Development of reliable interaction potential for and results of molecular dynamics simulations of ZrO_2 film growth

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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
  - correlated parameters such as ion energy and temperature

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

Outline

- Development of reliable interaction potential for ZrO_2
  [J. Houska, Comp. Mater. Sci. 111 (2016) 209–217]
- Results of growth simulations of ZrO_2
  [J. Houska, Surf. Coat. Technol. 304 (2016) 23–30]

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

crucial for success of classical MD: reliable potentials (force fields) describing interatomic interactions

Buckingham interaction potential

$$U = A\mathrm{e}^{-r/\rho} - Cr^{-6} + q_1 q_2 / 4\pi\varepsilon r$$

- State the art for ionic metal oxides
- 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

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wrong preferred coordination numbers

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unsuitable for reliable growth simulations

Literature potentials for ZrO_2 lead to undercoordination

Criterion of success: Zr coordination, N_{Zr}

Experiment:	$N_{Zr} = 8$ (c- & t-ZrO_2)
	$N_{Zr} = 7$ (m-ZrO_2)
Ab-initio:	$N_{Zr} \leq 7$ (a-ZrO_2)

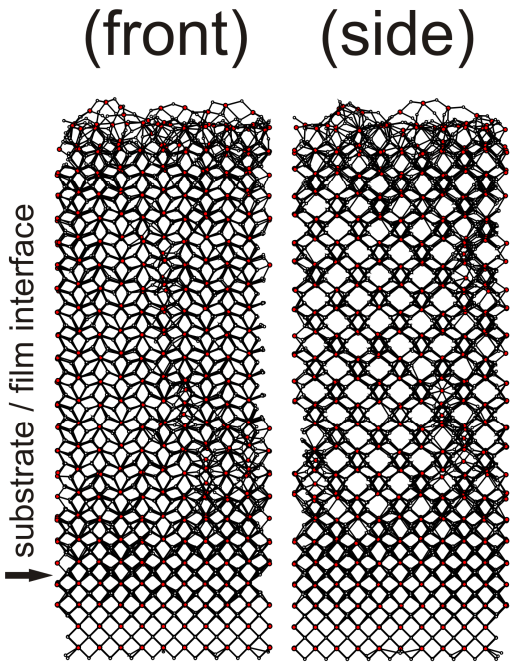
Growth by simulations on amorphous ZrO_2

Schelling 2001:	$N_{Zr} < 6$
Dwiwedi 1990+Kilo 2003:	$N_{Zr} < 5$
Lewis 1985:	$N_{Zr} = 0$ (desorption)
Noordhoek 2014 (variable-charge):	$N_{Zr} < 4$

Growth by simulations on cubic ZrO_2

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

Literature potentials for ZrO_2 lead to undercoordination



N_{Zr} = 6 (grown film)

N_{Zr} = 8 (substrate)

Growth by simulations on cubic ZrO_2

Schelling 2001:

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

Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1 q_2 / 4\pi\varepsilon r$$

Starting point:

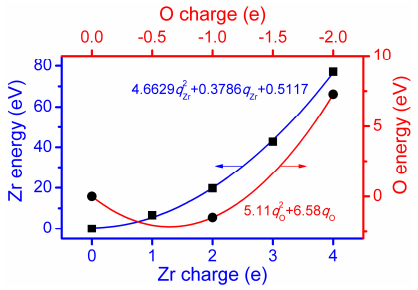
full-charge Schelling pot. (A, ρ, C at q_{Zr} = +4e, q_O = -2e)

- incorrect N_{Zr}

Solution:

partial-charge (q_{Zr} between 0 and +4e)

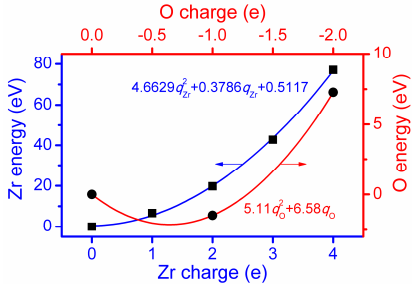
- additional degree of freedom ⇒ correct N_{Zr}
- closer to the experiment
- avoiding too high potential energies of ionization



Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1 q_2 / 4\pi\varepsilon r$$

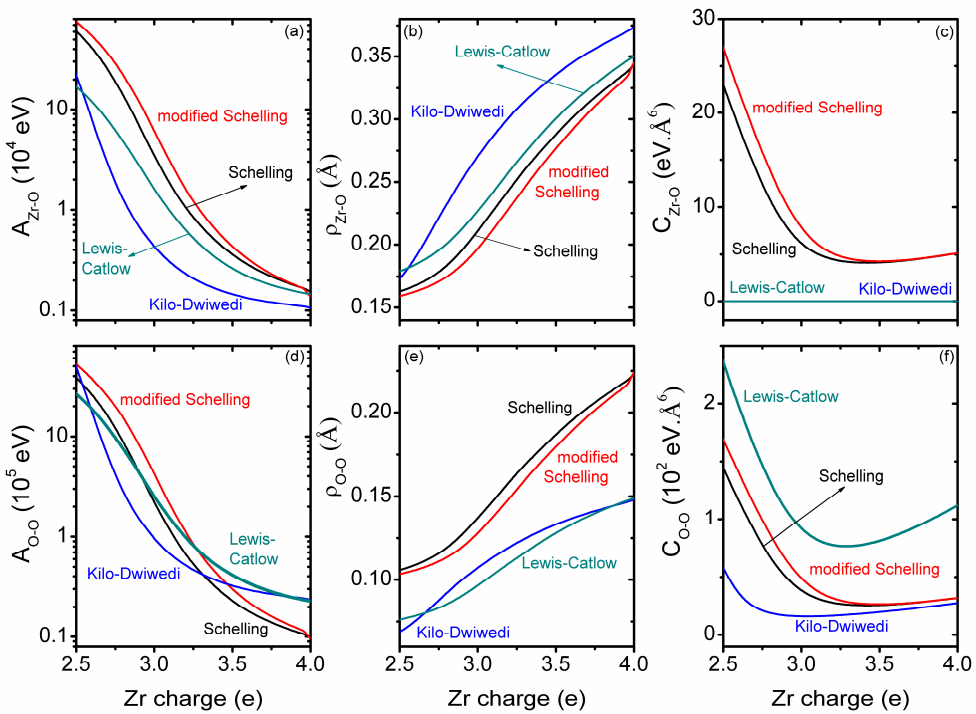
1) Starting-point potential - correct lattice const. and energies
2) $q_{Zr} = q_{Zr} - \Delta q_{Zr} \Rightarrow$ new (incorrect) lattice const. and energies
3) changing the length scale
   $\Rightarrow$ new A, ρ, C, q_{Zr}
   $\Rightarrow$ correct lattice constants
4) changing the energy scale at preserved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



Fitting of reliable ZrO_2 potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1 q_2 / 4\pi\varepsilon r$$

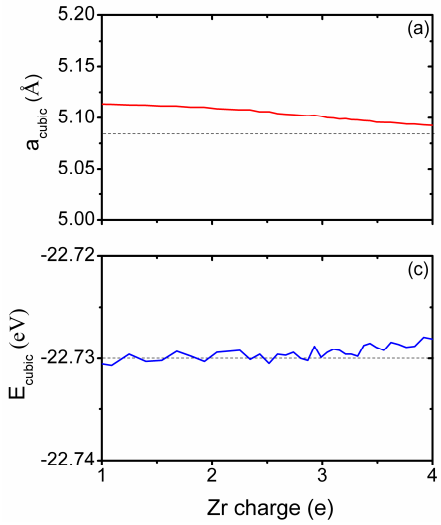
Results : q_{Zr}-dependent short-range parameters A, ρ, C
(shown for various starting-point potentials, one is used below)



