

Molecular dynamics study of the growth of various crystalline phases of metal oxides

J. Houska

*Department of Physics and NTIS - European Centre of Excellence,
University of West Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic*



EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
INVESTING IN YOUR FUTURE





Molecular dynamics study of the growth of various crystalline phases of metal oxides

J. Houska

*Department of Physics and NTIS - European Centre of Excellence,
University of West Bohemia, Univerzitni 8, 306 14 Plzen, Czech Republic*

Acknowledgment

- European Regional Development Fund through project "NTIS - New Technologies for Information Society", European Centre of Excellence, CZ.1.05/1.1.00/02.0090
- Alexander von Humboldt Foundation through fellowship No. 1140782
S. Mraz, J.M. Schneider - RWTH Aachen



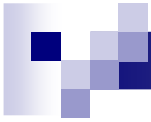
EUROPEAN UNION
EUROPEAN REGIONAL DEVELOPMENT FUND
INVESTING IN YOUR FUTURE





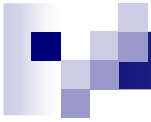
Motivation

- Reproduce growth of metal oxides using classical MD
- ⇓
- Relationships between growth conditions and phase formation
- ⇓
- Define pathways for synthesis of desired phases



Outline

- Methodology
- Growth of TiO_2
4 Figs. from [*J. Houska, S. Mraz and J.M. Schneider, J. Appl. Phys. 112, 073527 (2012)]*
- Growth of Al_2O_3
4 Figs. from [*J. Houska, Surf. Coat. Technol. 235, 333 (2013)]*
- Effect of bombardment by high-energy atoms including Ar
4 Figs. from [*J. Houska, Surf. Coat. Technol. 254, 131 (2014)]*
- Conclusions



Simulation protocol

- Recursive atom-by-atom simulation protocol
 - 1) **Substrate** or previously nucleated grain
(given size, composition, structure, temperature T)
 - 2) **New atoms**
(given flux composition, energy E)
 - 3) **Fixed-energy (NVE) run**
(particle collisions and energy dissipation)
 - 4) **Fixed-temperature (NVT) run**
(to reestablish the deposition temperature)
 - 5) **Removal** of resputtered/desorbed particles and return to 2
- Varied energy or EDF, temperature, growth template
- Disentangled nucleation and growth



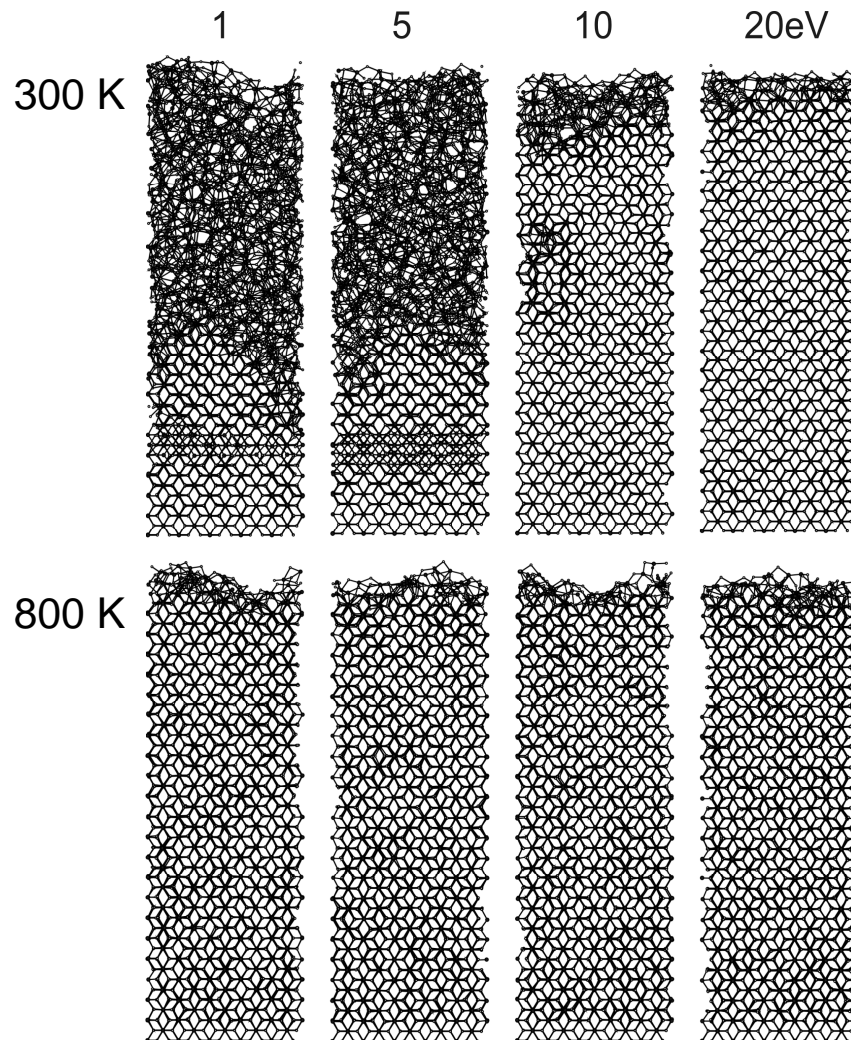
Partial-charge Buckingham interaction potential

- Crystalline phases = local energy minima: insufficient
- Open surface growth tests
- In the case of ionic (not covalent) crystals:
 - reactive bond order potential (REBO; many fitting parameters) performs horribly
 - simple 2-body potential (few fitting parameters) performs very well
- In the case of potentials including Coulombic component
 - 'full charge' potentials (e.g. $\text{Ti}^{+4}\text{O}^{-2}$ or $\text{Al}^{+3}\text{O}^{-2}$) lead to high potential energies delivered into materials
 - 'partial charge' potentials (often close to O^{-1}) lead to more reliable results



growth of rutile TiO_2 (001)

effect of ion energy, E , at $T = 300$ or 800 K

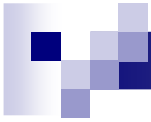


■ Experiment:

