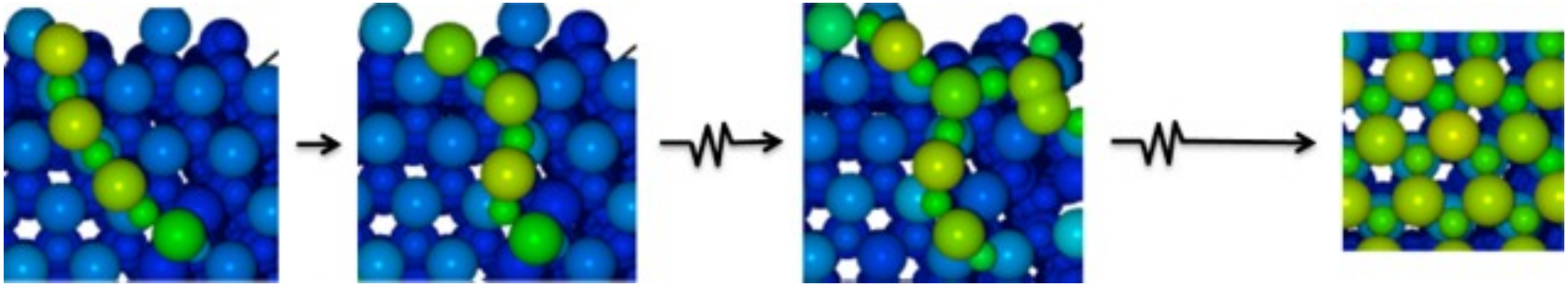
The ballistic-chemical etching event is over in 1.5 ps

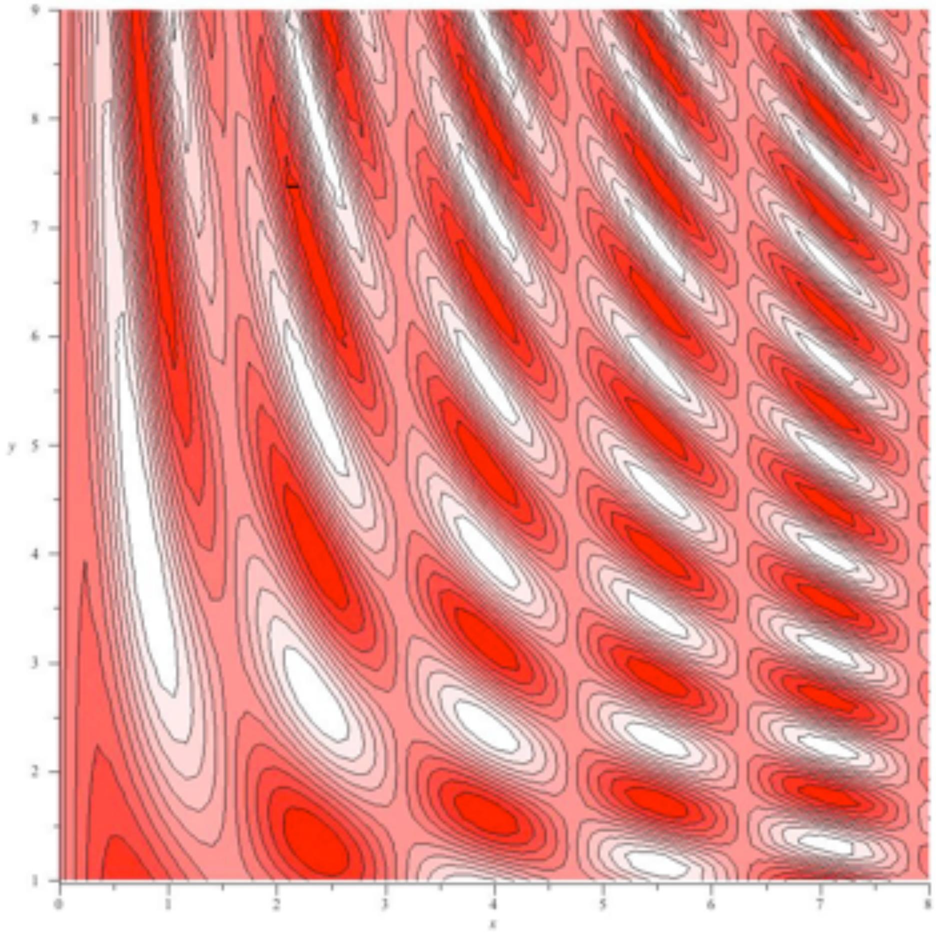
Example of an complex transition which cannot be guessed : String vibration on a ZnO surface (ReaXFF)



Small spheres represent Zn, large spheres O atoms

ZnO strings form on the surface and move with barriers of around 0.3 eV.
When interacting with other such strings they form the hexagonal structures for the next crystalline layers

A 2-dimensional example to illustrate the problem



Diffusion of atoms between impacts Corresponds to the jumps we see in this two-dimensional example.

Note that the jumps between the different basins of attraction occur over the saddle points on this two-dimensional surface.

The problem is we have no idea where the saddle points are and how high the barriers are. Guessing will not work.

We need a method to determine the transitions without guessing what they are

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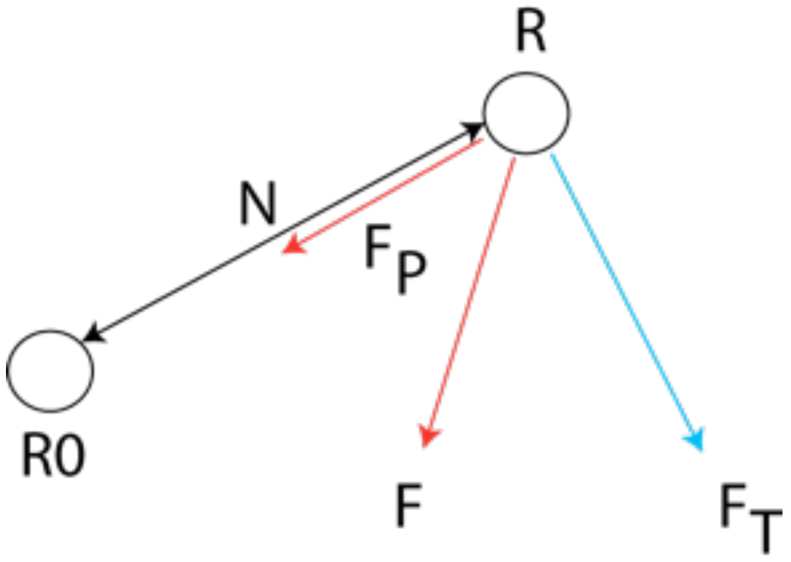
ART Method

The first step is to offset from the origin in a random direction.

At each step a displacement vector with unit normal **N**, connecting **R** to the original local minimum **R₀** is. calculated



ART - Translation

- Once decomposed a modified force, G, is created a:

$$\mathbf{G} = \mathbf{F} - (1+\alpha)(\mathbf{F}.\mathbf{N})\mathbf{N}$$

  - alpha is a control parameter that influences the aggressiveness of the search.

A large alpha will climb away from the minimum rapidly but may miss the saddle point by overshooting. Too small a value can miss some of the saddles.

Different saddles are found by different initial random displacements.

OTF-Kinetic Monte Carlo

(Henkelmann and Jonnson J. Chem. Phys. **115** 9657 2001)

$$r_{ij} = \nu \exp(-\frac{E_{ij}}{k_B T})$$

- On-the-fly KMC : system sizes typically 800-8000 atoms in our systems.

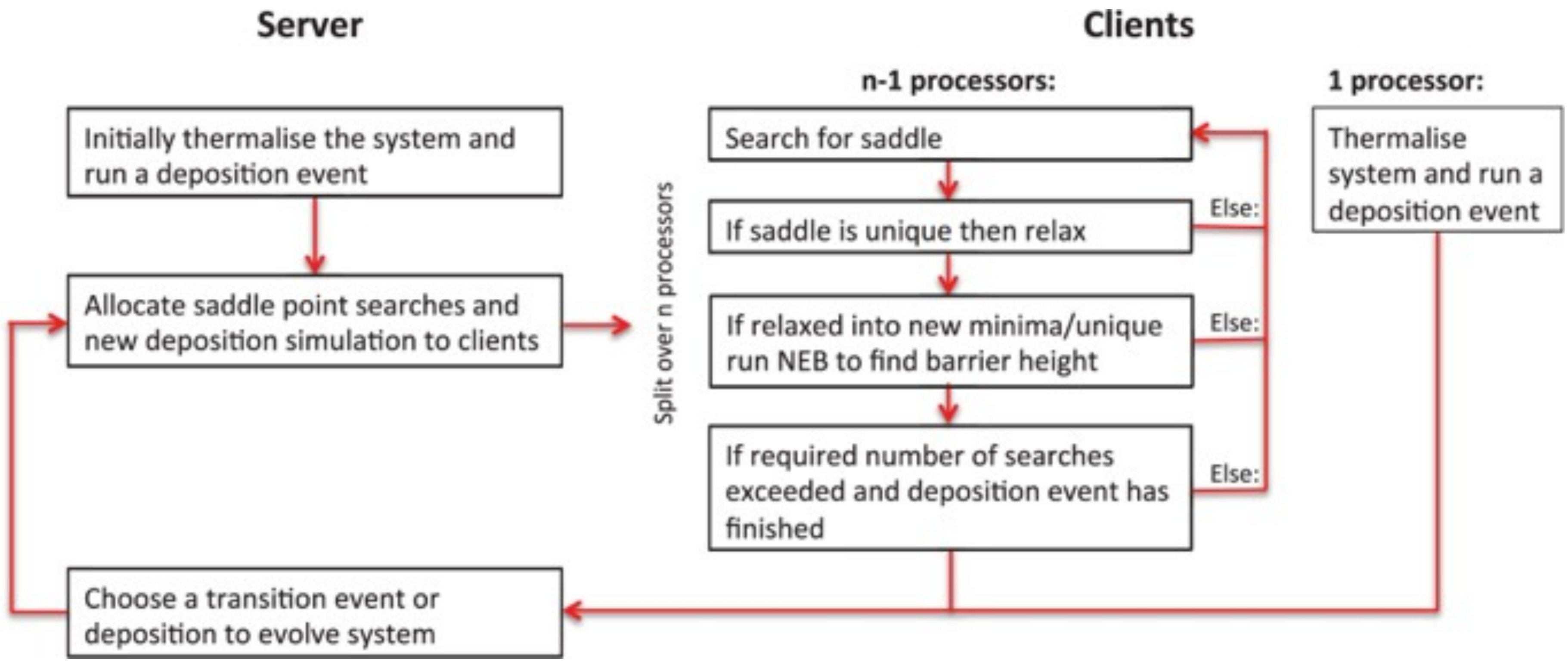
- For each minimum found, a list of *n* unique transitions from i to j with rates r_{ij}, *j=1..n* is constructed. Typically the search is terminated when no new unique transition is found after a fixed number of saddle searches, *or* when a fixed number of transitions have been found *or* after a fixed search time.