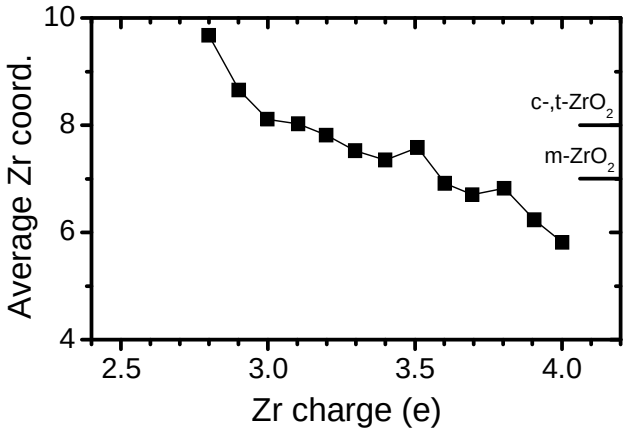
Fitting of reliable ZrO_2 potential

Newly fitted partial-charge potentials lead to

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



different coordination numbers
obtained by growth on a-ZrO_2



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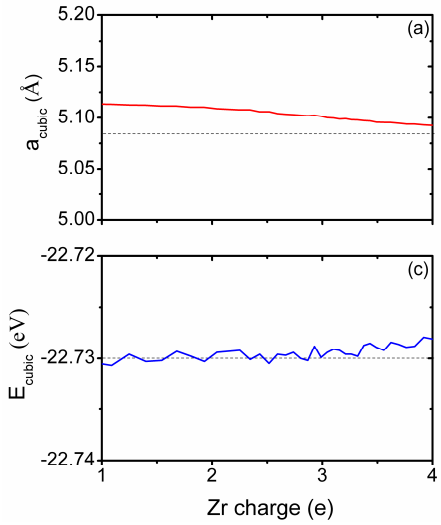
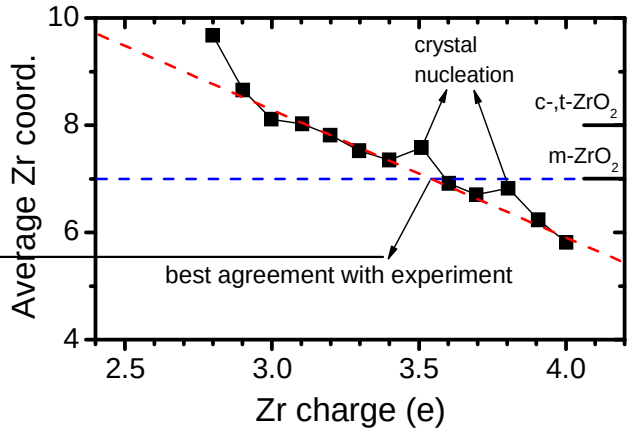


different coordination numbers
obtained by growth on a-ZrO_2

experimental N_{Zr} for $\boldsymbol{q_{Zr} = 3.542}$



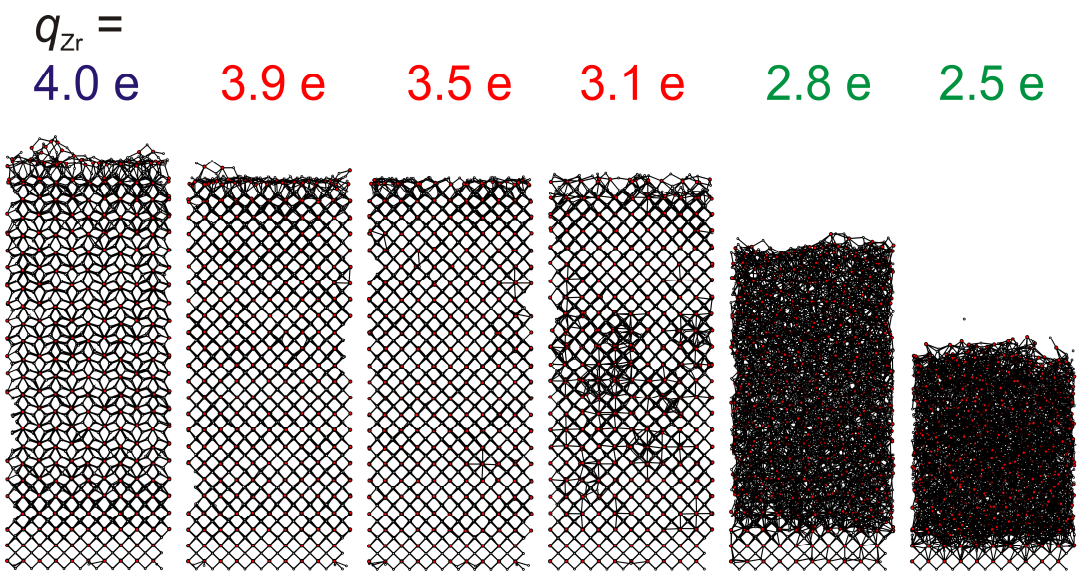
Test of fitted ZrO_2 potentials

- Growth on a-ZrO_2: experimental N_{Zr} for q_{Zr} = 3.542
- Growth on c-ZrO_2 (under optimum growth conditions):

