

Pathways for the preparation of technologically important metal oxides

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Motivation

- Reproducing the film growth by MD allows one to disentangle
 - crystal nucleation and crystal growth
 - effects of individual parts of the total particle flux
 - experimentally correlated process parameters



- Reproduce film (metal oxide) growth
 - classical molecular dynamics
 - reliable interaction potentials (force fields)



- Relationships between growth conditions and
 - film densification
 - crystal nucleation (non-epitaxial template)
 - crystal growth (epitaxial template)

Outline

- Simulation protocol

- Reliable interaction potential

 - details for ZrO_2

[J. Houska, Comp. Mater. Sci. 111 (2016) 209–217]

 - briefly for Al_2O_3 , TiO_2

[J. Houska, Comp. Mater. Sci. 134 (2017) 1-7]

- Results of growth simulations

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[J. Houska et al., J. Appl. Phys. 112 (2012) 073527]

- Conclusions

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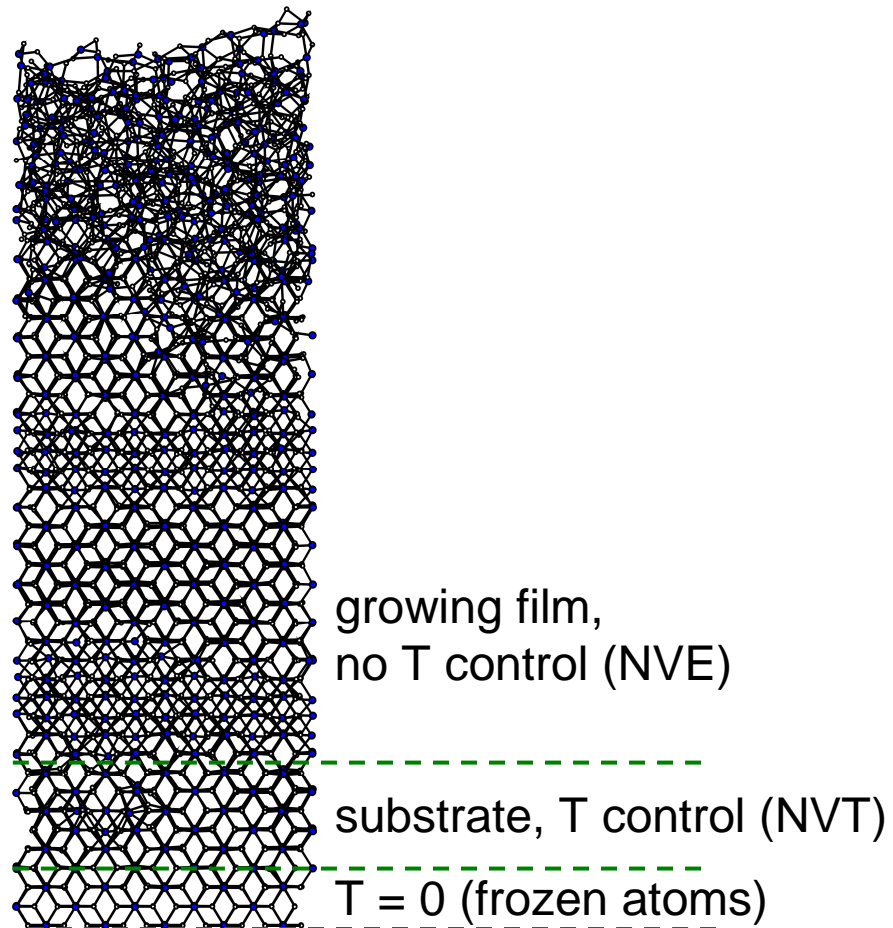
- Conclusions

Recursive atom-by-atom simulation protocol

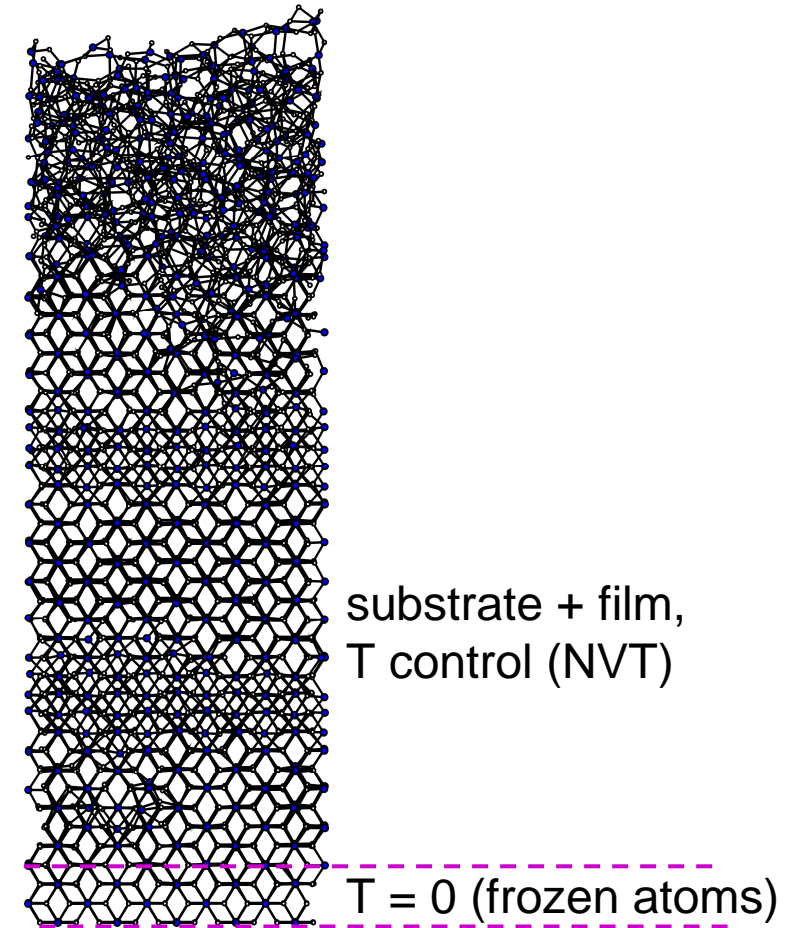
- 1) **Substrate or previously nucleated crystal**
(given structure & temperature)
- 2) **New atoms**
(given energy distribution function)
- 3) **Fixed-energy (NVE) run**
(particle collisions and energy dissipation)
- 4) **Fixed-temperature (NVT) run**
(to reestablish the deposition temperature)
- 5) **Removal** of resputtered/desorbed particles and return to 2

Recursive atom-by-atom simulation protocol

step 3 (NVE run)

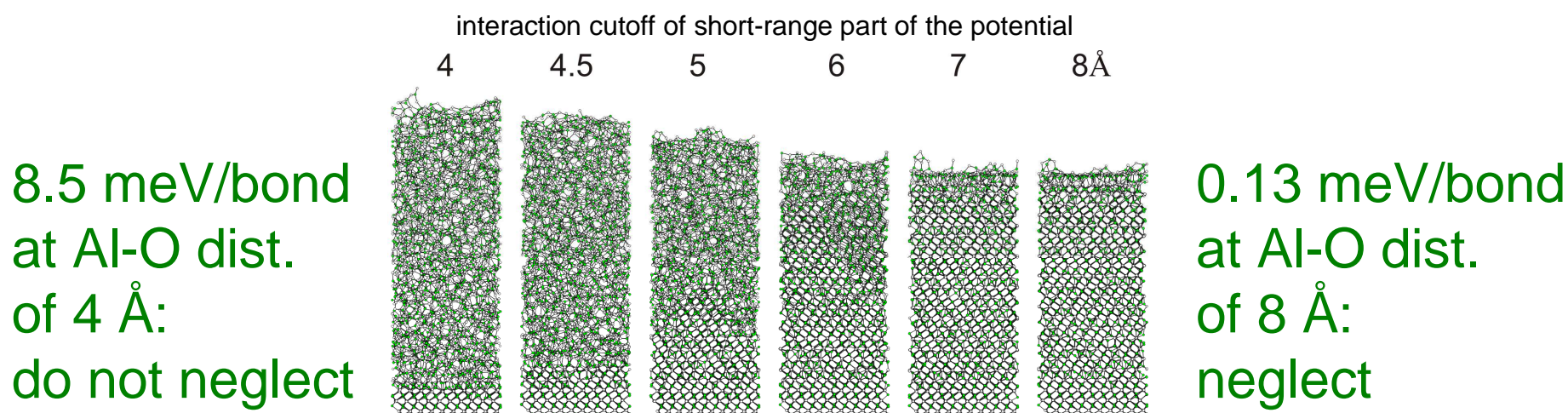


step 4 (NVT run)



Crucial prerequisite: reliable interaction potential (force field)

- must exhibit energy minima corresponding to the crystalline phases of interest (lattice constants, formation energies, etc.)
- must lead to correct results, e.g. coordination numbers, of the open surface film growth simulations (next slides)
- must be used with sufficiently long interaction cutoff



example for Al_2O_3 using Matsui potential

[M. Matas et al., Mol. Simul. 43 (2017) 1436-1441]

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Buckingham interaction potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r$$

- State the art for ionic metal oxides; more complex potentials (reactive, variable charge) did not lead to better results
- Potential parameters in the literature for most materials:



crystal phases of interest constitute energy minima:
correct lattice constants and formation energies



fitted with other simulation protocols in mind



wrong preferred coordination numbers



unsuitable for reliable growth simulations

Literature potentials for ZrO_2 lead to undercoordination

Criterion of success: Zr coordination, N_{Zr}

Experiment: $N_{\text{Zr}} = 8$ (c- & t- ZrO_2)

$N_{\text{Zr}} = 7$ (m- ZrO_2)

Ab-initio: $N_{\text{Zr}} \leq 7$ (a- ZrO_2)

