Numerical modeling of low-T oxide film growth

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dépasser les frontières

Navier

ÉQUIPES LUMINESCENCE - MPN - NAVIER - (N)ME - SOPRANO
g-MAG
MATERIAUX POUR L'ASTRONOMIE GRAVITATIONNELLE

Rhéophysique

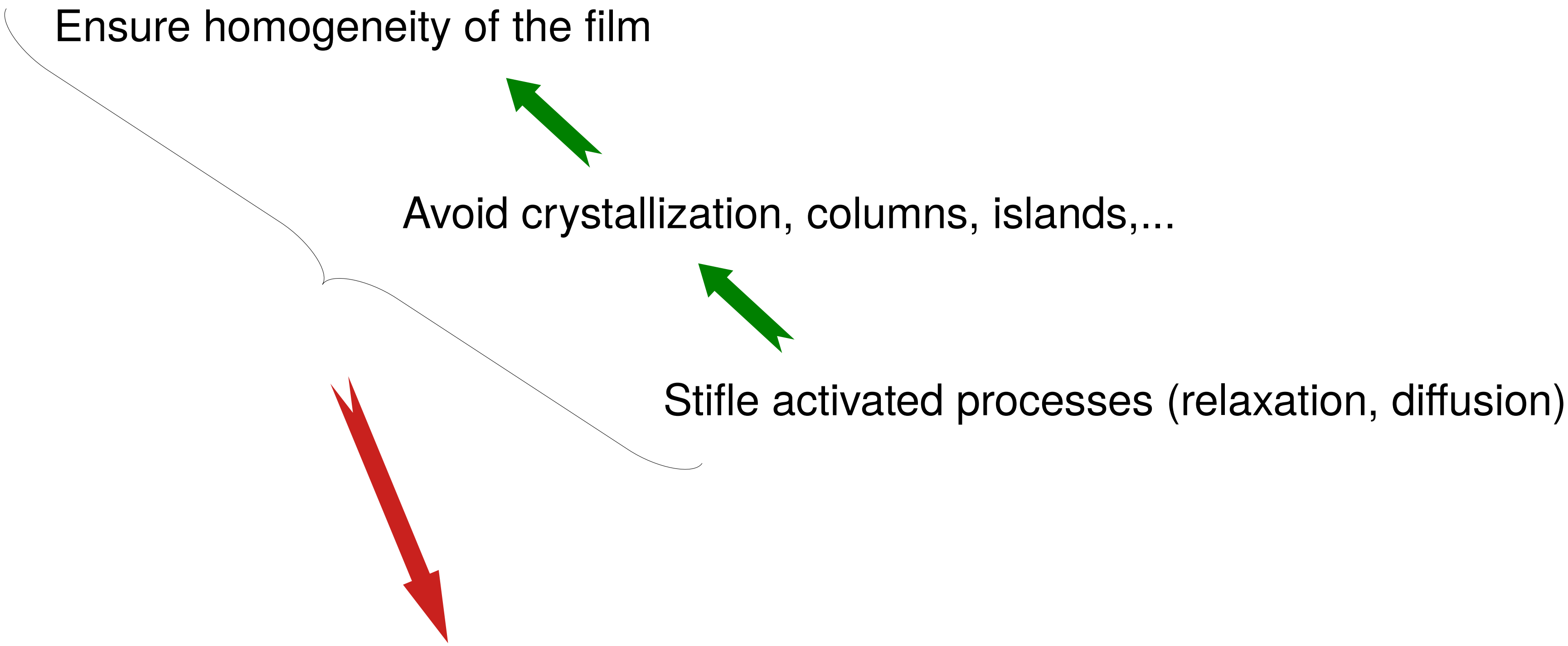
IFSTTAR

Collaboration with Essilor
PhD of S. Gelin

essilor

S. Gelin, D. Poinot, S. Chatel, P. J. Calba, and A. Lemaitre.
Microstructural origin of compressive in situ stresses in electron-gun-evaporated silica thin films. Phys. Rev. Materials, 3(5):055608, (2019).

Why low-T deposition?



Ensure homogeneity of the film

Avoid crystallization, columns, islands,...

Stifle activated processes (relaxation, diffusion)

Films have not experienced any equilibrium state

$\neq$ usual glasses obtained by thermal quench from liquids

We know little of film micro-structures

Stress in ophthalmic coatings

Ophthalmic antireflective coatings:

- SiO2, ZrO2
- electron gun vaporization

Large quenched-in stresses (a few 100 MPa)