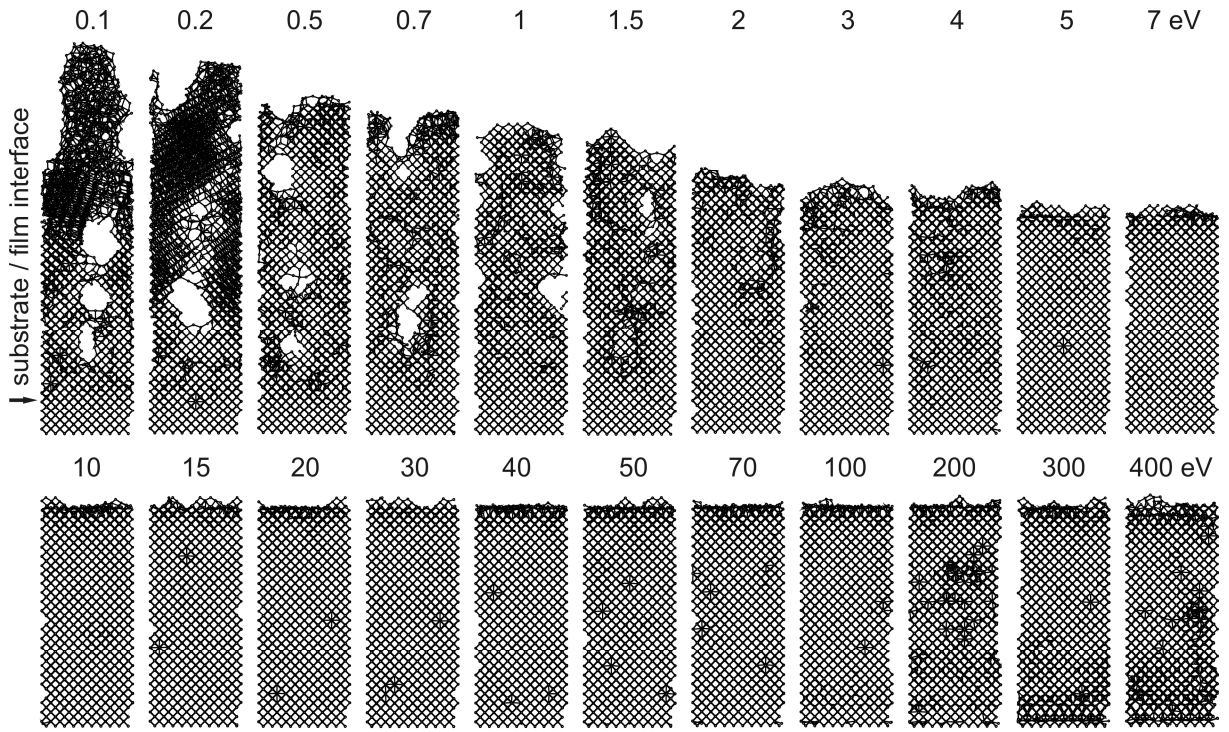
  q_{Zr} = 4.0 : undercoordination, fictitious rutile-like