Growth by simulations on amorphous ZrO_2

Schelling 2001: $N_{\text{Zr}} < 6$

Dwiwedi 1990+Kilo 2003: $N_{\text{Zr}} < 5$

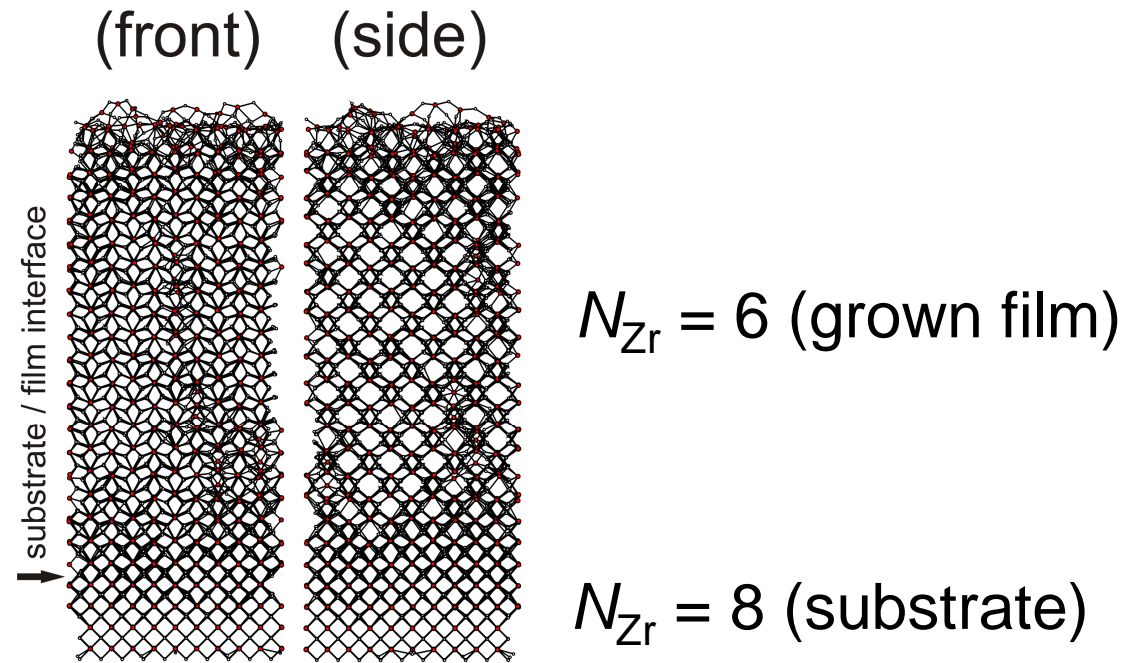
Lewis 1985: $N_{\text{Zr}} = 0$ (desorption)

Noordhoek 2014 (variable-charge): $N_{\text{Zr}} < 4$

Growth by simulations on cubic ZrO_2

Schelling 2001: $N_{\text{Zr}} = 6$ (fictitious rutile-like structure)

Literature potentials for ZrO_2 lead to undercoordination



Growth by simulations on cubic ZrO_2

Schelling 2001:

$N_{\text{Zr}} = 6$ (fictitious rutile-like structure)

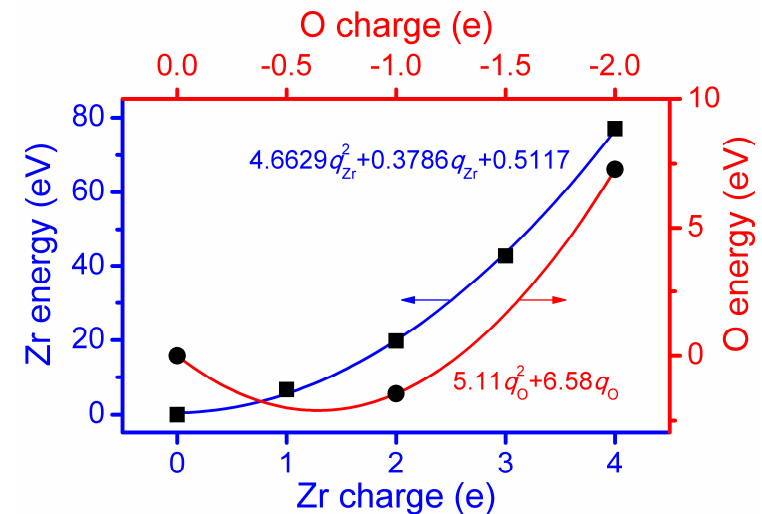
Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r$$

Starting point: **full-charge** Schelling pot. (A, ρ, C at $q_{\text{Zr}} = +4e$)

Solution: **partial-charge** (q_{Zr} between 0 and $+4e$)

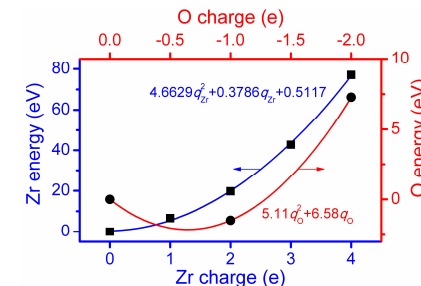
- additional degree of freedom \Rightarrow correct N_{Zr}
- closer to the experiment
- avoiding too high potential energies of ionization
(delivered into growing films
in parallel to the kinetic energy)



Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r$$

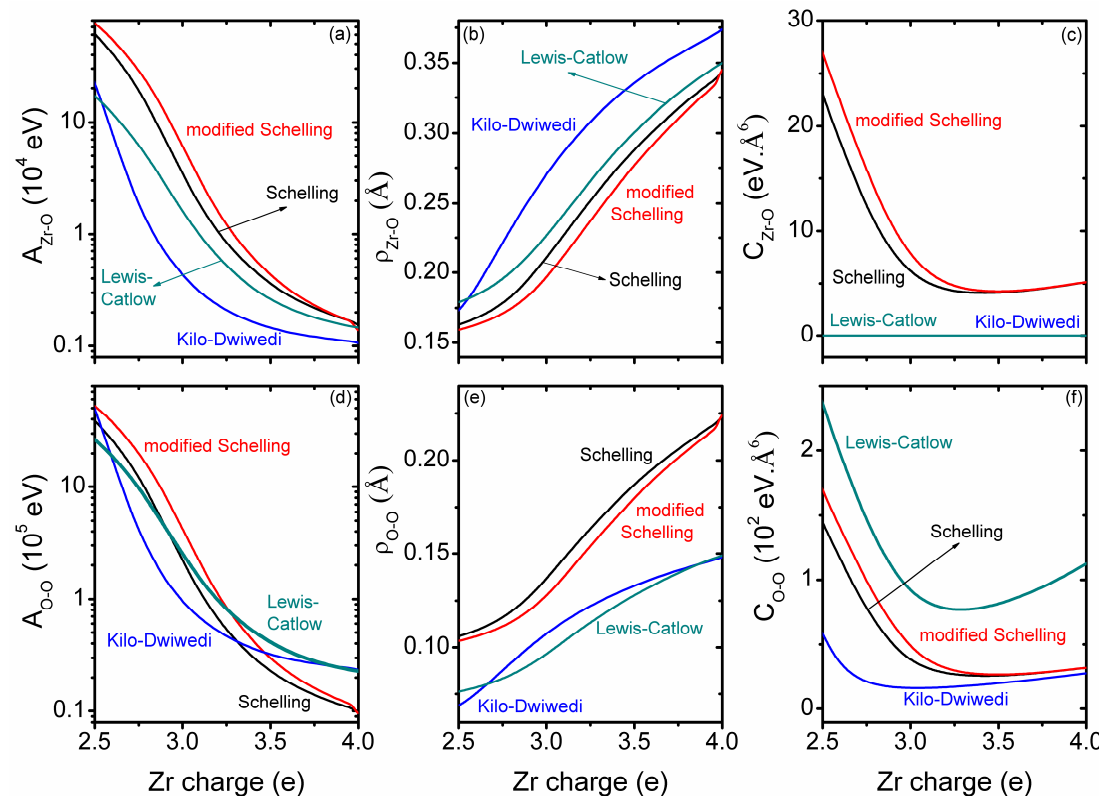
- 1) Starting-point potential - correct lattice const. and energies
- 2) $q_{\text{Zr}} = q_{\text{Zr}} - \Delta q_{\text{Zr}} \Rightarrow$ new (incorrect) lattice const. and energies
- 3) changing the length scale
 \Rightarrow new $A, \rho, C, q_{\text{Zr}}$
 \Rightarrow correct lattice constants
- 4) changing the energy scale at preserved length scale
(quadratic dependence of ionization energy on q_{Zr} ,
thus quadratic equation for the rescaling factor)
 \Rightarrow new $A, \rho, C, q_{\text{Zr}}$
 \Rightarrow correct formation energies
- 5) return to 2



Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r$$

Results : q_{Zr} -dependent short-range parameters A , ρ , C
(shown for various starting-point potentials, one is used below)



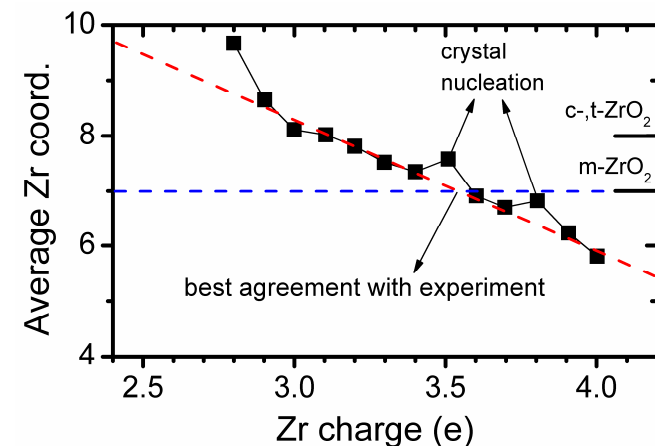
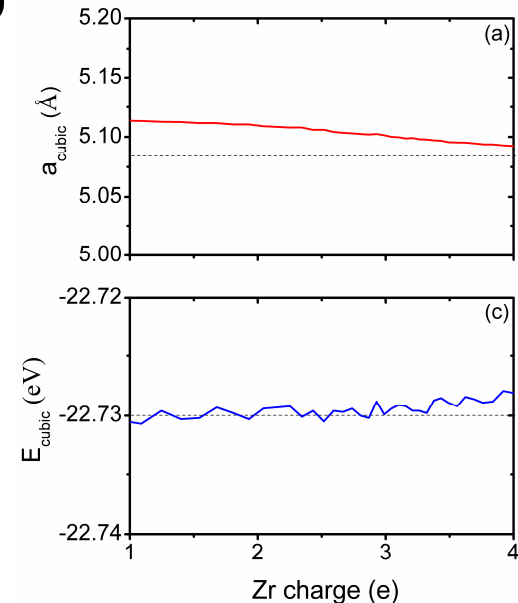
Fitting of reliable ZrO_2 potential

