

Pathways for the preparation of functional coatings by simulations at various scales

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Outline

- Modelling at higher than atomic scale:
thermochromic $\text{ZrO}_2/\text{V}_{1-x}\text{W}_x\text{O}_2/\text{ZrO}_2$
[J. Houska et al., *Sol. Energy Mater. Sol. Cells* 191, 365-371 (2019)]
[D. Kolenaty, J. Vlcek et al., *Sci. Rep.* 10, 11107 (2020)]
- Ab-initio modelling at atomic scale:
maximum achievable N content in amorphous Si-C-N
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- Classical modelling at atomic scale:
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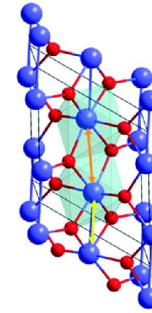
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Thermochromic VO₂

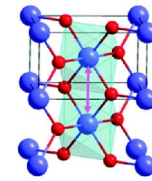
Low temperature (monoclinic):

- semiconductor (band gap)
- transparent
- low electrical and thermal conductivity



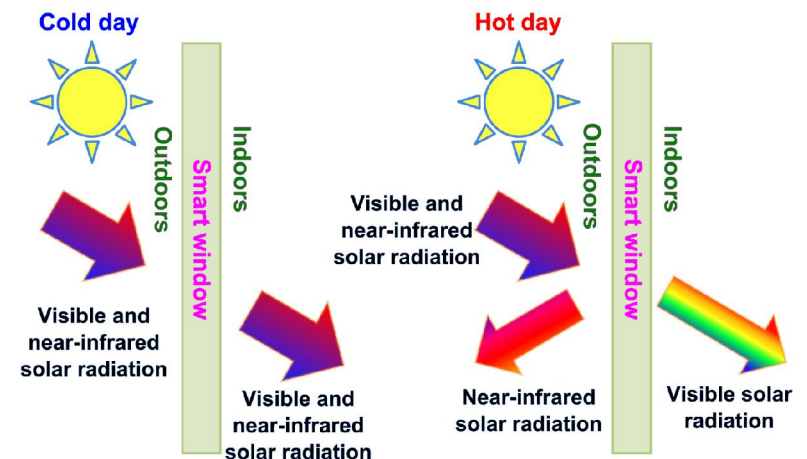
High temperature (tetragonal rutile):

- metallic
- opaque in IR
- high electrical and thermal conductivity



Transition temperature shifted to the room temp. by W doping

Applications including smart energy-efficient windows



Low-*T* deposition of crystalline VO₂ (Vlcek et al.)

High power impulse magnetron sputtering
of V in Ar+O₂ plasma



highly ionized fluxes with many metal ions



crystallinity & densification without bias at
250 °C on crystalline substrate
300 °C on amorphous glass substrate
(literature before 2016: ≥ 400 °C)

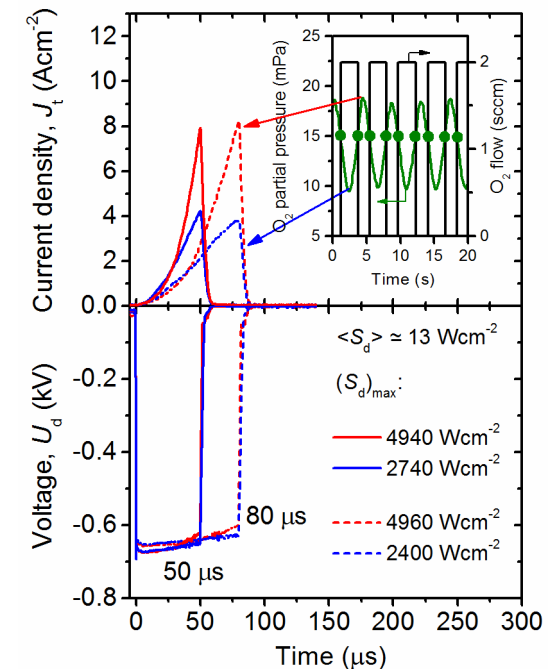
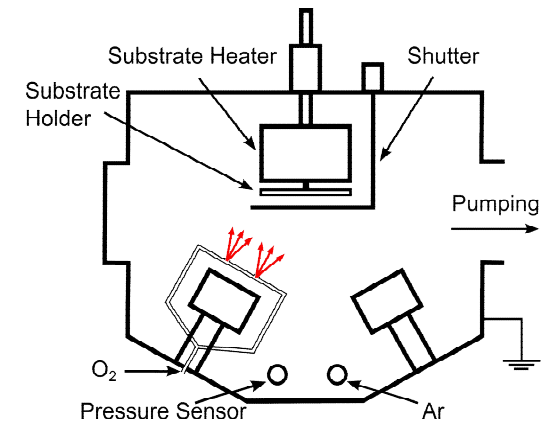
Patented pulsed reactive gas flow control



exactly as much oxygen as we need



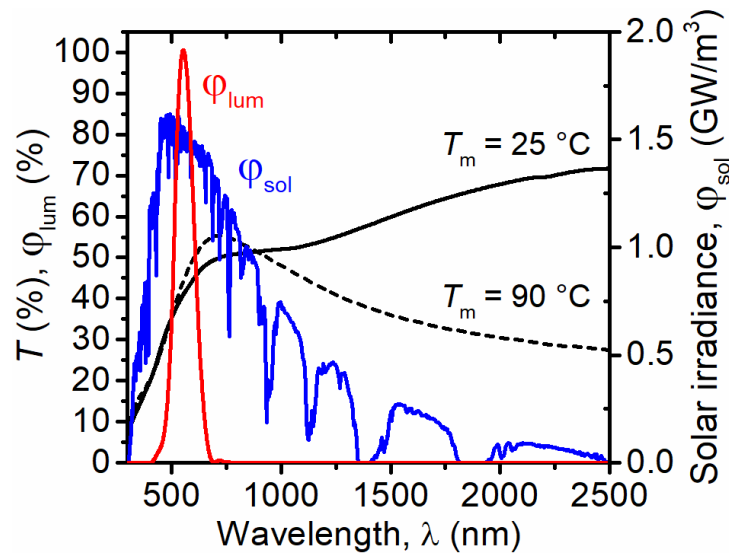
VO₂ film stoichiometry ($\times V_2O_5$, $\times V_2O_3$)



Thermochromic VO₂

One of challenges: maximize both

- luminous transmittance, T_{lum} and
- modulation of solar transmittance, ΔT_{sol}



$$T_{lum} = \int_{380}^{780} \phi_{lum}(\lambda) \phi_{sol}(\lambda) T(\lambda, T_m) d\lambda / \int_{380}^{780} \phi_{lum}(\lambda) \phi_{sol}(\lambda) d\lambda$$

$$T_{sol} = \int_{300}^{2500} \phi_{sol}(\lambda) T(\lambda, T_m) d\lambda / \int_{300}^{2500} \phi_{sol}(\lambda) d\lambda$$

How to maximize T_{lum} and ΔT_{sol}

$$T_{lum} = \int_{380}^{780} \phi_{lum}(\lambda) \phi_{sol}(\lambda) T(\lambda, T_m) d\lambda / \int_{380}^{780} \phi_{lum}(\lambda) \phi_{sol}(\lambda) d\lambda$$

$$T_{sol} = \int_{300}^{2500} \phi_{sol}(\lambda) T(\lambda, T_m) d\lambda / \int_{300}^{2500} \phi_{sol}(\lambda) d\lambda$$

Varying VO₂ thickness \Rightarrow tradeoff
(thin films have high T_{lum} , thick films have high ΔT_{sol})

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(thin films have high T_{lum} , thick films have high ΔT_{sol})

1st order antireflection layers \Rightarrow tradeoff

(first-order maximum of T_{lum} overlaps with minimum of ΔT_{sol})

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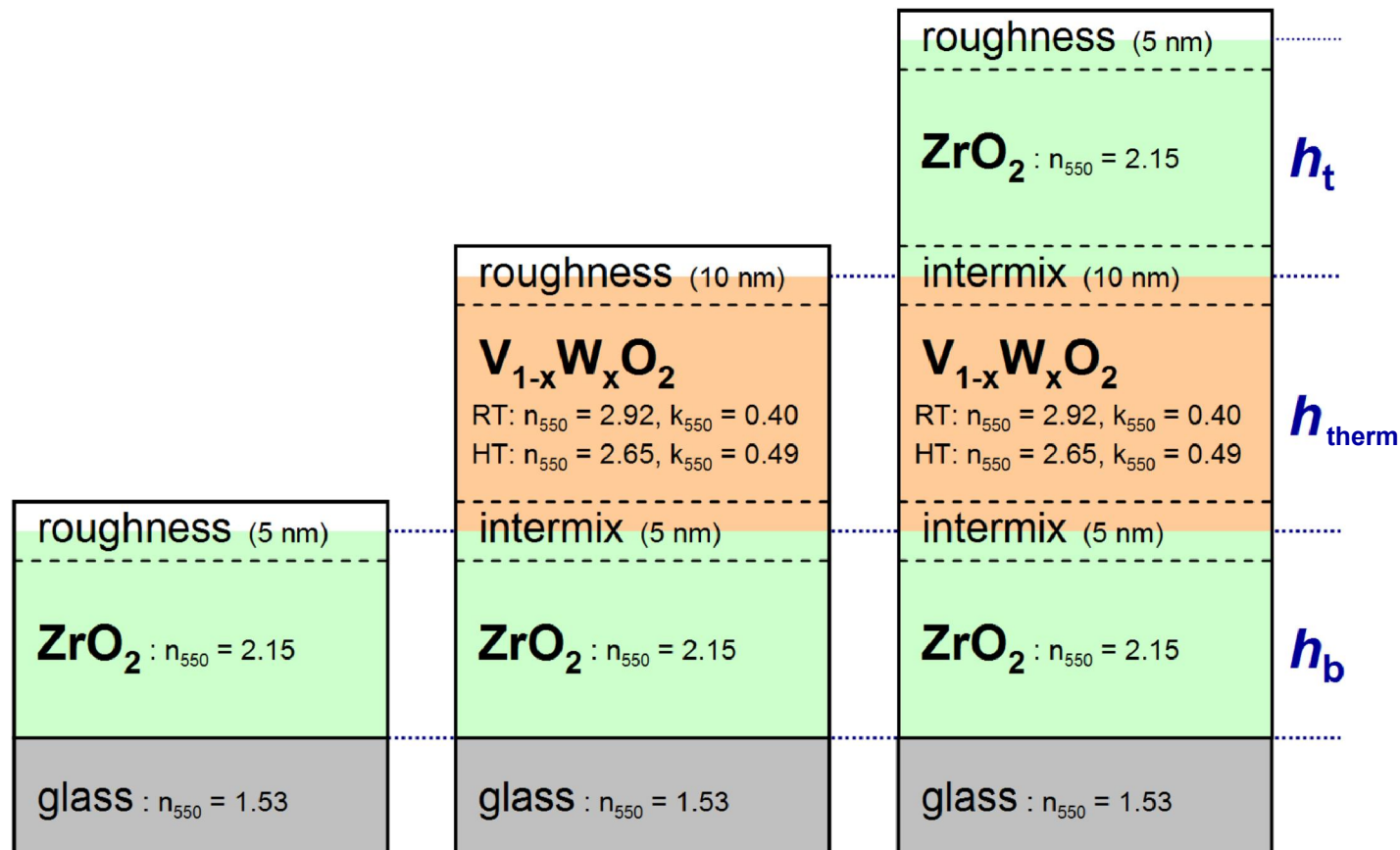
2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}