- Normally we assume a fixed prefactor but could use the Vineyard method instead.
  (G.H. Vineyard J. Phys. Chem. Solids **3** 121(1957))
  The sum of the transition rates, R is calculated and a random numbers, P_r and u between 0 and 1 are generated and multiplied by R.

- We cumulatively step through the rates R_i until we exceed P_r.R. The selected transition R_i is performed and the time of the system is increased by Δt where:

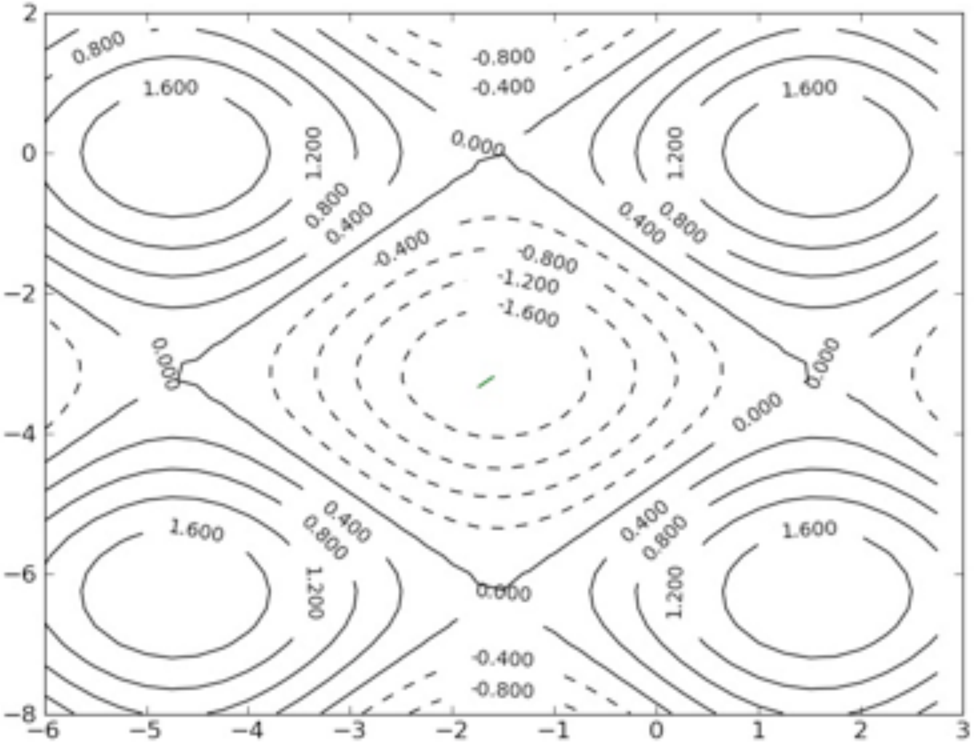
$$\Delta t = -\frac{\log u}{R}.$$

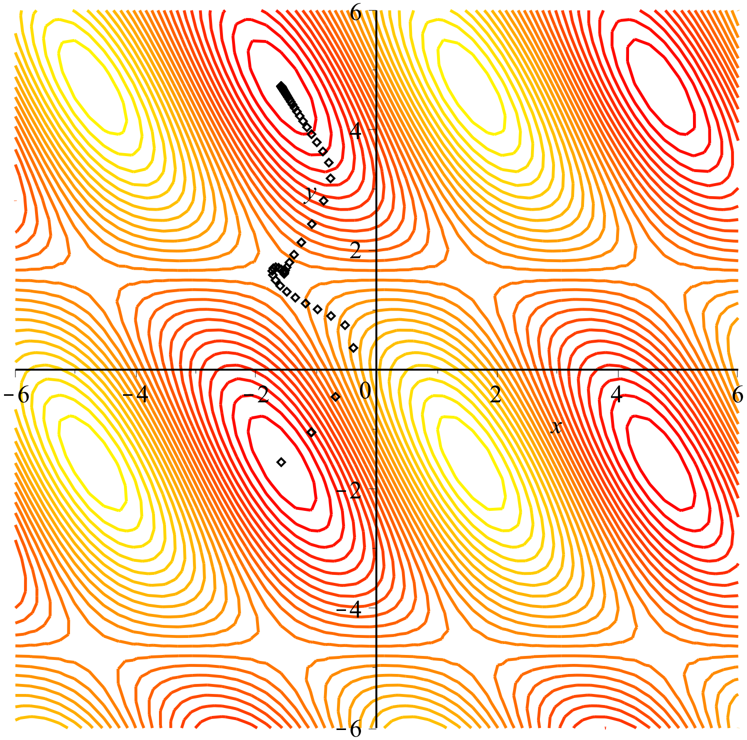
OTF-KMC method



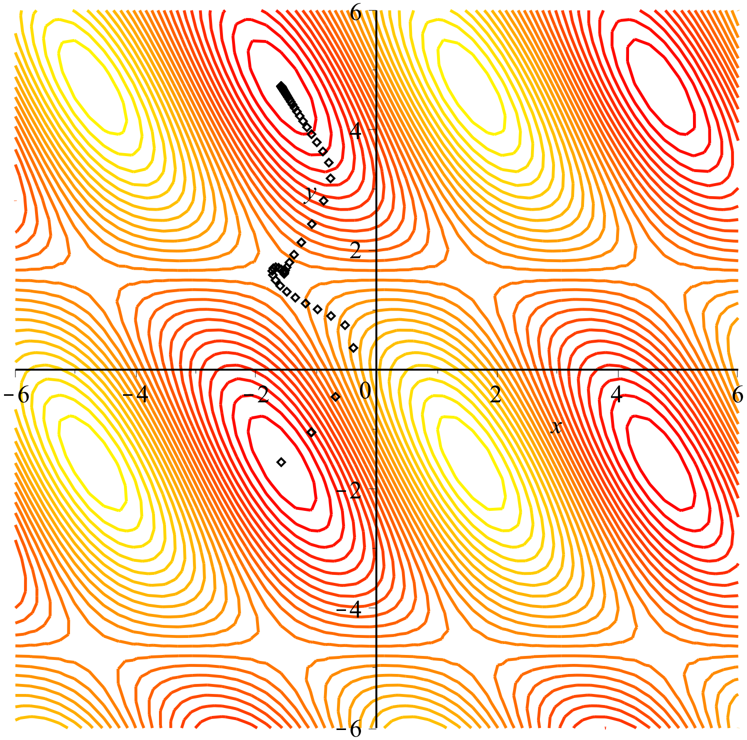
Code is written in Python and wraps around standard MD packages. In our case LBOMD and LAMMPS. The code was developed by Louis Vernon now at LANL and other PhD students in the group

Saddle searching methods





Saddle searching methods



The technique is time consuming so we need computational tricks to improve efficiency e.g. :

(1) Minimise the number of searches while retaining good statistics; typically we would perform > 200 such searches

(2) Initialise our initial search directions so as to sample the search space in the best way

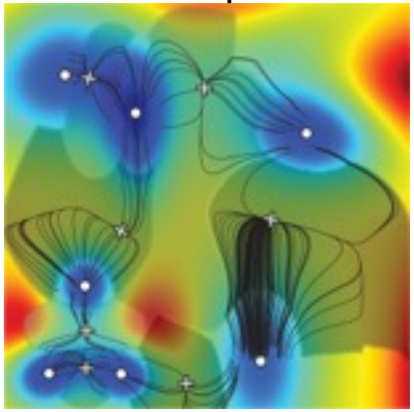
(3) Minimise the search space volume, i.e. only consider the defective regions

(4) Re-use previously determined transitions by recognising similar geometries (Pederson and Jonnson use path skipping also)

Dimer plus Lanczos algorithm

At a local minimum all eigenvalues of the Hessian matrix **H** are positive.

$$\mathbf{H} = \begin{bmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_{3N} \partial x_1} & \frac{\partial^{3N} E}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_{3N} \partial x_{3N}} \end{bmatrix}.$$



Pedersen and Jonnson SIAM 2011

At a rank 1 saddle (most of them) one of the eigenvalues of the Hessian matrix is negative.

Method: Use the dimer method to climb out of the basin of attraction of the minimum until one of the eigenvalues of the Hessian is negative, i.e. $C < 0$

Reverse the force along the direction of the negative eigenvalue (determined by the Lanczos method) and use the conjugate gradient algorithm, which now thinks the saddle is a minimum.