Newly fitted partial-charge potentials lead to

the same lattice constants and energies
(fitted for c- & t- ZrO_2 , shown for c- ZrO_2)

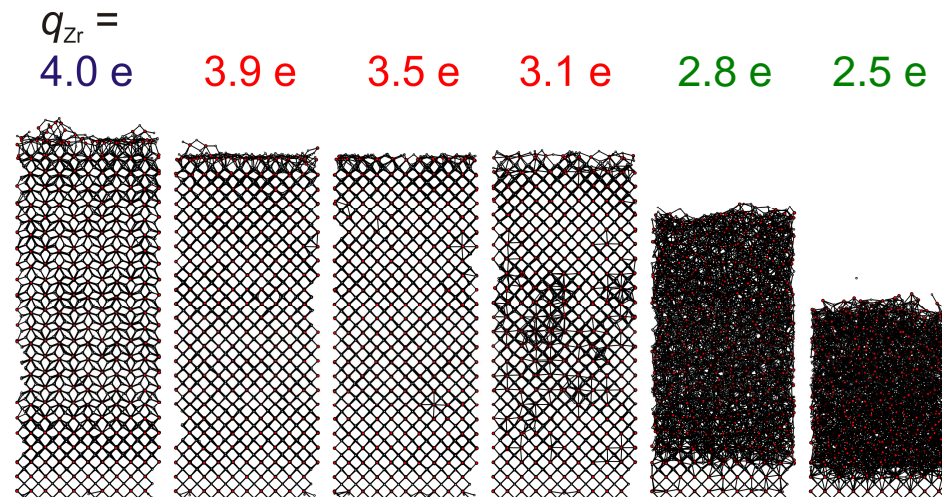
... but ...

different coordination numbers,
experimental N_{Zr} for $q_{\text{Zr}} = 3.542 \text{ e}$



Test of fitted ZrO_2 potentials

- Growth on a- ZrO_2 : experimental N_{Zr} for $q_{\text{Zr}} = 3.542$ e
- Growth on c- ZrO_2 (under optimum growth conditions):
 - $q_{\text{Zr}} = 4.0$: undercoordination, fictitious rutile-like
 - q_{Zr} around 3.5 : indeed, c- ZrO_2 growth
 - q_{Zr} too low : overcoordination, amorphization



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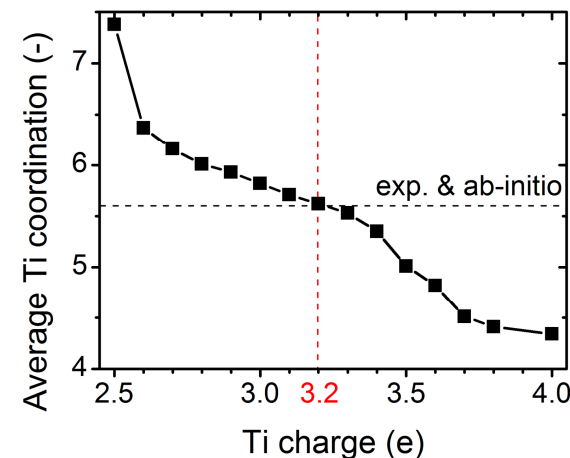
Fitting of reliable TiO_2 potential

Some literature potentials work well (e.g. partial-charge potentials by Matsui et al. for Al_2O_3 and other oxides), but there are many opposite examples (e.g. Post 1986 for TiO_2)

Let's apply the fitting procedure presented for cubic ZrO_2 to rutile and anatase TiO_2 . Again, the fitted partial-charge potentials lead to the same lattice constants and energies (this time for both rutile and anatase TiO_2)

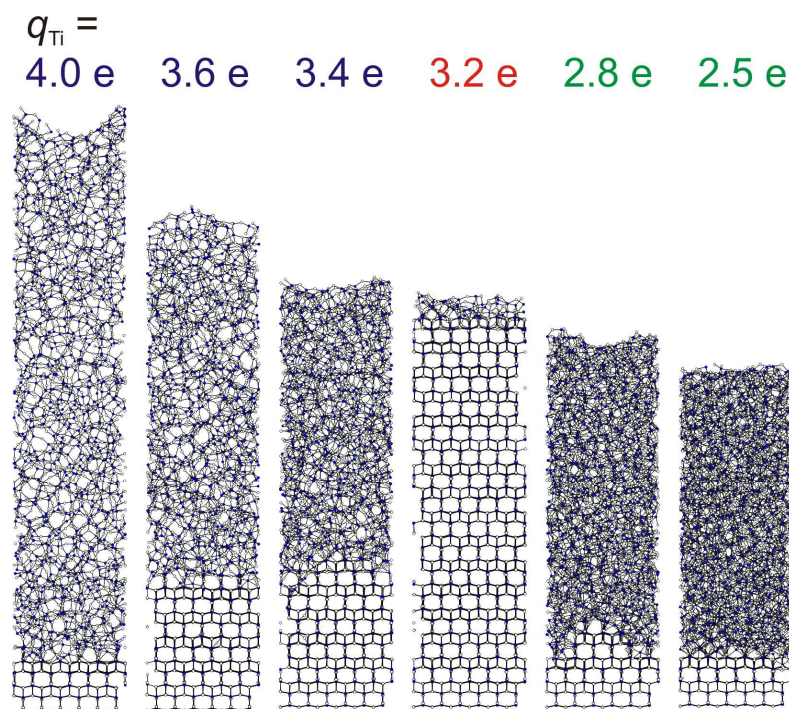
... but ...

different coordination numbers,
experimental N_{Ti} for $q_{\text{Ti}} = 3.197 e$



Test of fitted TiO_2 potentials

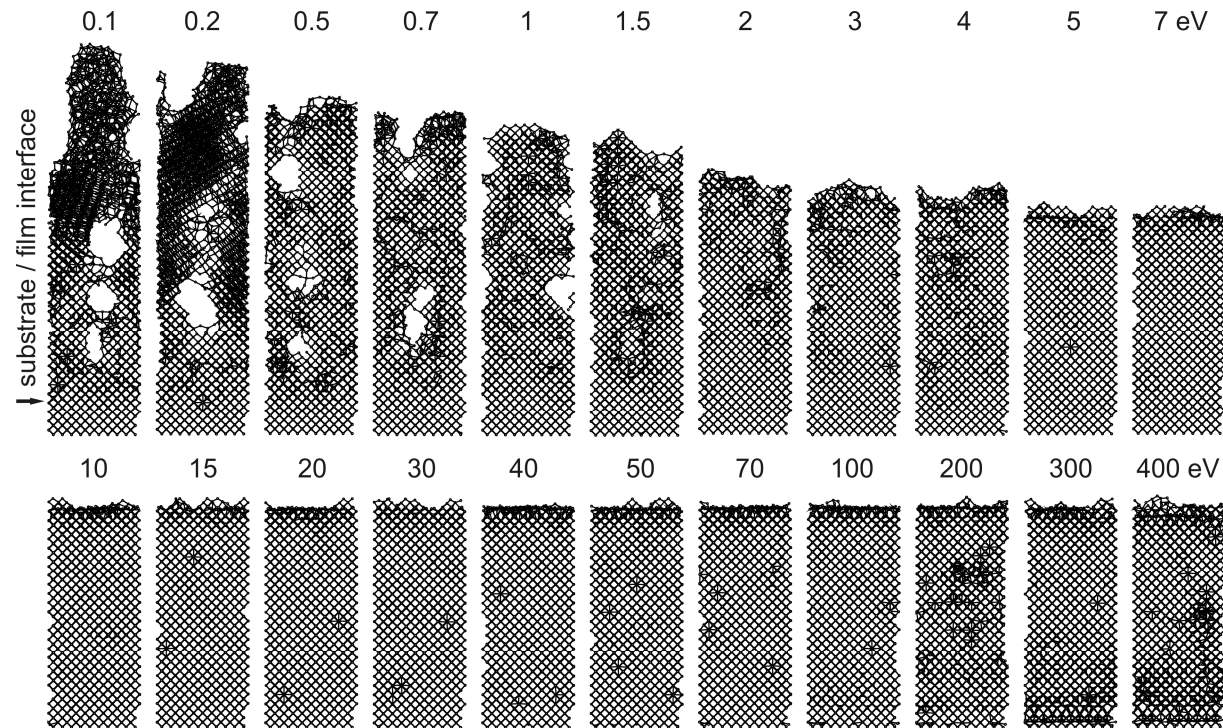
- Growth on a- TiO_2 : experimental N_{Ti} for $q_{\text{Zr}} = 3.197$ e
- Growth on anatase TiO_2 (under optimum growth conditions):
 - q_{Ti} too high : undercoordination, amorphization
 - q_{Ti} around 3.2 : indeed, anatase TiO_2 growth
 - q_{Ti} too low : overcoordination, amorphization or fictitious cubic



