

Use of Molecular Dynamics for Collapse Free Cleaning Through Surface Modification Treatment

Innovation for a Sustainable World

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Topics

◆ Introduction to Molecular dynamics and SMT

◆ Simulation model validations:

- Contact angle
- Young modulus

◆ Simulations of fins dynamics: wet vs. dry

- Collapse
- Restoration

◆ Conclusions

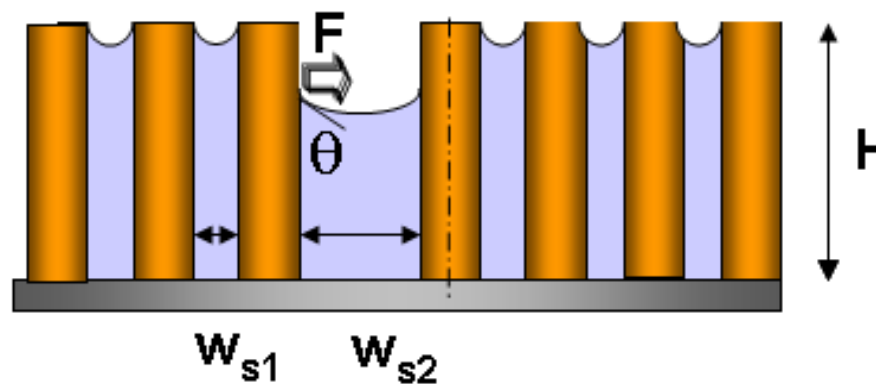
Introduction

◆ Pattern collapse



◆ Reduction of capillary forces:

- High temp and high flow IPA (Hot IPA)
 - Low γ : IPA
- Surface treatment
 - $\cos \theta$ will be close to “ZERO”



$$F_c = 2\gamma \cos \theta \frac{H}{w_s}$$

F_c : capillary force per unit length

γ : surface tension

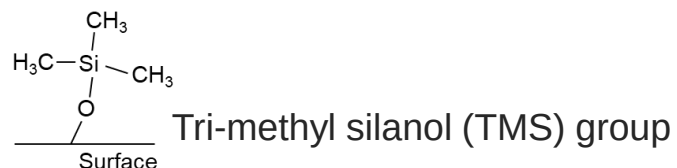
θ : contact angle

H : liquid height

w : space width

◆ Pattern collapse suppression technology

- Surface modification treatment (SMT) with TMS terminated surface [1] → Contact angle $\sim 90^\circ$

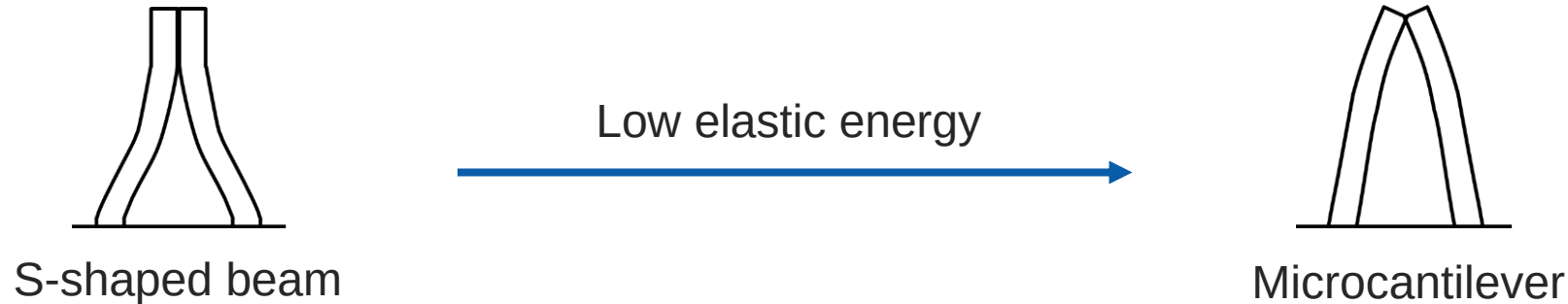


[1] H. Jeong *et al.*, “Combined molecular dynamics simulations and reaction kinetics study on wettability of trimethylsilyl functionalized silicon surfaces”, *Surf. Interfaces*, **35**, 102463 (2022)

Introduction

◆ Issue

- Pattern collapse may occur even with SMT with 2 different configuration:



➔ Collapse results from balance between Adhesion Vs. Elastic Energies [2]

Key point: The dynamics of the structure in nano-scale

◆ Objective of this molecular dynamics (MD) simulation study

- To investigate the dynamics of the SMT-fins in wet and dry conditions
- To discuss the adhesion and the elastic energies balance to determine pattern collapse