How to maximize T_{lum} and ΔT_{sol}

2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}

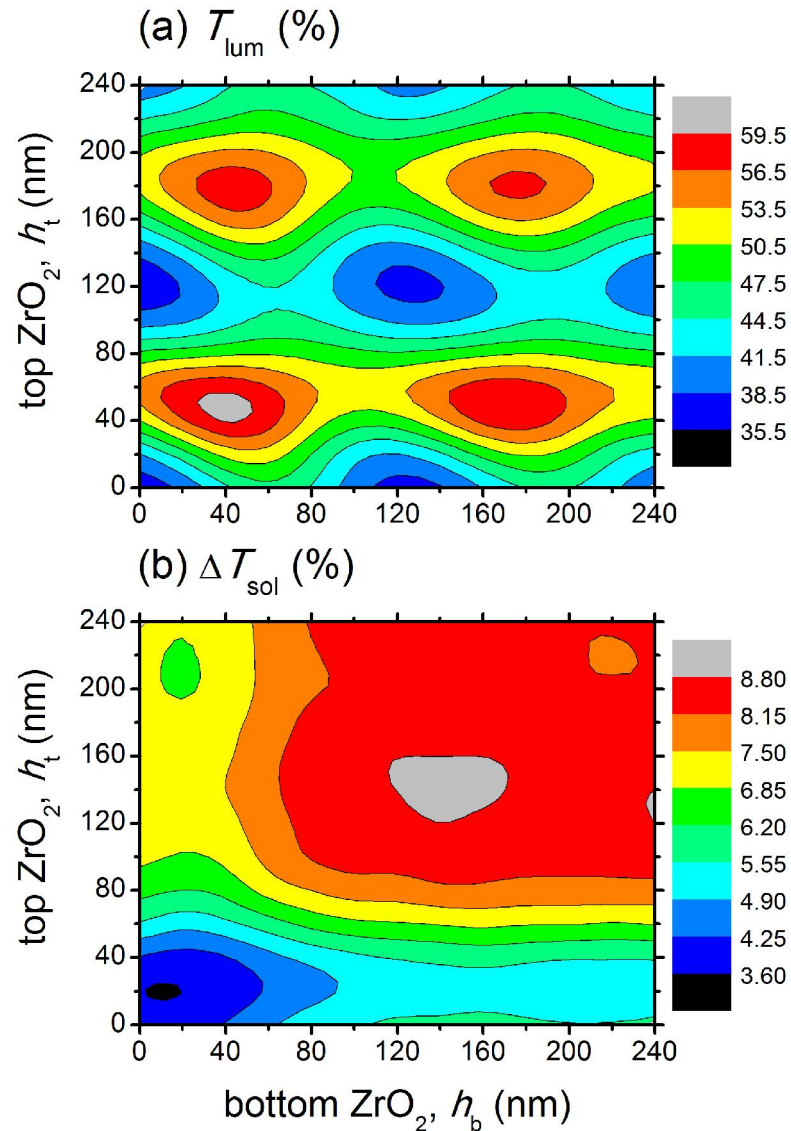
chosen material of antireflection layers: ZrO_2

chosen VO_2 or $\text{V}_{1-x}\text{W}_x\text{O}_2$ thickness in calculations below: 50 nm



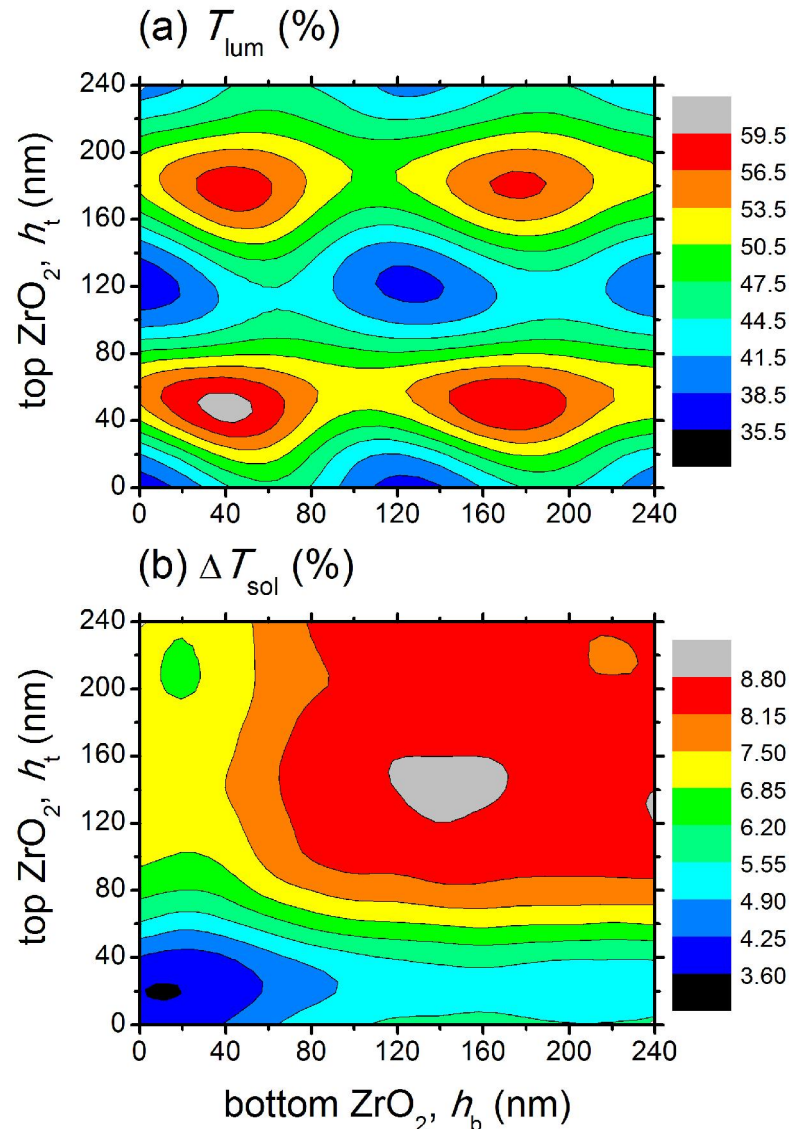
How to maximize T_{lum} and ΔT_{sol} (at $h_{\text{therm}} = 50$ nm)

2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}



How to maximize T_{lum} and ΔT_{sol} (at $h_{\text{therm}} = 50$ nm)

2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}



Peafowl-like figure for T_{lum} :

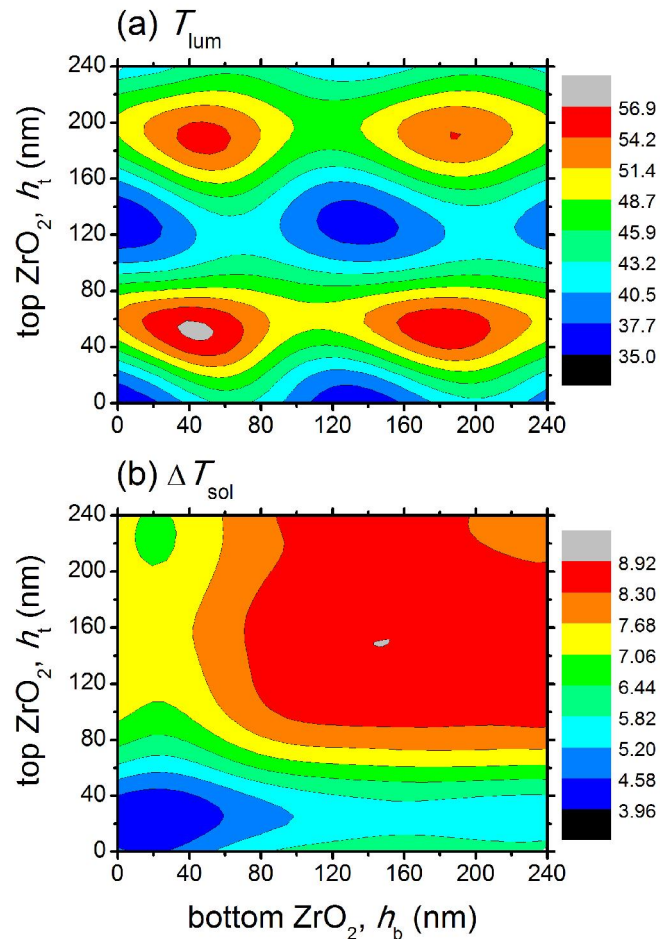
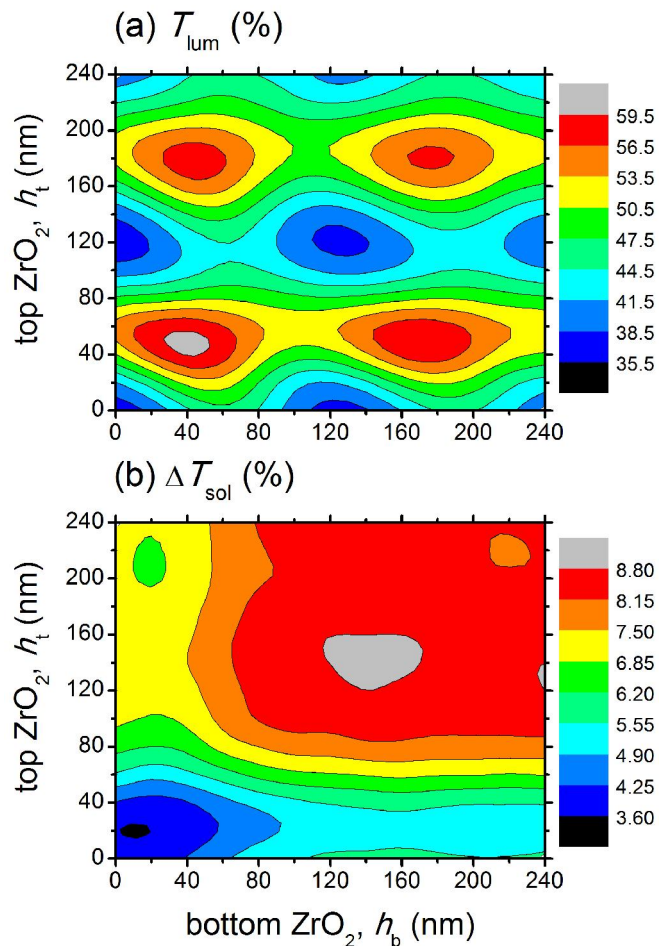
1st order maximum of T_{lum}
(ZrO_2 thickness of ≈ 40 nm)
corresponds to **low** ΔT_{sol}

2nd order maximum of T_{lum}
(ZrO_2 thickness of ≈ 180 nm)
corresponds to **high** ΔT_{sol}

Recommendation almost independent of the beam angle

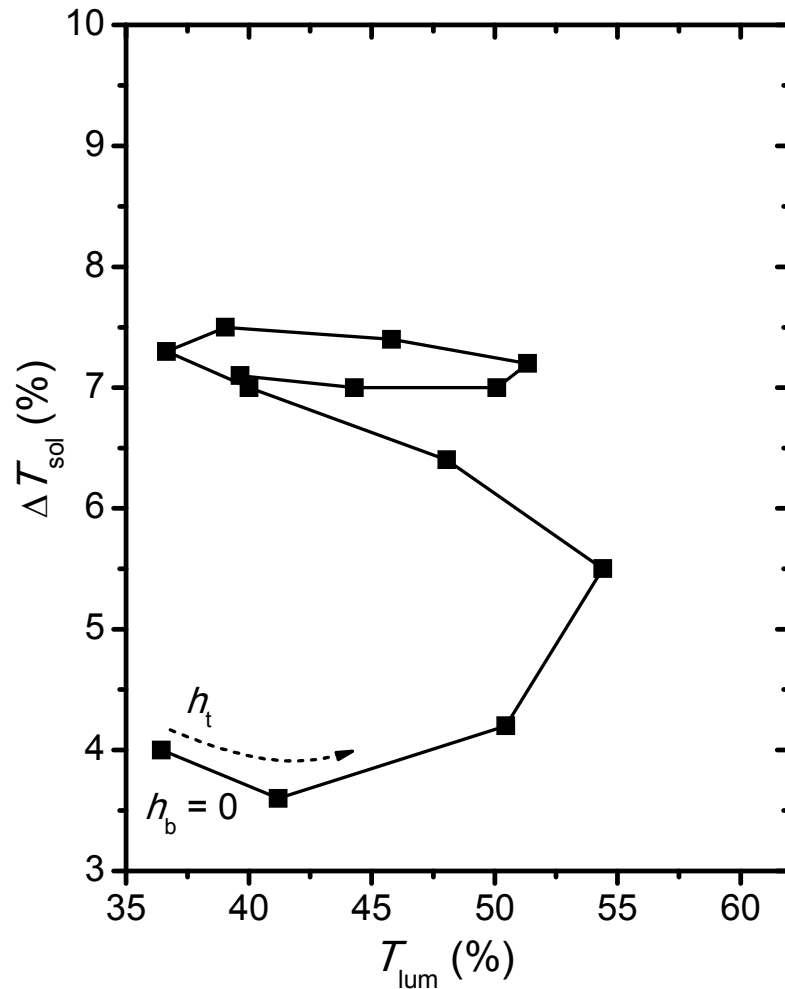
normal beam

45° beam, refraction towards normal:
45° in air = 19° in ZrO_2 , $\cos 19^\circ = 0.95$
 \Rightarrow 190 instead of 180 nm)