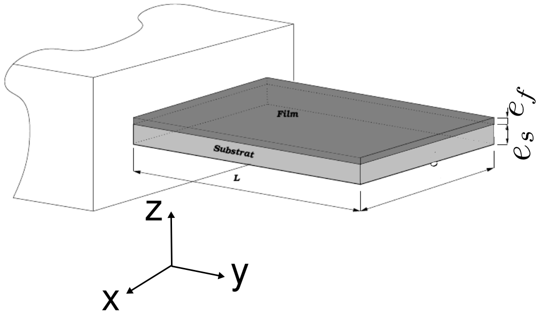
- delamination when cutting
- stability

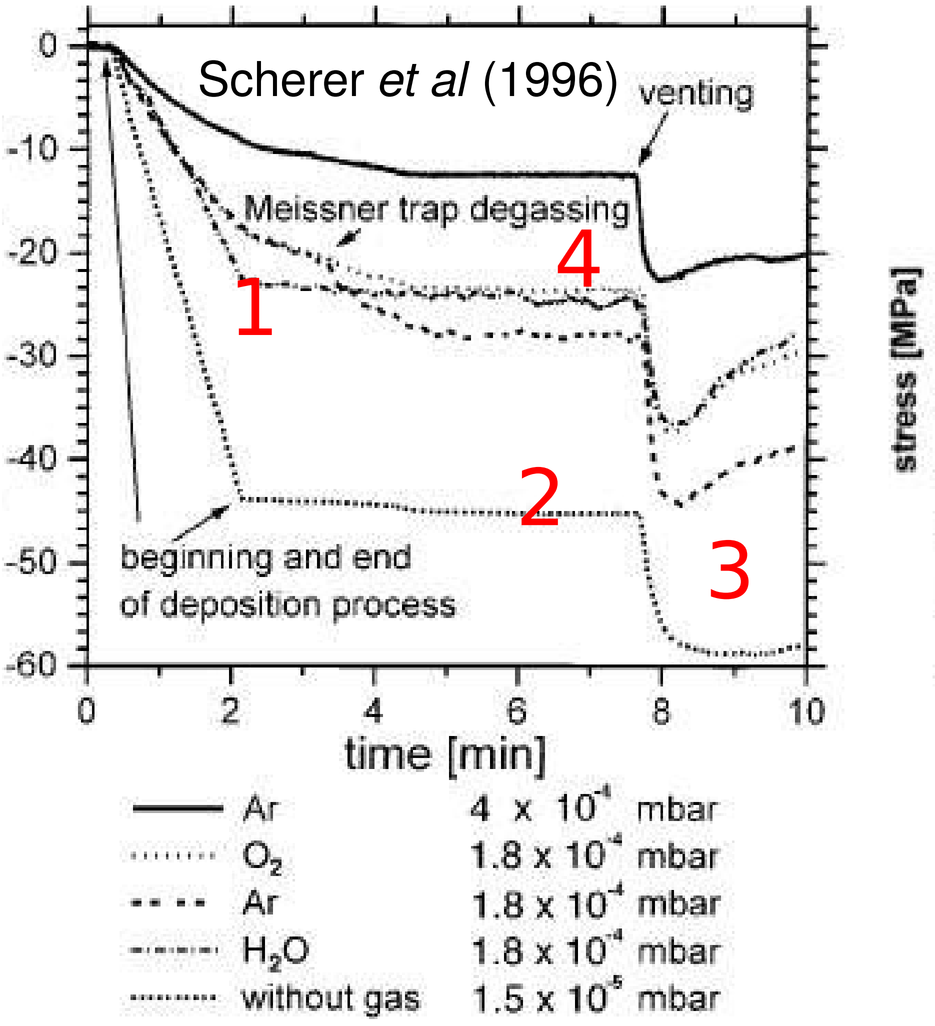
Films are strongly **anisotropic**

Stationary growth => stress **homogeneous**

Stress more compressive after venting

O2 or Ar have similar effects





Objective: numerical modeling

Low T oxide growth

Lefèvre *et al* (2001)

Evaporation

High + low energy particles

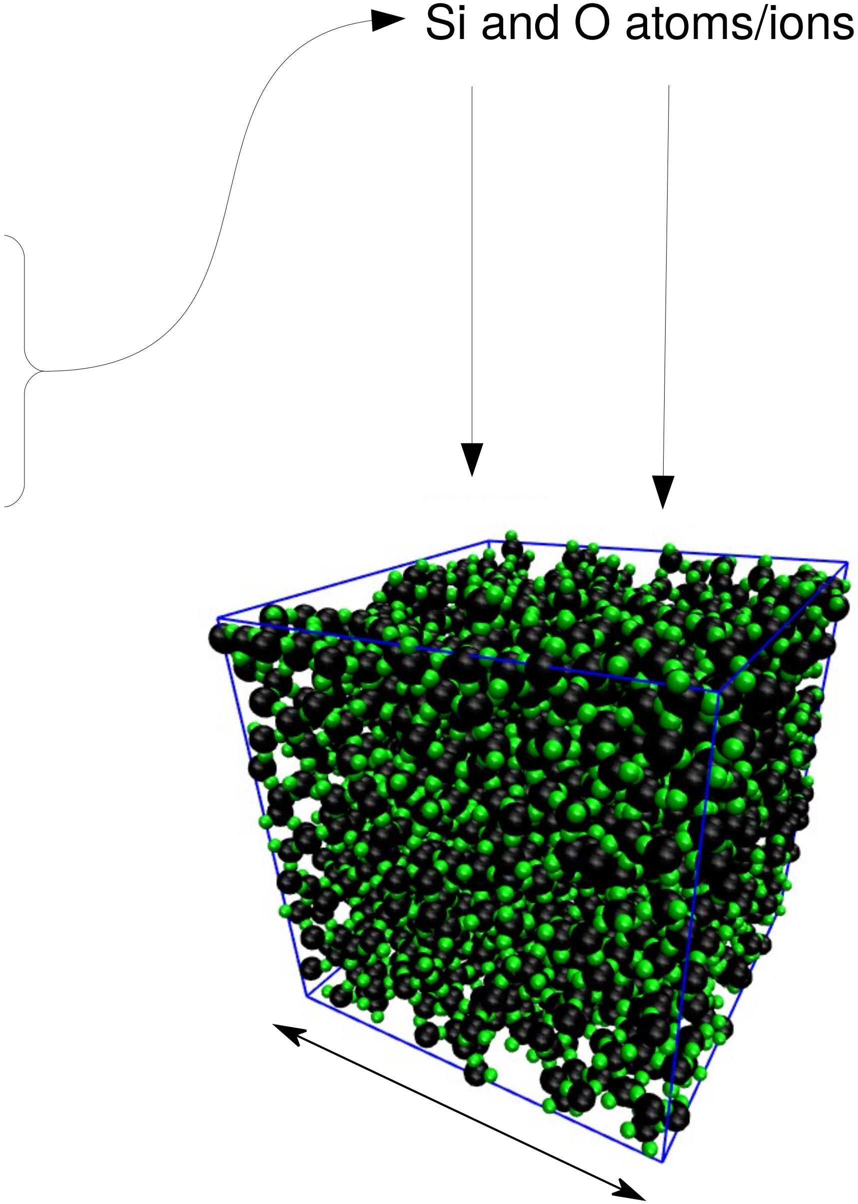
Taguchi & Hamaguchi (2007)

Grigoriev *et al* (2015, 2016, 2017, 2018)

Sputtering

Issue with oxygen rebounds

No steady growth



Simulations focus on the growing film

Do not reproduce processes occurring during vaporization and transport

Need to introduce assumptions about impacting particles

The good news

Si—O bond energy ~ a few eVs

➡ unbreakable by thermal activation at room temperature

diffusion timescales (4.9eV) >>>> age of the universe >>>> deposition duration

➡ in experimental high vacuum, nothing happens between impacts

It suffices to simulate impacts, and neglect processes occurring in-between

On a 10nm x 10nm surface
1 impact every 0.5ms
each impact ~ a few ps

Low-T deposition simulations can access experimental timescales !!!