- deposition of rutile requires high E and/or T

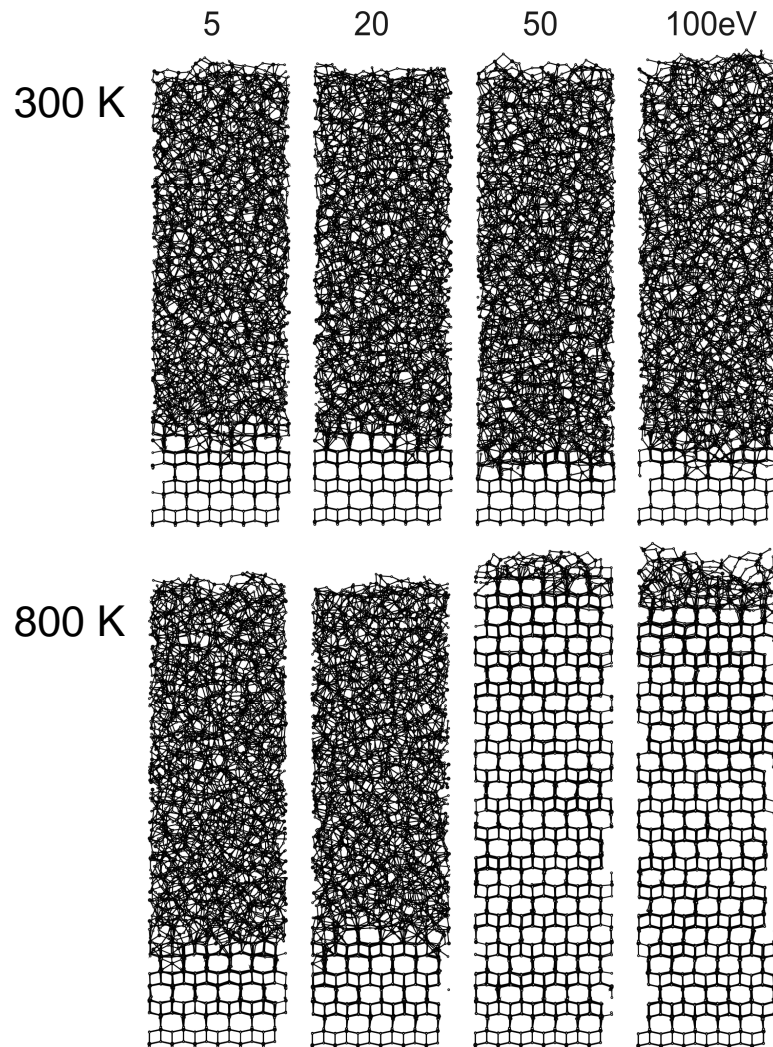
■ Simulation:

- high E and/or T is needed for nucleation only
- nucleated rutile grows in a wide range of conditions
- independent of crystal orientation (not shown)



growth of anatase TiO_2 (001)

effect of ion energy, E , at $T = 300$ or 800 K



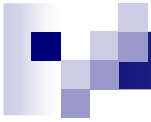
■ Simulation:

- amorphization at too low E or low T
- amorphization at too high E (not shown)



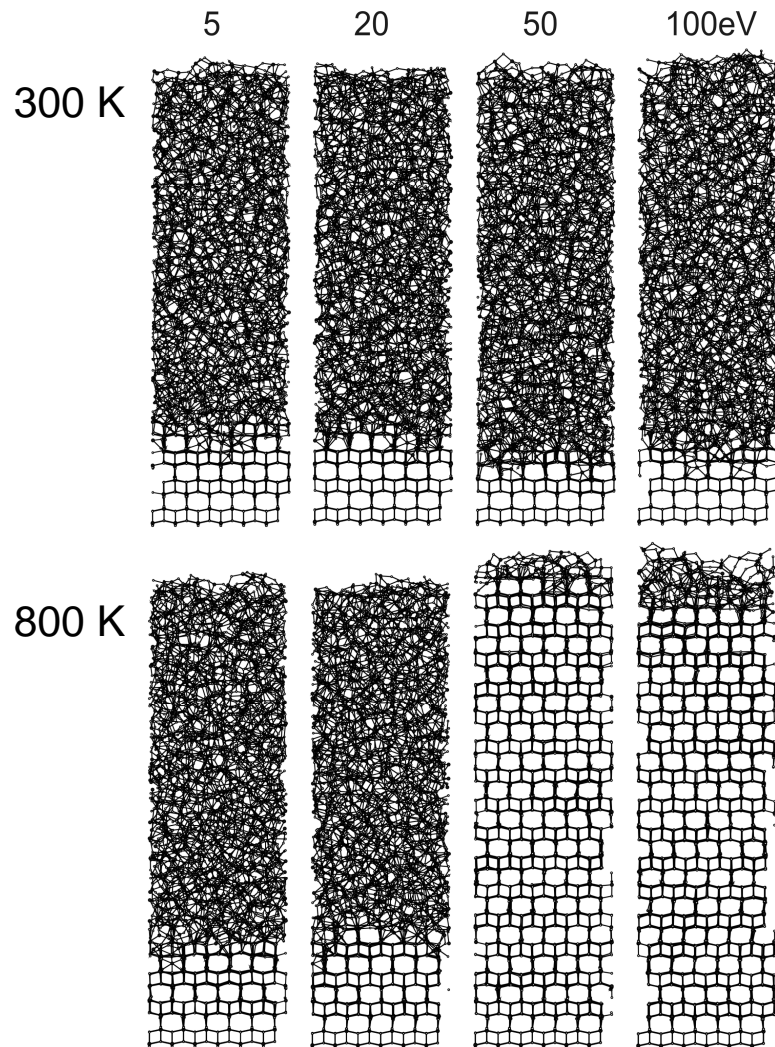
■ Qualitative difference

- presence of anatase is controlled by growth
- presence of rutile is controlled by nucleation



growth of anatase TiO_2 (001)

effect of ion energy, E , at $T = 300$ or 800 K



■ Qualitative difference

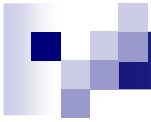
- presence of anatase is controlled by growth
- presence of rutile is controlled by nucleation