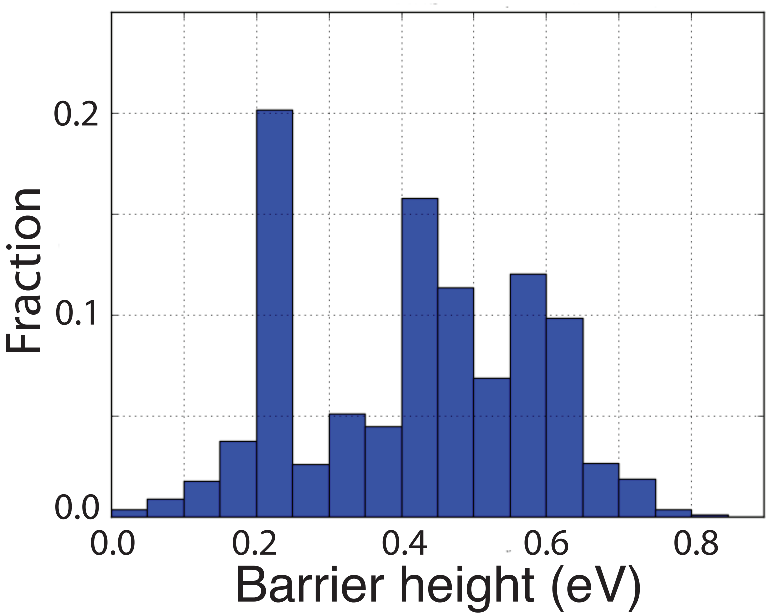
Faster than the previous method

This is currently our preferred method for determining saddles.

Sputtering with realistic dose rates

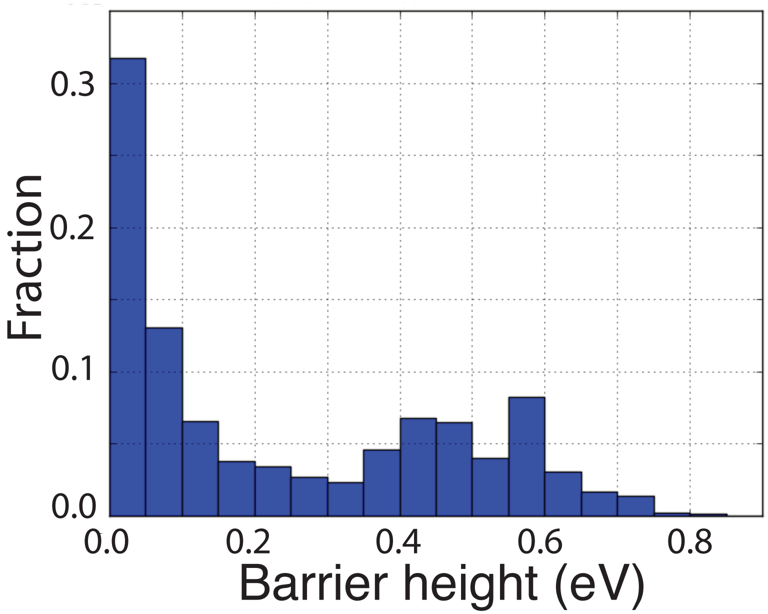
- Au {0 1 0} and (3 11 0} surfaces impacted at 500 eV with both Au and Ar ions. Ackland potential +ZBL.
- Surface areas 4 nm x 4 nm with 8,000 atoms in the system
- MD runs for 20 ps followed by OTF-KMC with a dose rate of ~ 2.5×10^{15} ions.$cm^{-2}s^{-1}$
- Bottom layer is held fixed. 350K thermostat for next 3 layers. PBC's is x and z.

All barriers for 500 eV sputtering of Au



(a)

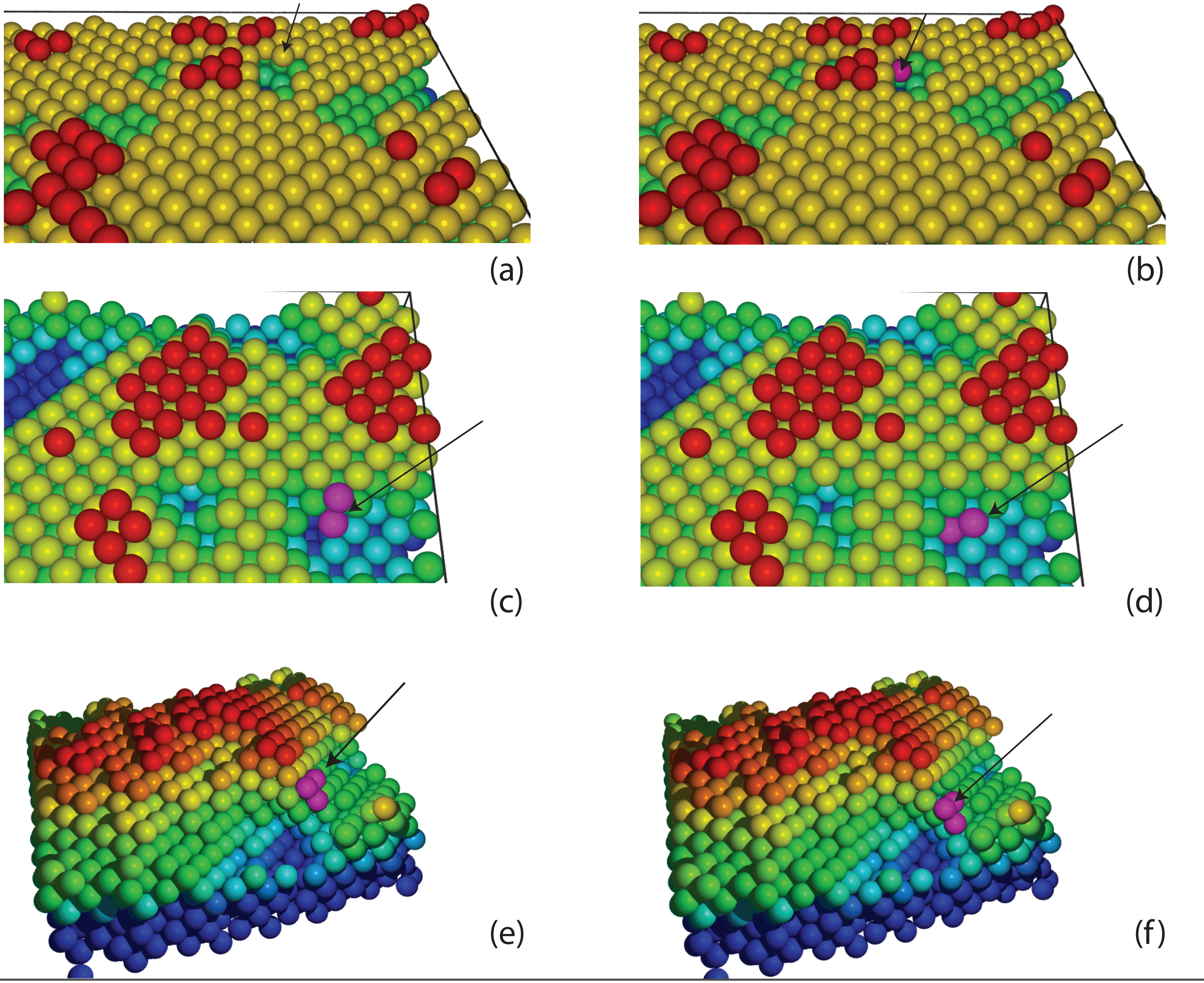
Au impact



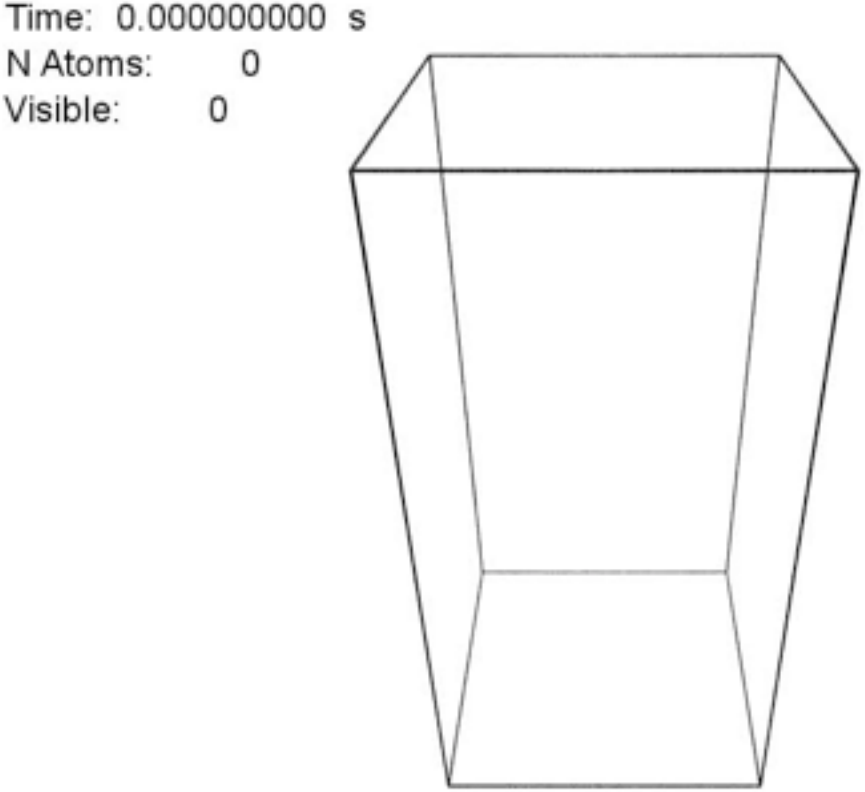
(b)