How to maximize T_{lum} and ΔT_{sol} (at $h_{\text{therm}} = 50 \text{ nm}$)

2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}



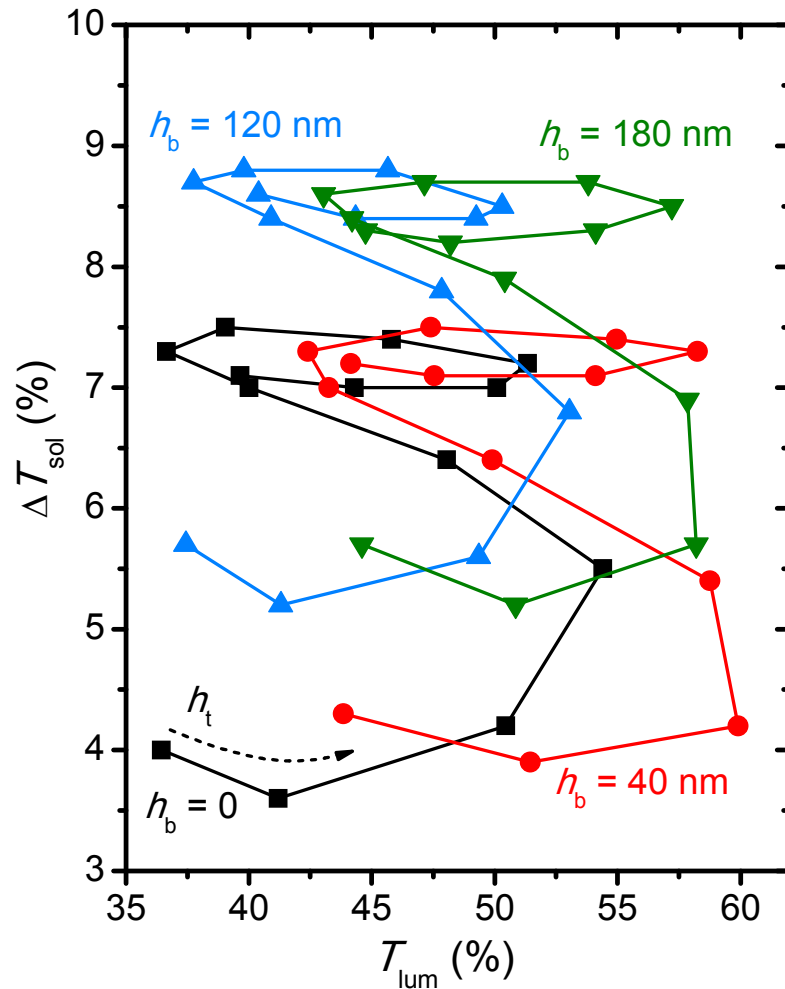
1st order maximum of T_{lum}
(ZrO₂ thickness of $\approx 40 \text{ nm}$)
corresponds to **low** ΔT_{sol}
(handle of lasso)

2nd order maximum of T_{lum}
(ZrO₂ thickness of $\approx 180 \text{ nm}$)
corresponds to **high** ΔT_{sol}
(loop of lasso)



How to maximize T_{lum} and ΔT_{sol} (at $h_{\text{therm}} = 50 \text{ nm}$)

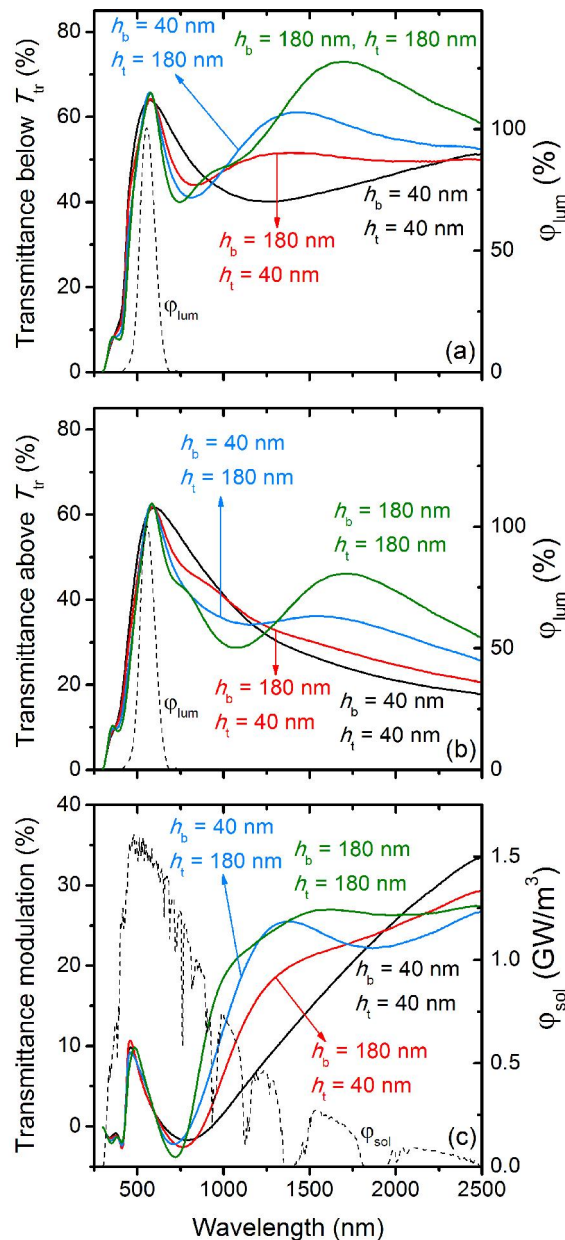
2nd order antireflection layers \Rightarrow improves both T_{lum} and ΔT_{sol}



recommendation (lasso-like dependence) valid for any thickness of the other AR layer \Rightarrow both AR layers should be second order



How to maximize T_{lum} and ΔT_{sol} (at $h_{\text{therm}} = 50$ nm)

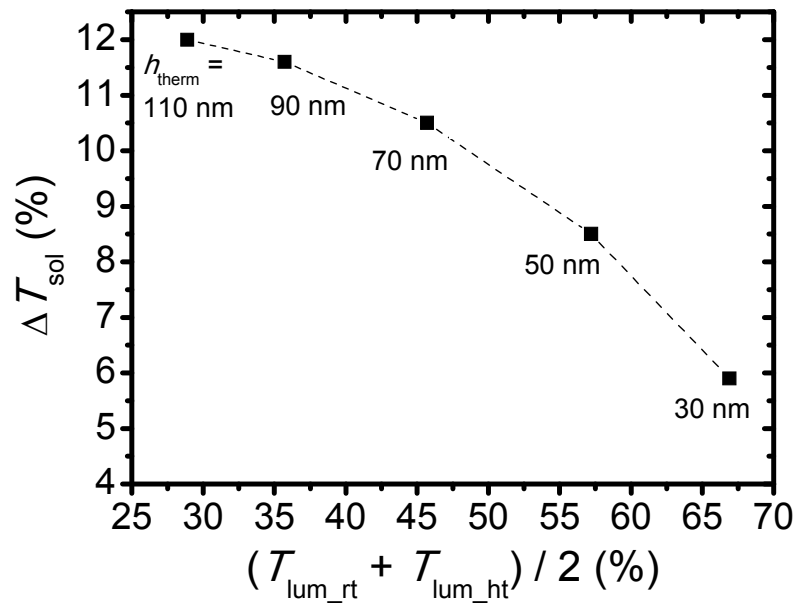


$h_b = h_t = 40$ nm (1. order max.):
high transmittance modulation
only at high λ (> 2000 nm), i.e.
multiplied by low solar intensity

$h_b = h_t = 180$ nm (2. order max.):
high transmittance modulation
at medium λ (wide range 800-
2000 nm), i.e. multiplied by high
solar intensity

in other words: optimum
antireflection layers actually
harm ΔT_{2500} , but improve
the integral quantity ΔT_{sol}

Maximize T_{lum} and ΔT_{sol} - experimental verification



Tradeoff between T_{lum} and ΔT_{sol}
(depending on VO_2 thickness)

figure for optimum
thickness of AR ZrO_2 :
 $h_{\text{b}} = h_{\text{t}} = 180 \text{ nm}$

Maximize T_{lum} and ΔT_{sol} - experimental verification

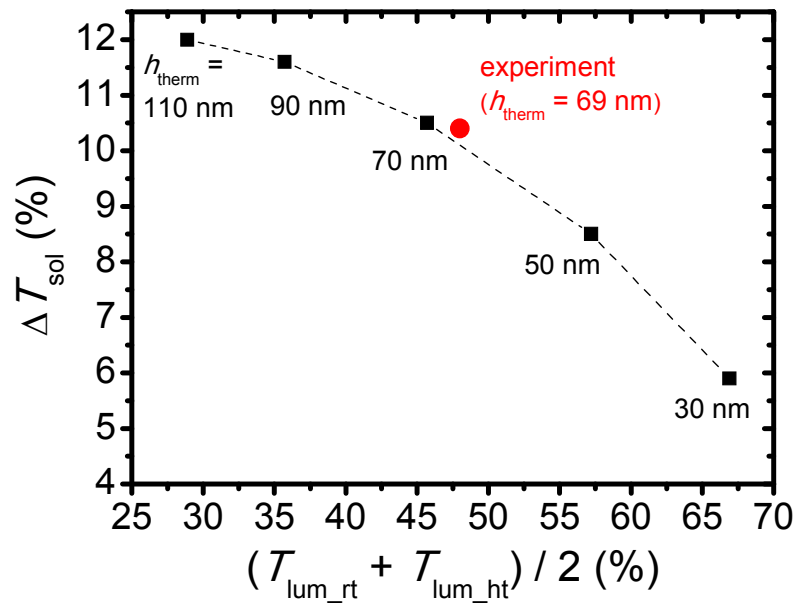


figure for optimum thickness of AR ZrO_2 :
 $h_b = h_t = 180 \text{ nm}$

Tradeoff between T_{lum} and ΔT_{sol}
(depending on VO_2 thickness)

VO_2 (actually $\text{V}_{0.982}\text{W}_{0.018}\text{O}_2$)
thickness $h_{\text{therm}} = 69 \text{ nm}$:
agreement with prediction

Experimental values

$T_{\text{lum}} = 48\%$

$\Delta T_{\text{sol}} = 10.4\%$

transition at 20°C due to $\text{W}_{0.018}$

[D. Kolenaty, J. Vlcek et al.,
Sci. Rep. 10, 11107 (2020)]

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Motivation

Dependence of hardness / band gap / thermal stability / ... of amorphous CN_x / SiN_x / Si-C-N ... on the N content, [N].

Wide range of maximum achievable [N] values (by atom-by-atom techniques, not e.g. polymerization) in the literature.

CN_x as an example

$\beta\text{-C}_3\text{N}_4$ predicted to be superhard. CN_x synthesised by low-pressure atom-by-atom growth interesting (friction coefficient, elastic recovery, ...) but amorphous and substoichiometric

Contradictory reported maximum [N] in a- CN_x in a wide range ≈ 23 to $\approx 45\%$ (only atom by atom growth)

≈ 23 to $\approx 57\%$ (also techniques like N_2^+ implantation).

What is the reliable maximum? Can we prepare C_3N_4 ?