Experiment

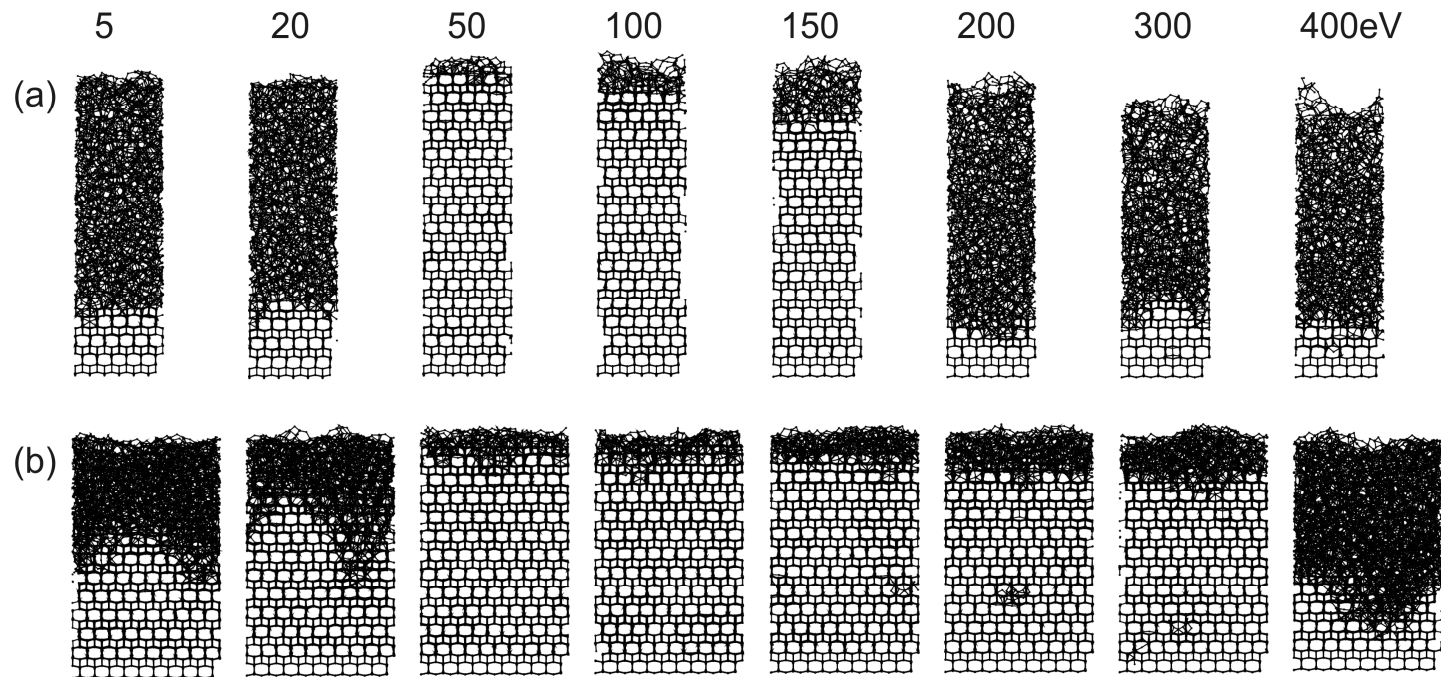
[S. Mraz in J. Houska, S. Mraz and J.M. Schneider, *J. Appl. Phys.* 112, 073527 (2012)]

- anatase obtained in low-density DC plasma
- rutile survived high-density RF plasma (but required higher T)



growth of anatase TiO_2 (001)

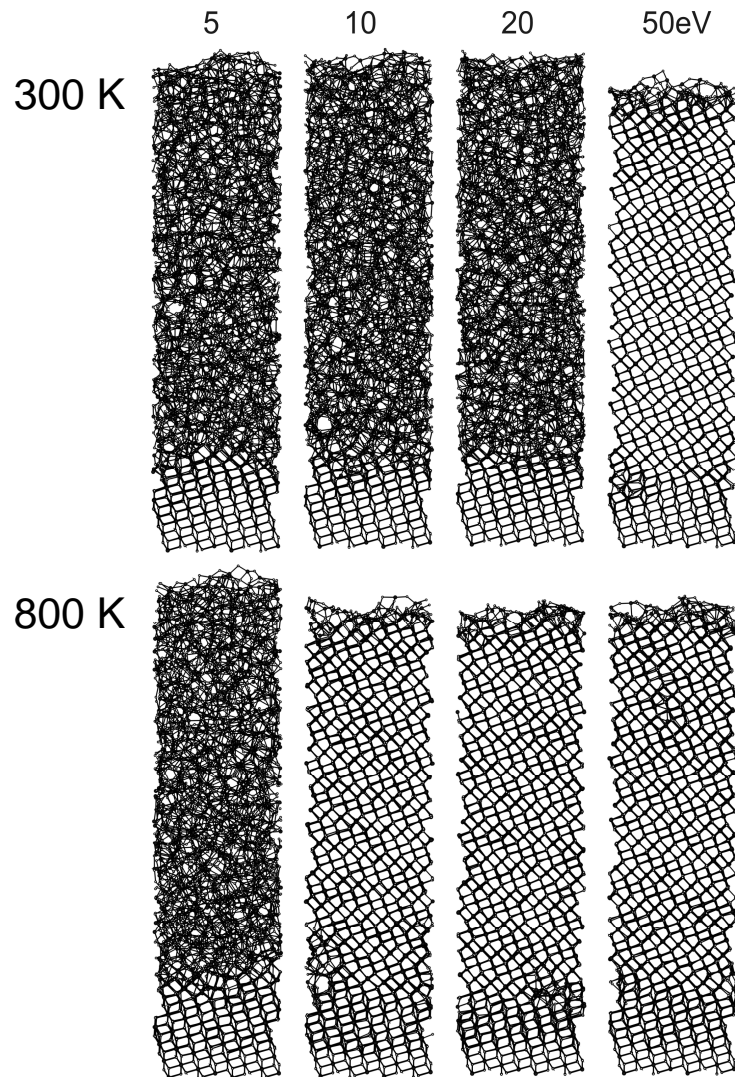
effect of ion energy and crystal size, E , at $T = 800$ K