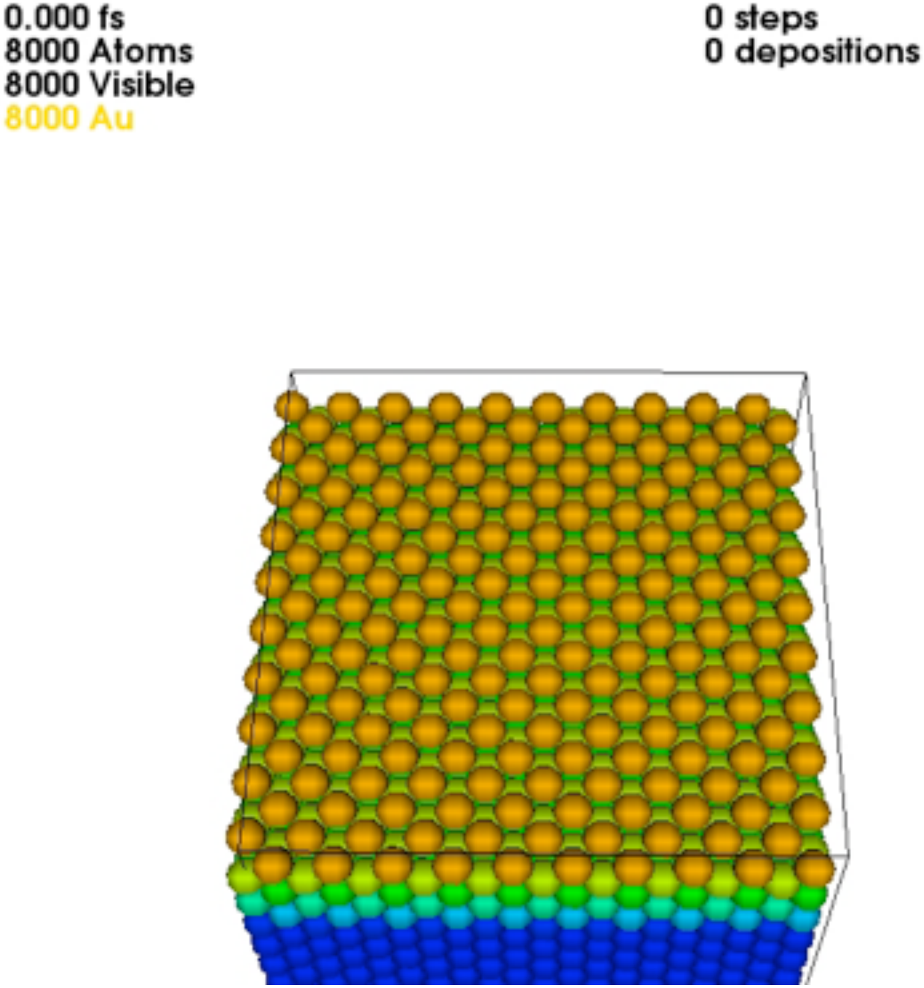
Ar impact

Healing mechanisms between impacts

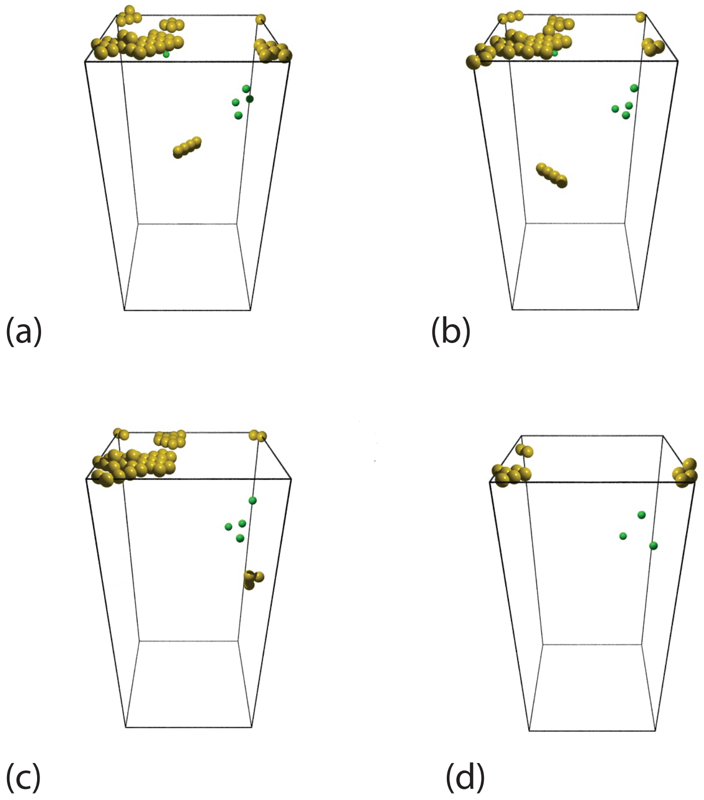


500 eV Ar incident normally on Au{010}

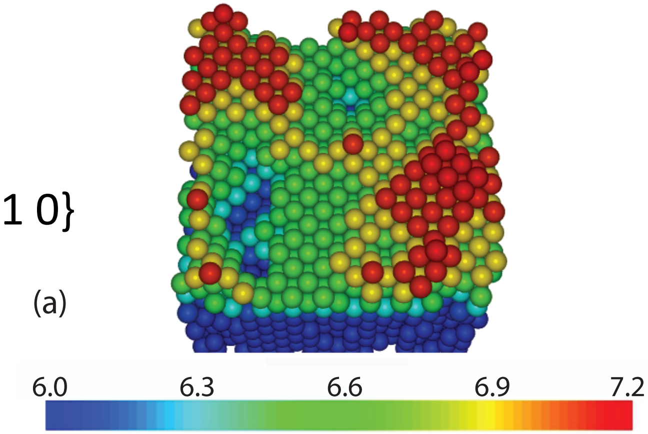




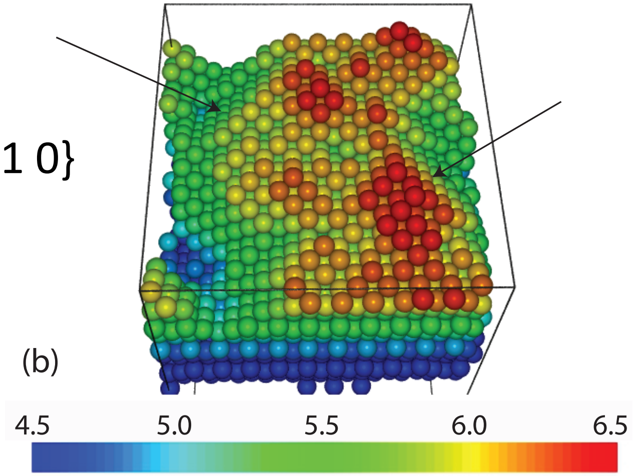
500 eV Ar on Au



{0 1 0}



{3 11 0}



height in nm

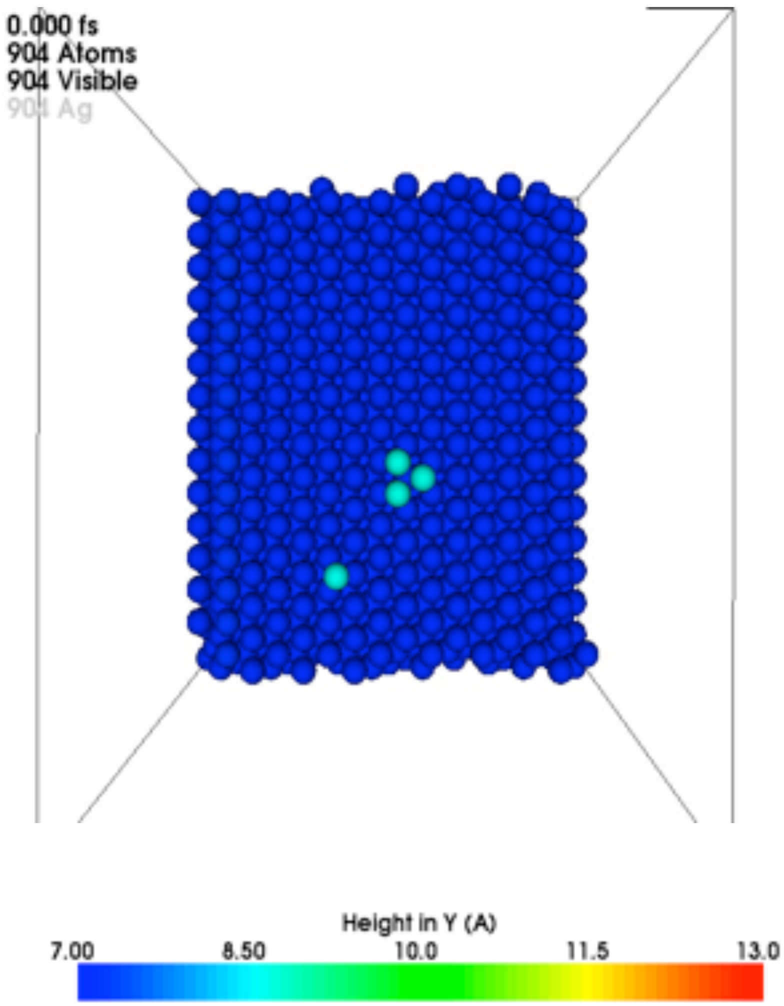
Ag{111} growth

- Ackland EAM potential
- {111} surface, 900 atoms in system
- Begin with a trimer on surface
- Periodic boundary conditions used, with bottom layer fixed and next layer thermalised, rest of lattice free
- Block transitions with energy barriers above 1.0 eV

Ag {111} growth

- 40 eV deposition at 350K, simulates growth by magnetron sputtering

- 3 monolayers of atoms added



Ag {111} growth

- 40 eV deposition at 350K, simulates growth by magnetron sputtering

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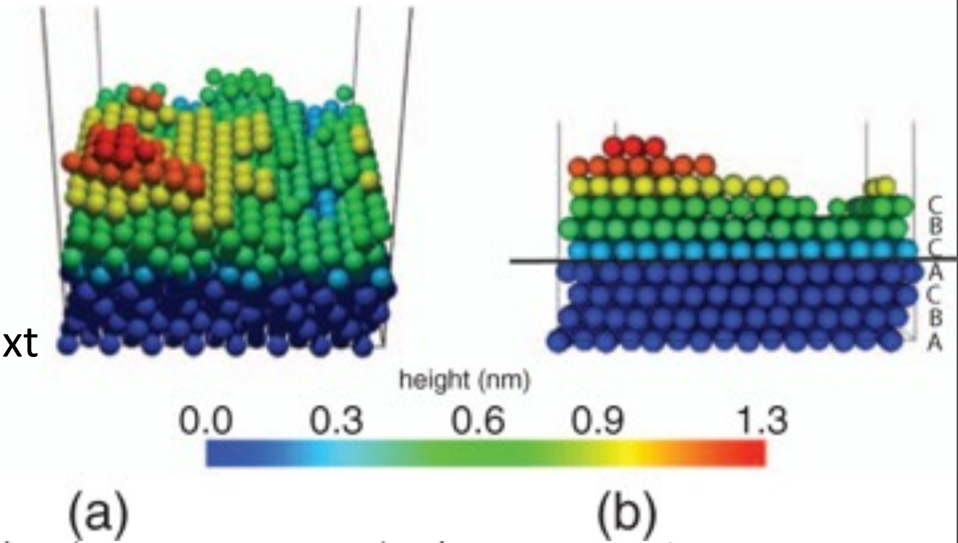
Ag {111} growth