Literature

- Highest [N] by N_2^+ ion beam or other N-rich precursors
- [N] often measured by techniques which cannot distinguish bonded N (in networks) and unbonded N_2 (in voids)
- Higher N contents at lower deposition temperatures (shorter time for N_2 formation and N_2 diffusion to atmosphere)

Hypothesis

Maximum N content in amorphous Si-C-N is largely given by the formation, presence, and loss of N_2 molecules

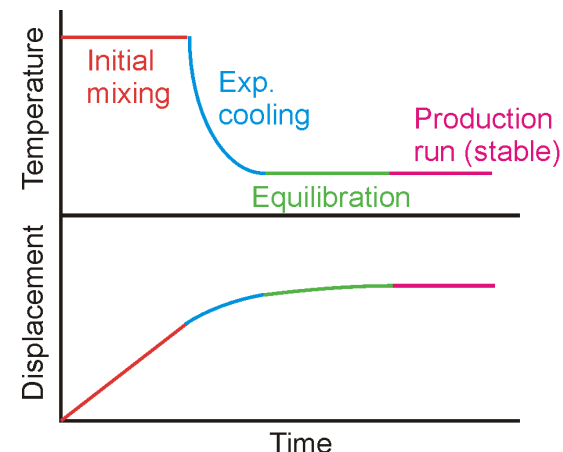
Aim of this part

Predict maximum stable N content in Si-C-N by extensive (wide range of compositions and densities) ab-initio DFT simulations, and explain the contradictory experimental data

Amorphous structure of given composition and density

Search for a local energy minimum, usually arising from rapid quenching of a localized melt after an energetic ion impact

- high-temperature mixing of a molten phase (6000 K)
- cooling to a representative deposition temperature (450 K)
- low-temperature equilibration
- collect energies and bonding statistics



Thermal spikes are subpicosecond, materials are covalent (\times low- T aging of metallic glasses) \Rightarrow length of each step 0.5 ps (longer simulations in selected cases for cross-check purposes)

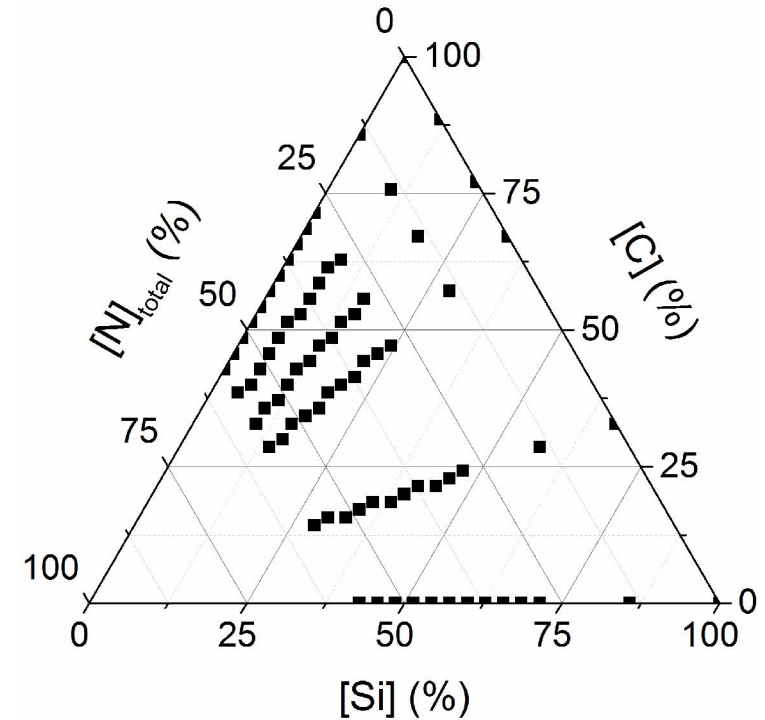
Car-Parrinello molecular dynamics implemented in CPMD code, norm-conserving Goedecker pseudopot., LDA xc functional, plane wave basis set with a wavefunction cutoff of 60 Ry

List of ab-initio simulations

6 compositions before including N:
 $[\text{Si}]/[\text{Si}+\text{C}] = 0 \text{ to } 100\%$

13 contents of bonded+unbonded N:
 $[\text{N}]_{\text{total}} = 0 \text{ to } 57\%$

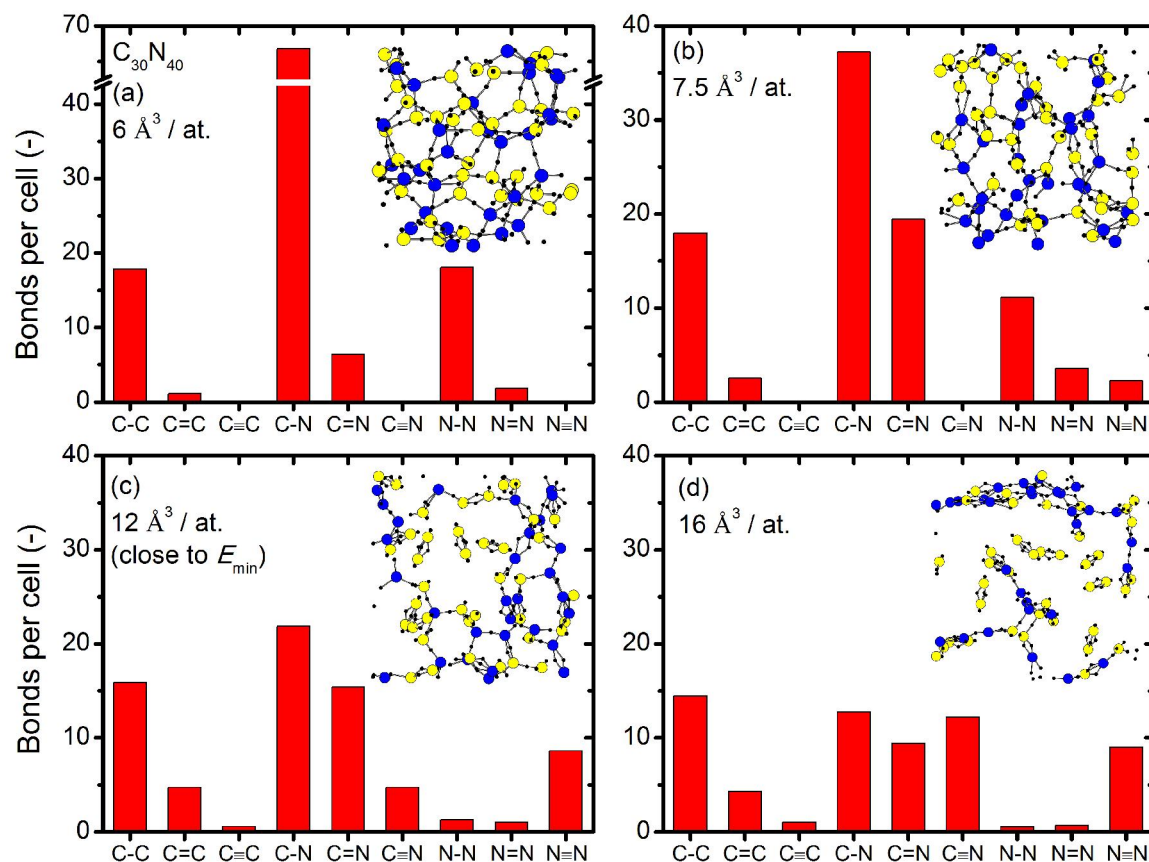
13-19 inverse atomic densities:
 $V = 6 \text{ to } 16\text{-}22 \text{ \AA}^3/\text{at.}$
(includes all relevant crystalline
and reported amorphous phases)



Statistical noise suppressed by repeating each simulation
5× with different random initial coordinates of 70 atoms

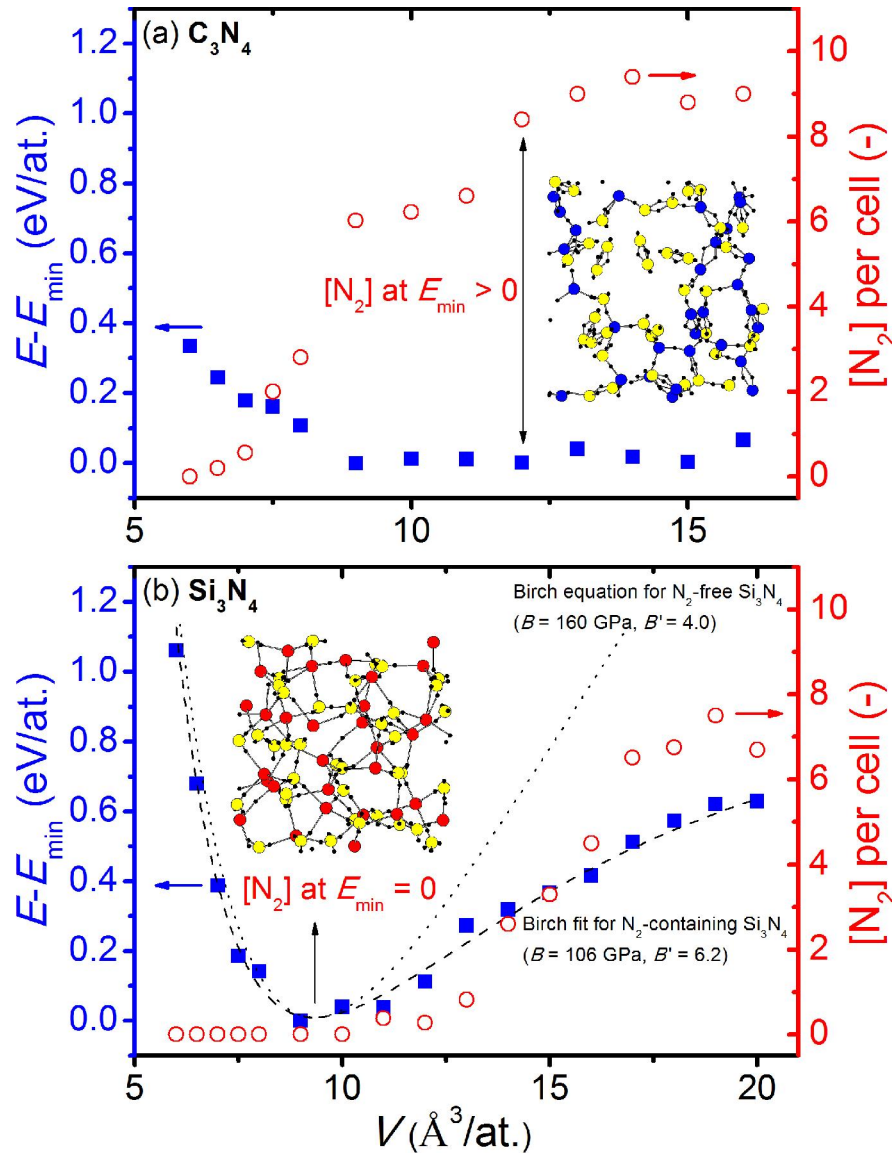
Results based on $6 \times 13 \times (13 \text{ to } 19) \times 5 = 5600$ LQ simulations
(impossible in 1990's when the experimental interest started)

Example of the role of density



- All structures of α - C_3N_4 (even the high-density N_2 -free one) include considerable fraction of NN bonds
- Decreasing density leads to increasing fraction of double and triple C=C, C=N, C≡N, N=N, N≡N (unbonded molecules)

Example of the role of composition



- Increasing V leads to increasing $[N_2]$ and decreasing $[N]_{\text{network}}$ (bonded)