- Anatase (not rutile) growth limited also by maximum E
- Dependence on crystal width

growth of anatase TiO_2 (111)

effect of ion energy, E , at $T = 300$ or 800 K



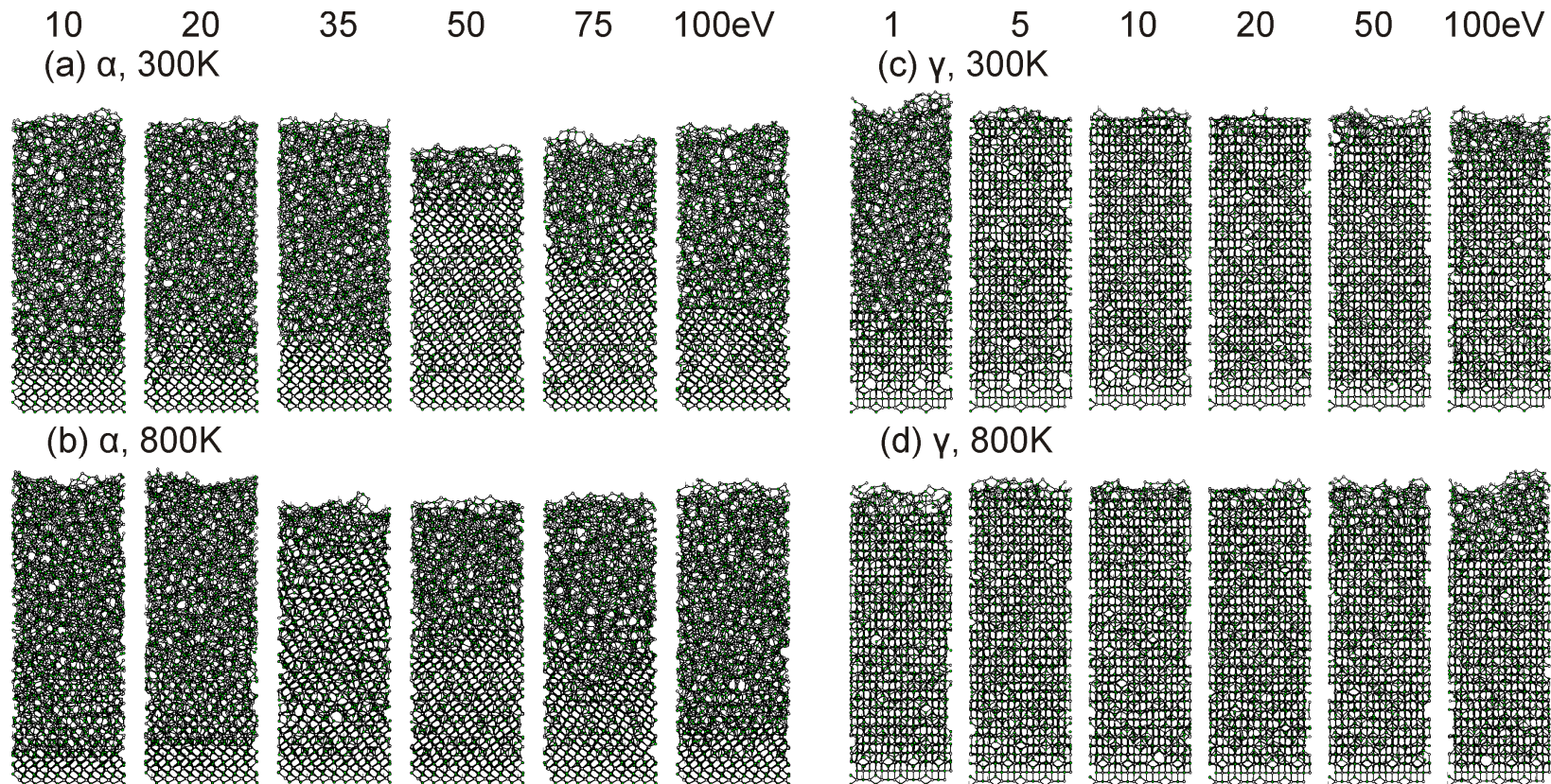
■ Simulation:

- (111) anatase amorphizes or converts to distorted rutile
- same observation also for (110) anatase (not shown)

■ Experiment

- indeed, (111) and (110) anatase not observed experimentally

growth of α -Al₂O₃ (0001) and γ -Al₂O₃ (001)
effect of ion energy, E , at $T = 300$ or 800 K