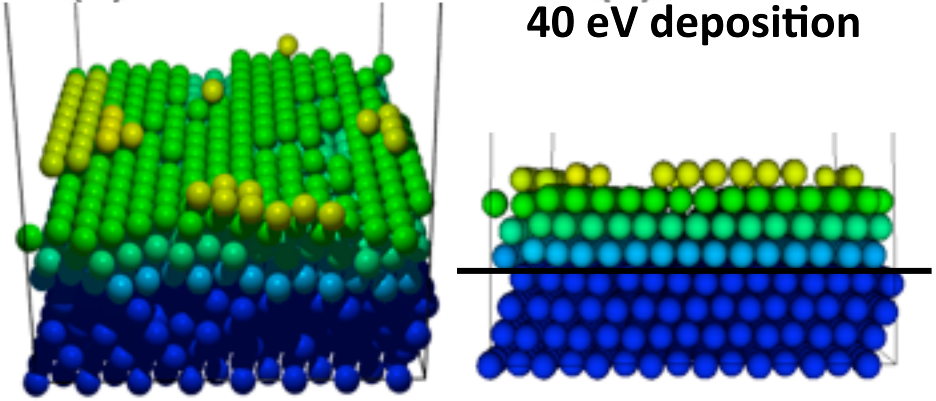
- **1 eV evaporation process:**
  - no complete layers
  - stacking fault
  - no mixing
- **40 eV sputter deposition:**
  - complete layers
  - correct stacking
  - mixing

1 eV deposition after 0.3s

Text

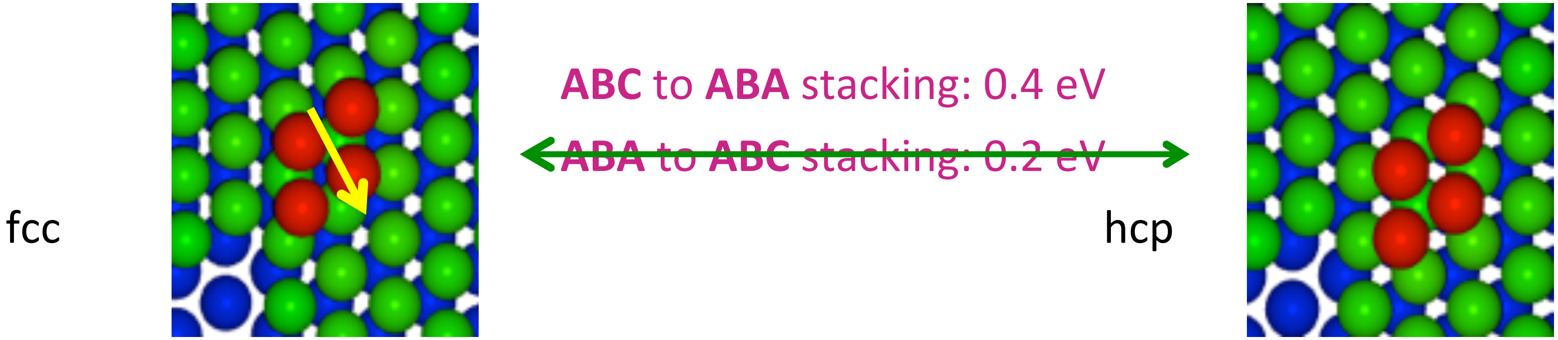


40 eV deposition



Modelling Ag {111} growth

- **Stacking faults:** accessible barriers



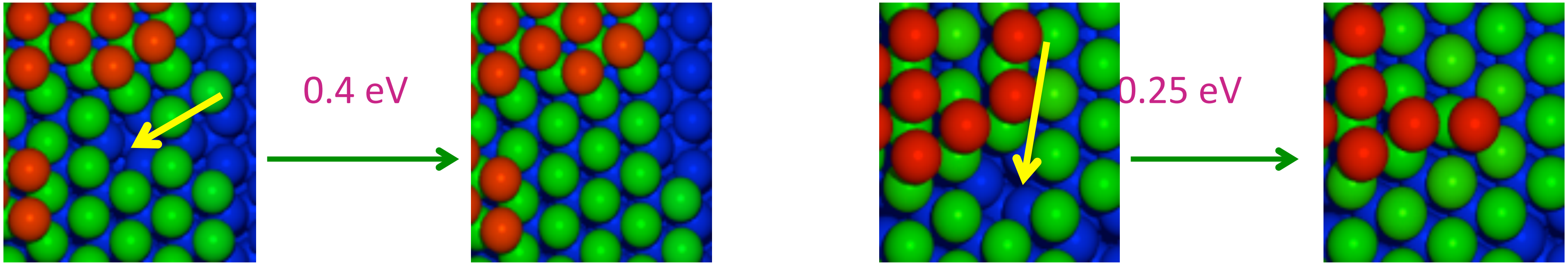
fcc

ABC to ABA stacking: 0.4 eV

ABA to ABC stacking: 0.2 eV

hcp

- **Hole filling:** Deposition <u>or</u> multi-atom concerted motion



0.4 eV

0.25 eV

Twin boundaries form when two 4/5 atom clusters are pinned by the addition of another atom in different position

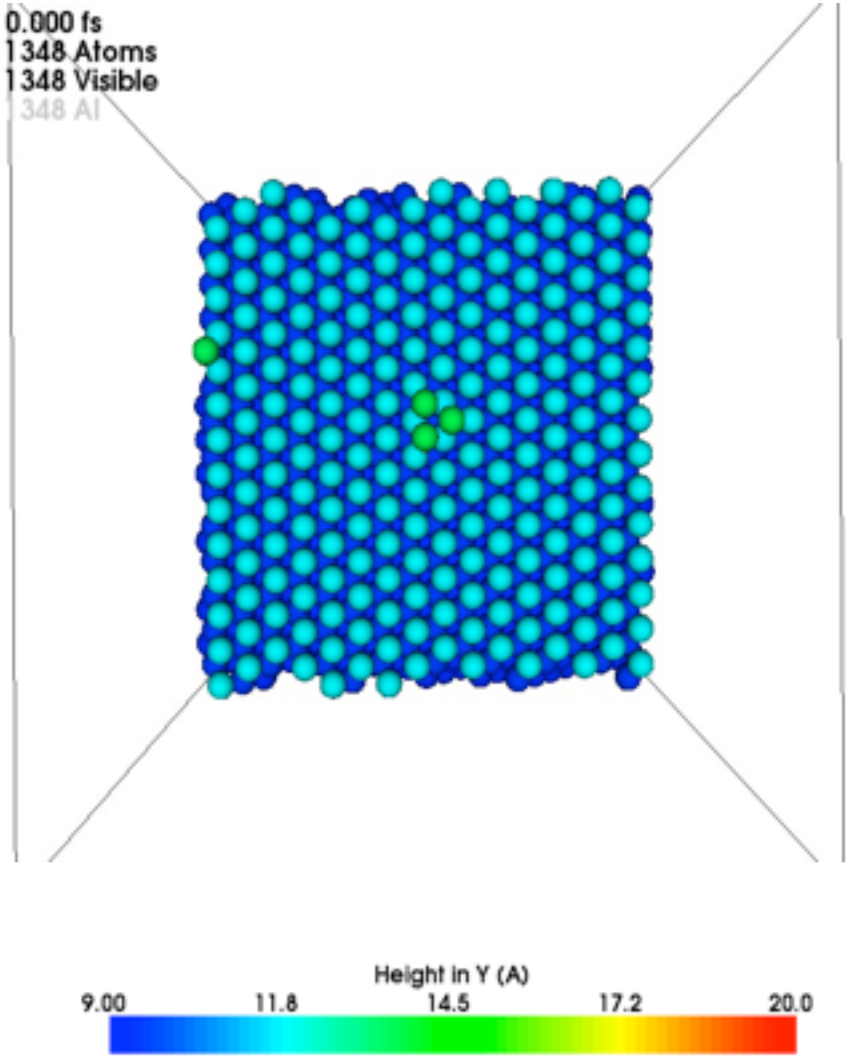
Modelling Al growth

- Voter and Chen potential
- {111} surface, 1344 atoms in system, 6 layers
- Begin with a trimer on surface
- Periodic boundary conditions used, with bottom layer fixed and next layer thermalised, rest of lattice free