  q_{Zr} around 3.5 : indeed, c-ZrO_2 growth

  q_{Zr} too low : overcoordination, amorphization

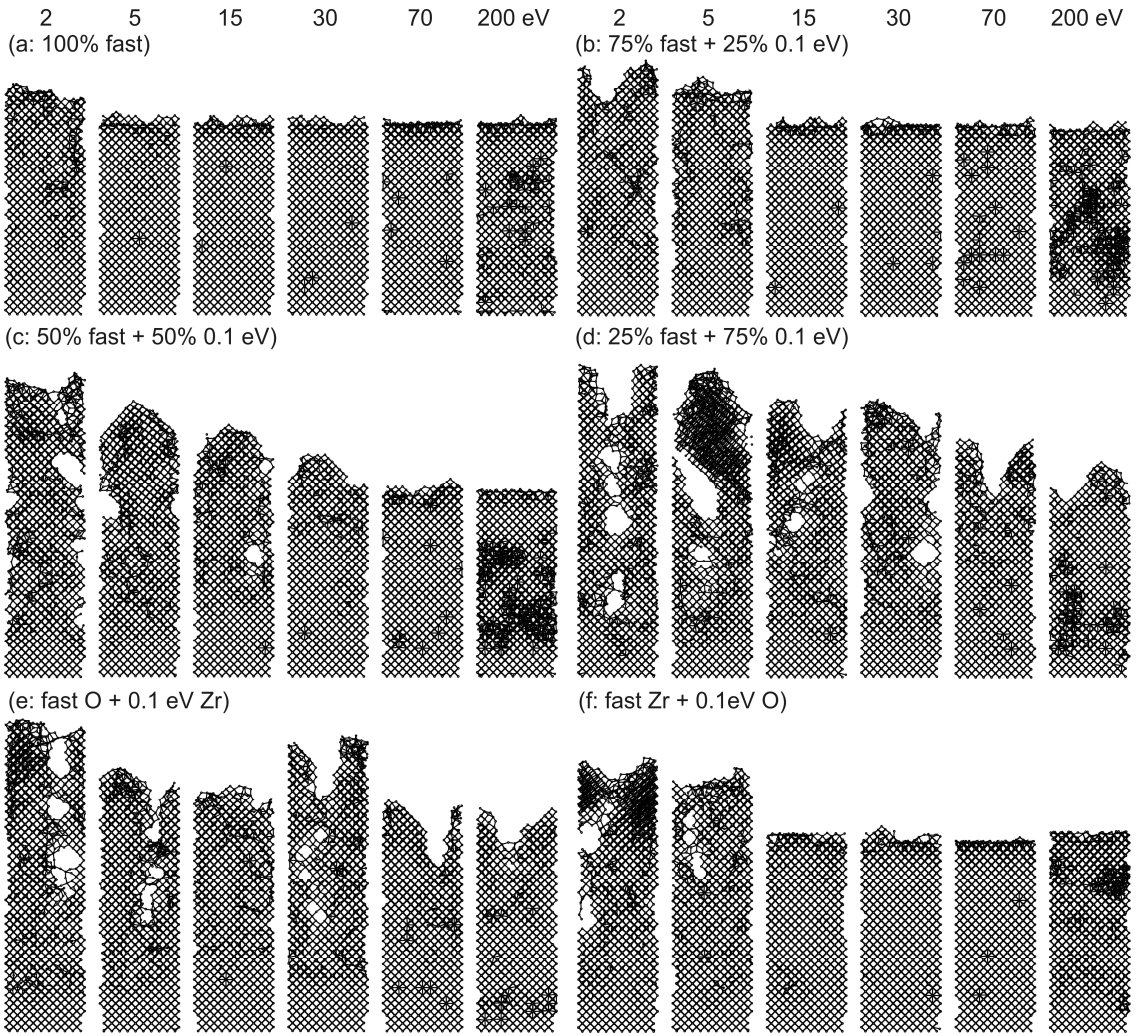


c-ZrO_2 growth - effect of energy, *E*



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

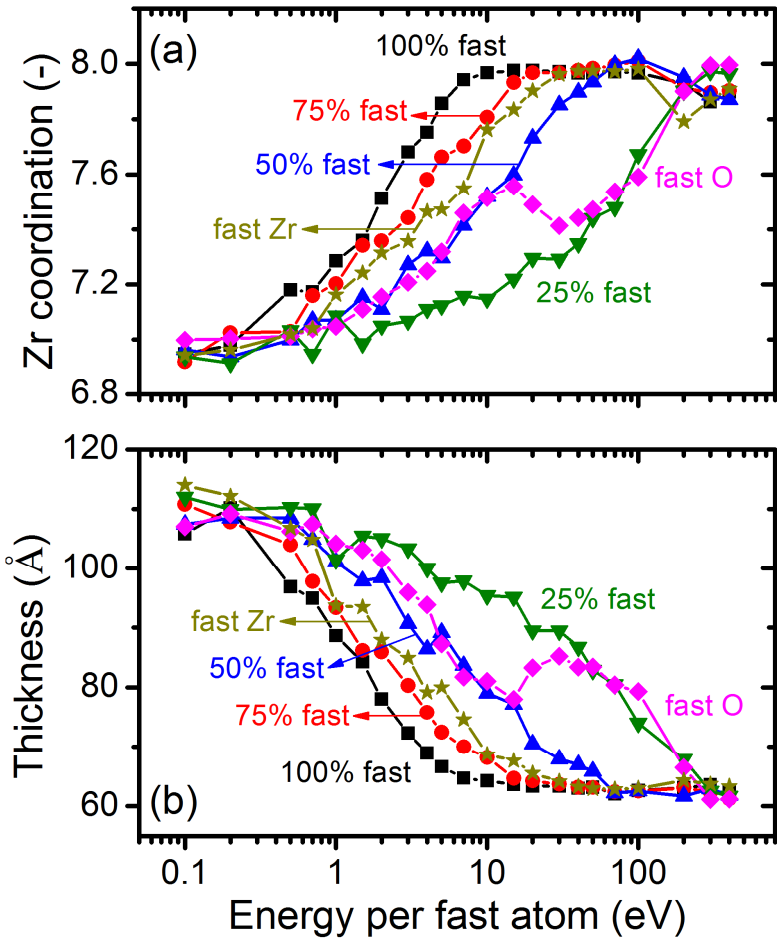
c-ZrO_2 growth - effect of energy distribution function