[2] T. Koide *et al.*, “Nano-Structures Stiction Suppression by Molecular Structure Optimized Surface Energy Reduction Agent “, *ECS Trans.* **69**, 8, 131-138 (2015)

Introduction

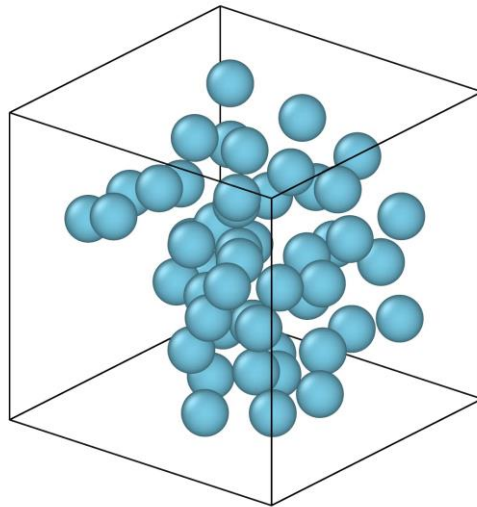
◆ Basic concepts of MD simulation

- Atomic interactions (e.g., van der Waals, electrostatic) are expressed as functions.

$$E = \sum_i \sum_j \left[4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right\} + \frac{q_i q_j e^2}{r_{ij}} \right]$$

i, j : Atom
 ϵ : Energy well depth
 σ : Atomic radius
 r : Distance
 q : Charge
 e : Elementary charge

- Atomic motions and forces are calculated using Newton's equations of motion.



Newton's equations of motion

$$m_i \frac{d^2 r_i}{dt^2} = F_i \left(= - \frac{dE}{dr_i} \right)$$

Topics

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◆ Simulation model validations:

- Contact angle
- Young modulus

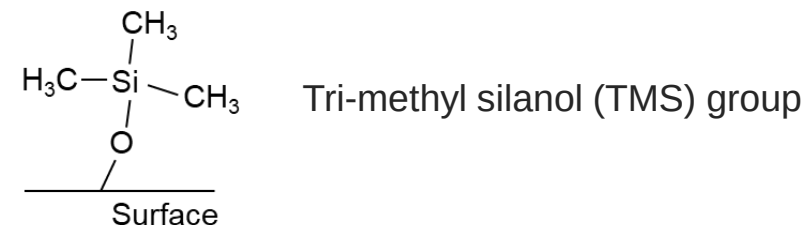
◆ Simulations of fins dynamics: wet vs. dry