Al {111} growth

- 1 eV depositions at 350K, simulates an evaporation deposition process

- 3 monolayers of atoms added



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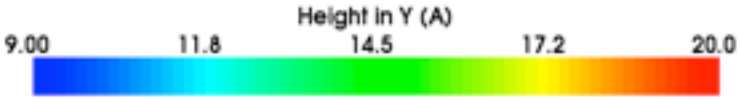
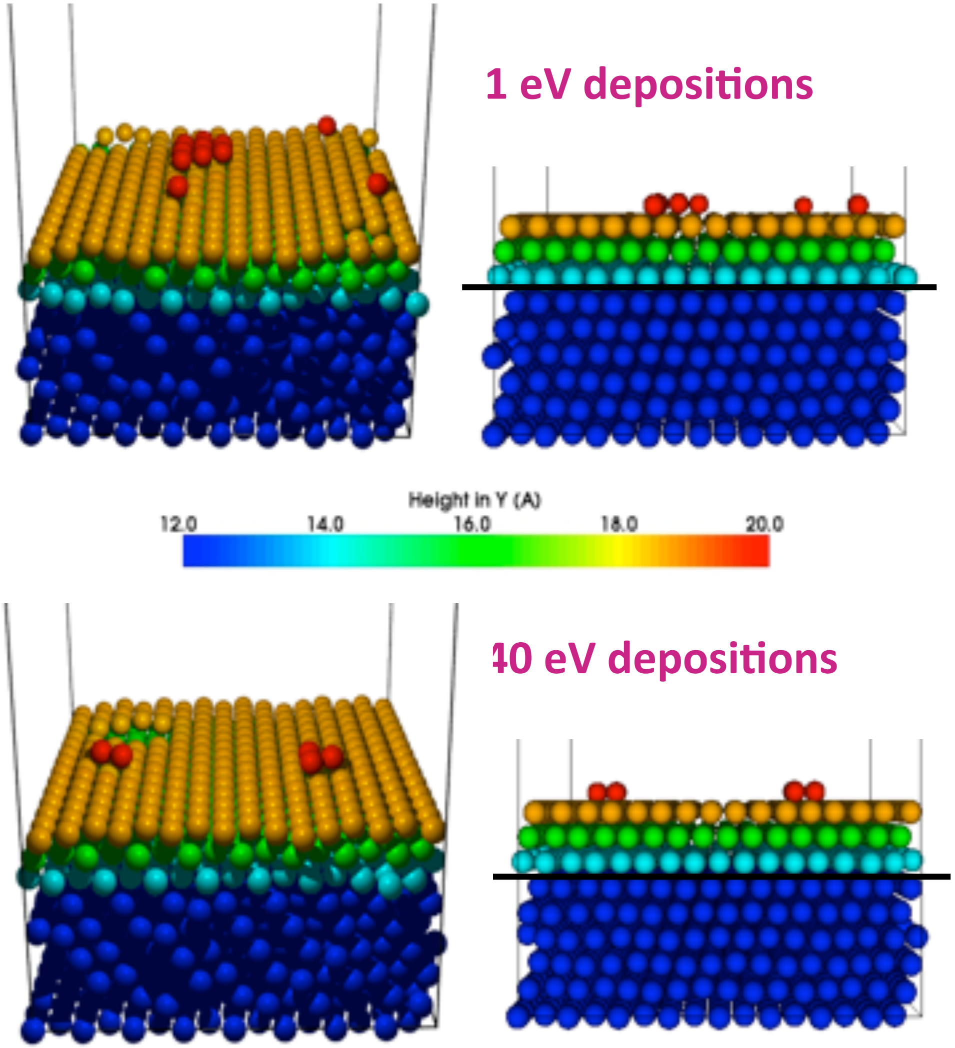


Al {111} growth

- **1 eV evaporation process**
    - - 2 complete layers
    - - correct stacking
    - - little mixing

- **40 eV sputter deposition:**
    - - 2 complete layers
    - - correct stacking
    - - mixing

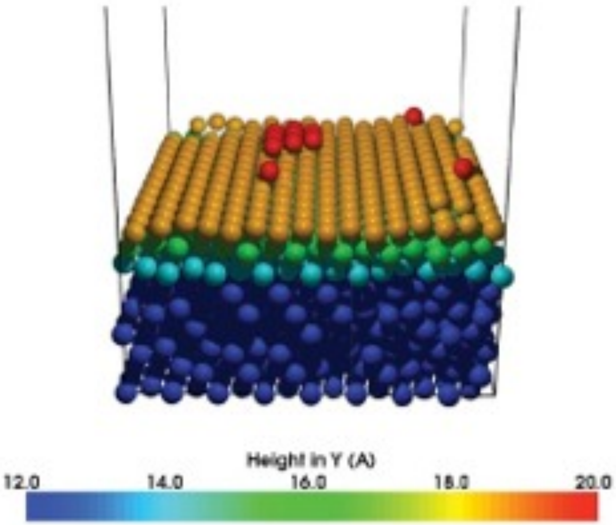


1 eV depositions

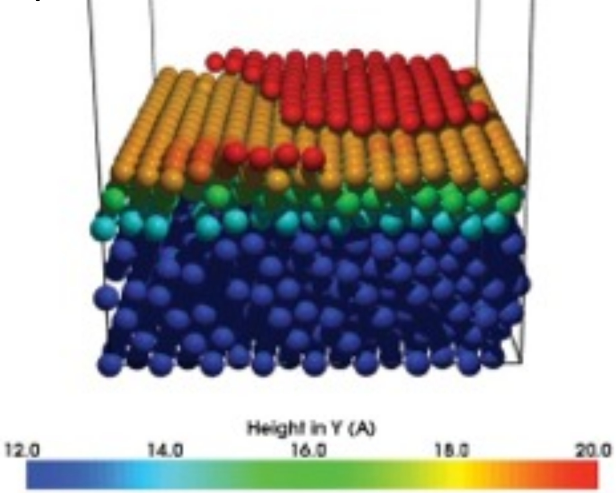
40 eV depositions

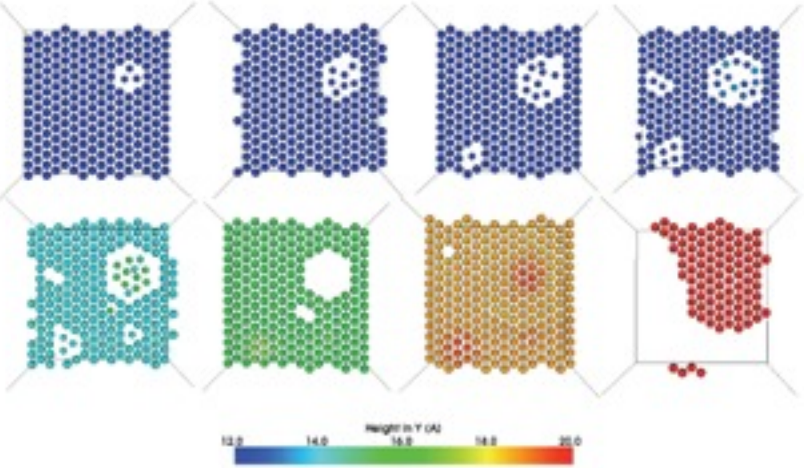
Al {111} growth : Does ion assist with evaporation deposition help ?

Evaporation : no ion assist



Evaporation : with Ar ion assist





Why are Ag and Al so different ?

- Ag ES barrier is 0.42 eV:
- Al ES barrier is 0.07 eV:
- Ar diffuses to the surface in the case of Ag

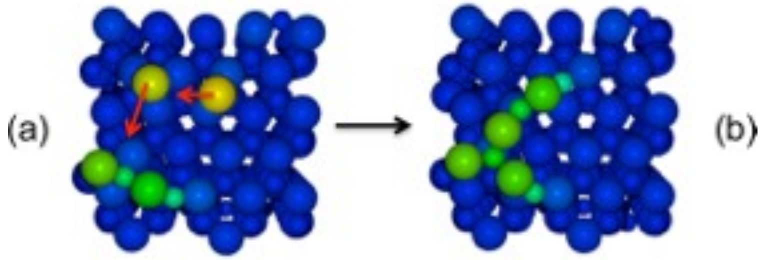
For Al evaporation deposition produces smooth uniform films for Ag the added energy of magnetron sputtering or ion assist is required to produce the more uniform films

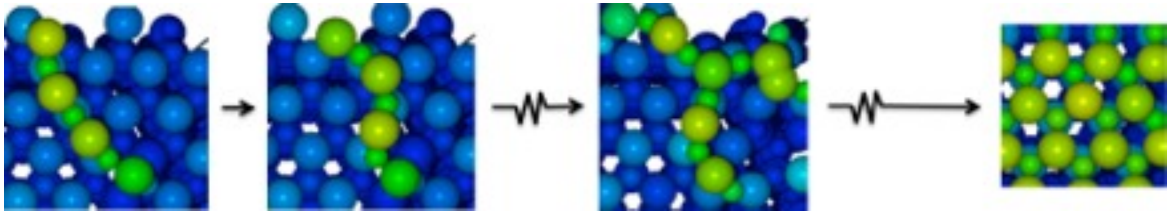
Modelling ZnO growth

- Variable charge ReaxFF potential
- Periodic boundary conditions; bottom layer fixed, next layer thermalised, rest of lattice free
- Block transitions with barriers above 1.0 eV, and block O dimers rotating where no net diffusion occurs
- ZnO, Zn, O, O_2 ad-atoms deposited onto O-terminated surface at various mixes depending on deposition process