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

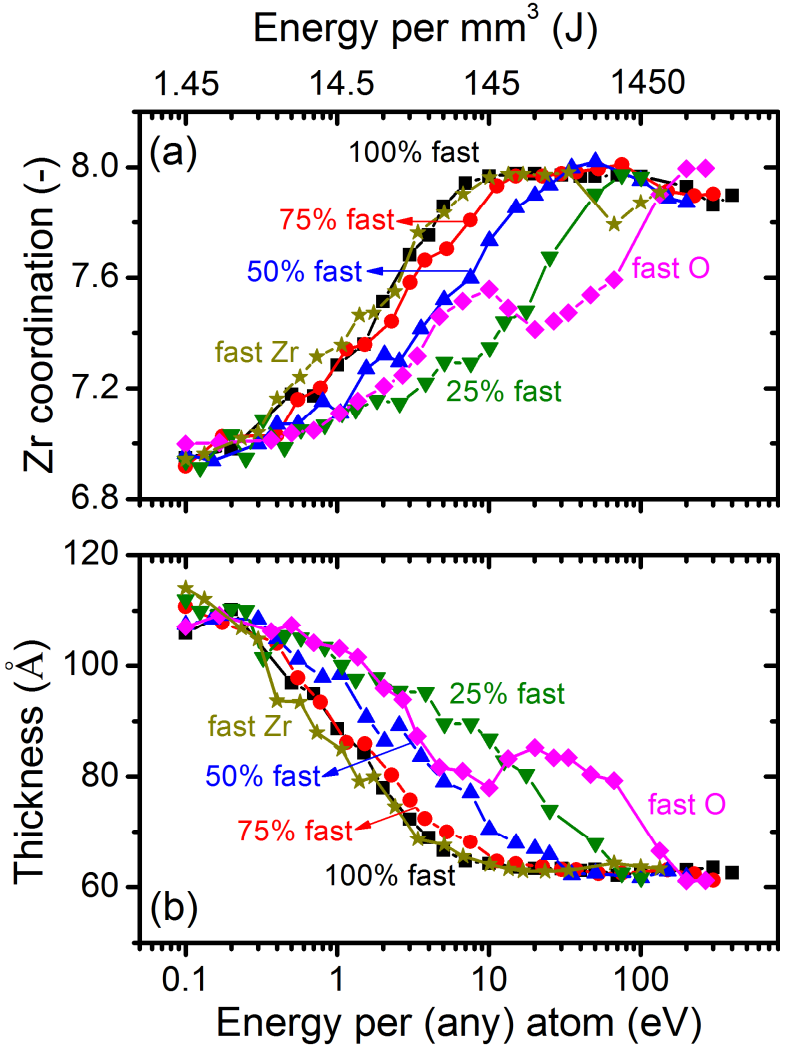
c-ZrO_2 growth - effect of energy distribution function

(quantification of the above results)



- Increasing fraction of slow atoms ⇒ 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-ZrO_2 growth - effect of energy distribution function



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

- Dependencies still do not overlap

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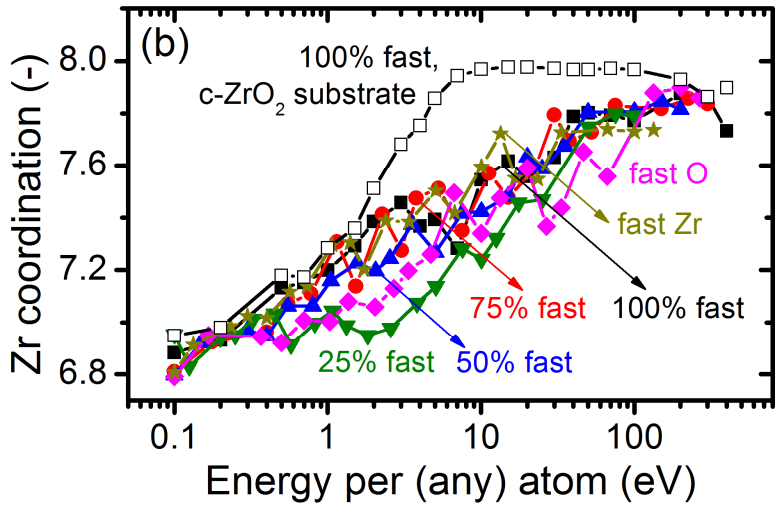
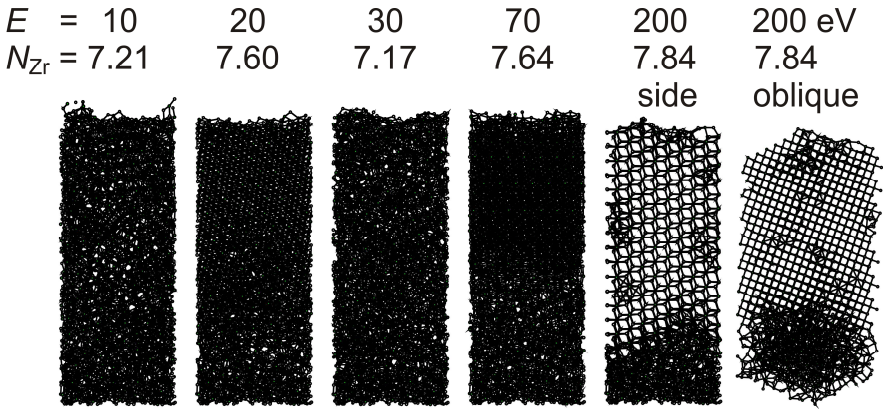
- Presence of slow atoms cannot be compensated by higher energy of fast atoms (ions) - correct average energy is not enough for crystal growth

