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Silicon nitride crystallization study via molecular dynamics and the ultra-fast 3-body (UF3) machine-learned interatomic potential

Tesia D. Janicki[1], Jason Gibson[2], Carlos Chacon[1], Edwin Chiu[1], Scott Grutzik[1], Khalid Hattar[3], Paul Kotula[1], Hojun Lim[1], Calvin Parkin[1], Jennie Podlevsky[1], Aashique Rezwan[1], Richard Hennig[2], Chris Bishop[1], J. Matthew D. Lane[1]

[1]Sandia National Laboratories
[2]University of Florida
[3]University of Tennessee-Knoxville

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APS March Meeting, Minneapolis, MN

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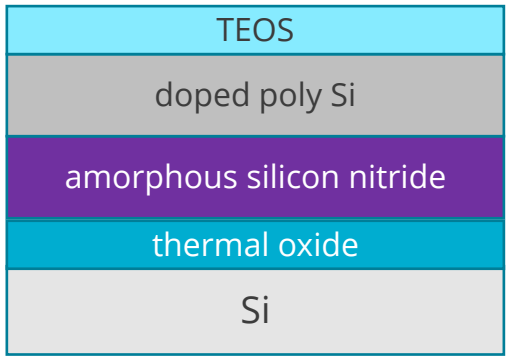
U.S. DEPARTMENT OF ENERGY

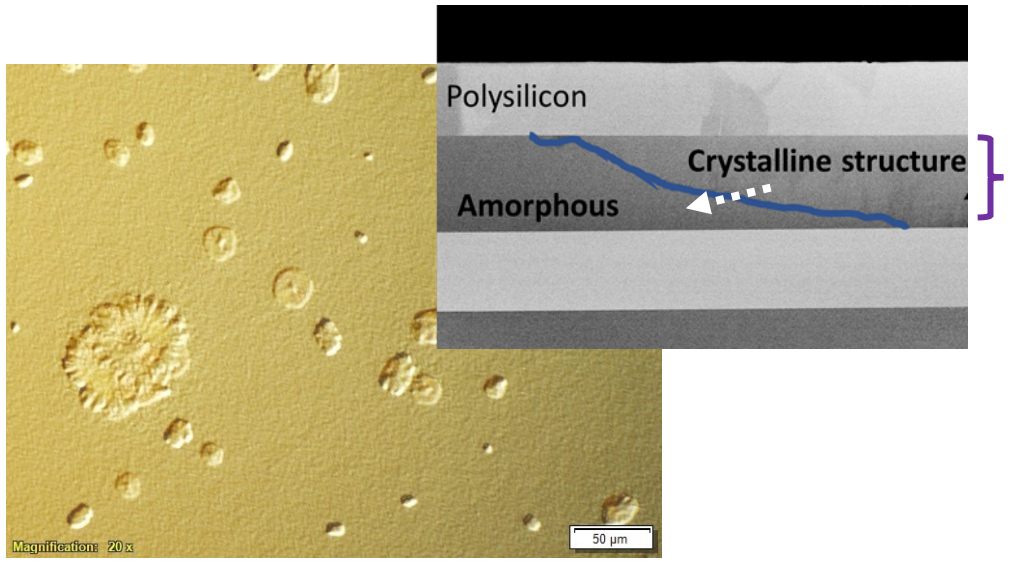
NNSA

Silicon nitride in microelectronics

Silicon nitride is ubiquitous in microelectronics fabrication across industry.



Anneal at
T > 1300K



Christopher Bishop, et al. Experimental characterization and modification of Silicon Nitride crystallization reaction kinetics for microelectronics applications. *EMC June 2023*

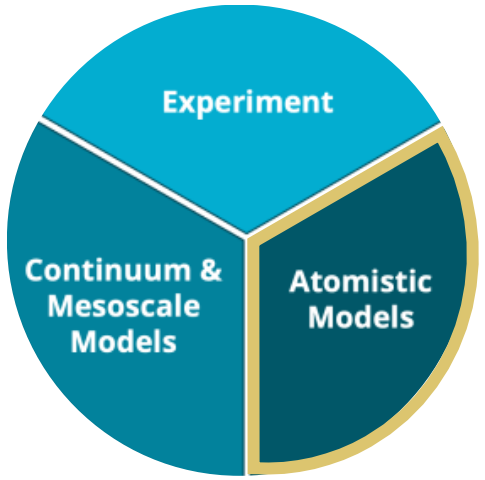
Spurious crystallization of Si_3N_4 occurs at lower temperatures in layer stack than in bulk films.