- Collapse
- Restoration

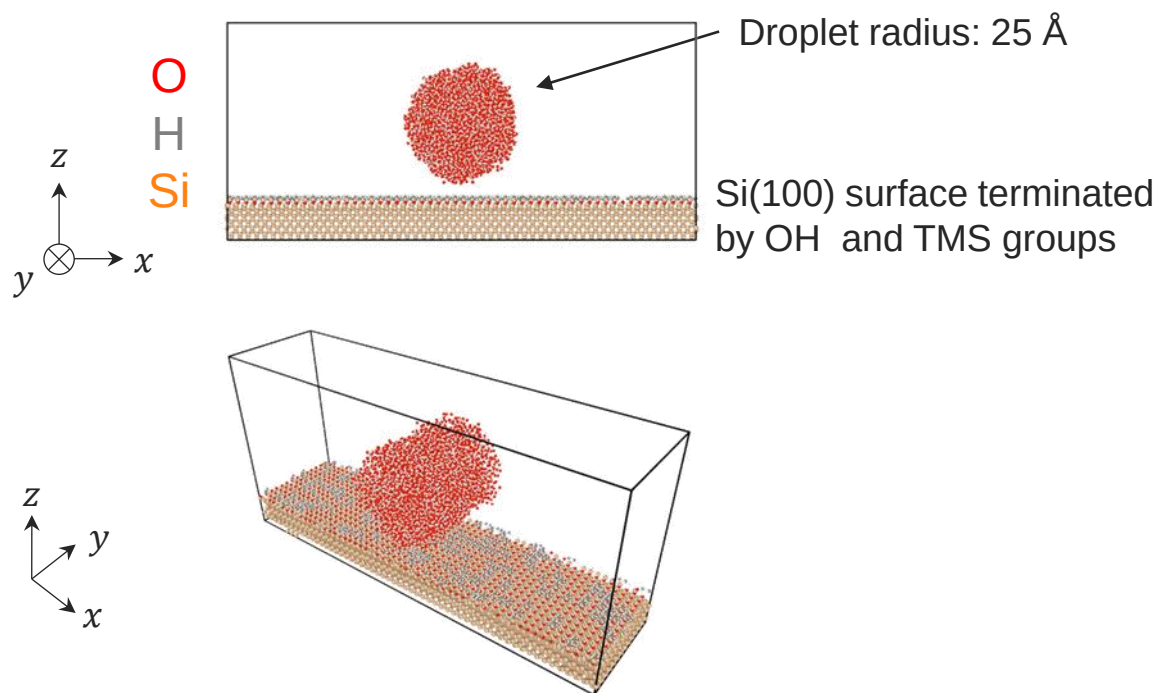
◆ Conclusions

Method: Water contact angle measurement

- ◆ Water contact angles (WCA) on Si(100) surfaces were measured.
- ◆ Si surfaces were terminated by OH groups and Tri-methyl silanol (TMS) groups.
- ◆ Modification rates of TMS were varied from 0 to 98%.



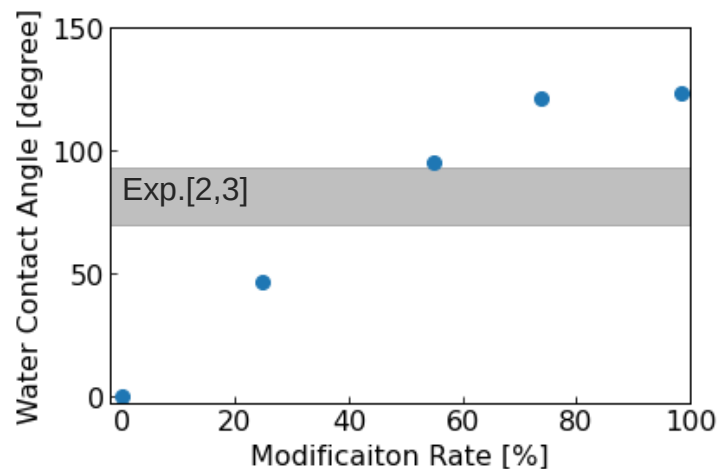
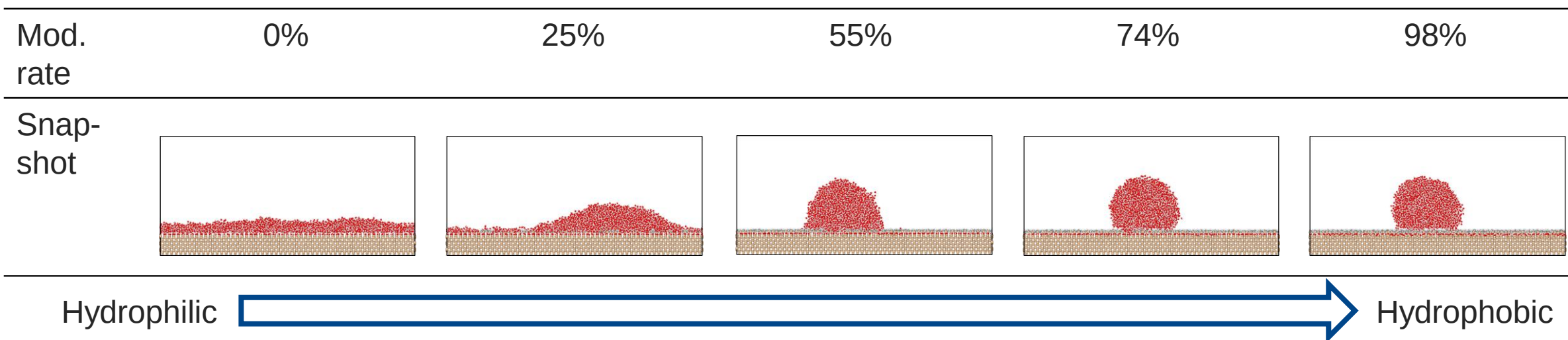
Simulation model



Simulation details

Number of molecules	3,515 water molecules
Substrate	0-98%TMS-Si(100)
System temperature	300 K
System dimensions	$L_x \times L_y \times L_z = 215.04 \times 53.76 \times 100.00 \text{ Å}$
Boundary conditions	Periodic boundary condition: x -, y -direction Specular boundary condition: z -direction
Equilibrium ensemble	NVT ensemble
Fixed atoms	Bottom Si atoms
Timestep	0.25 fs
Iterations	Equilibrium steps: 14,000,000 (3500 ps) Production steps: 2,000,000 (500 ps)

Results: Water contact angle measurement



- The modification rates of TMS groups on SiO_2 were 52.8~58.3%[1].
- The WCA of TMS modified SiO_2 were varied from 65 to 93 degrees[3,4].
- This hydrophilic to hydrophobic trend is confirmed in another MD research[5].