Amorphous ZrO_2 growth and c-ZrO_2 nucleation





- Dependencies closer to each other

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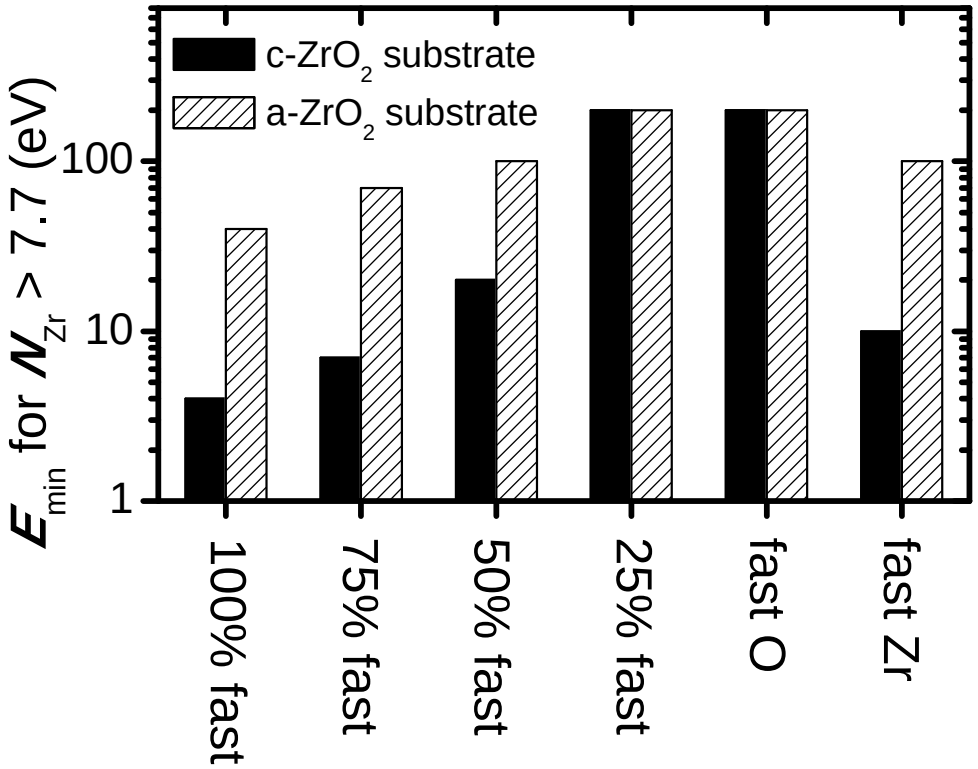
- Correct average energy is not enough for crystal growth, but ±enough for densification of amorphous
- Frequent c-ZrO_2 nucleation at energy of fast atoms (for various energy distribution functions) ≥200 eV