Growth Mechanisms

- Zn_xO_x strings form on surface and vibrate with small barriers



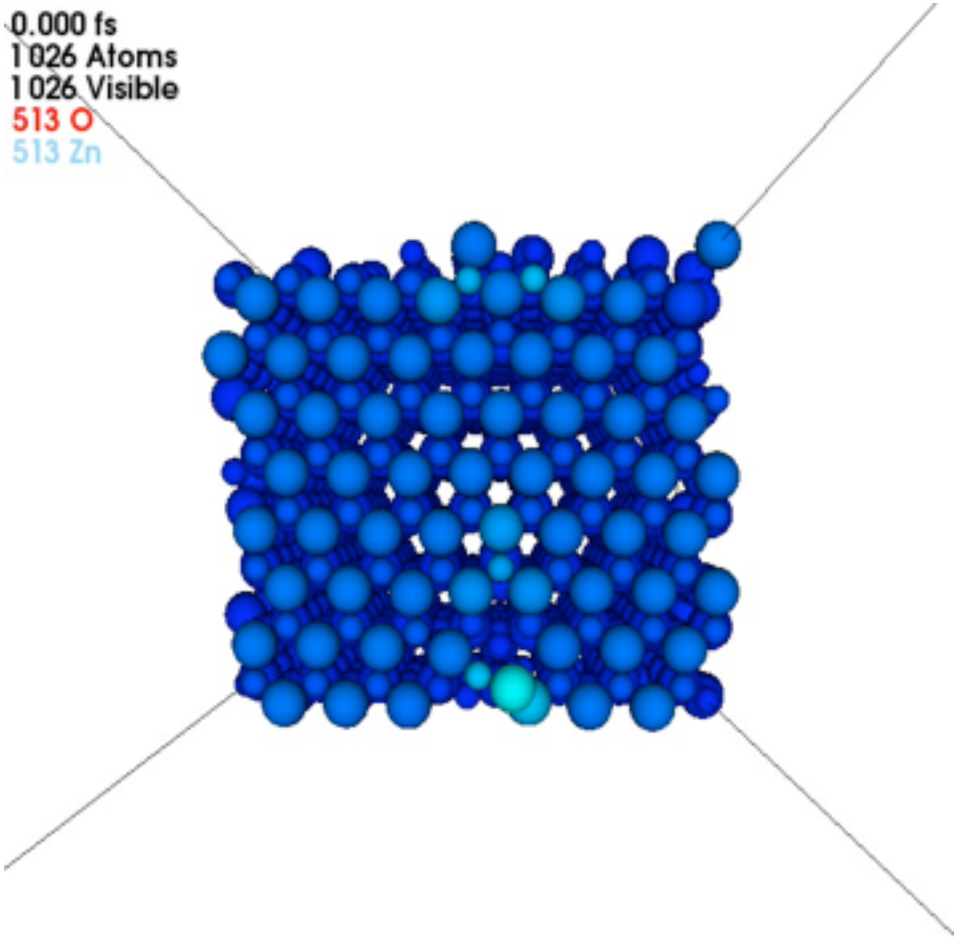


- Strings form hexagonal structures in the wurzite or zincblende form:

ZnO growth

- **40 eV deposition of O rich Zn_xO_y mixture** at 350K
- Large spheres O atoms
- Small spheres Zn atoms

- ~ 1/2 s simulated
- 1 layer added



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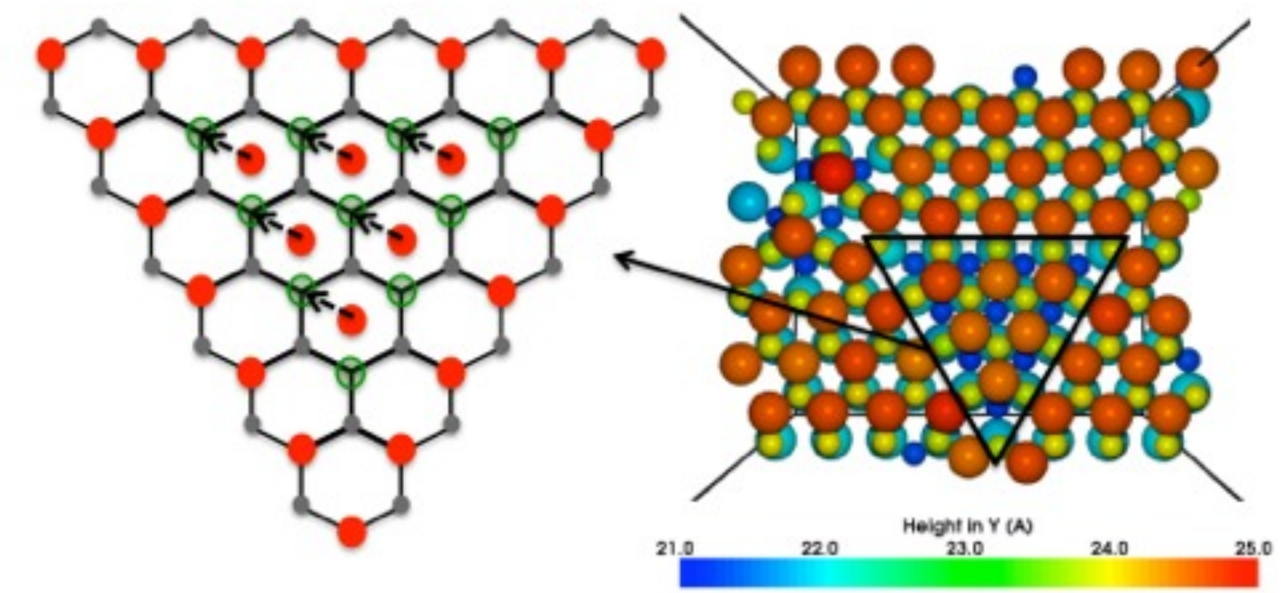
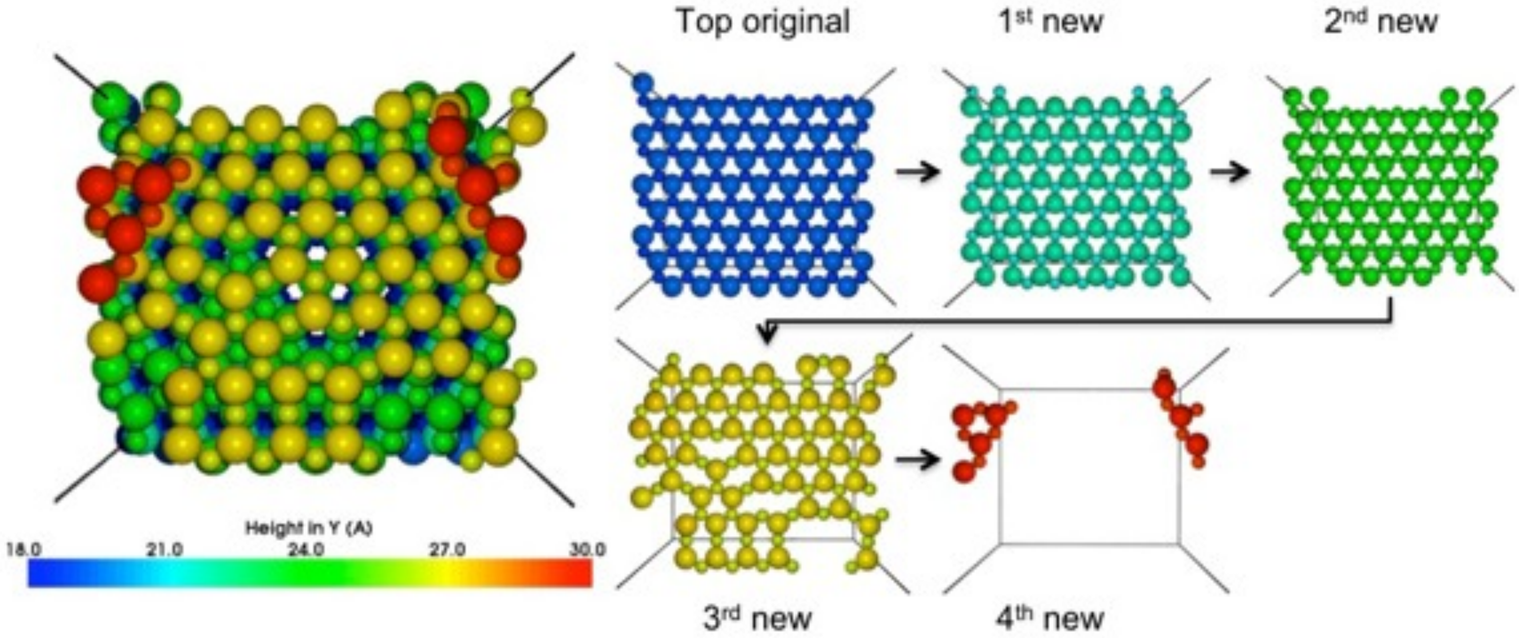
Stacking Fault formation in ZnO growth



Post-deposition annealing at 900K improves the crystalline structure



TiO_2 growth

- Variable charge potential modified by Louis Vernon
- Initial rutile 1536 atom lattice with 8 layers
- Periodic boundary conditions used, with bottom layer fixed and next layer thermalised, rest of lattice free
- Block transitions with barriers below 0.4 eV and above 1.0 eV
- A mixture of O, O_2, Ti, TiO and TiO_2 clusters are deposited

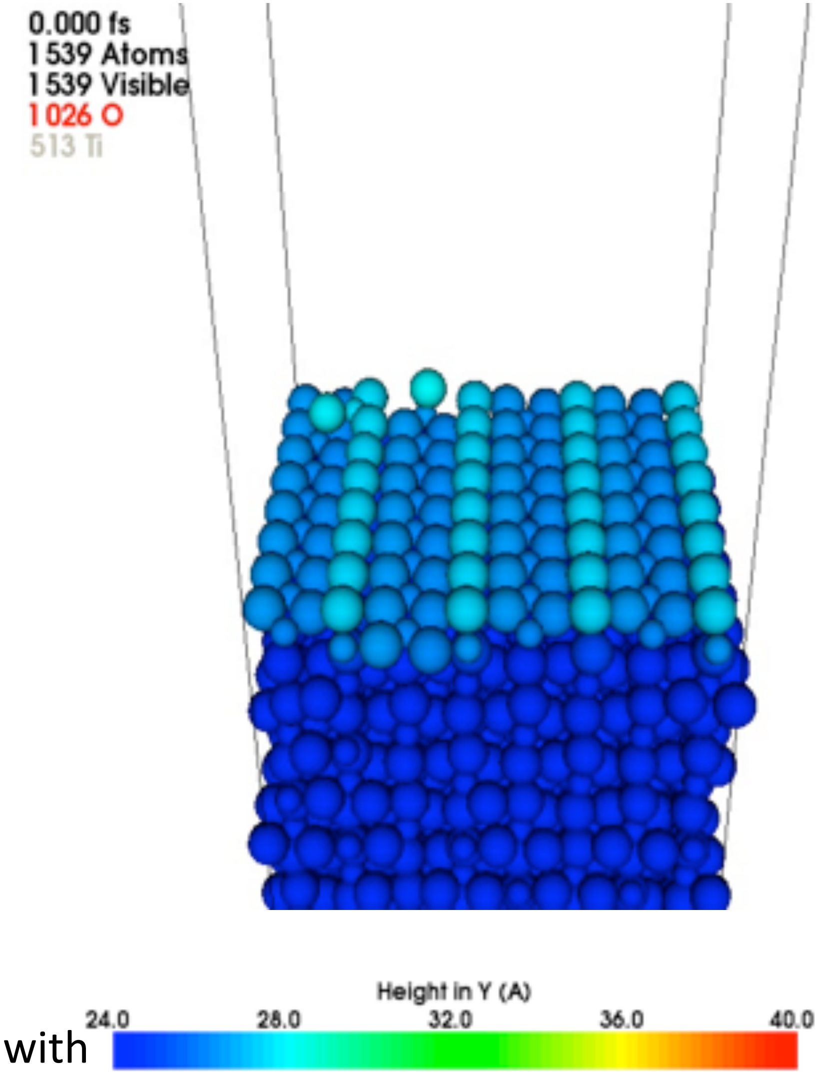
Rutile Growth Mechanisms

- Ti atoms form interstitials. O atoms decorate the surface.
- Titania growth via migration of first layer Ti interstitials up to the surface in the presence of an O rich surface

- O atoms are mobile on the surface
- The presence of O atoms above Ti interstitial reduces energy barrier for diffusion to the surface.