Outline

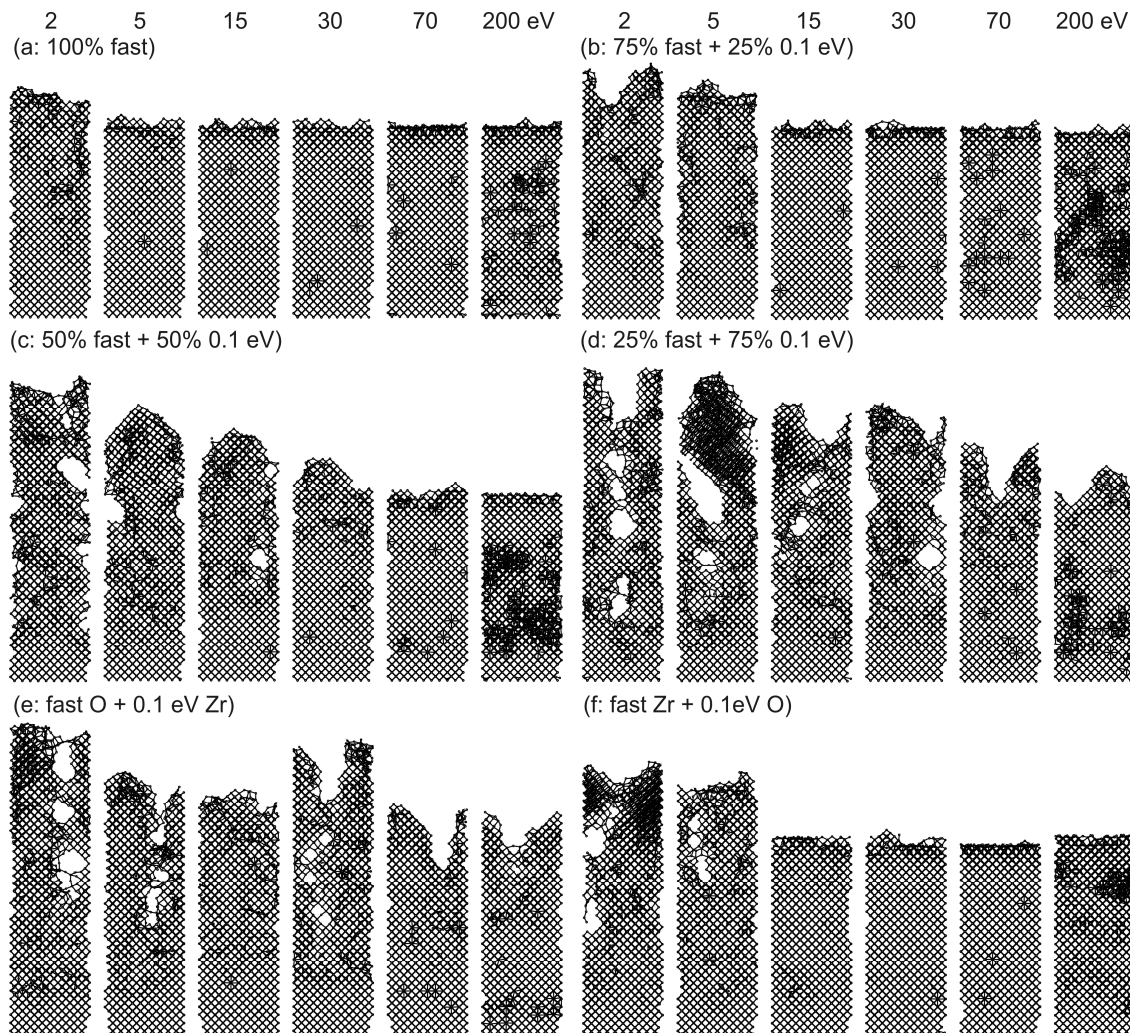
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c-ZrO₂ growth - effect of energy, E



- Densification with increasing energy
- Same energy of all atoms \Rightarrow fully densified at $E \geq 5$ eV
- Defects at $E > 100$ eV

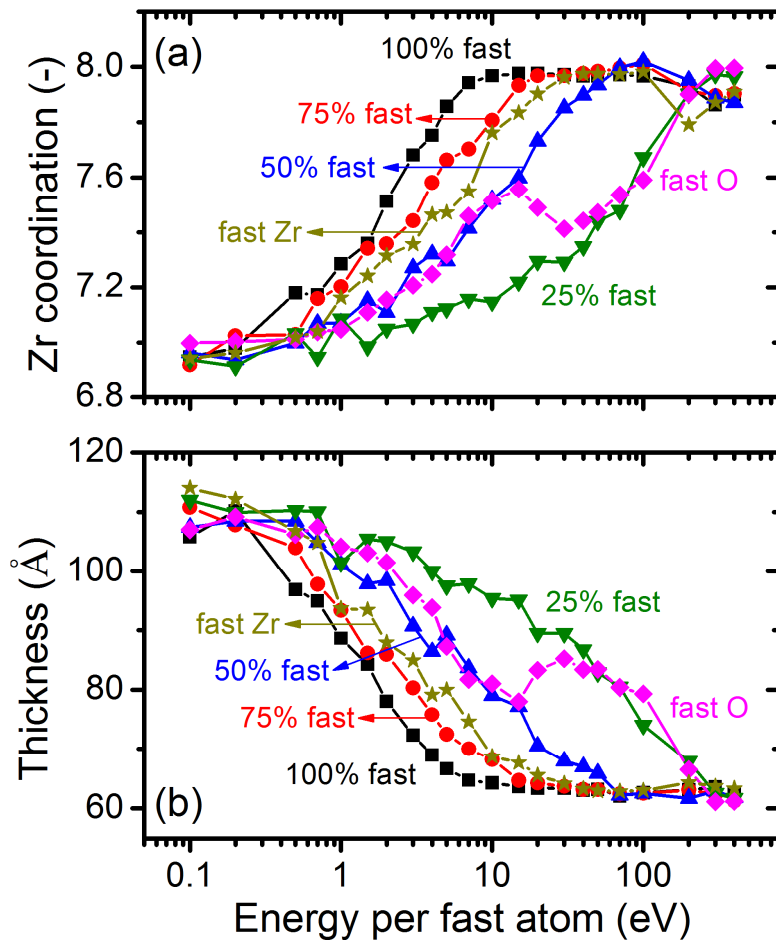
c-ZrO₂ growth - effect of energy distribution function



- Increasing fraction of slow atoms \Rightarrow less densified
- Fast heavy Zr (33% of all atoms): densification
×
Fast light O (66% of all atoms): poor densification

c-ZrO₂ growth - effect of energy distribution function

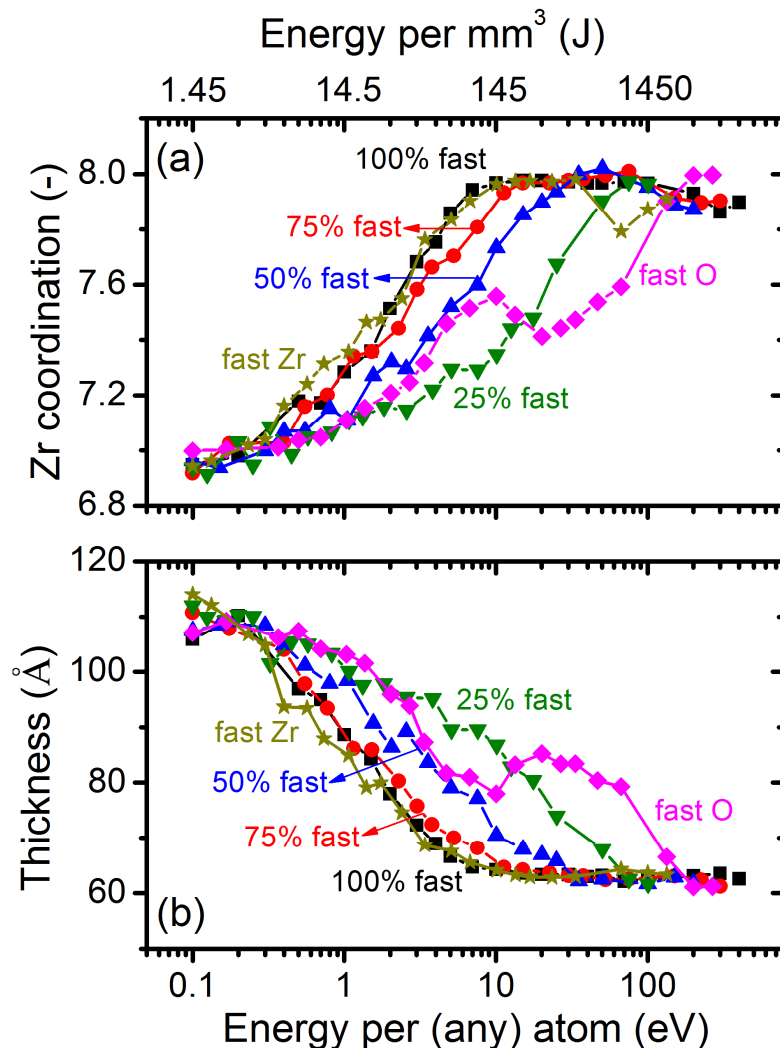
(quantification of the above results)



- Increasing fraction of slow atoms \Rightarrow less densified (low N_{Zr} , high thickness)
- Fast heavy Zr: densification
×
Fast light O: poor densification
- Reproducible local N_{Zr} minima (limit for inducing specific kind of defect)

c-ZrO₂ growth - effect of energy distribution function

(same data as a function of energy **per any atom**, not fast atom)