[1] H. Jeong *et al.*, *Surf. Interfaces*, **35**, 102463 (2022)

[3] F. R. Jones, Optimization of the Reaction of Hexamethyldisilazane on a Fumed Silica Surface (1999)

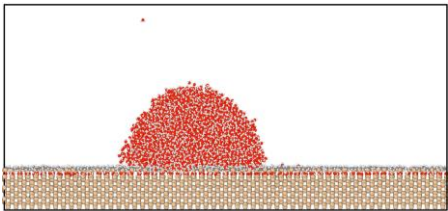
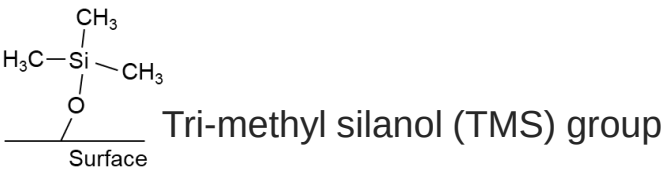
[4] N. Martinez, Wettability of silicon, Silicon dioxide, and Organosilicate Glass, University of North Texas (2009)

[5] V. Silverio, *Colloids Surf. A Physicochem. Eng. Asp.*, **570**, 210-217 (2019)

Validation of the simulation model

◆ Water contact angle measurement

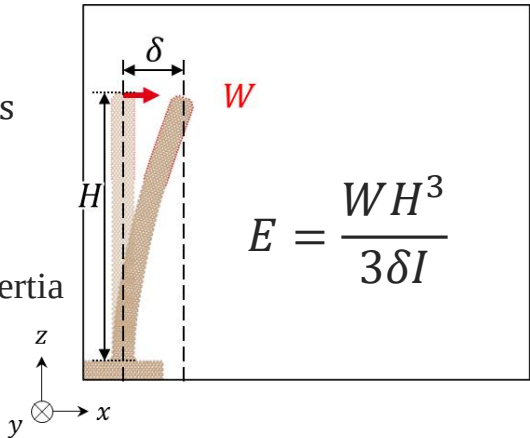
- Modification rate: Tri-methyl silanol (TMS) groups coverage rate



	Experimental	This simulation
Modification rate [%]	52.8-58.3 [3]	55.0
Water contact angle [°]	93 [4]	95

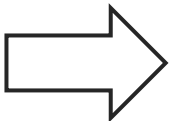
◆ Young's modulus measurement

E : Young's modulus
 W : Load on tip
 H : Fin length
 δ : Bending length
 I : Moment of the inertia



Young's modulus of Si(110)	Experimental	This simulation
Bulk [GPa]	169 [6]	174.7
<10 nm [GPa]	90-110 [6]	107.7

[3] F. R. Jones, Optimization of the Reaction of Hexamethyldisilazane on a Fumed Silica Surface (1999)
[4] N. Martinez, Wettability of silicon, Silicon dioxide, and Organosilicate Glass, University of North Texas (2009)
[6] H. Sadeghian *et al.*, *Appl. Phys. Lett.*, **94**, 221903 (2009)



These results indicate our simulation model is valid.

Topics

- ◆ Introduction to Molecular dynamics and SMT
- ◆ Validation by contact angle prediction
- ◆ Simulations of fins dynamics: wet vs. dry
- ◆ Effect of SMT on collapse prevention and reparation
- ◆ Conclusions

Topics

◆ Introduction to Molecular dynamics and SMT

◆ Simulation model validations:

- Contact angle
- Young modulus

◆ Simulations of fins dynamics: wet vs. dry

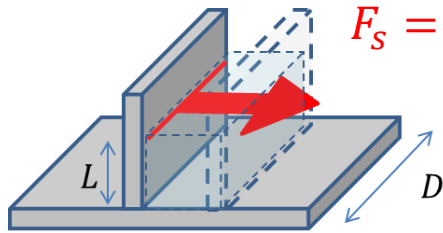
- Collapse
- Restoration

◆ Conclusions

Method: Fins dynamics simulations

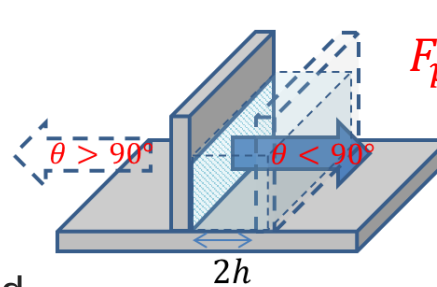
◆ There are 2 factors related to pattern collapse [7]

➤ Surface tension of liquid

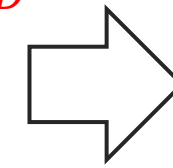


γ_l : Surface tension of liquid
 D : Width

➤ Force due to Laplace pressure



L : Liquid height
 h : inter-pattern distance



Pattern collapse

◆ Maximizing the both factors to cause collapse intentionally.