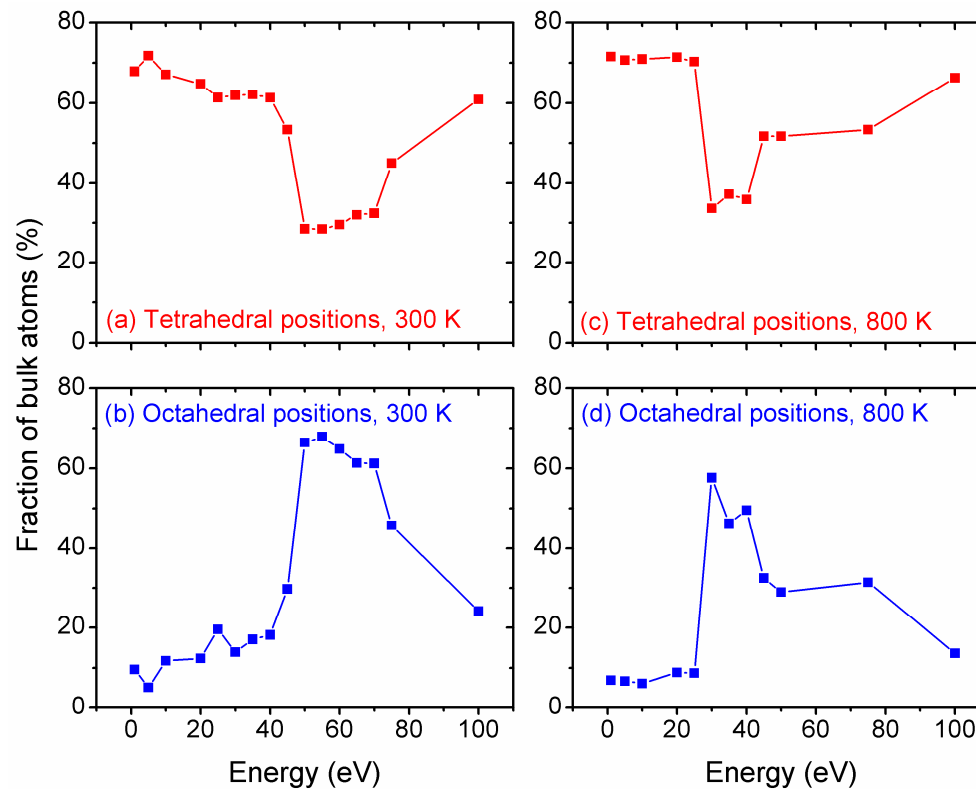


- α -Al₂O₃: energy window (50eV at 300K, 35eV at 800K)

- γ -Al₂O₃: growth at almost any energy

growth of $\alpha\text{-Al}_2\text{O}_3$ (0001) (in more detail)

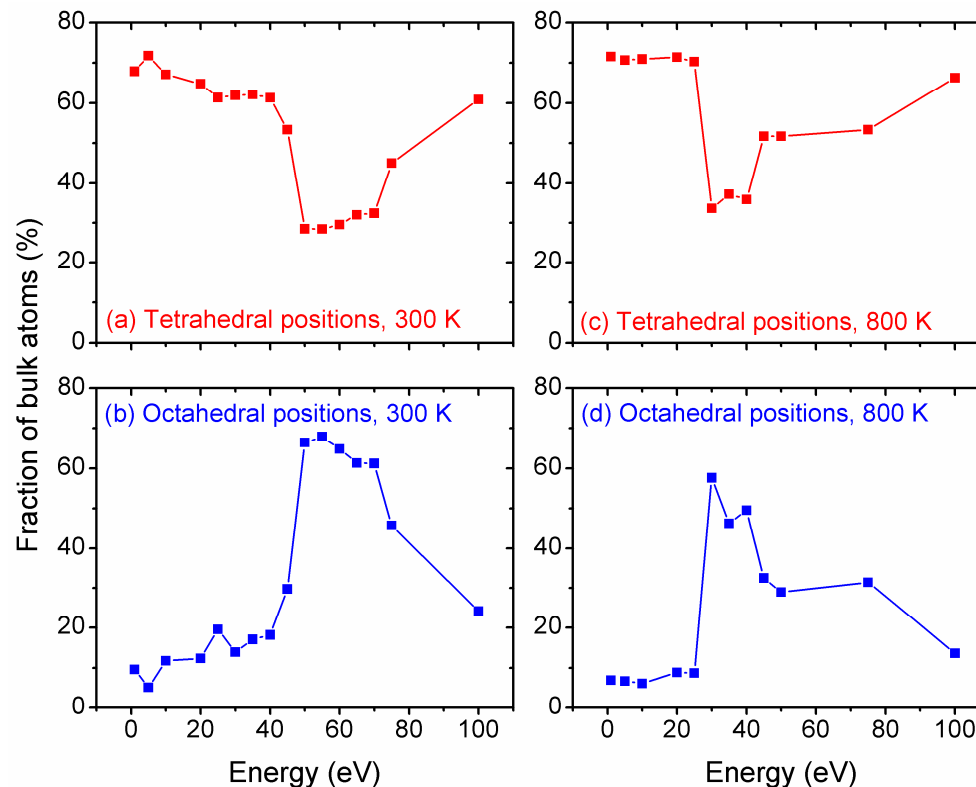
effect of ion energy, E , at $T = 300$ or 800 K



- $\alpha\text{-Al}_2\text{O}_3$: octahedrally coordinated Al only
- **T = 300 K:**
maximum at 50-70 eV
- **T = 800 K:**
maximum at 30-40 eV

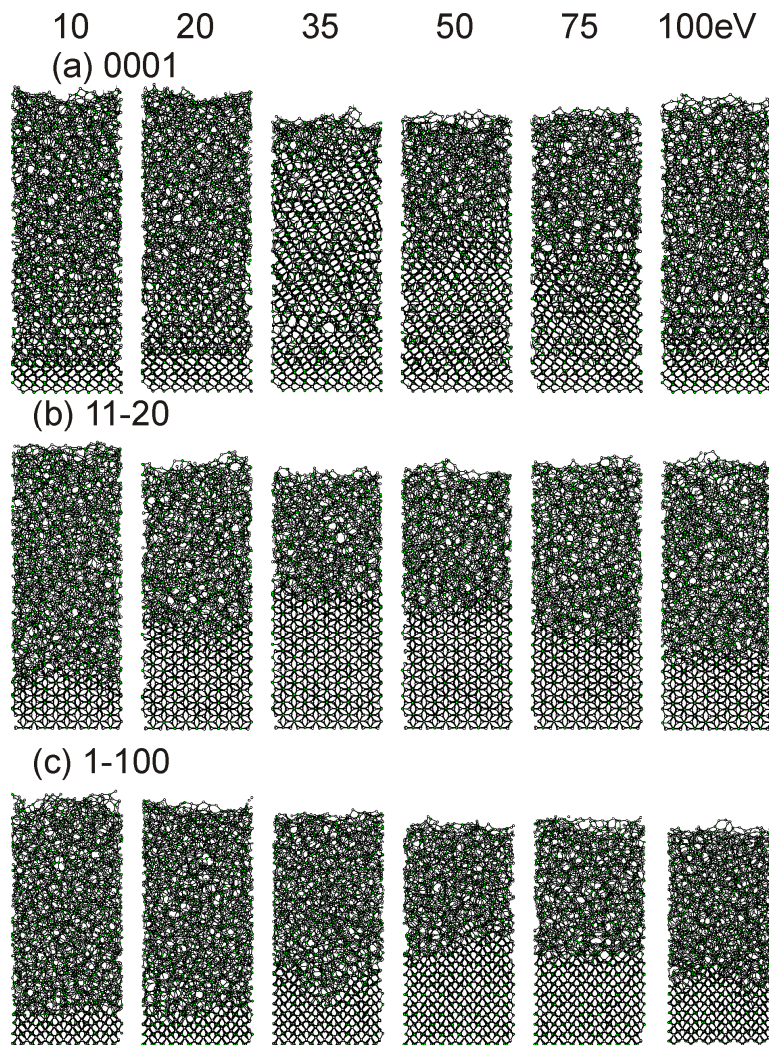
growth of $\alpha\text{-Al}_2\text{O}_3$ (0001) (discussion)

effect of ion energy, E , at $T = 300$ or 800 K

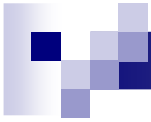


- **too low E :**
insufficient to "punch" Al to octahedral positions
- **too high E :**
accumulation of ion-induced defects leads to amorphization