- C_3N_4 : at the lowest energy $[N_2] \approx 9$ per 70-atom cell

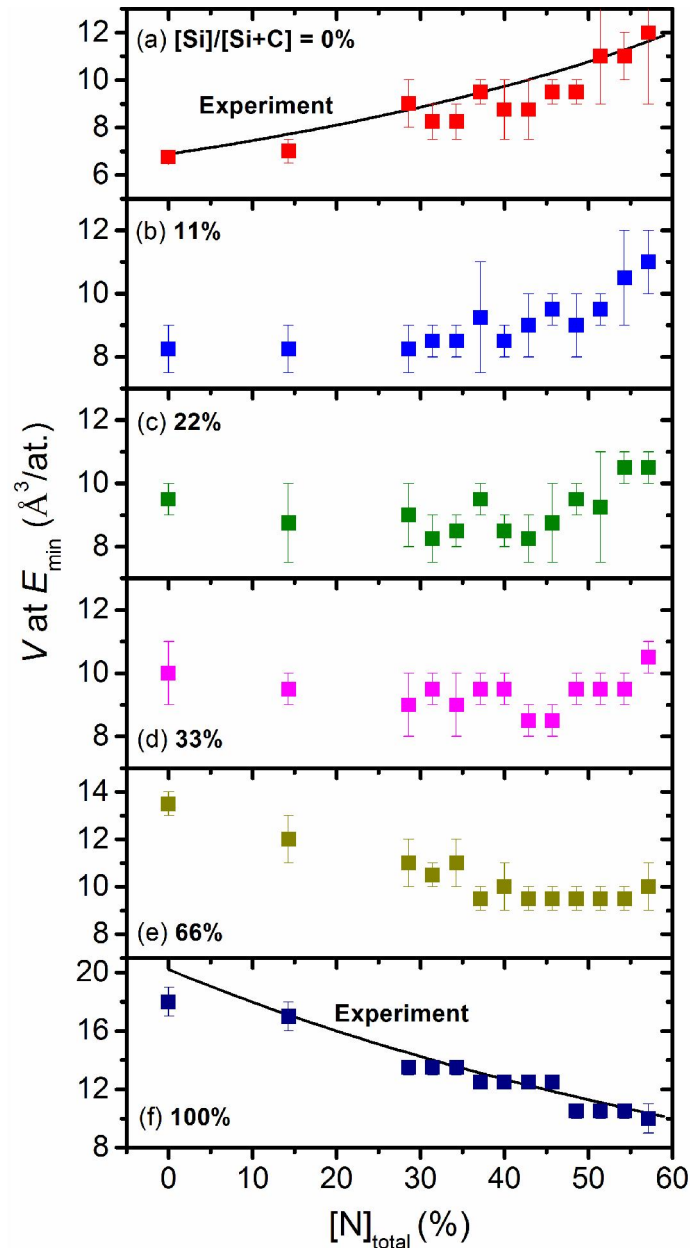


$$[N]_{\text{total}} = 40/70 = 57\%$$

$$[N]_{\text{network}} = (40 - 2 \times 9) / (70 - 2 \times 9) = 42\%$$

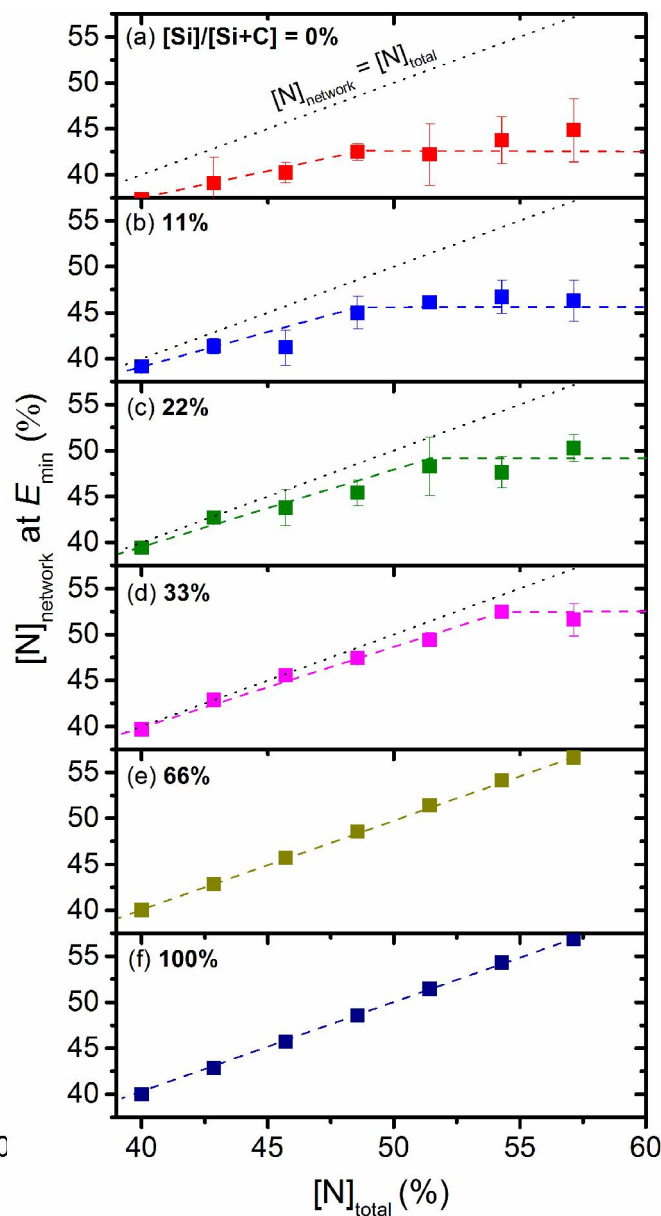
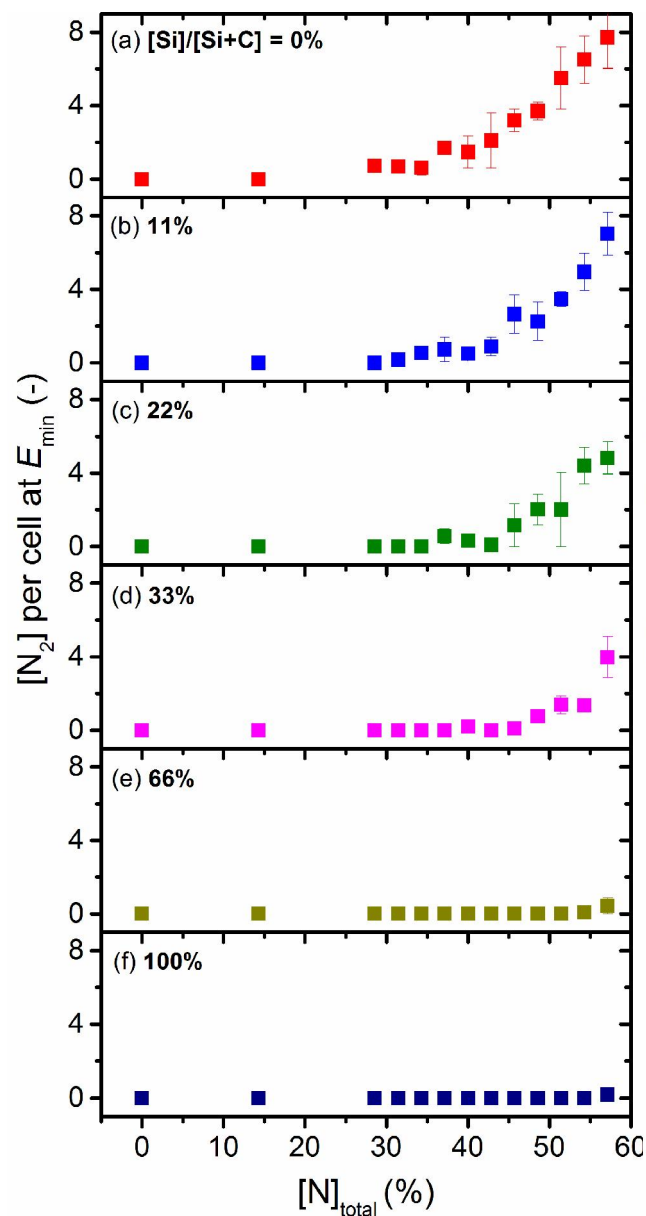
- Si_3N_4 : at the lowest energy $[N_2] \approx 0$

All 78 lowest-energy densities



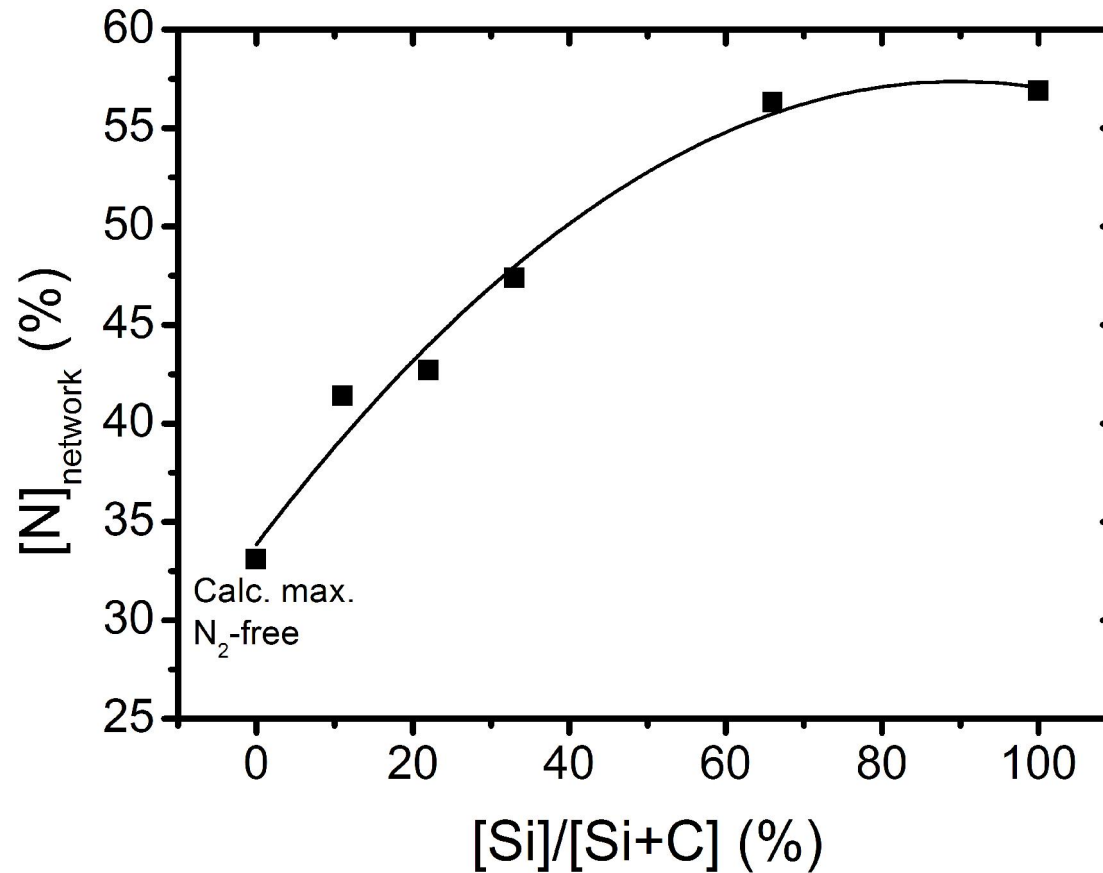
- C-rich compositions:
 V increases with $[\text{N}]_{\text{total}}$
 (volume for N_2 -containing voids)
- Si-rich compositions:
 V decreases with $[\text{N}]_{\text{total}}$
 (no N_2 -containing voids, large Si)
- Materials are allowed to contain unbonded $\text{N}_2 \Rightarrow$ good agreement with the experiment, achieved without any fitted parameters
[CN_x Valladares et al.]
[SiN_x Yen et al.]

All 78 lowest-energy contents of bonded and unbonded N



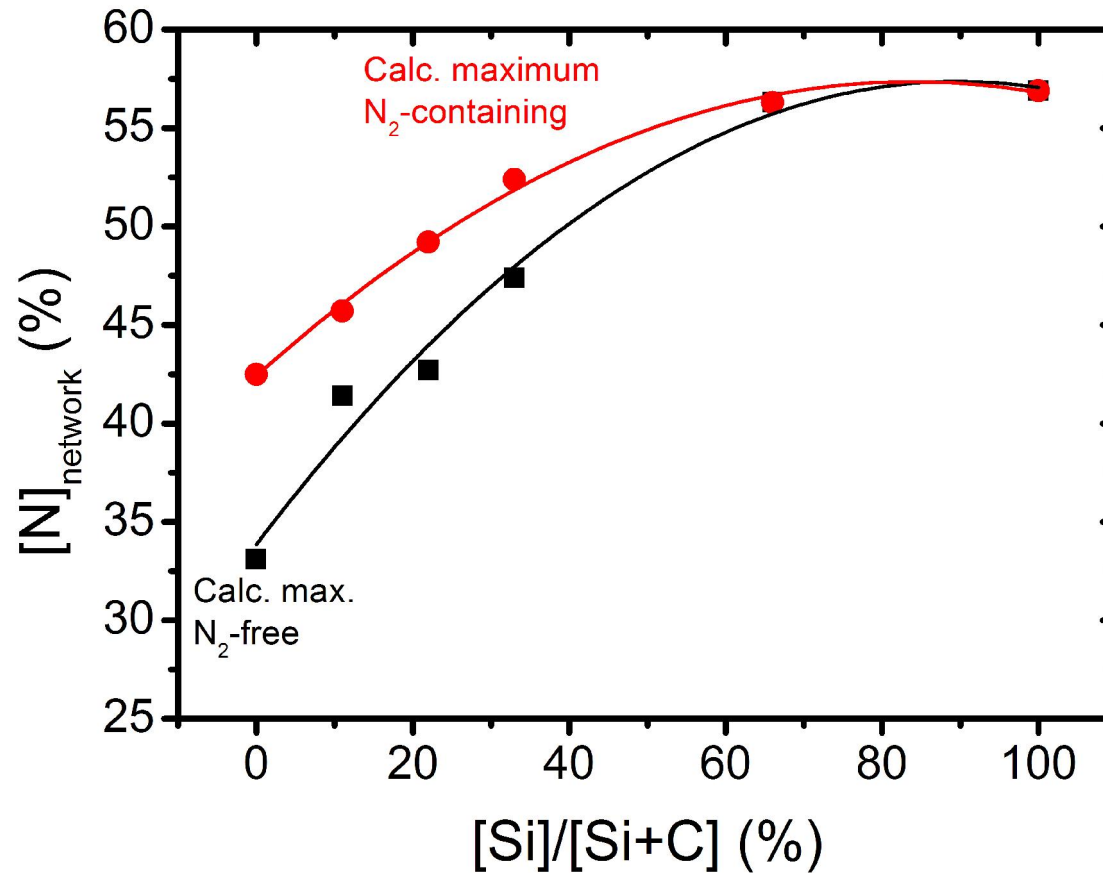
- Above certain $[N]_{\text{total}}$ onset: increasing $[N_2]$, \approx constant $[N]_{\text{network}}$
- The $[N]_{\text{total}}$ onset and the saturation $[N]_{\text{network}}$ increase with $[\text{Si}]/[\text{Si}+\text{C}]$
- N-rich networks stabilized by N_2 : N_2 diffuses out
 \Downarrow
lower $[N]_{\text{total}}$
 \Downarrow
lower $[N]_{\text{network}}$