These effects can be mitigated via temperature control.

Core science questions regarding the nature of crystallization remain.

- What causes nucleation?
- What is the growth mechanism (e.g. rates)?
- What parameters offer mechanistic control (e.g. stress, composition)?
- Can we model/predict these phenomena?

Interdisciplinary Approach



- What causes nucleation?
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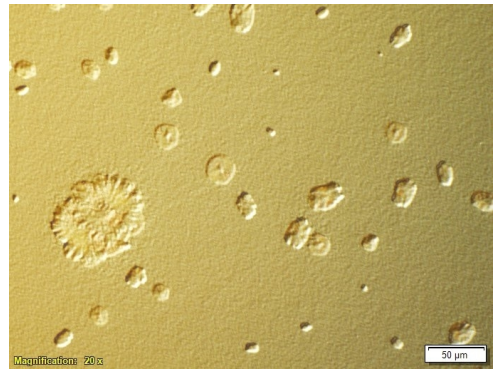


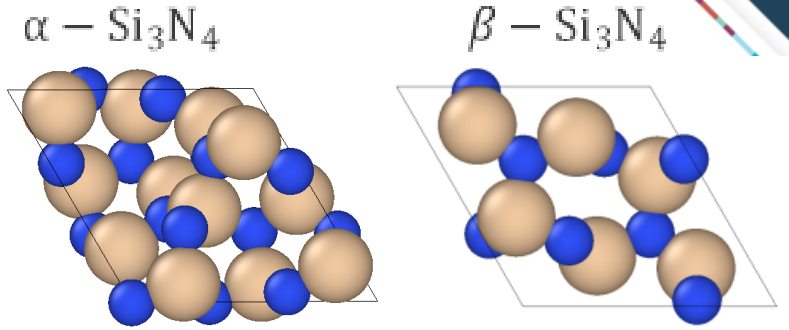
Goals for Atomistic Models

- Accurately model structural properties in silicon nitride.
- Show that we can reproduce experimental growth behaviors.
- Extract mechanistic details where possible.

Ultra-**F**ast **3**-Body (**UF3**)

Silicon Nitride System: Experiment and MD Approaches

Crystal	Stoichiometric Si_3N_4 possesses 2 stable trigonal polymorphs at ambient pressure. Experiments only observe α nucleation & growth. Simulations only seed for the α phase in our models.
Amorphous Structure	Experiments use chemical vapor deposition (CVD) to deposit amorphous films. Simulations use a melt/quench to generate the amorphous phase.** In ambient pressure, Si_3N_4 dissociates near the melting point. $Si_3N_4(s) \rightarrow 2N_2(g) + 3Si(g, l)$
Interface Dynamics & Crystal Growth	Rates of experimental crystallization near 1400K are ~10^{-8} m/s Simulations use high temperature MD simulations and extrapolate to experimental temperatures using time/temperature superposition.



Interatomic Potentials

Empirical potentials are trained for specific problems and often lack transferability.

Marian, Gastreich & Gale: MG2[1]

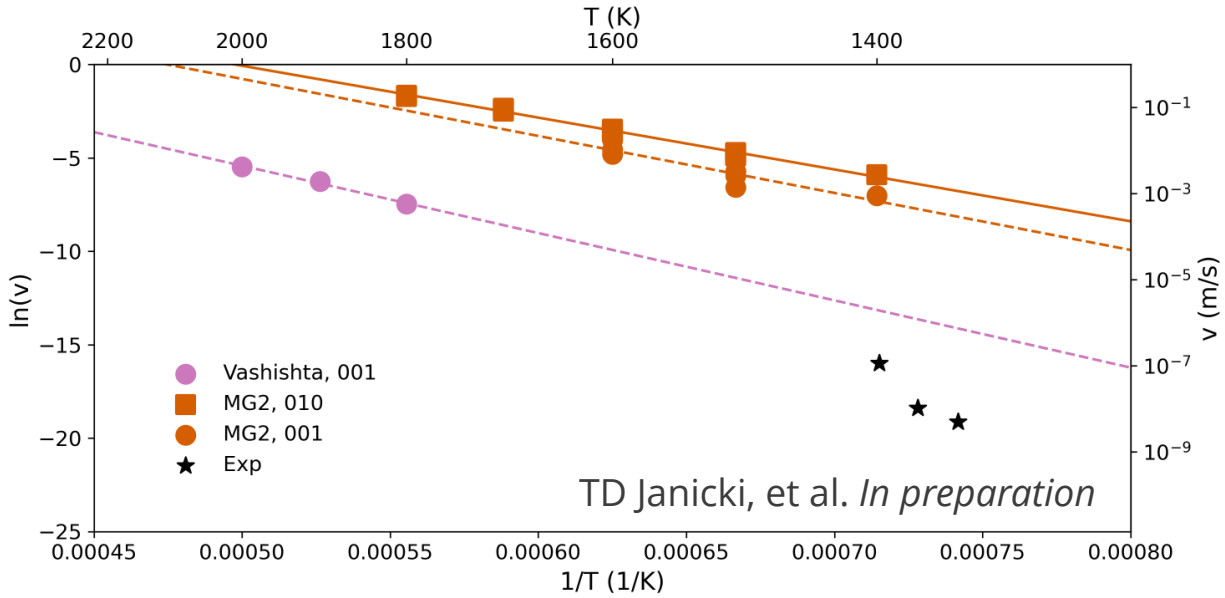
- 2-body
- Designed for structure in SiN and Si-B-N
- Performs well for amorphous structural properties