The bad news

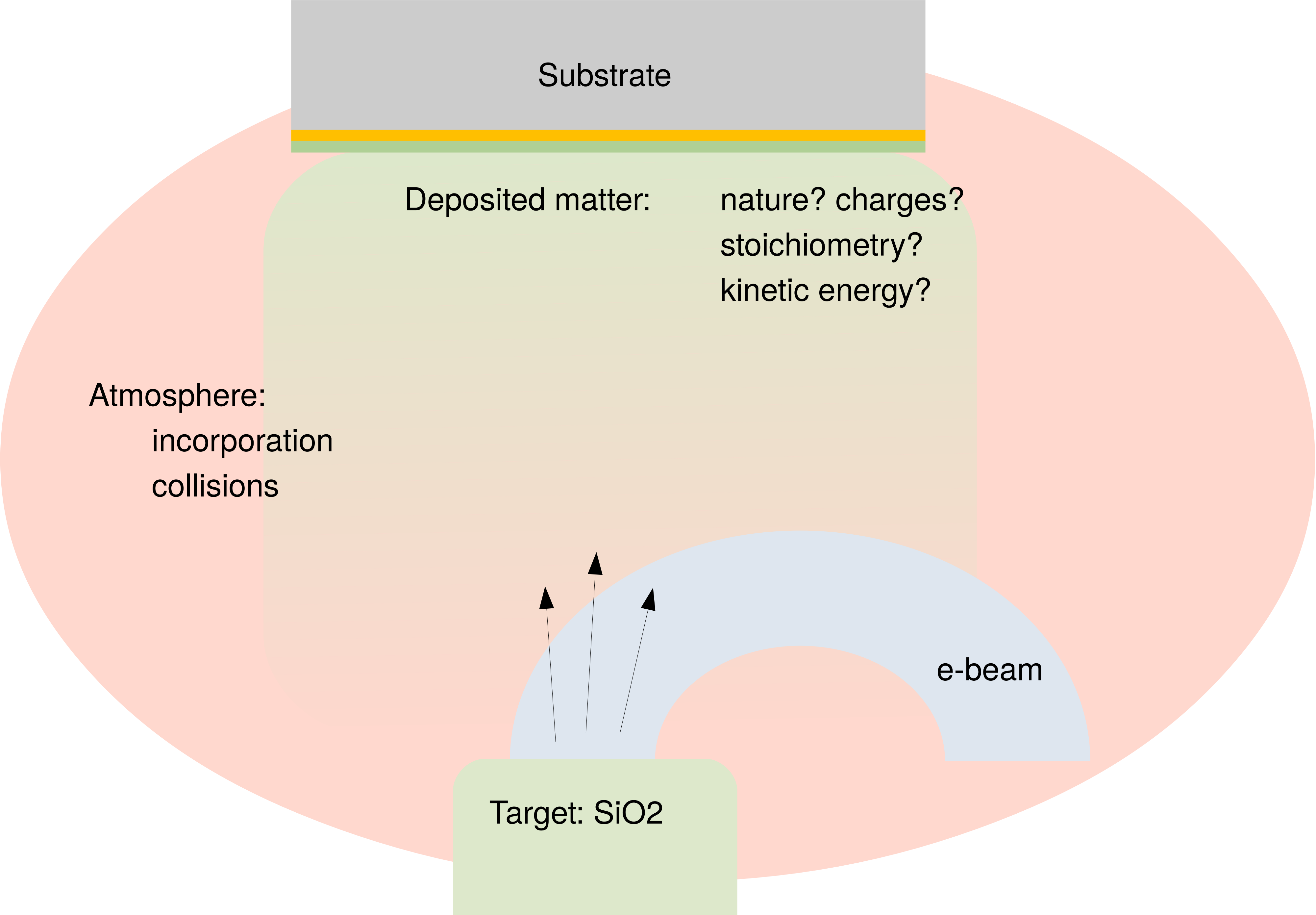
MD simulation timestep = ps to fs

→ cannot access experimental timescales

Cannot access chemical reaction timescales esp. involving water
(Attempts exist to mitigate the problem using Monte Carlo methods, but...)

So, simulations can model only deposition in a high vacuum / no water

The deposition process: e-beam



Substrate

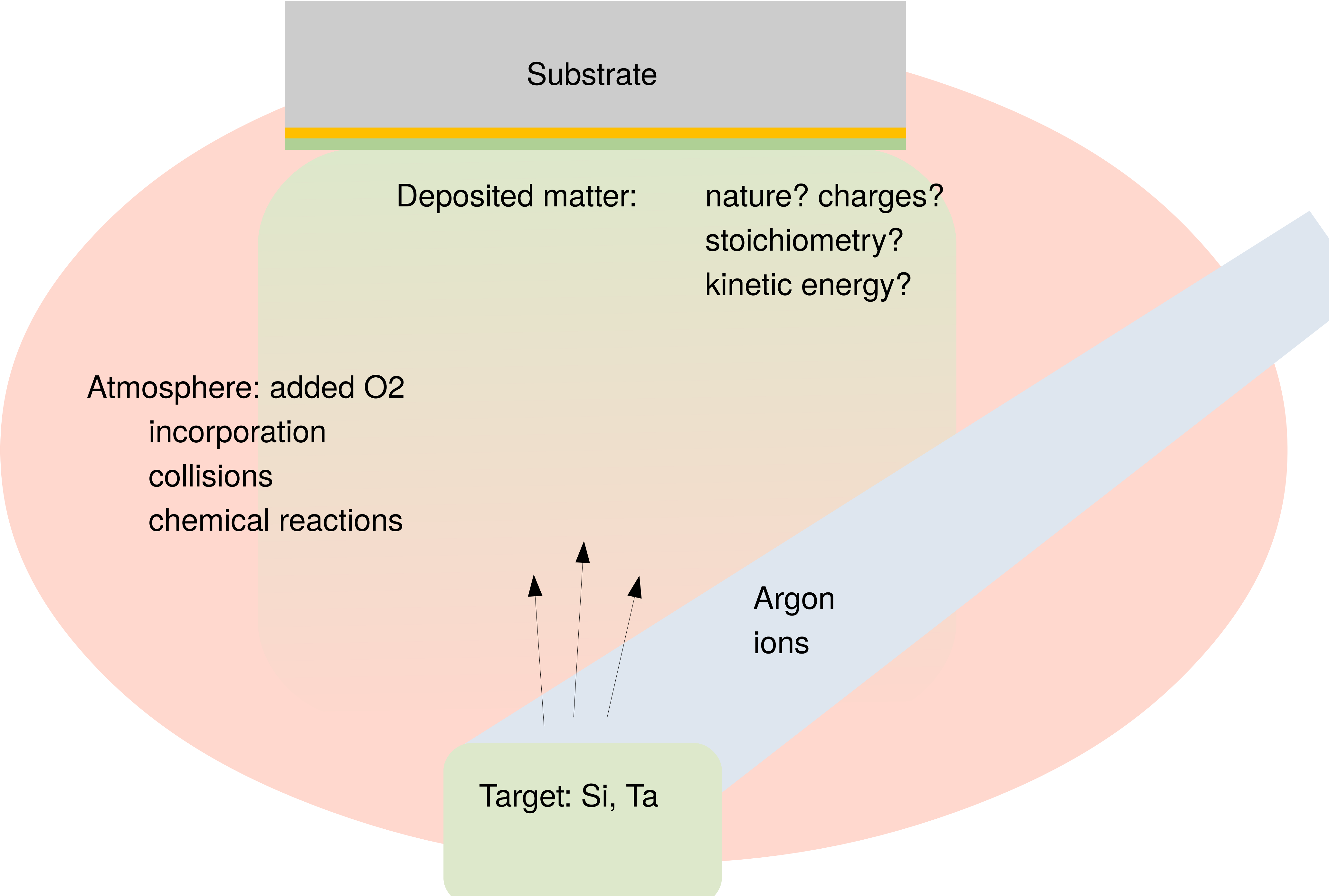
Deposited matter: nature? charges?
stoichiometry?
kinetic energy?

Atmosphere:
incorporation
collisions

e-beam

Target: SiO2

The deposition process: ion beam sputtering



Substrate

Deposited matter:

nature? charges?
stoichiometry?
kinetic energy?