Maximum achievable content of bonded N



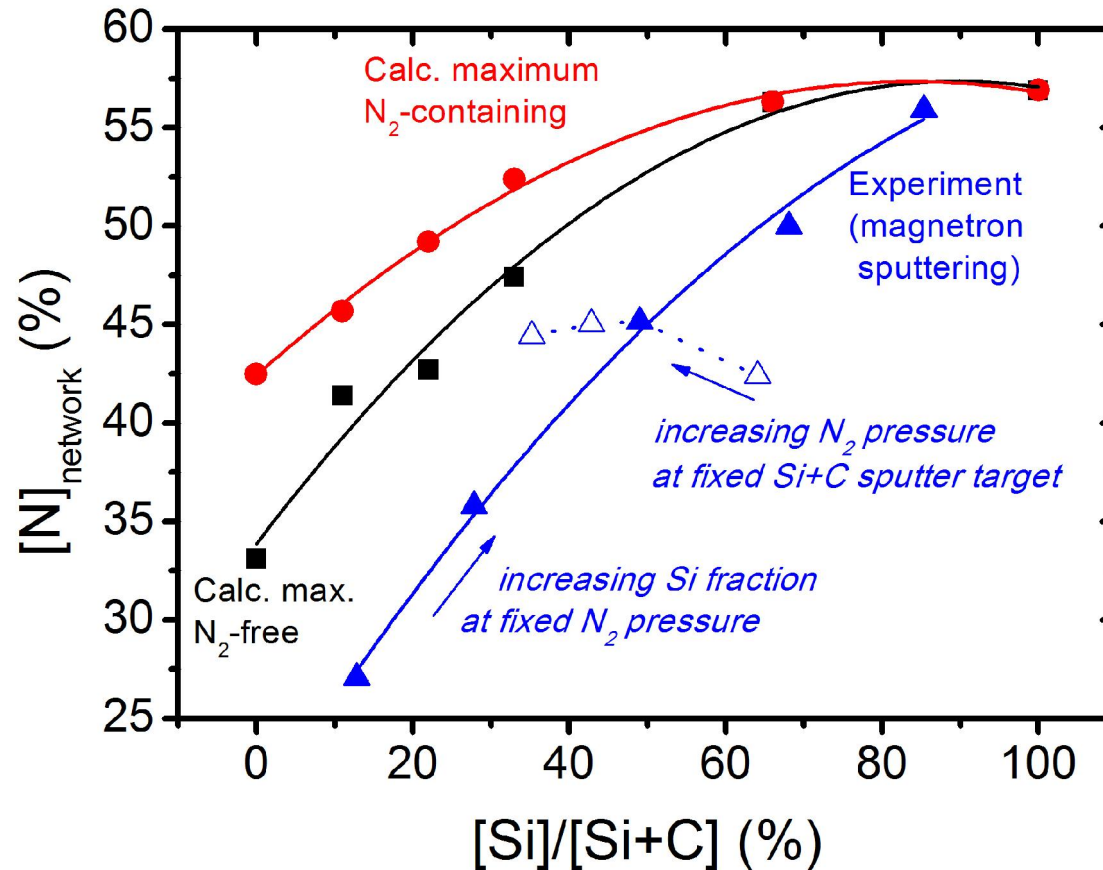
- N₂-free: $[N]_{\text{network}} \leq -0.00292 \times ([Si]/[Si+C])^2 + 0.524 \times [Si]/[Si+C] + 33.8$

Maximum achievable content of bonded N



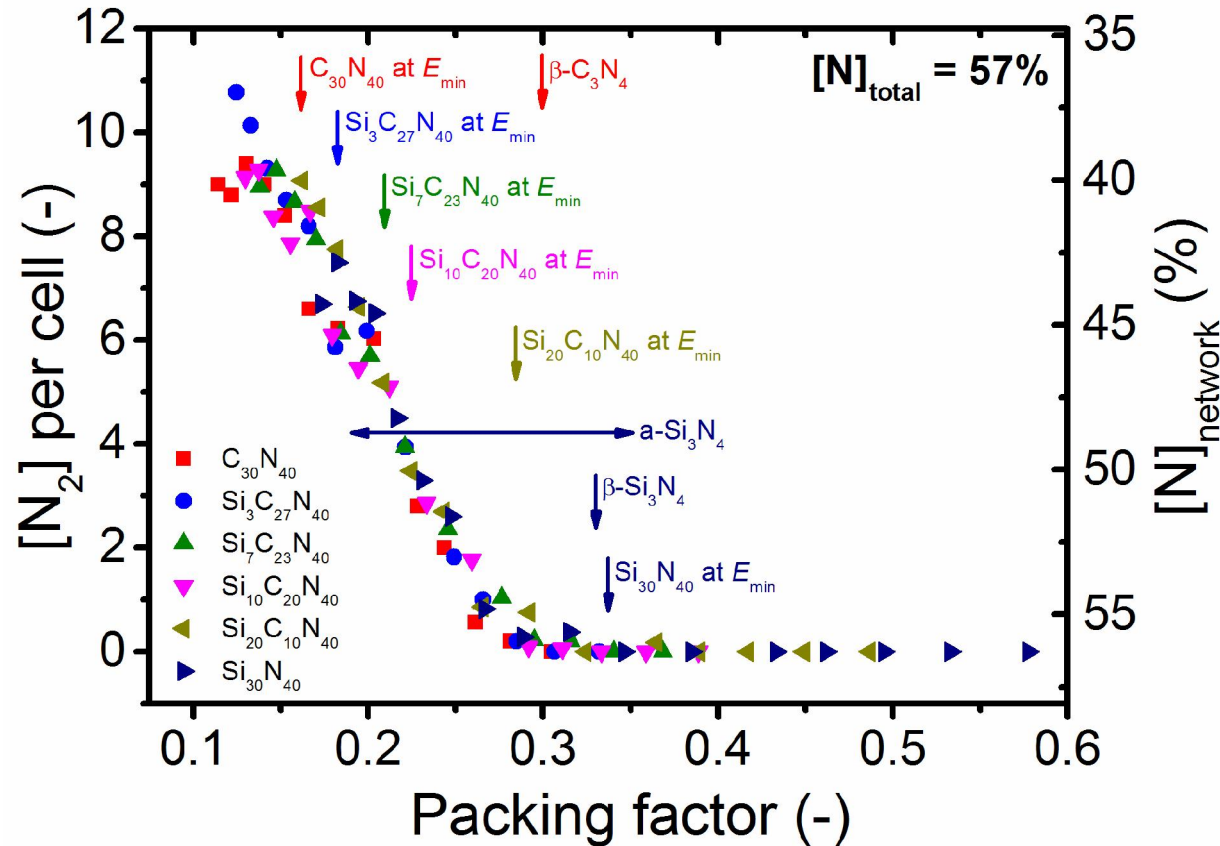
- N_2 -free: $[N]_{\text{network}} \leq -0.00292 \times ([Si]/[Si+C])^2 + 0.524 \times [Si]/[Si+C] + 33.8$
- N_2 -containing: $[N]_{\text{network}} \leq -0.00212 \times ([Si]/[Si+C])^2 + 0.356 \times [Si]/[Si+C] + 42.4$

Maximum achievable content of bonded N



- N_2 -free: $[N]_{\text{network}} \leq -0.00292 \times ([Si]/[Si+C])^2 + 0.524 \times [Si]/[Si+C] + 33.8$
- N_2 -containing: $[N]_{\text{network}} \leq -0.00212 \times ([Si]/[Si+C])^2 + 0.356 \times [Si]/[Si+C] + 42.4$
- Consistent with magnetron sputtering [Vlcek, Kormunda, Cizek et al.]

Maximum achievable content of bonded N



- $[N_2]$ per 200 atoms = $[N]_{\text{total}} (1 - \text{packing factor} / 0.28)$ independently of $[Si]/[Si+C]$ (shown) and $[N]_{\text{total}}$ (not shown)
- However, N_2 formation depends on the composition because the lowest-energy packing factor depends on the composition

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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 growth
 - used for covalent films, ionic oxides, metallic glasses, ..., here an example for ZrO_2
 - classical molecular dynamics
 - reliable interaction potentials (force fields)



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

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

Buckingham interaction potential for ZrO_2

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

Full charge ($q_{\text{Zr}} = +4e$) potentials in the literature:



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



fitted with other simulation protocols in mind



wrong preferred coordination numbers N_{Zr}



unsuitable for reliable growth simulations

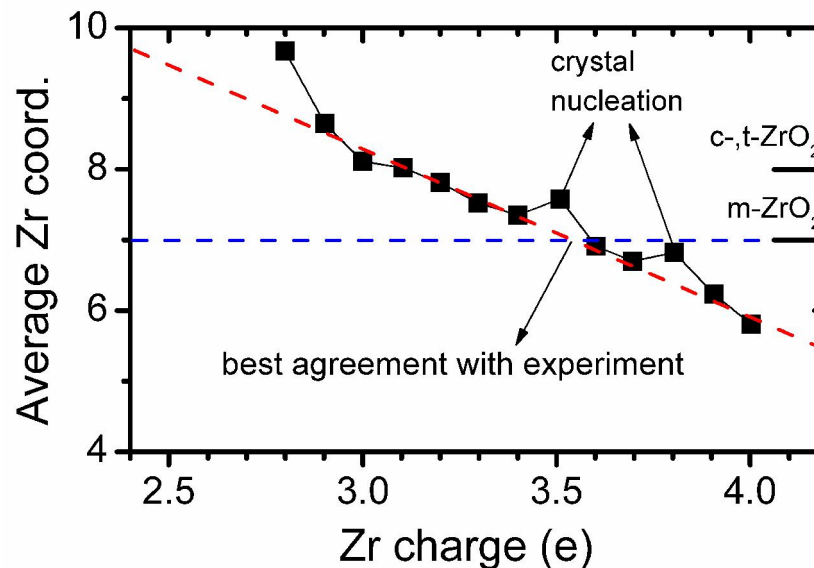
Solution: fitting own **partial-charge** (q_{Zr} between 0 and +4e)
interaction potential optimized for growth simulations