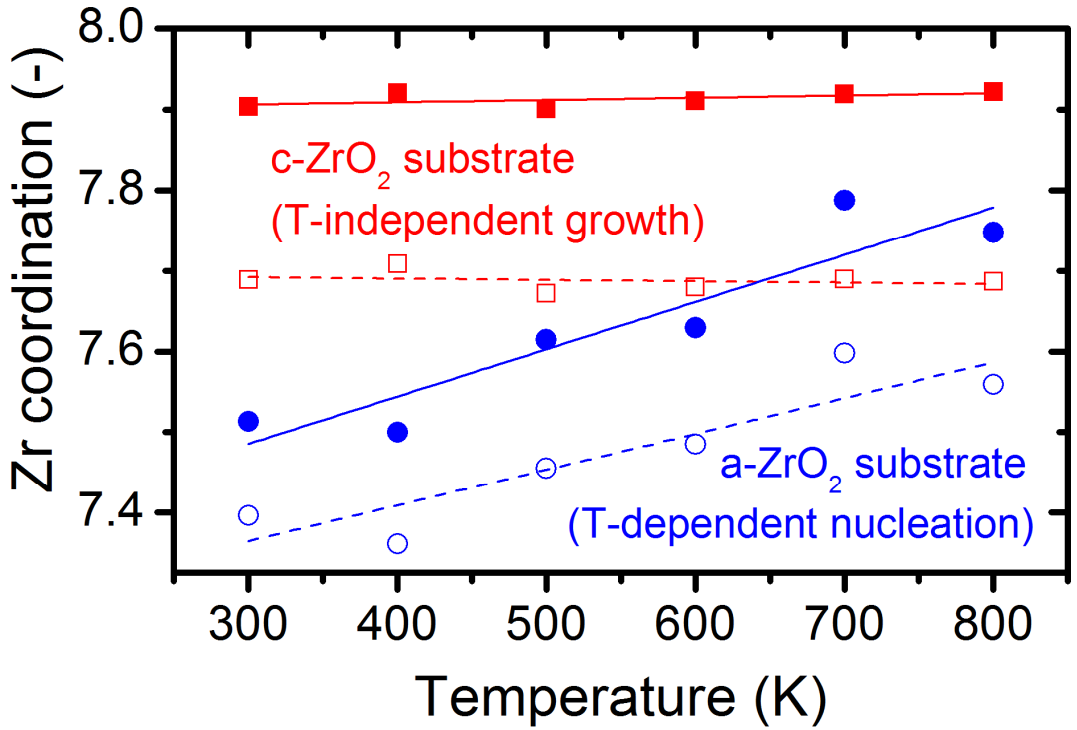
Growth × nucleation: effect of energy and EDF



minimum energy of fast atoms leading to crystallinity & densification (N_{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



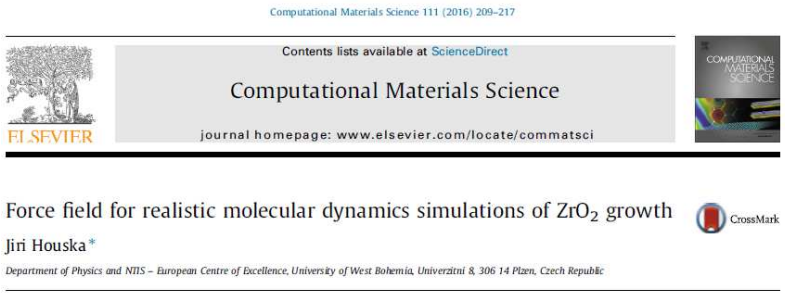
full symbols:
average over 3.0 - 400 eV

empty symbols:
average over 0.1 - 400 eV

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

Conclusions

- Procedure for improvement (coorrect coordination numbers!) of literature interaction potentials $\Rightarrow$ reliable ZrO_2 potential
- Crystal growth (5 eV limit at optimum EDF)
- Crystal nucleation (200 eV limit)
- EDF-dependent & mass/momentum-dependent growth
- T-independent growth $\times$ T-dependent nucleation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Force field for realistic molecular dynamics simulations of ZrO_2 growth

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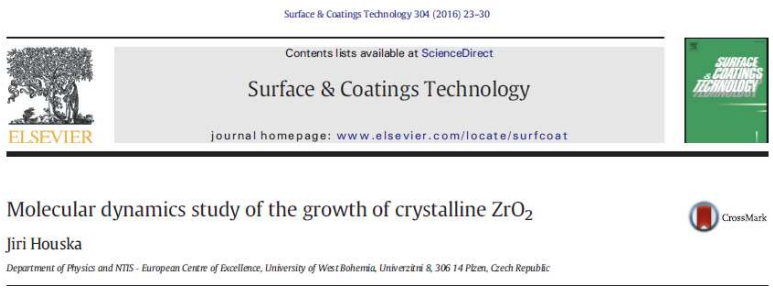
Surface & Coatings Technology 304 (2016) 23–30

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Molecular dynamics study of the growth of crystalline ZrO_2

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