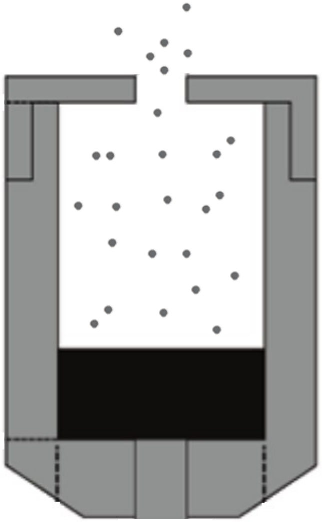
Atmosphere: added O2
- incorporation
- collisions
- chemical reactions

Argon
ions

Target: Si, Ta

The evaporation myth

Knudsen cell



$$\mathrm{SiO_2(s)} \rightleftharpoons \mathrm{SiO(g)} + 1/2\mathrm{O_2(g)}$$

$$p_J^{e_c}(e_c) = \frac{1}{(k_B T)^2}\, e_c \exp\left(-\frac{e_c}{k_B T}\right)$$

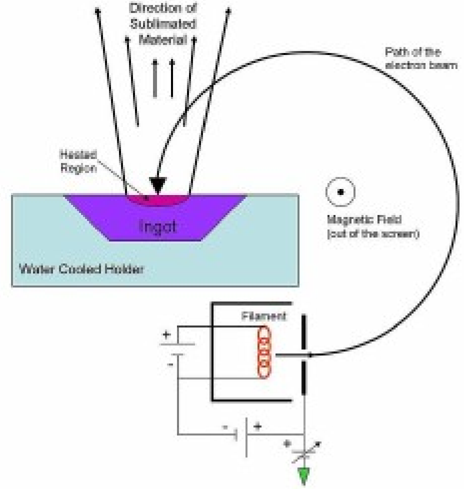
$\langle e_c \rangle = 2k_B T$, that is 0.26 eV at 1500 K

No SiO2 deposition

Joule heated crucible

$$\langle e_c \rangle = 2k_B T\ ?$$

Electron gun



All sort of issues:

- silica is an electric insulator charge concentration
- secondary, Auger electrons

Proposed assumptions and tests

There is experimental evidence that heating ≠ e-beam vaporization

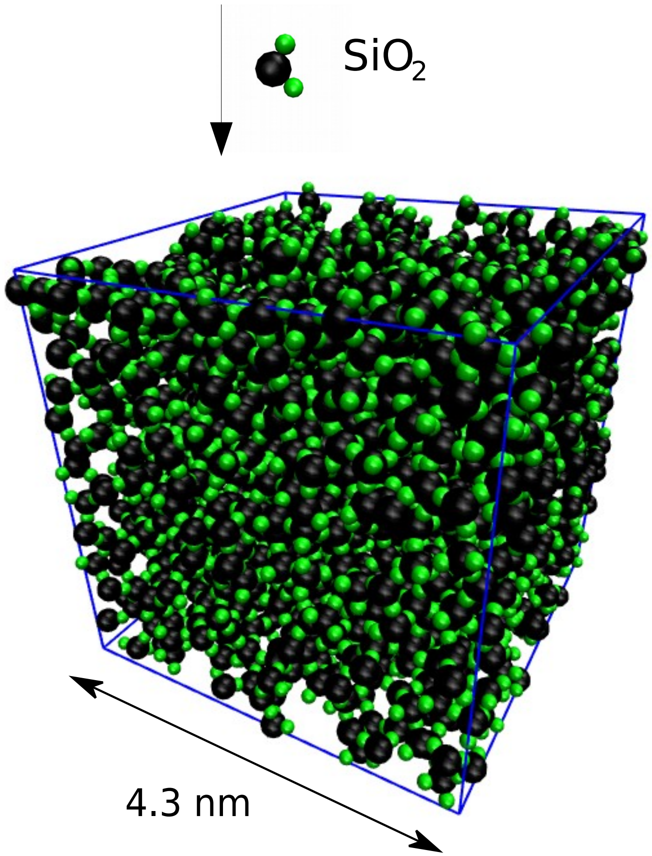
So, <u>we do not know what reaches the growing film</u>

There are experimental & numerical hints that atomic or molecular oxygen **rebounds**

↳ particles (SiO2, SiO, SiO3,...) are vaporized, not single atoms

velocities are unknown

Possible kinetic effect could be experimentally tested by introducing collisionnal slowing down using non-reactive gases