- Use water as high surface tension liquid.
- Set a non-uniform wet state as an initial system.

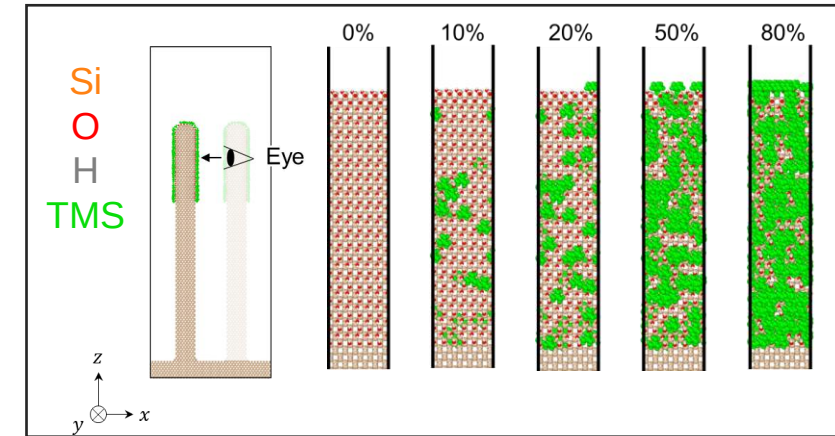
[7] S. Farshid Chini *et al.*, “Understanding Pattern Collapse in Photolithography Process Due to Capillary Forces”, *Langmuir*, **26**, 16, 13707-13714 (2010)

Method: Fins dynamics simulations

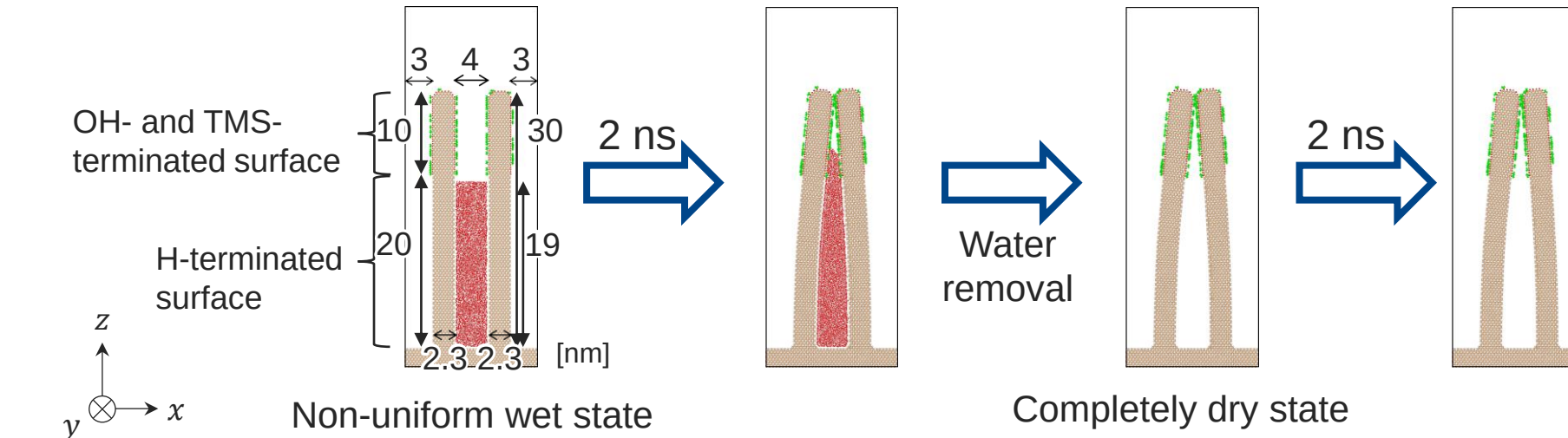
◆ Model details

- Models: Si based fin
- Top 10 nm: OH and TMS groups termination
- Other: hydrogen atom termination
- Water molecules: placed between fins with a width of 4 nm
- TMS modification rates: 0 to 80%
- Periodic boundary conditions: in x - and y -directions