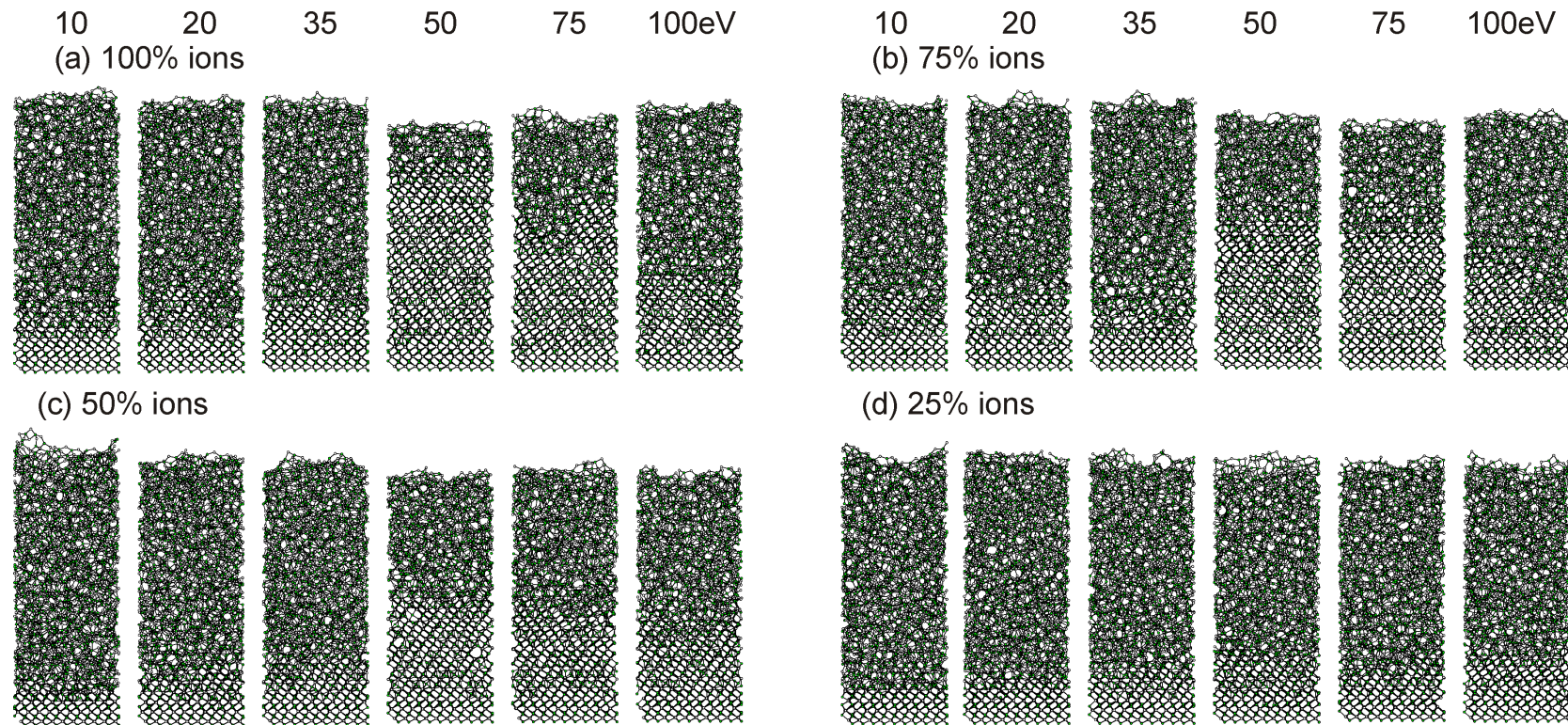
growth of $\alpha\text{-Al}_2\text{O}_3$ (0001, 11-20, 1-100) effect of crystal orientation (and E) at $T = 800$ K



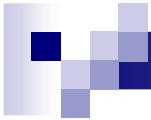
- **$\alpha\text{-Al}_2\text{O}_3$ (0001 - reminder):**
 - E window for crystal growth
 - defects and distortions
- **$\alpha\text{-Al}_2\text{O}_3$ (11-20 and 1-100):**
 - no defects or distortions
 - prone to abruptly amorphize at any E



growth of $\alpha\text{-Al}_2\text{O}_3$ (0001) effect of low- E film-forming particles at $T = 300$ K