Numerical simulations

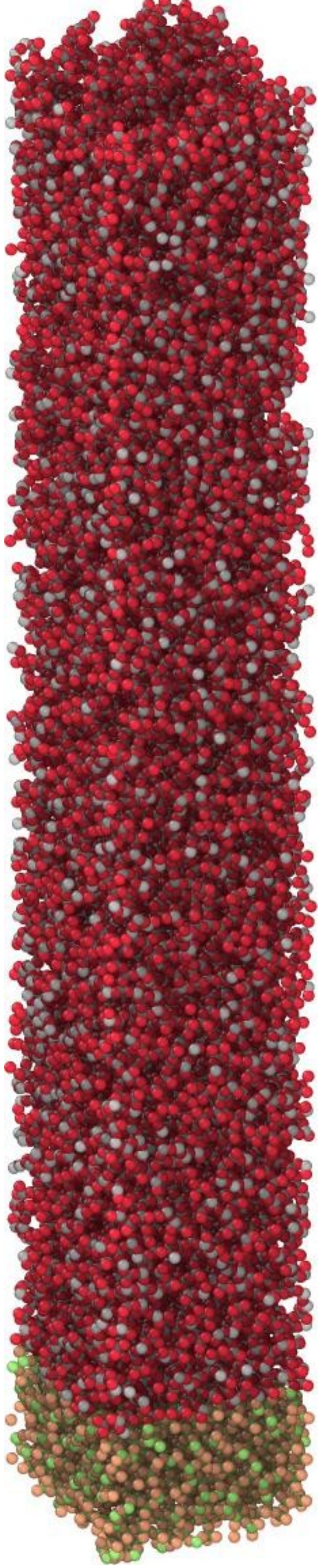
45Å x 45Å substrate

<u>Main results</u>

Systematically reaches steady growth

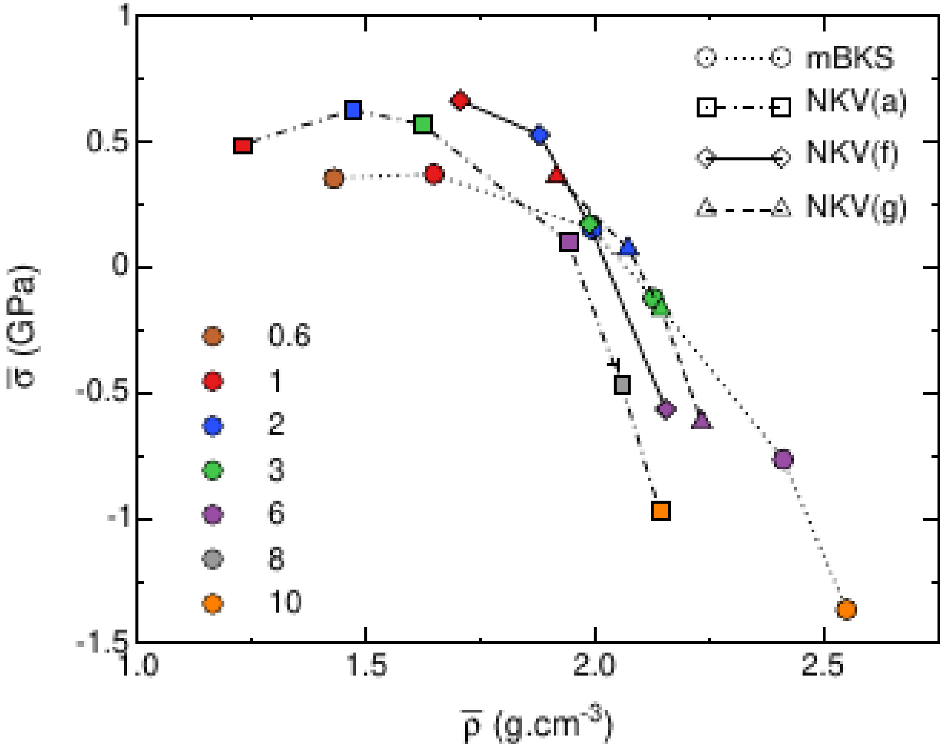
Tests:

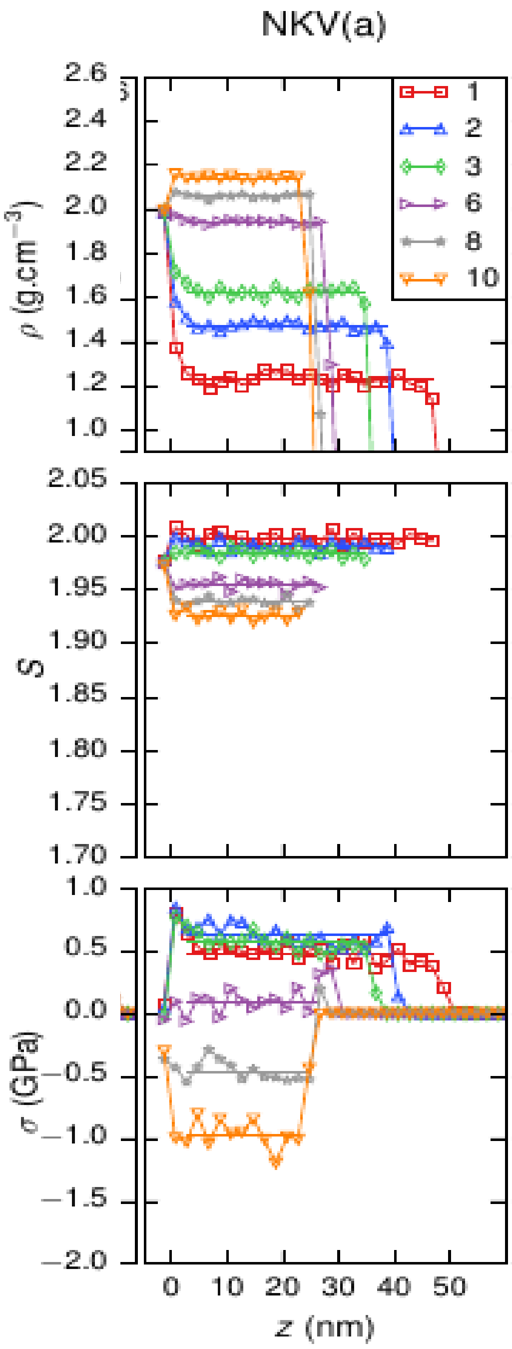
- no size effect
- no substrate effect
- no internal kinetic energy effect
- insensitive to velocity scatter

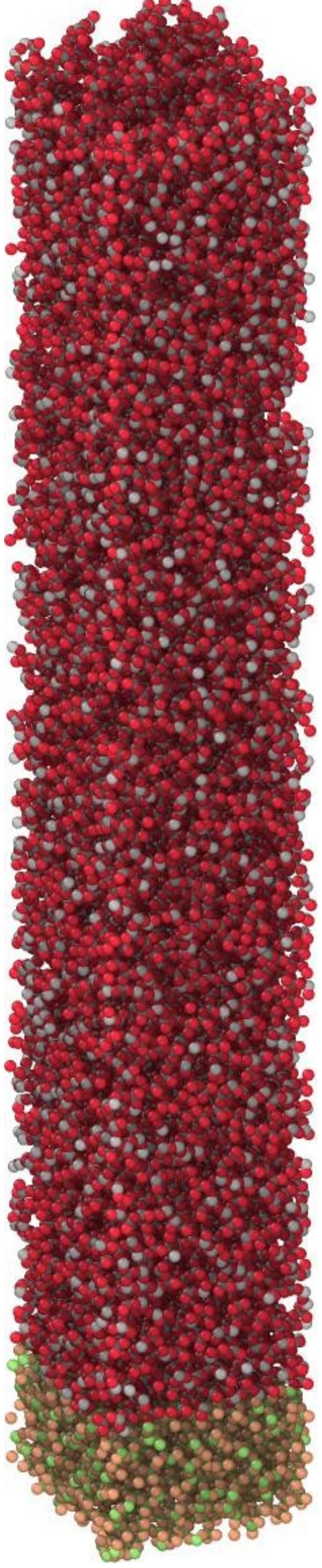


Numerical simulations

45Å x 45Å substrate





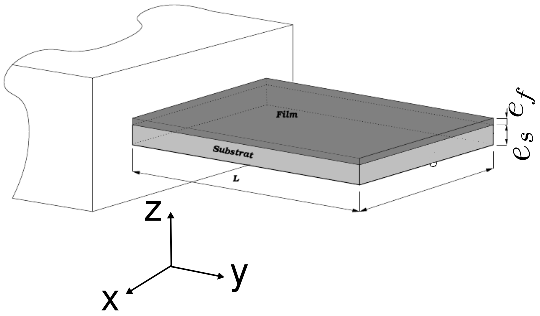


Back to experiments

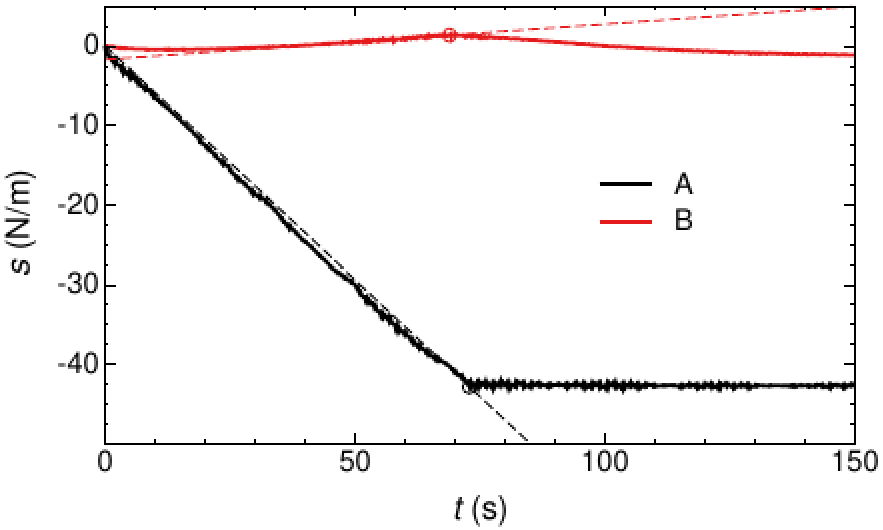
- try to experimentally approach the high vacuum limit
- try and test possible collisional slowing down effect