Buckingham interaction potential for ZrO_2

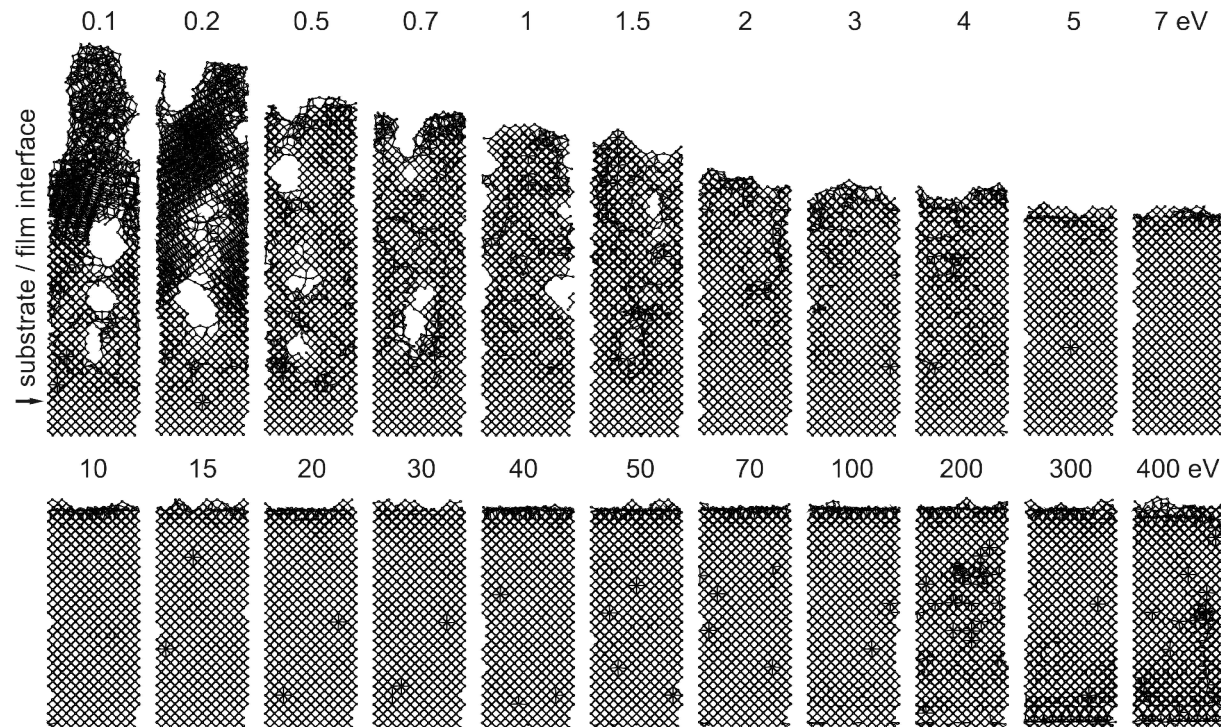
$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r$$

Solution: fitting own **partial-charge** (q_{Zr} between 0 and +4e)
interaction potential optimized for growth simulations

- 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)

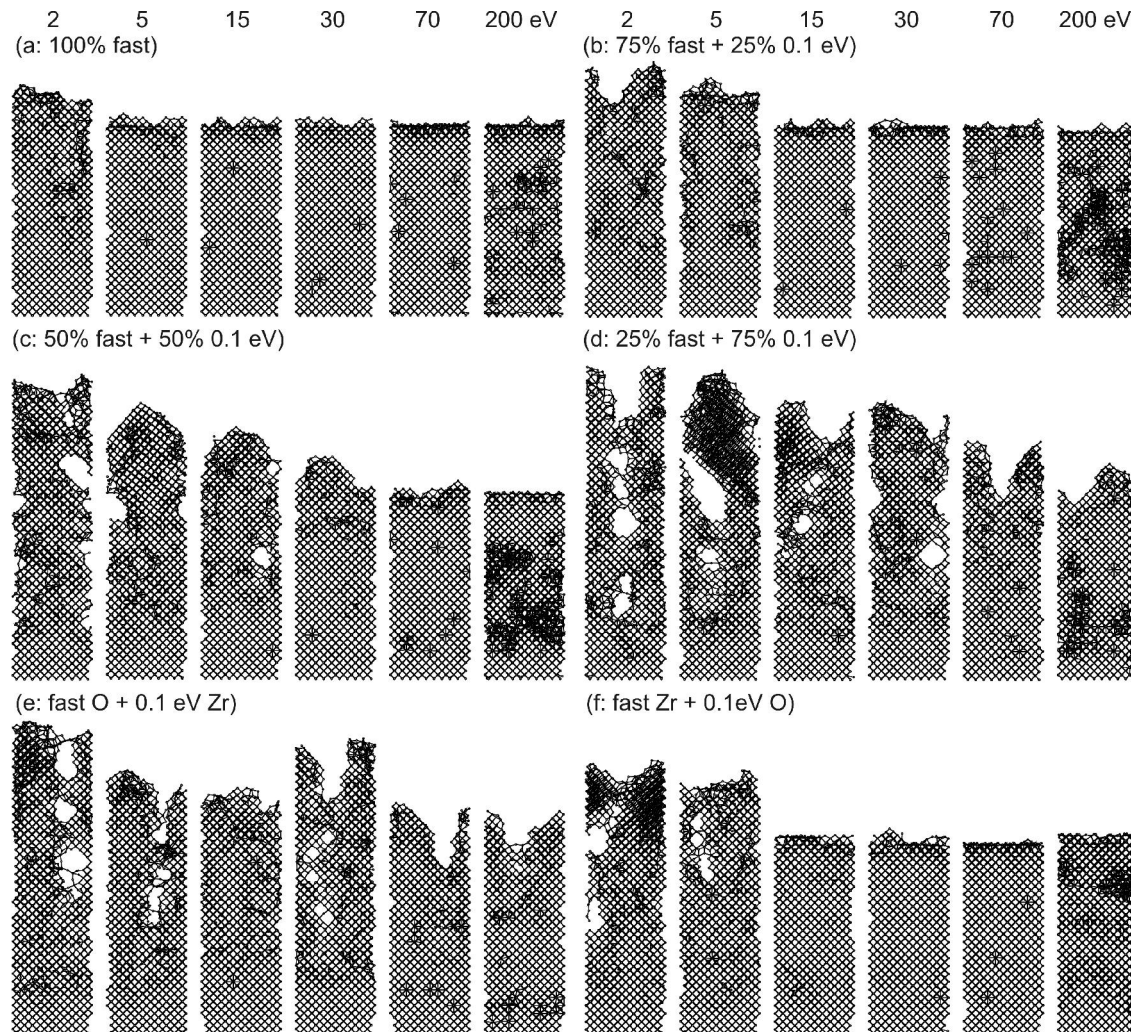


c-ZrO₂ growth - effect of energy, E



- 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

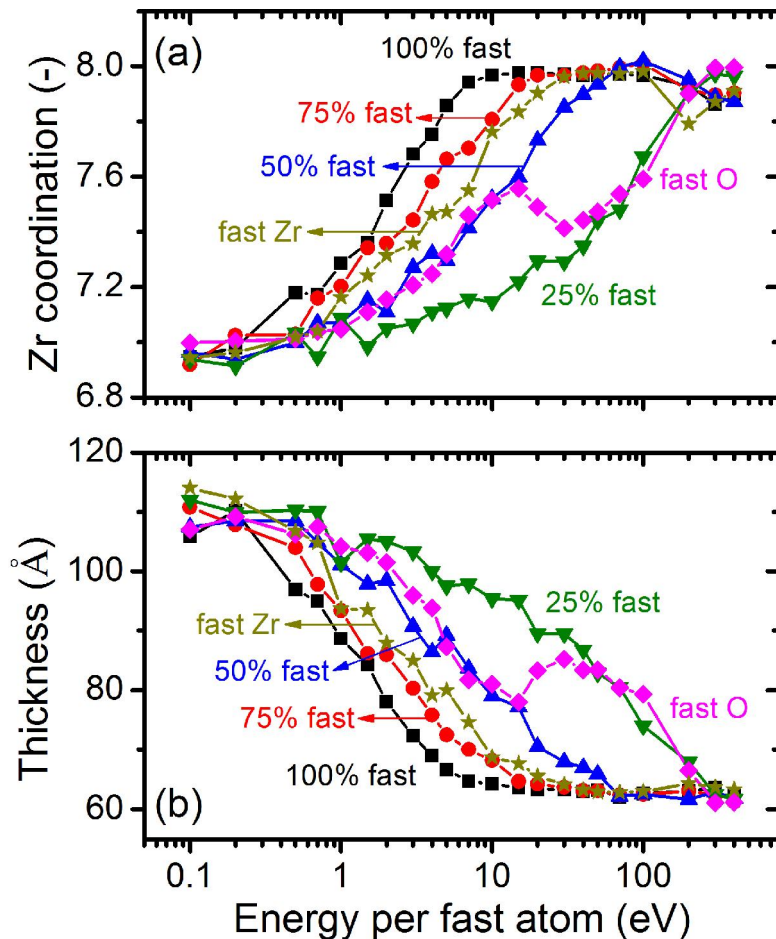
- Fast heavy Zr (33% of all atoms): densification

×

- Fast light O (66% of all atoms): poor densification

c-ZrO₂ growth - effect of energy distribution function

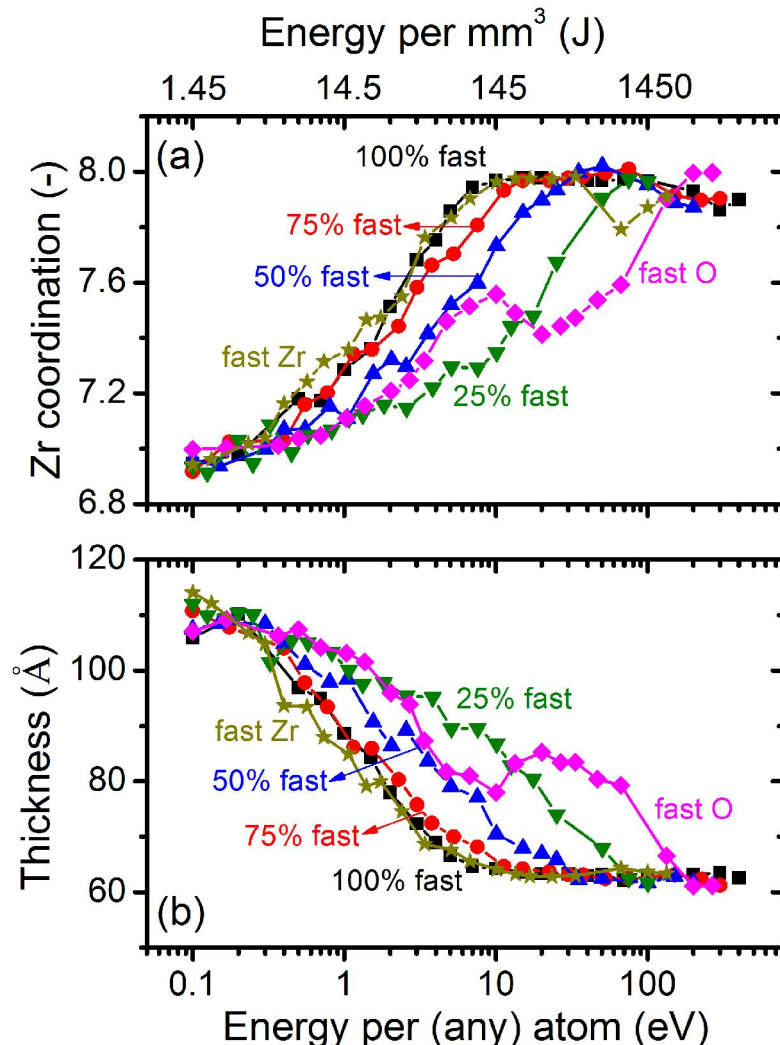
(quantification of the above results)



- 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)