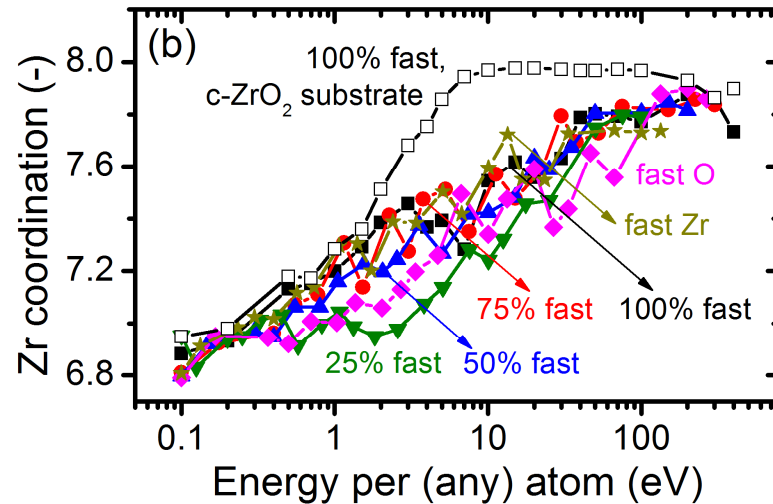


■ Dependencies still do not overlap

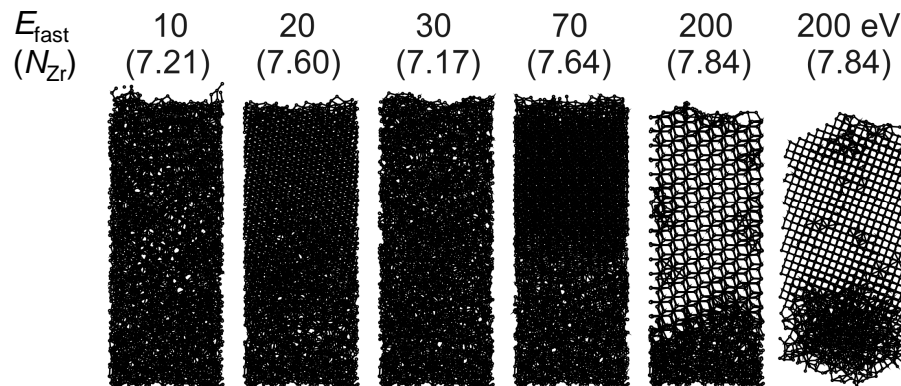


■ Presence of slow atoms cannot be compensated by higher energy of fast atoms (ions) - correct average energy is not enough for crystal growth

Amorphous ZrO_2 growth and c- ZrO_2 nucleation

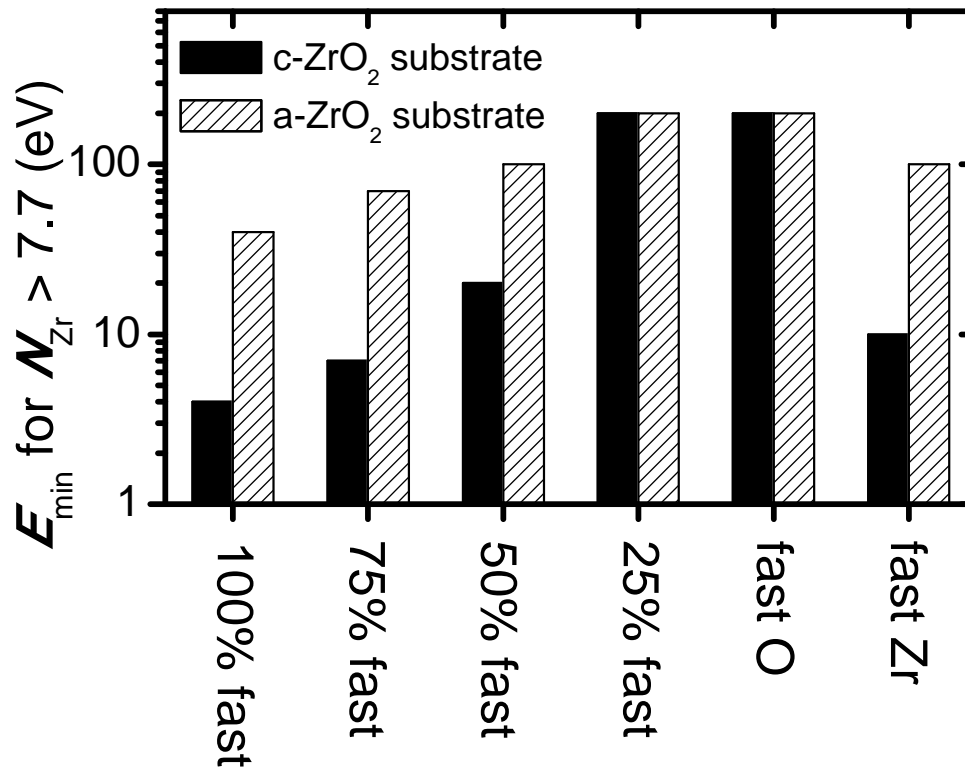


- Dependencies closer to each other
 \Downarrow
- Correct average energy is not enough for crystal growth, but \pm enough for densification of amorphous



- Frequent c- ZrO_2 nucleation at energy of fast atoms (for various energy distribution functions) ≥ 200 eV

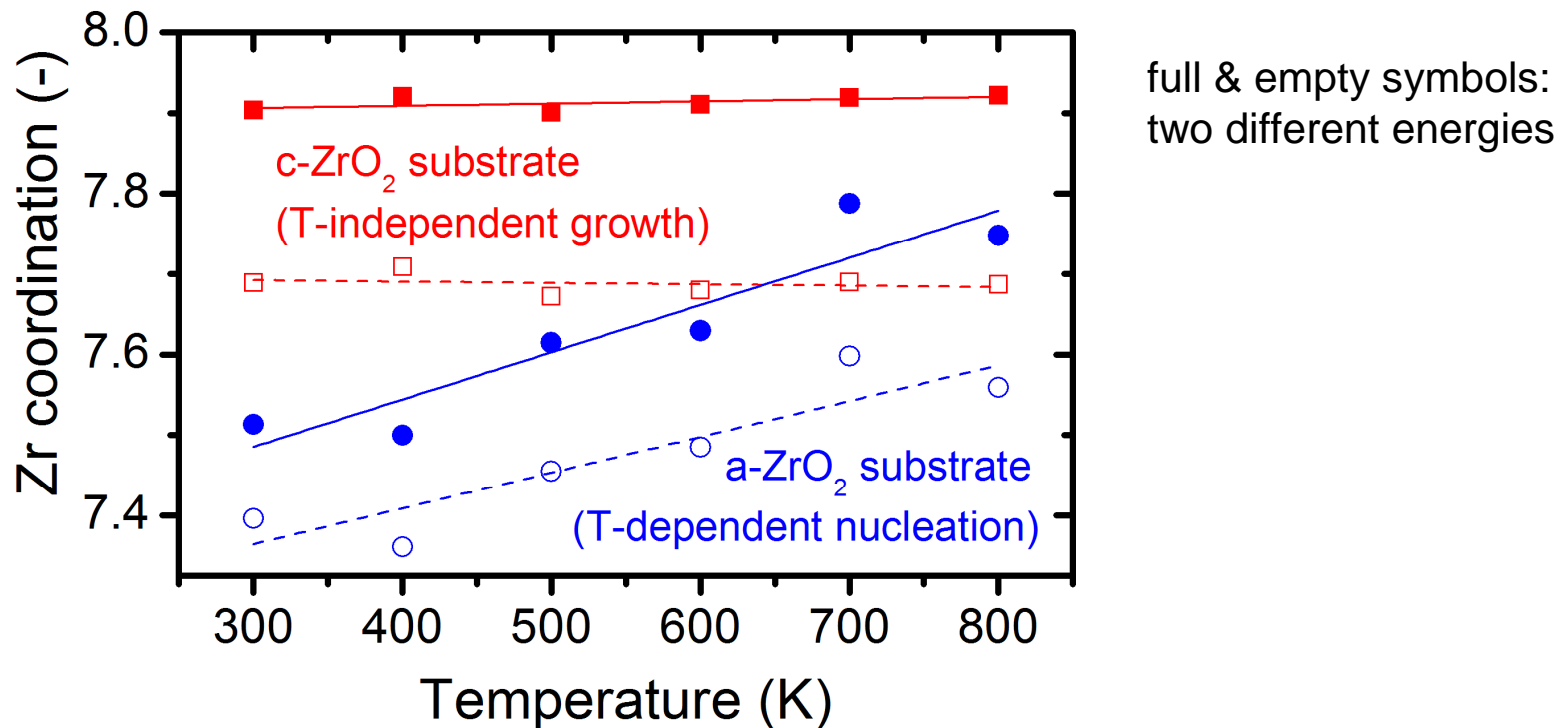
Growth × nucleation: effect of energy and EDF



minimum E of fast atoms
leading to crystallinity &
densification ($N_{\text{Zr}} > 7.7$)

- Epitaxial growth can be utilized at optimum EDF only:
then, **5 eV** of all atoms is enough for dense crystal growth
- Non-optimum EDF or amorphous substrate:
200 eV of some atoms is needed for frequent (re)nucleation