	Experimental parameters			Estimated values	
	P_{ini} (mbar)	P_{dep} (mbar)	N	n_c	$r_{\mathrm{H_2O}}$
A	3×10^{-7}	7×10^{-6}	5	0.09	1.9×10^{-2}
B	3×10^{-7}	2×10^{-4}	3	2.7	1.9×10^{-2}

	$\overline{\rho}$ ($\mathrm{g\cdot cm^{-3}}$)	x_{O}	x_{H}	$\overline{\sigma}$ (MPa)
A	2.00 ± 0.05	2.07 ± 0.10	0.3	-389 ± 32
B	1.7 ± 0.1	2.05 ± 0.10	0.3	31 ± 6



$$s(e) = \int_0^e \sigma_{yy}(z)\mathrm{d}z$$

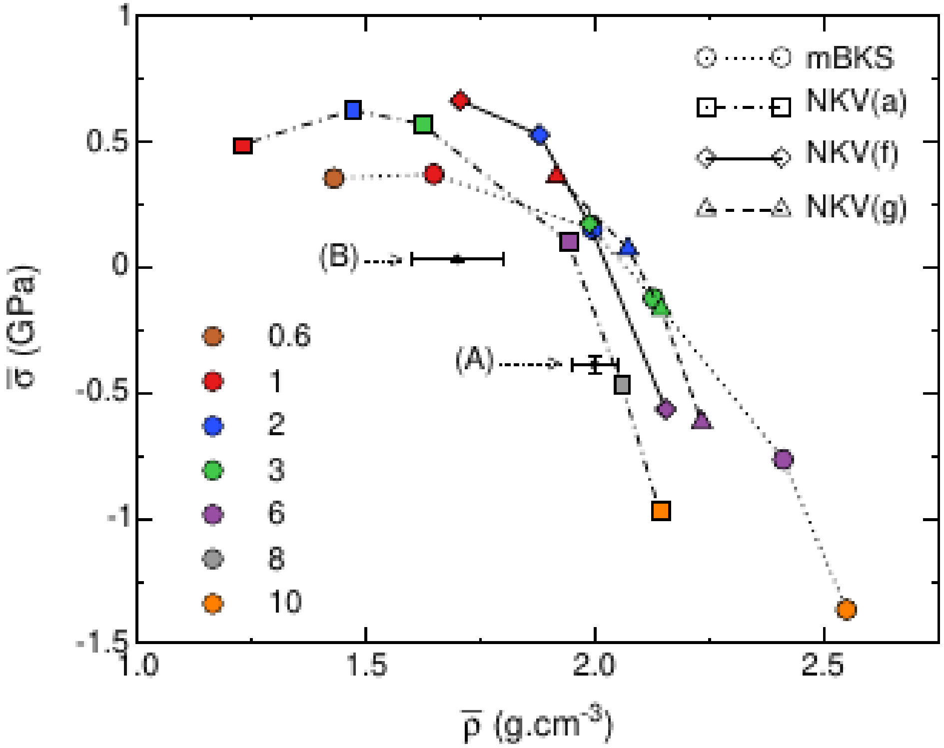


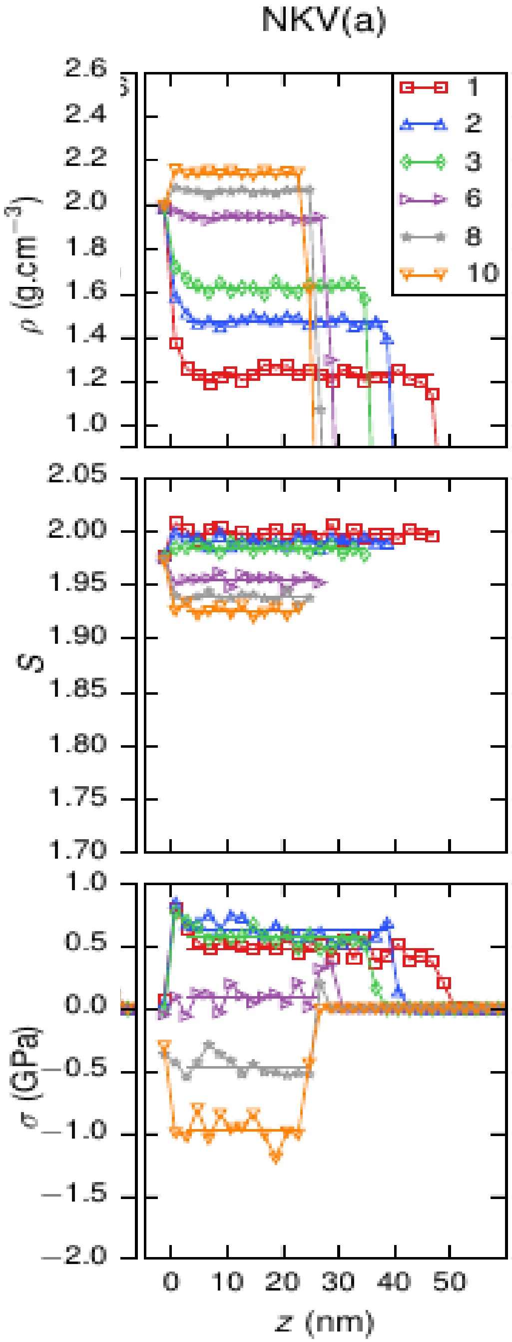
Stress compressive near ideal vacuum

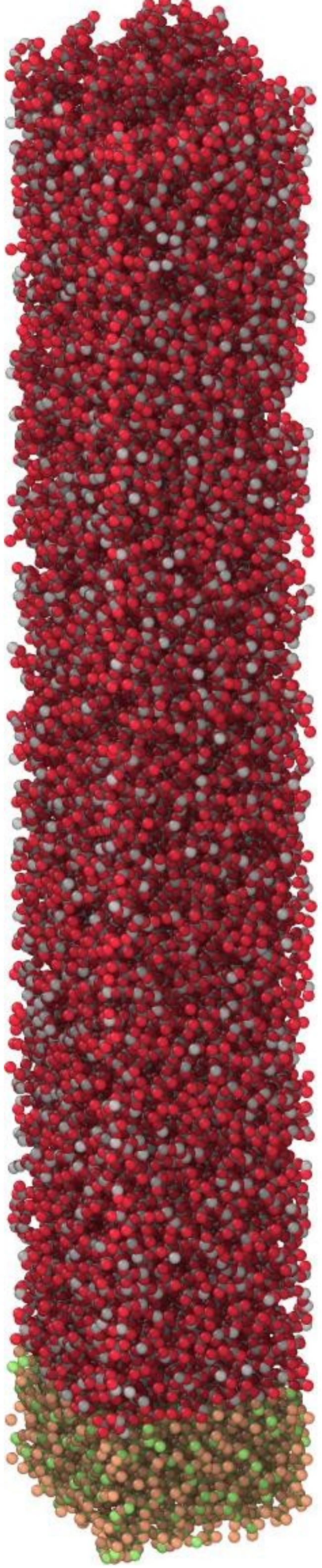
Strongly sensitive to slowing down effects