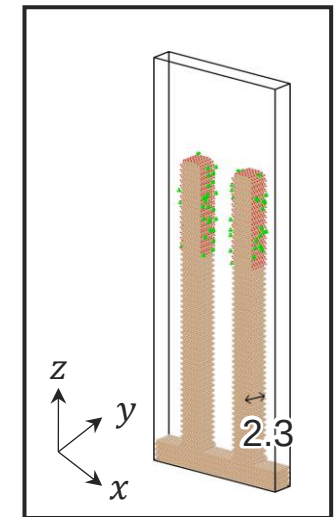
Enlarged view of the tip



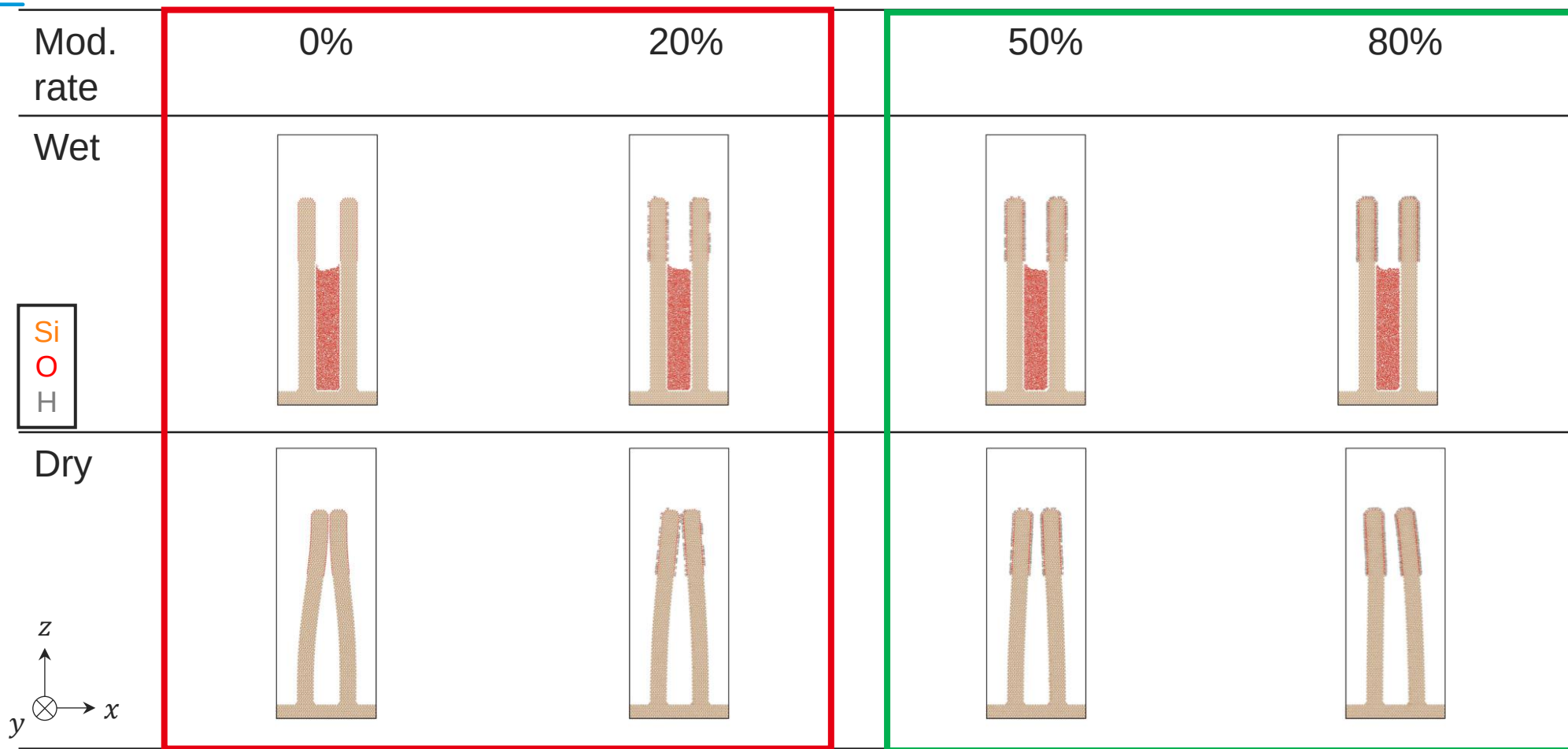
◆ Calculation flow



Bird view



Results and discussion: Fins dynamics in wet and dry conditions



Contact

No contact

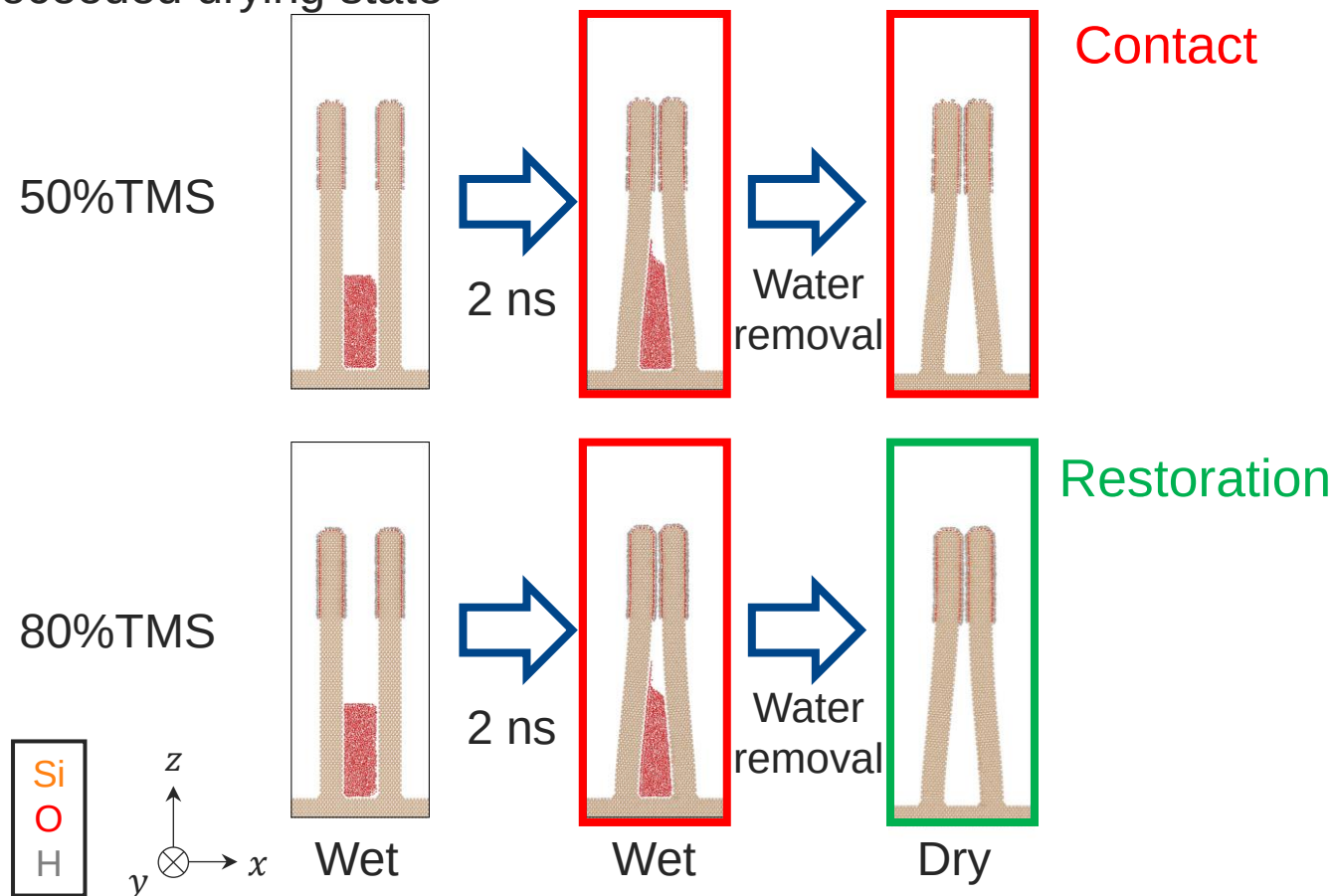
- The low modification rates models: Water OH groups interactions are strong and keep contact.
- The high modification rates models: Water-OH groups interactions are weakened by TMS.

TMS groups have the effect of preventing fins contact.

Results and discussion: Fins dynamics in wet and dry conditions

◆ Lowering the water height level in the 50% and 80% TMS models

- To simulate a proceeded drying state

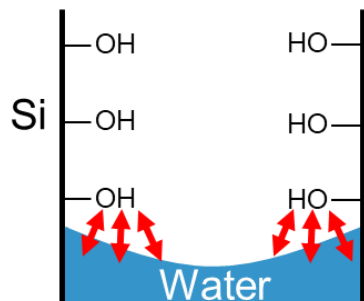


If the **modification rate is high**, patterns could be **restored**.

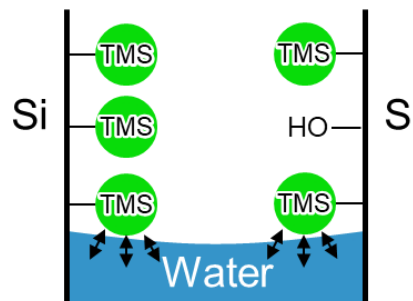
Short summary: the effect of TMS groups

◆ TMS groups have 2 effects in preventing collapse.