Growth × nucleation: effect of temperature



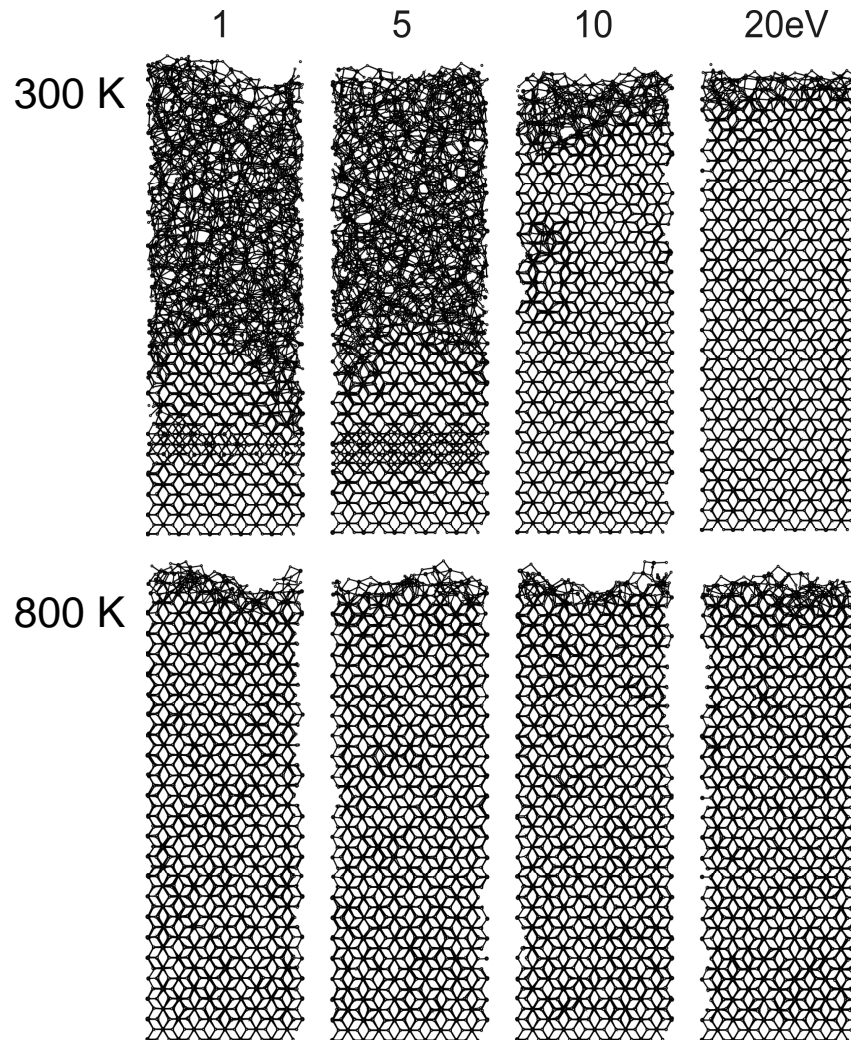
- Growth of existing crystals is almost T-independent
- Nucleation of crystals (on amorphous substrate) takes place on longer time scale, is T-dependent

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growth of rutile TiO_2 (001)

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



■ Experiment:

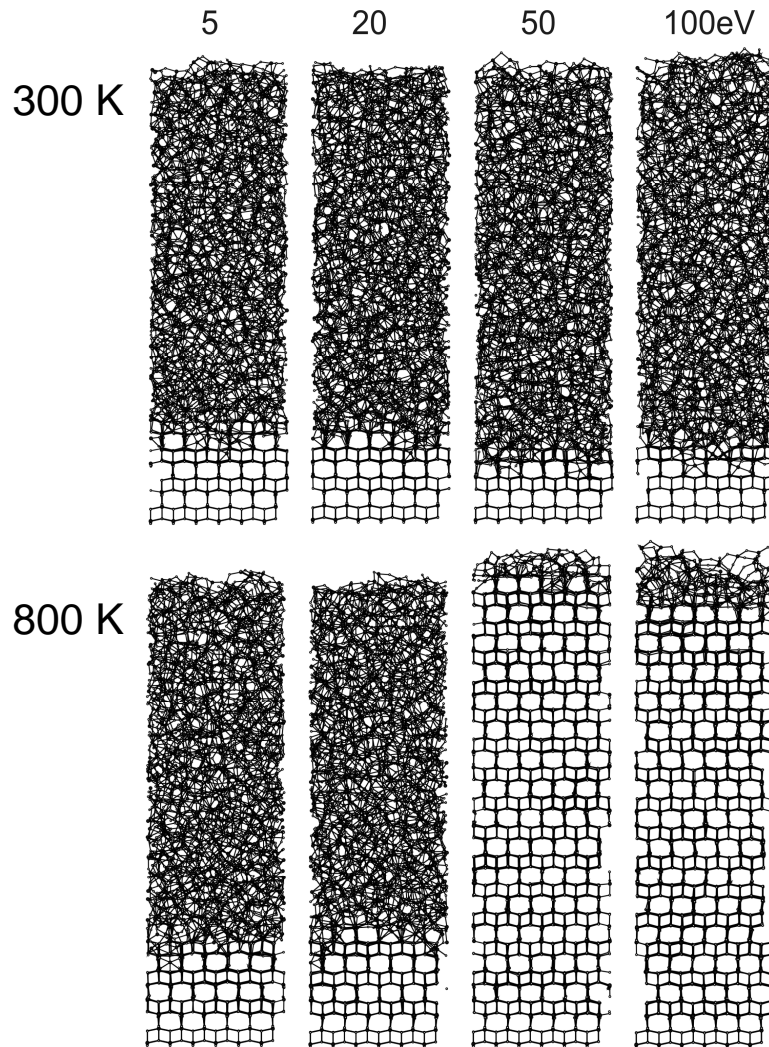
- deposition of rutile requires high E and/or T

■ 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)

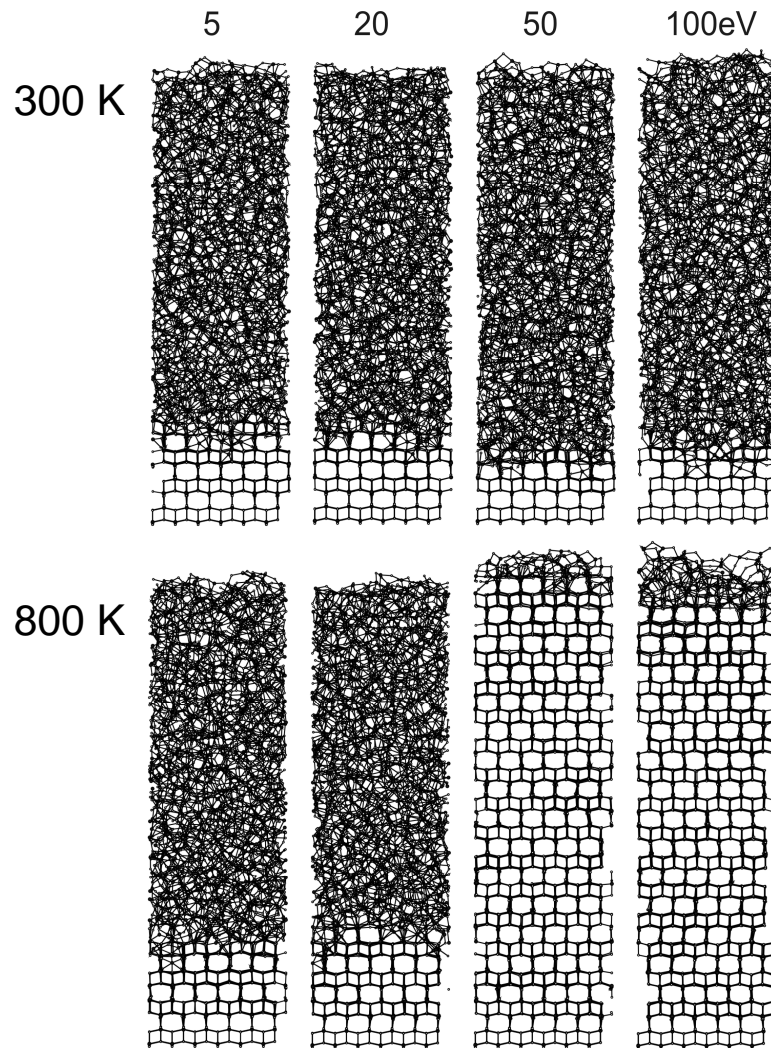


■ Qualitative difference

- 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



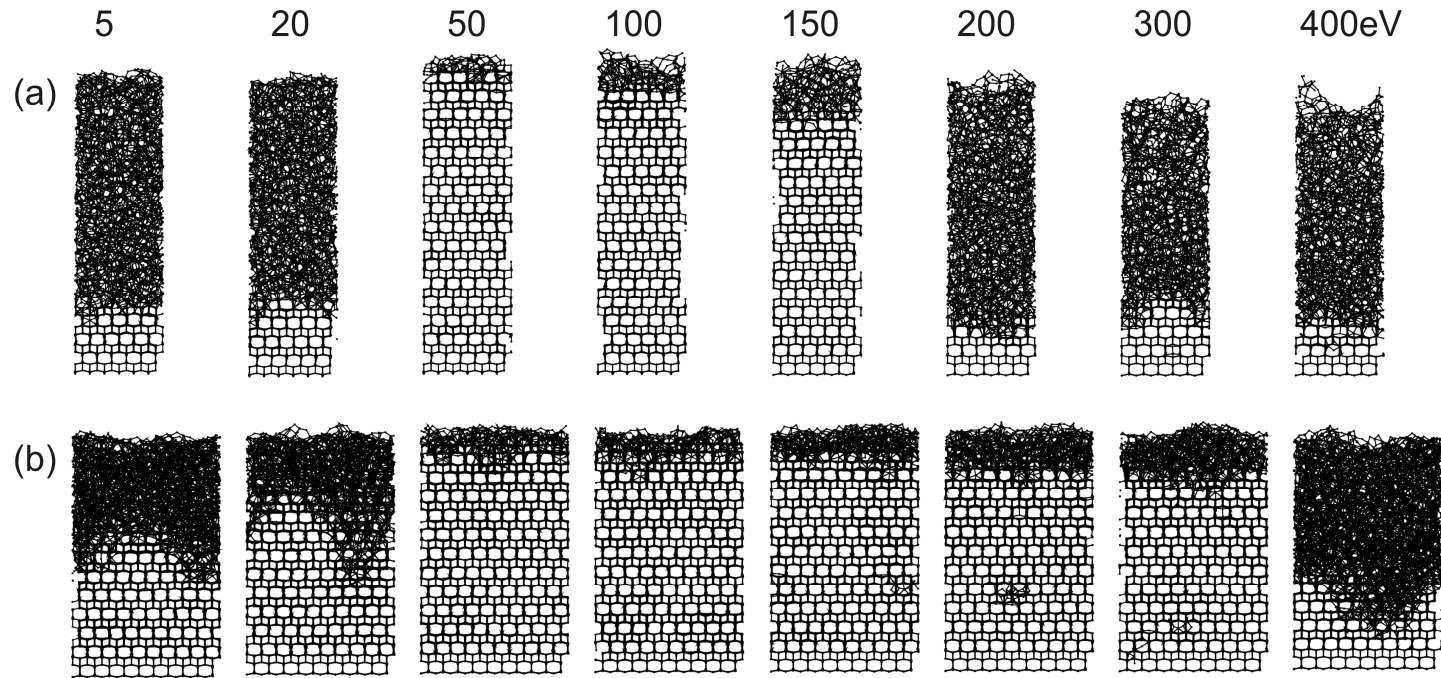
■ Experiment

[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)