Numerical simulations

45Å x 45Å substrate





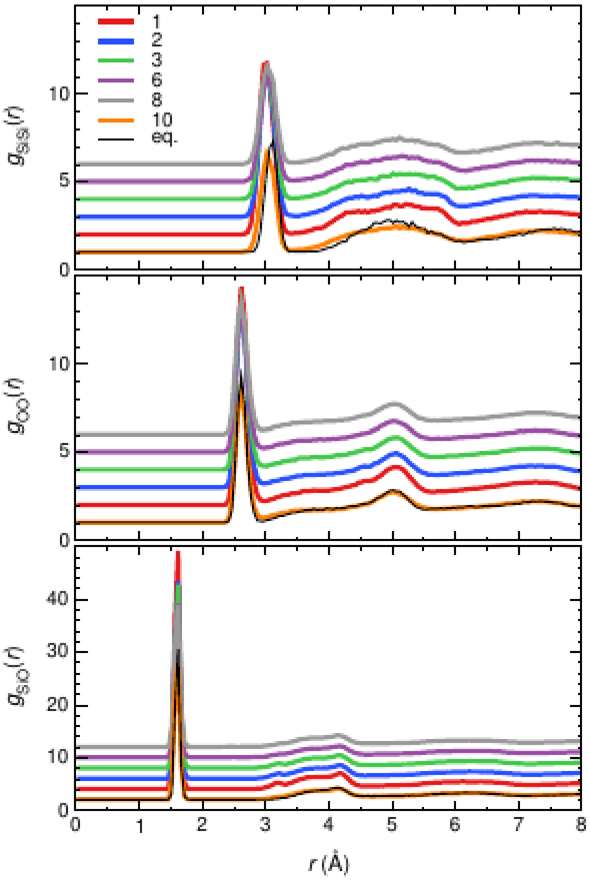


Density and stress do compare in high vacuum expmtl data yet, for e_k ~ 3eV

Predicted slowing down effect found in expmts.

Microstructural analysis

Pair autocorrelation function: not very informative



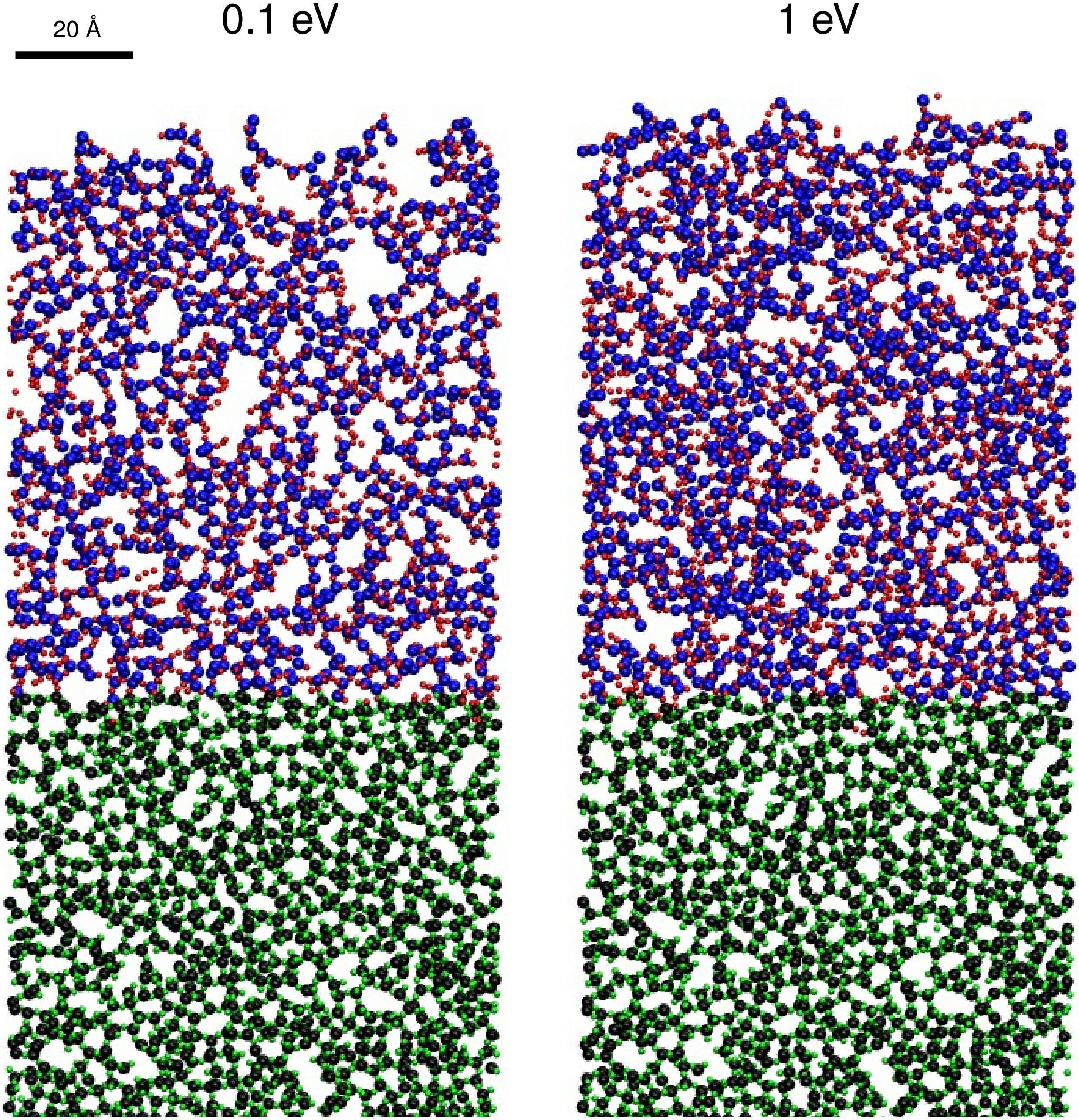
Neighbor counting

e_k	x_O	$\phi_{\text{Si-4}}(\%)$	$\phi_{\text{Si-3}}(\%)$	$\phi_{\text{O-2}}(\%)$	$\phi_{\text{O-1}}(\%)$
1	1.998	84.5	15.5	92.3	7.6
2	1.991	85.9	14.1	93.6	6.3
3	1.984	86.6	13.4	94.5	5.3
6	1.955	86.0	14.0	97.0	2.8
8	1.939	84.8	15.2	97.9	1.8
10	1.926	83.5	16.5	98.3	1.3
eq.	2.000	96.5	3.5	98.25	1.75