Sputter Deposition

- 40 eV deposition at 350K, simulates sputter deposition
- 4 monolayers added with molecules arriving stoichiometrically
- 6 s simulated



Including Ar improves slightly the structure slightly with
~ 1% Ar inclusion in the film

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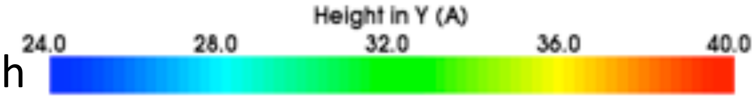
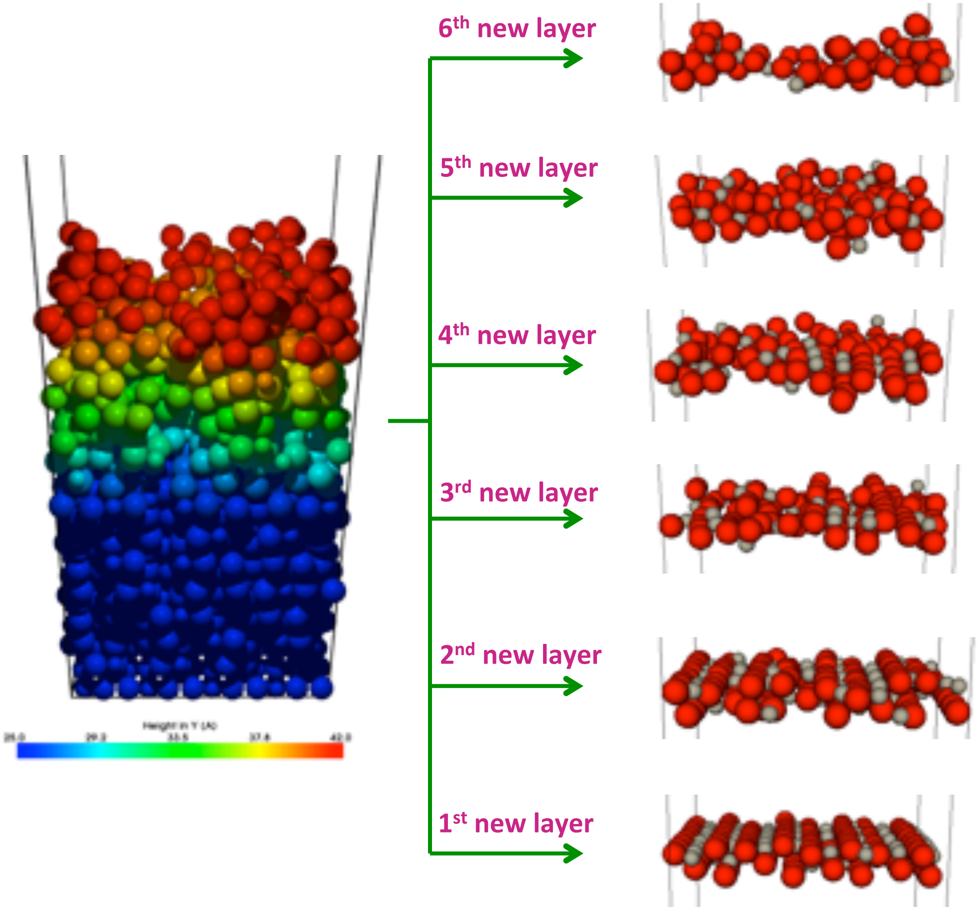


Modelling TiO_2 growth

1 eV ..evaporation process:



6th new layer

5th new layer

4th new layer

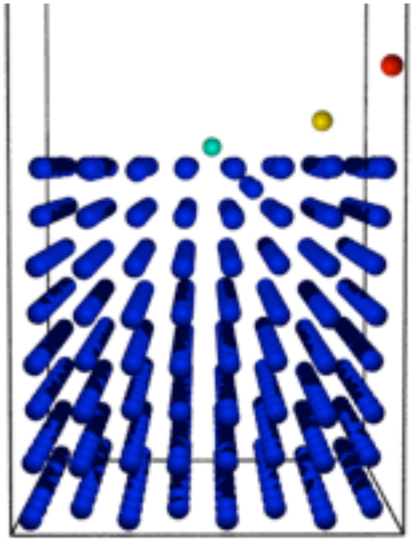
3rd new layer

2nd new layer

1st new layer

- Atoms missing from layers
- Low energy allows little diffusion
- Little mixing of original atoms

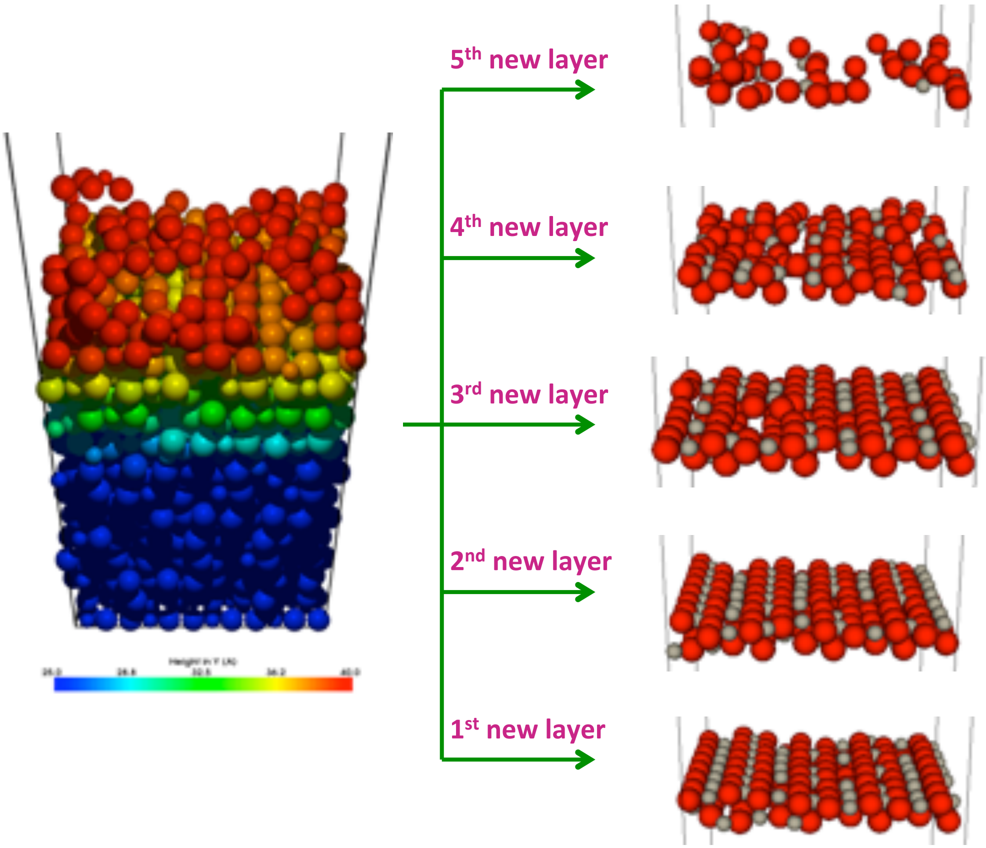
Ti:



Wednesday, 3 October 12

Modelling TiO_2 growth

40eV.. sputter deposition:



5th new layer

4th new layer

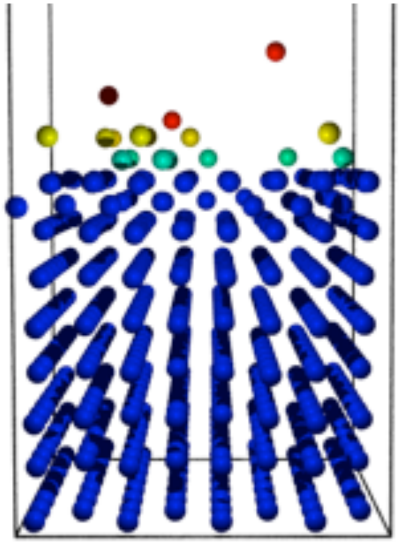
3rd new layer

2nd new layer

1st new layer

- 3 very good layers
- Mixing mechanism with original substrate, allowing rutile growth mechanism

Ti:



CONCLUSIONS

The methodology enables growth mechanisms to be identified but beware of finite size effects

Parameters can be varied on the computer to optimise the resulting growth

Defect mechanisms can be identified but limited by size effects

Fcc metals Ag and Al grow quite differently due to the different ES barriers and the diffusion barriers for incorporated Ar. So Al is crystalline when grown by evaporation whereas Ag is more crystalline when grown by sputtering

The oxides ZnO and TiO_2 have completely different growth mechanisms.
We can get good rutile growth with sputtering and crystalline ZnO by post annealing.

There is further scope to improve the methodology and to apply it to other systems

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