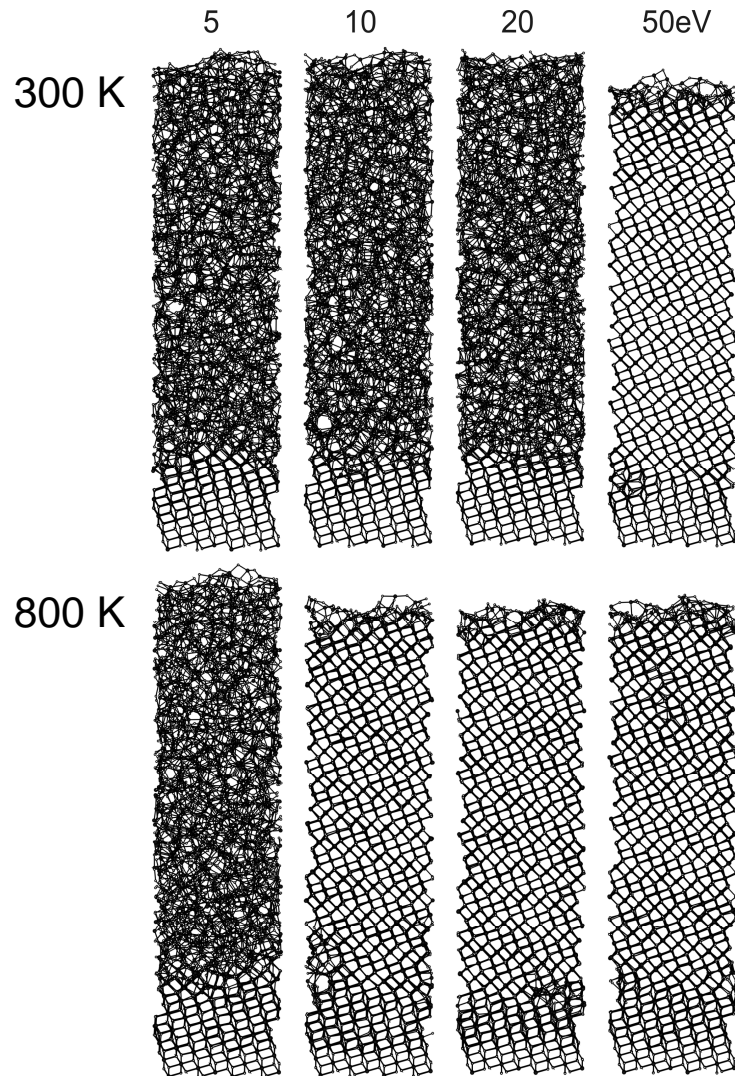
effect of ion energy and crystal size, E , at $T = 800$ K



- Anatase (not rutile) growth limited also by maximum E :
the limit depends on crystal width

growth of anatase TiO_2 (111)

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



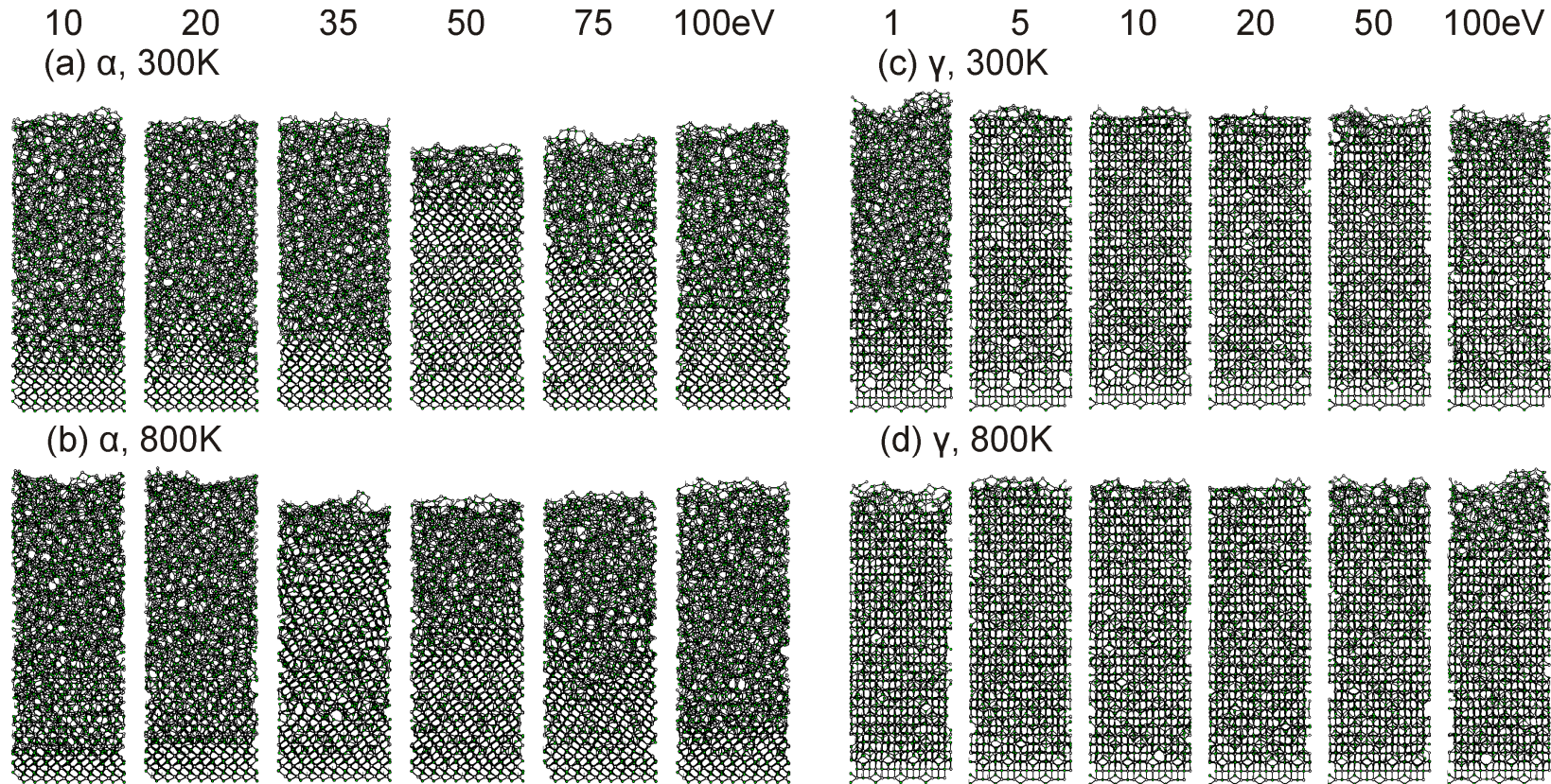
■ Simulation:

- (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 - Al_2O_3 (0001) and γ - Al_2O_3 (001) effect of ion energy, E , at $T = 300$ or 800 K

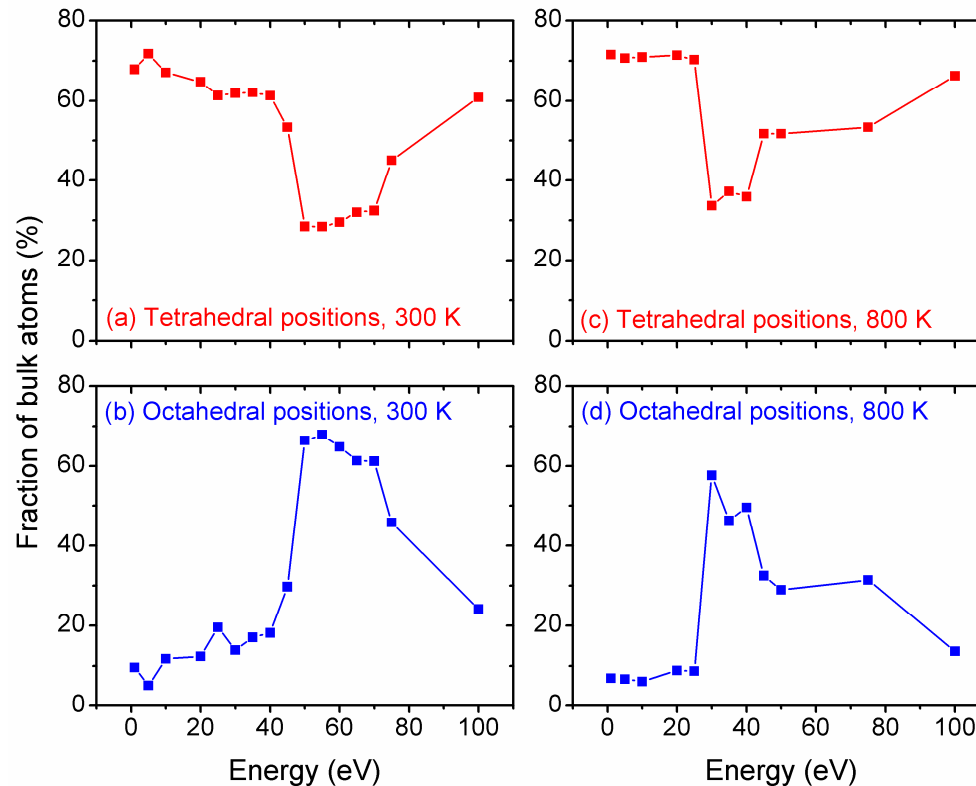


- α - Al_2O_3 : energy window (50eV at 300K, 35eV at 800K)