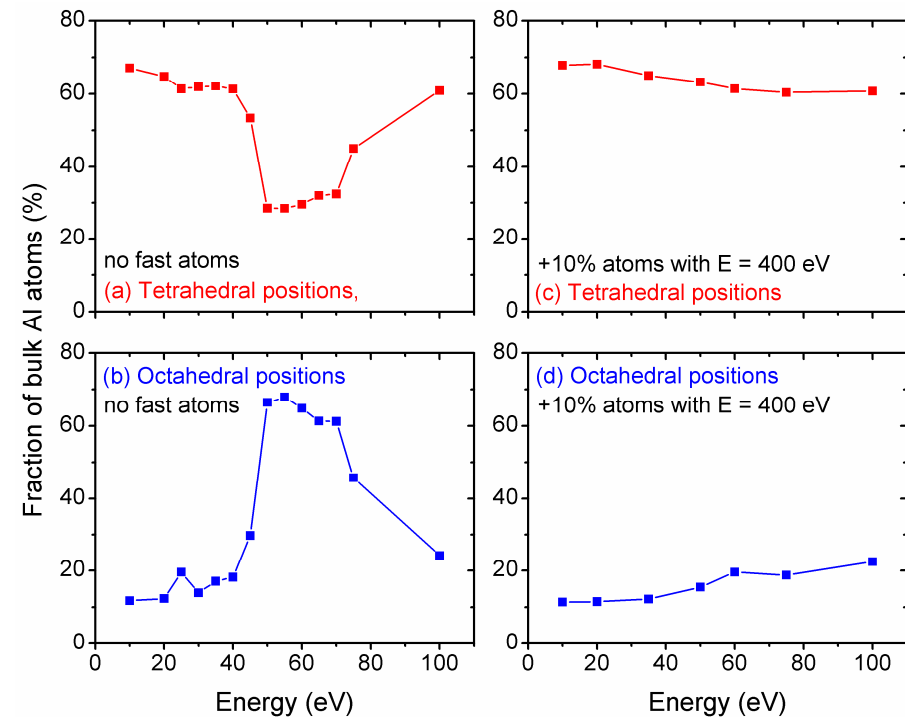
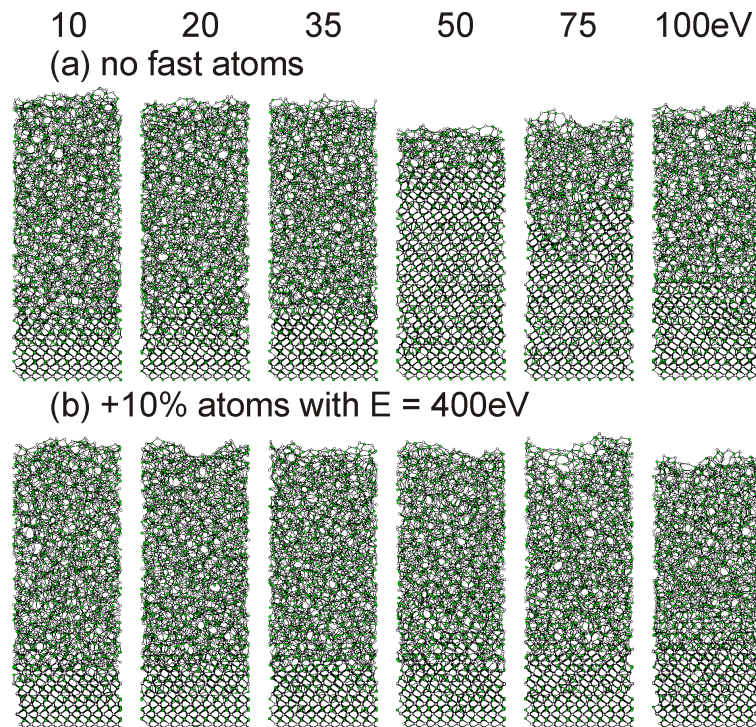


- **100% ions (all atoms have same E) \Rightarrow E window exists**
- **<100% ions (some atoms have $E = 1\text{eV}$) \Rightarrow amorphization**
(presence of neutrals cannot be compensated by higher ion E)

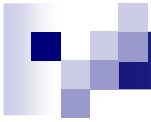


growth of $\alpha\text{-Al}_2\text{O}_3$ (0001)

effect of high- E (400 eV) film-forming particles *at* $T = 300$ K



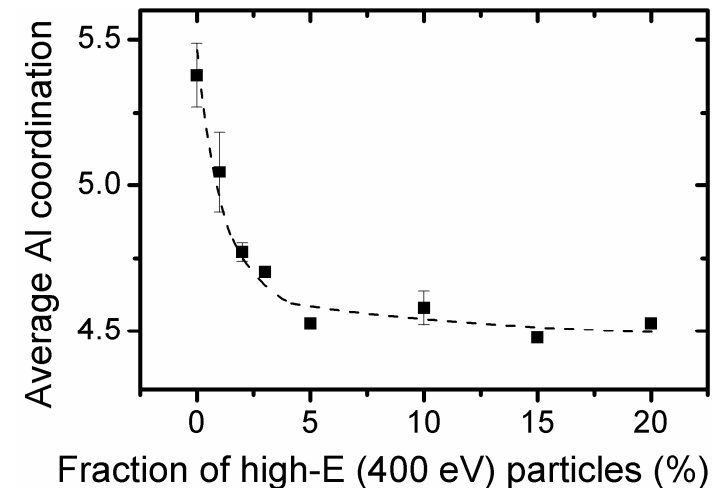
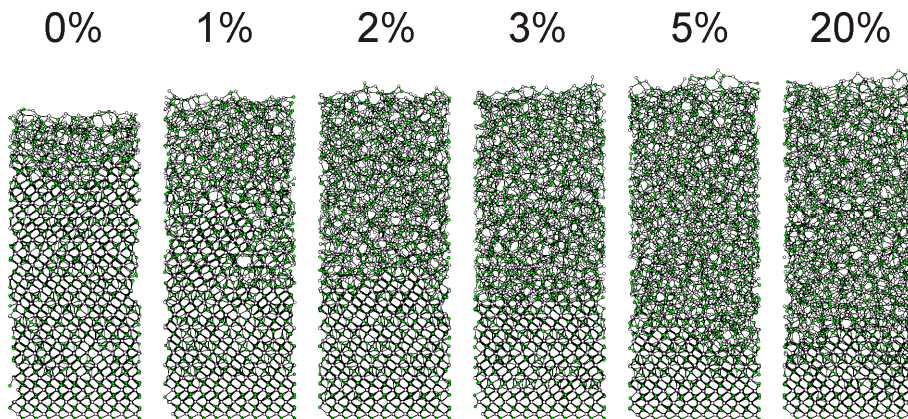
- correct E of 90% particles (50-70eV) \Rightarrow amorphization
- correct averaged E of all particles ($0.9 \times 20 + 0.1 \times 400 = 58$ eV) \Rightarrow also amorphization



growth of $\alpha\text{-Al}_2\text{O}_3$ (0001)