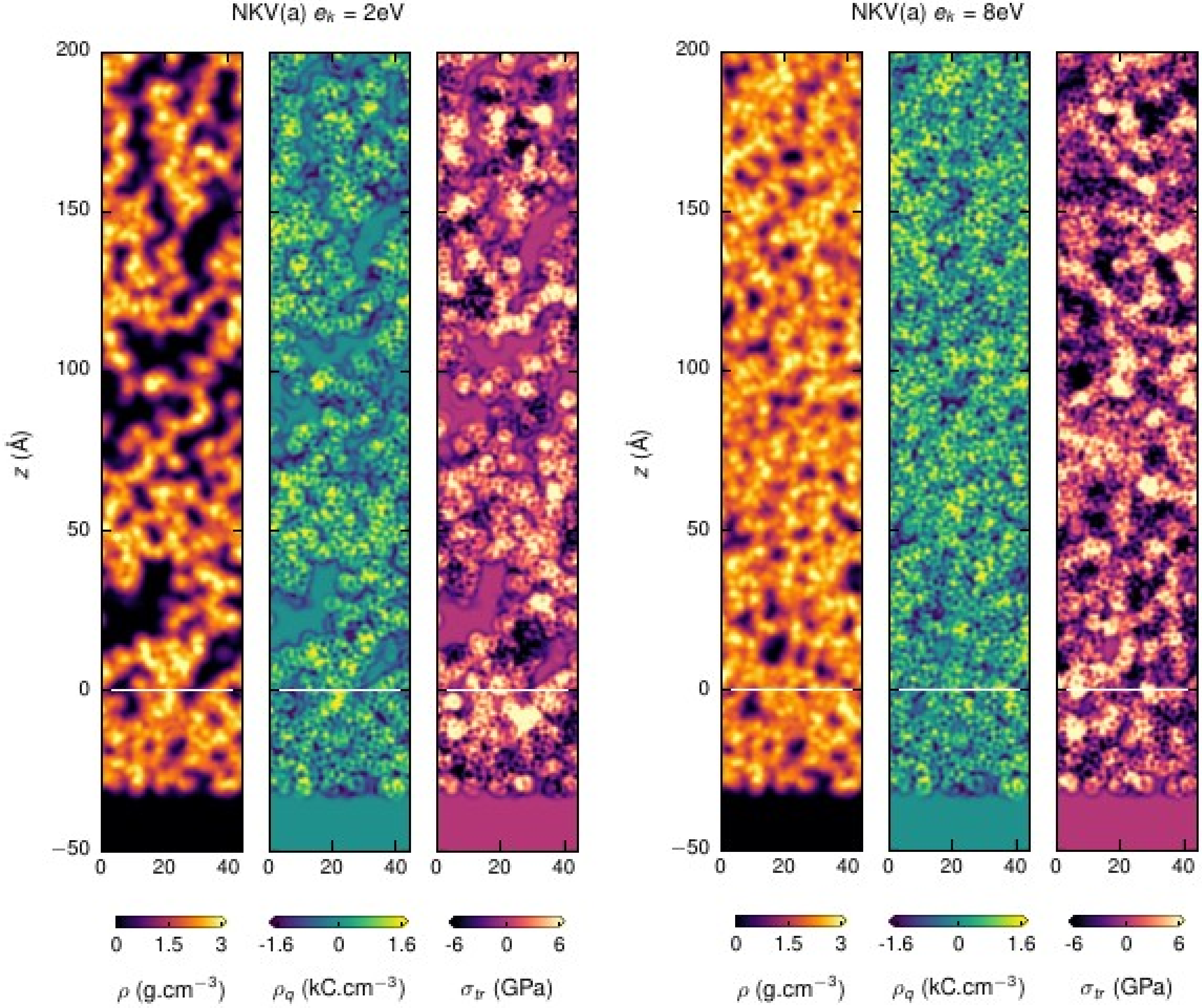
→ Significant fraction of defects

$$\phi_{\mathrm{Si}-3} \simeq 4 - 2x_{\mathrm{O}} + \phi_{\mathrm{O}-1}\, x_{\mathrm{O}}$$

Microstructural analysis



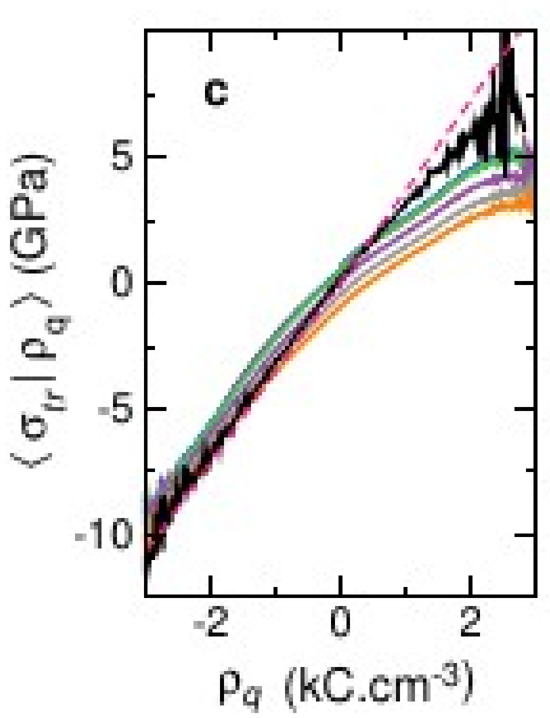
Coarse-grained fields



Formation of pores at low e_k

associated with lower density / more tensile stress

Origin of compressive stresses



Positively charged regions are found around Si atoms

They tend to be tensile <== cohesion of SiO bonds

In films:

- these regions are less tensile
- no significant difference in
  compressive (oxygen-rich) regions

➡ Si-O bond network comprises a significant number of defects
==> less coordinated / less able to develop tensile forces
==> loss of cohesion causes macroscopic stress to become compressive

➡ Suggests: post-deposition stress relaxation associated with oxidation

Conclusions and directions

- Oxygen-deficiency explains late stress relaxation / oxidation processes
- Kinetic energies of a few eV’s consistent with low stress in ZrO2

Working on: deposition of Ta2O5 films

→ Essential to characterize the deposited particles experimentally
(due to the complexity of the vaporization and transport processes)

→ Also need systematic assessment of residual gases

→ High-vacuum limit:
  - theoretically simpler
  - only way to connect with simulations
(which then provides pointers to understand other cases)

→ Important observables (not just loss)
  - in-situ and ex-situ stress
  - in-situ stoichiometry!…
  - defects?…