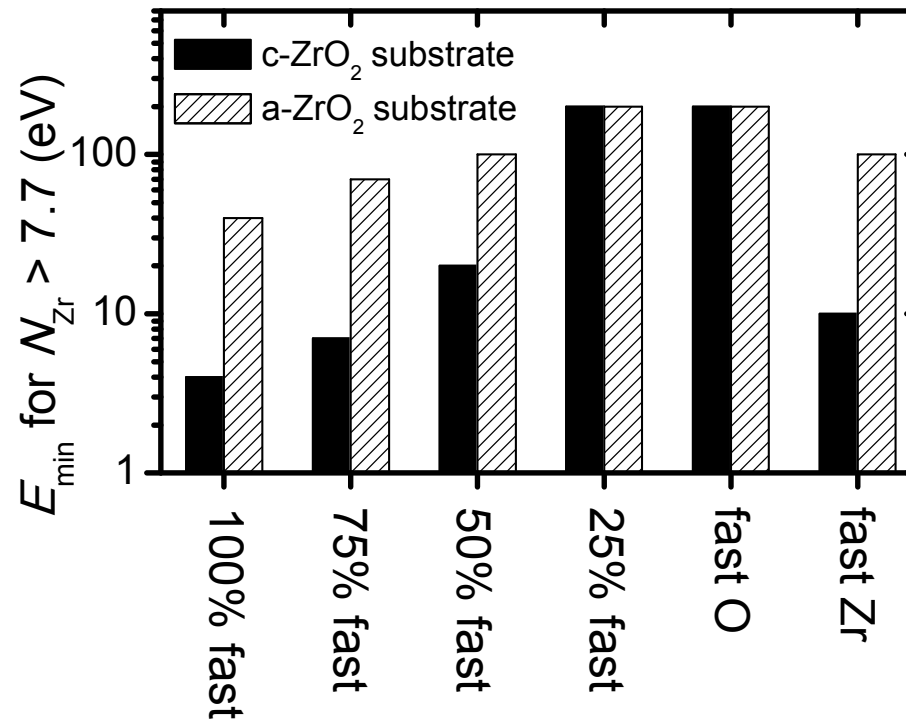
■ Dependencies still do not overlap



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

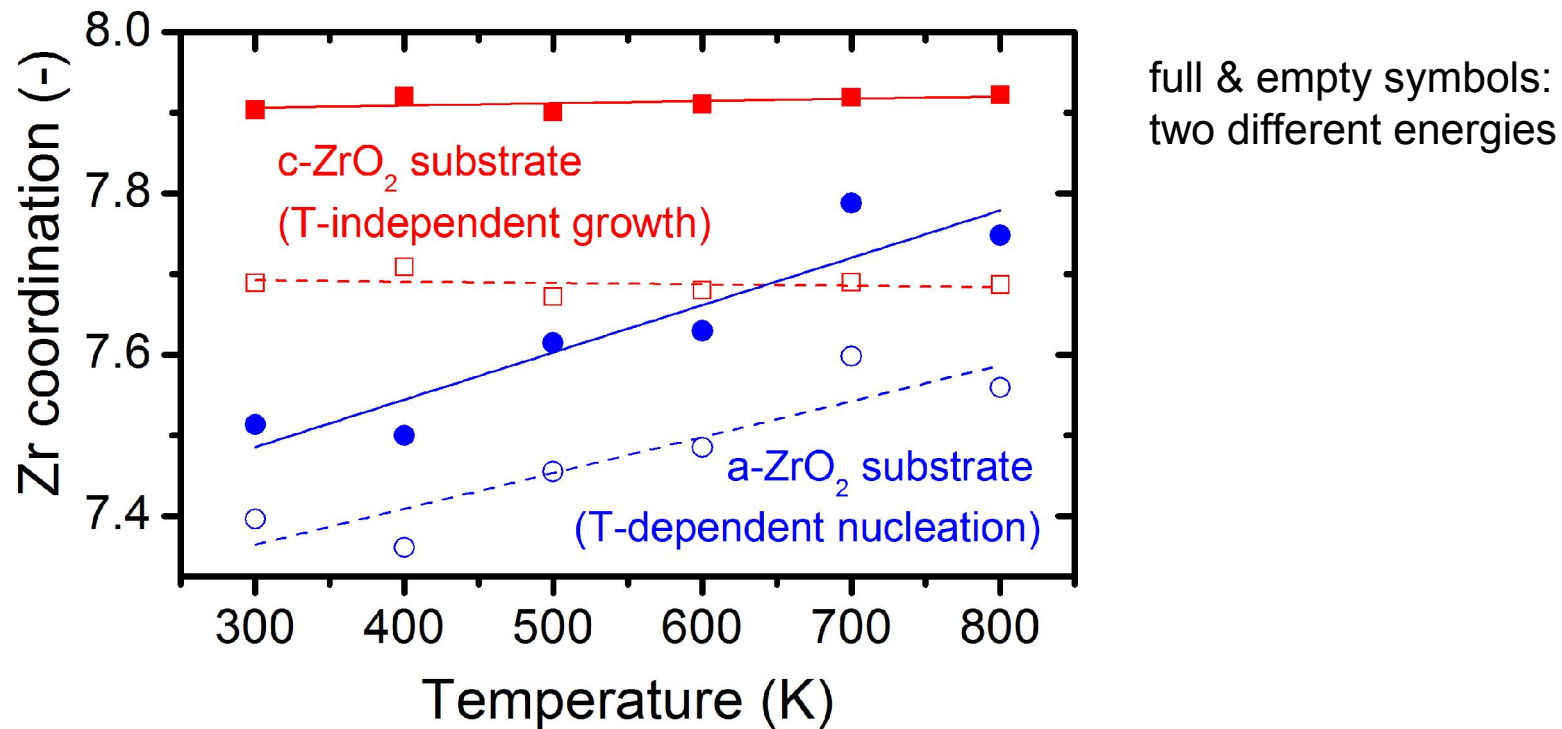
Growth on c-ZrO₂ (previous slides) × nucleation and growth on a-ZrO₂ (not shown):

minimum energy
of fast atoms
(at various EDFs)
leading to
crystallinity &
densification



- 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



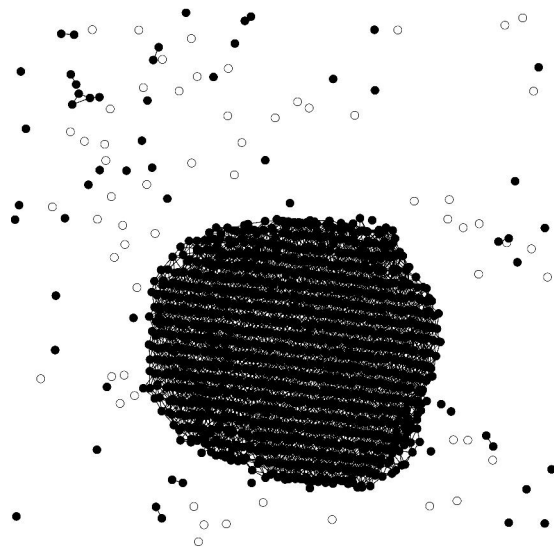
- Growth of existing crystals is almost T-independent
- Nucleation of crystals (on amorphous substrate) takes place on longer time scale, is T-dependent

Extension from films (flat substrate) to nanoparticles (spherical substrate)

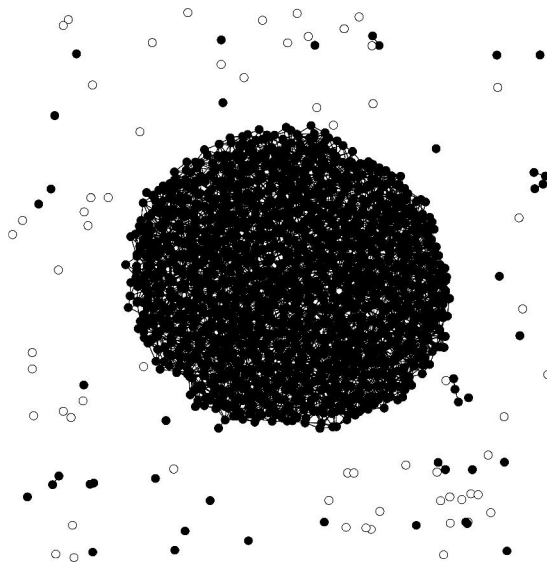
Effect of energies, temperatures, partial pressures on
crystalline faceted \times crystalline spherical \times amorphous

Experiments by Shukurov et al. (original speaker)

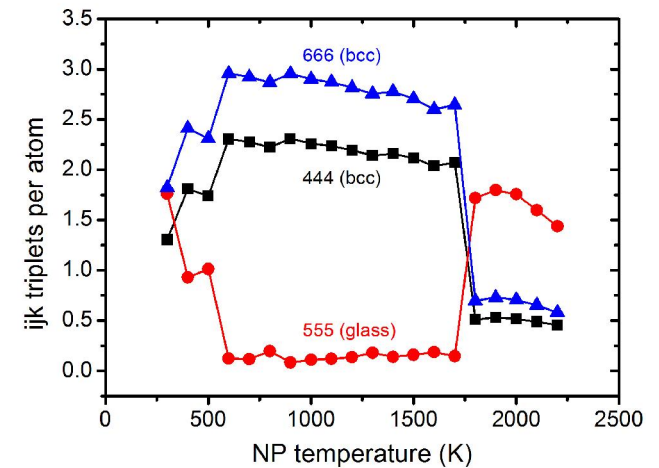
crystalline Nb



amorphous Nb



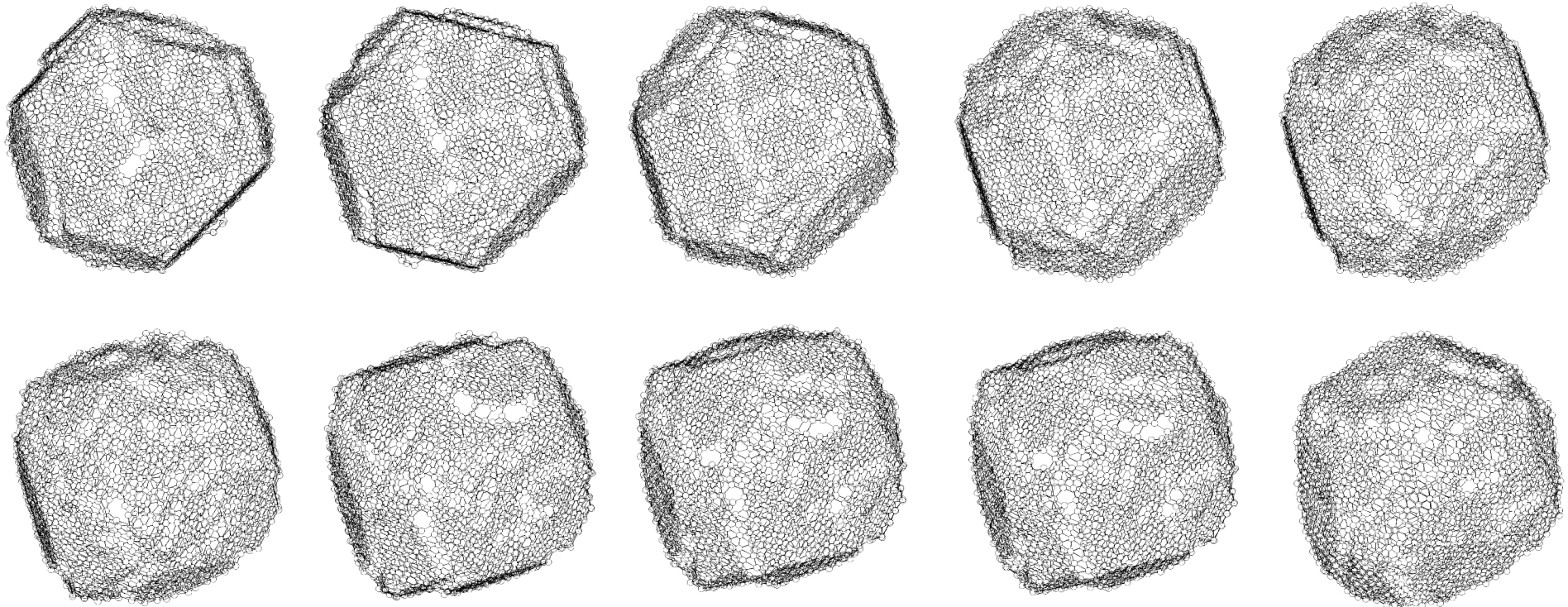
common neighbor
analysis



Extension from films (flat substrate) to nanoparticles (spherical substrate)

Wire model of nanoparticle surface, varied angle of view
(rotation in vertical plane with 10° step)

Varying cross section (hexagonal, square, spherical)
of the same nanoparticle



Conclusions

Support of experiment by simulations at various scales

- higher than atomic:
design of multilayered thermochromic coatings
- atomic ab-initio:
maximum achievable content of N in amorphous nitrides
- atomic classical:
pathways for the growth of technologically important crystals

Know and use various levels of theory and various simulation algorithms (not to stick e.g. to the easiest and most frequent ab-initio calculations of properties of monocrystals)

Acknowledgment

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