effect of high- E (400 eV) film-forming particles *at* $T = 300$ K

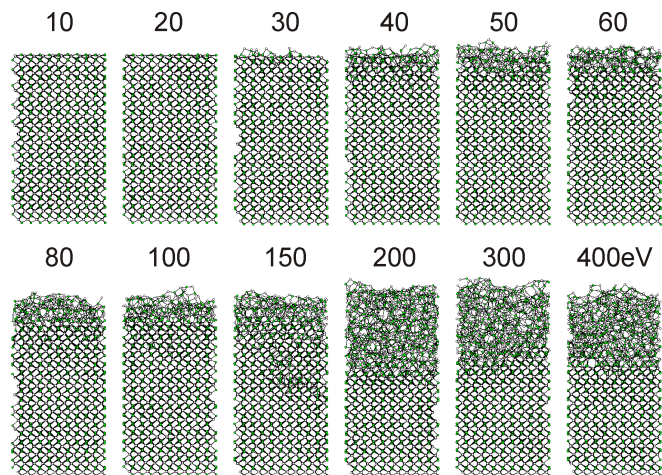
majority of atoms with optimum $E = 60$ eV
+ x% atoms with $E = 400$ eV



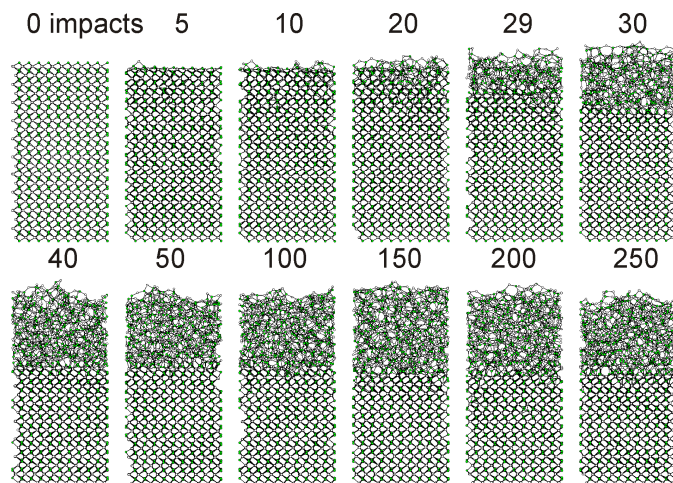
- $\leq 1\%$ 400 eV film-forming particles \Rightarrow eventual amorphization
- 3-5% 400 eV film-forming particles \Rightarrow instant amorphization

bombardment of $\alpha\text{-Al}_2\text{O}_3$ (0001) by Ar

effect of Ar energy and number of impacts



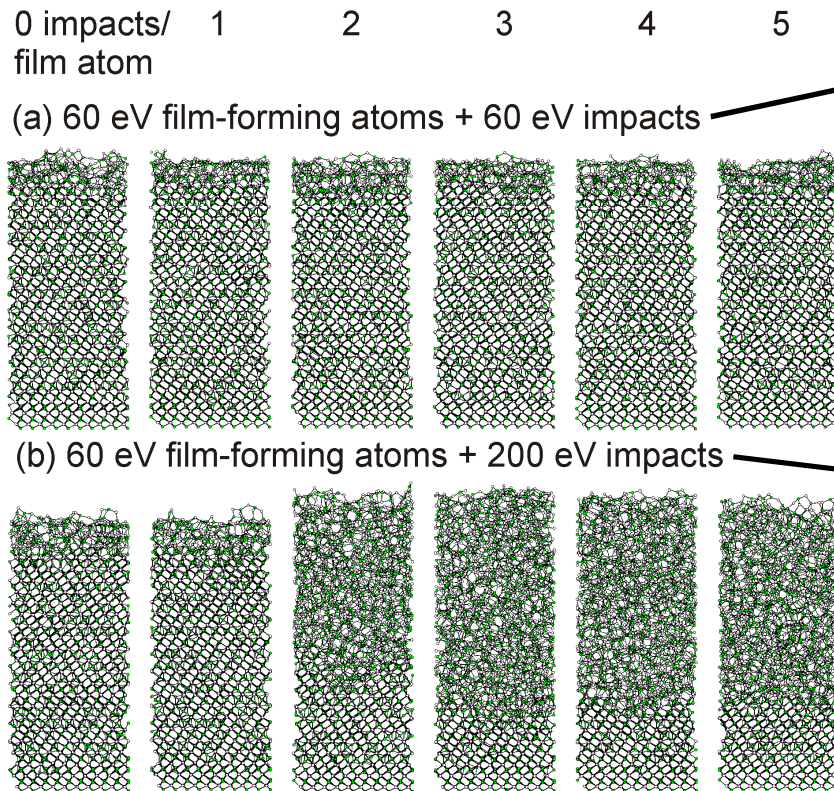
- fixed number of Ar impacts (250 per 6 nm²) \Rightarrow **threshold Ar energy (200 eV)**



- fixed Ar energy (400 eV) \Rightarrow **threshold (to some extent random) number of Ar impacts**

growth of $\alpha\text{-Al}_2\text{O}_3$ (0001) under Ar bombardment

effect of Ar energy and number of impacts



- **low Ar energy**
(20-60 eV): no effect
- **medium Ar energy** (not shown)
(100-150 eV): occasional
(random) amorphization
- **high Ar energy**
(200 eV): amorphization at
sufficiently high Ar flux
- **very high Ar energy** (not shown)
(300-400 eV): easier
amorphization, resputtering



Conclusions

- **TiO₂** : rutile - difficult nucleation, growth at almost any T and E
anatase - easy nucleation, growth at high T and optimum E
- **Al₂O₃** : γ phase - easy nucleation and growth
 α phase - E window (small crystals), e.g. 50-70 eV at 300 K or
minimum E (large crystals)
- **E window** : all film-forming particles must have the correct E
(correct averaged E is insufficient !)
- **Ar bombardment** : harmful, but quantitatively less harmful (e.g. 200 eV
limit) than energetic film-forming particles
- **Dependence on template orientation** (anatase TiO₂, α -Al₂O₃)