- γ - Al_2O_3 : growth at almost any energy

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

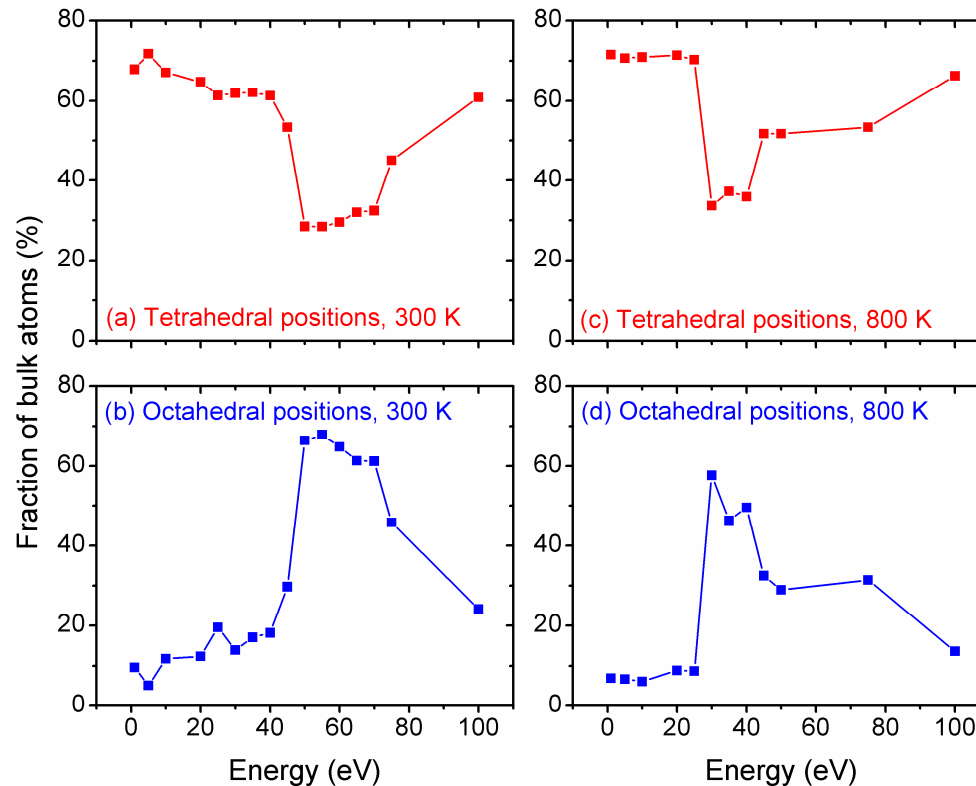
effect of ion energy, E , at $T = 300$ or 800 K



- $\alpha\text{-Al}_2\text{O}_3$: 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)

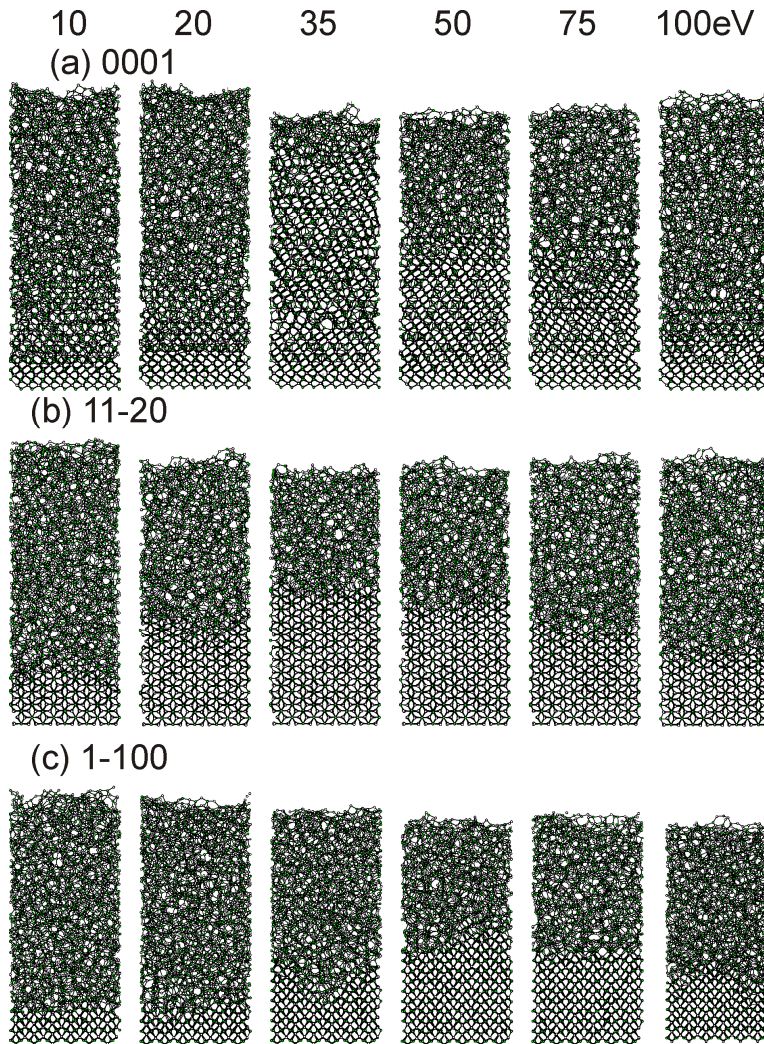
effect of ion energy, E , at $T = 300$ or 800 K



- **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)

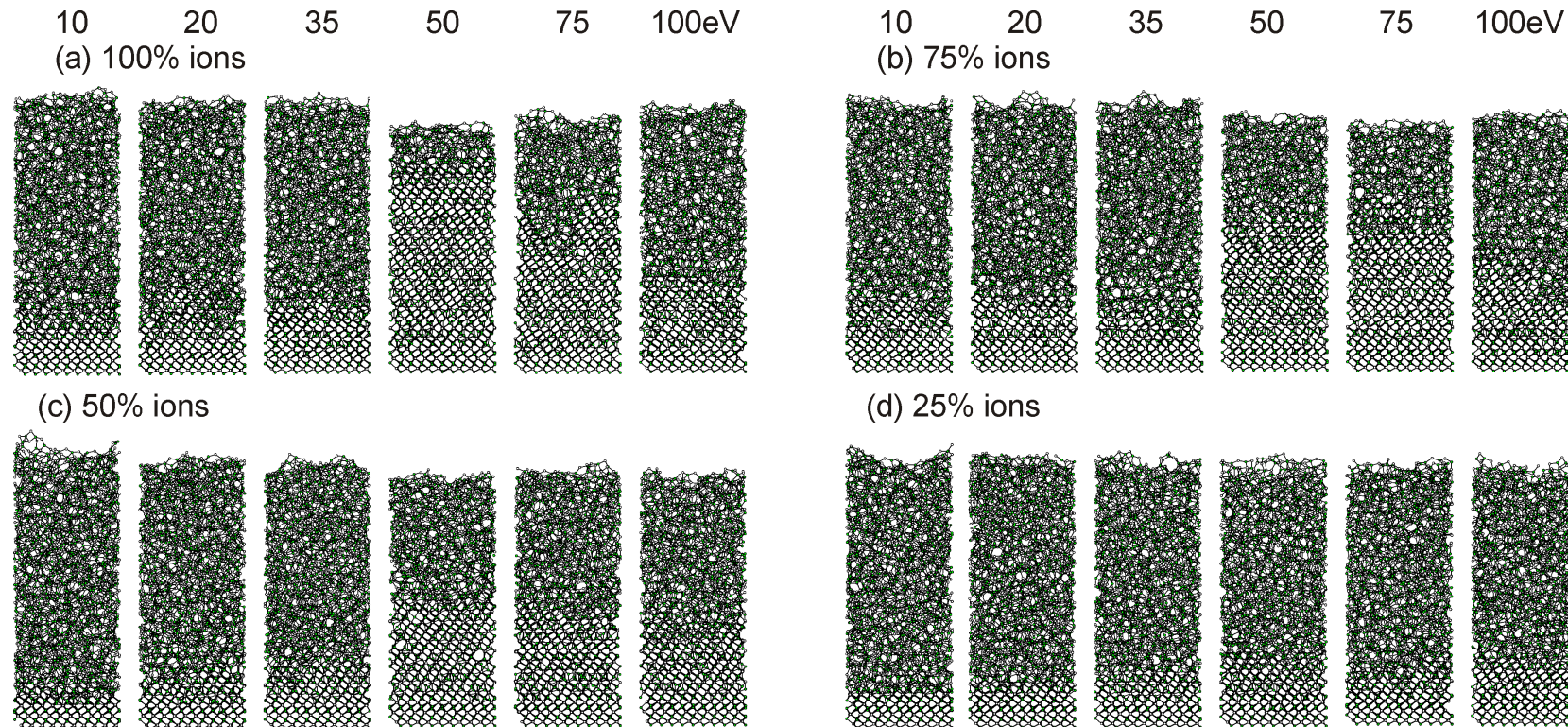
effect of crystal orientation (and E) at $T = 800$ K



- **$\alpha\text{-Al}_2\text{O}_3$ (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 $T = 300\text{ K}$



- **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)

Conclusions

- procedure for improvement (**coorrect coordination numbers**) of literature interaction potentials
- easy nucleation, easy growth $\gamma\text{-Al}_2\text{O}_3$
easy nucleation, difficult growth anatase TiO_2
difficult nucleation, easy growth c- ZrO_2 , rutile TiO_2
difficult nucleation, difficult growth $\alpha\text{-Al}_2\text{O}_3$
difficult nucleation: high- E tail of arriving atoms, high T
difficult growth: E window, high T , effect of orientation
- narrow EDF is beneficial (lower E per volume needed for densification) or necessary (phases requiring E window)
- densification by heavier atoms is more effective