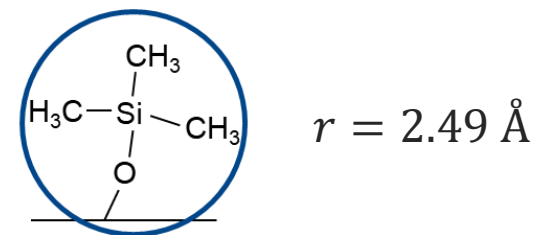
1. Weaken the interactions between water and OH groups on fins.



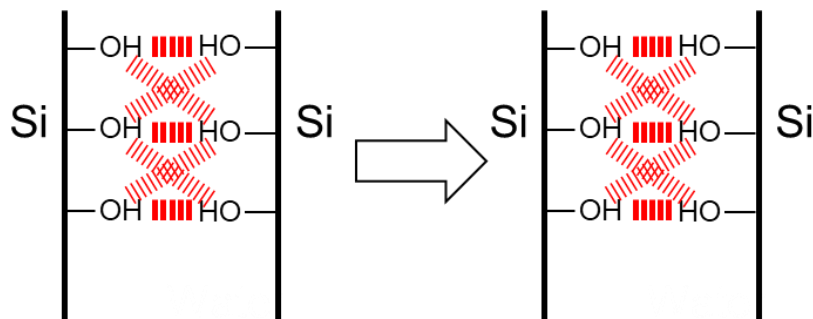
Strong Interactions



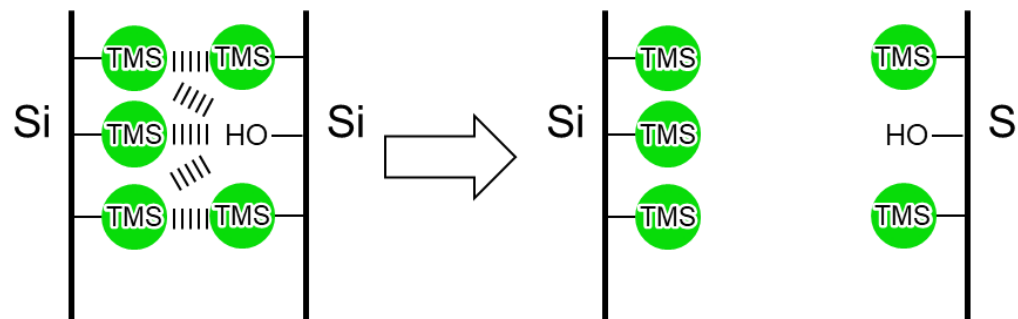
Weak Interactions



2. The interactions among TMS groups are weak and fins restoration could occur.



Do not restore



Restore

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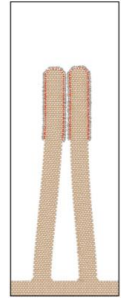
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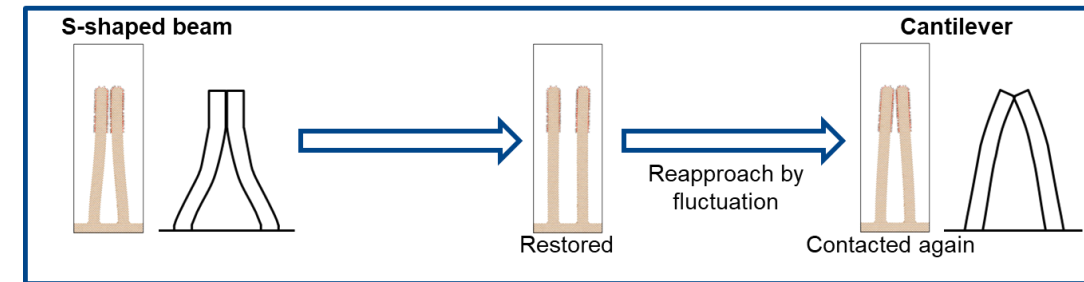
◆ Conclusions

Conclusion

- ◆ At high modification rate of TMS, fins restoration was directly observed.
 - High modification rate is important for restoration.



- ◆ Contact is kept when it deformed as a cantilever.



- ◆ Suggestions that might improve process results
 1. Distribute TMS groups uniformly and densely.
 2. Give enough energy for the structure to be restored and counterbalance adhesion energy

MD study aims here to improve chemical efficiency and cleaning process thanks to fast learning cycle, while at the same time reducing drastically physical prototypes and minimizing waste.

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