Vashishta[2]

- 3-body
- Designed for fracture problems
- Performs well for crystal mechanical properties

$$\ln(v) = \ln(v_o) - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

T : temperature
v : velocity
E_a : activation ener



[1] C. M. Marian, M. Gastreich and J. D. Gale. *Phys. Rev. B.* **62** (2000) 3117-3124
[2] P. Vashishta, R. K. Kalia, A. Nakano, W. Li and I. Ebbsjö. in *Amorphous Insulators and Semiconductors,* edited by M. F. Thorpe and M. I. Mitkova (Kluwer Academic, Netherlands 1997) 151-213

UF3 Development

- Training Workflow
- Structure — Genetic algorithm & aiMD
- Descriptor — Cubic B-splines
- Learning Model — Linear regression
- Property — Energy & Force
- Validation

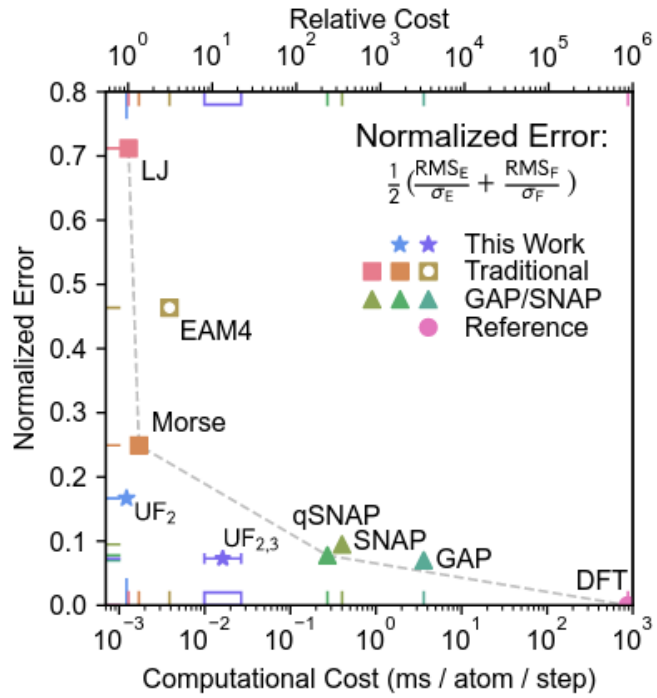
$$E = \sum_{ij} V_2(r_{ij}) + \sum_{ijk} V_3(r_{ijk})$$

$$V_2(r_{ij}) = \sum_{n=0}^{K} c_n B_n(r_{ij})$$

$$V_3(r_{ijk}) = \sum_{l=0}^{K_l} \sum_{m=0}^{K_m} \sum_{n=0}^{K_n} c_{lmn} B_l(r_{ij}) B_m(r_{ik}) B_n(r_{jk})$$

$$B_n = B_{n,3+1}(r) = \frac{r - t_n}{t_{n+d} - t_n} B_{n,3}(r) + \frac{t_{n+d+1} - r}{t_{n+d+1} - t_{n+1}} B_{n+1,3}(r)$$

Performance for 128-atom system of BCC Tungsten:



S. R. Xie, M. Rupp and R. G. Hennig. *NPJ Comput. Mater.* **9**, 162 (2023)

Parameters are interpretable, with force and energy mapped back to 2/3-body contributions

UF potentials show promise in both accuracy and efficiency

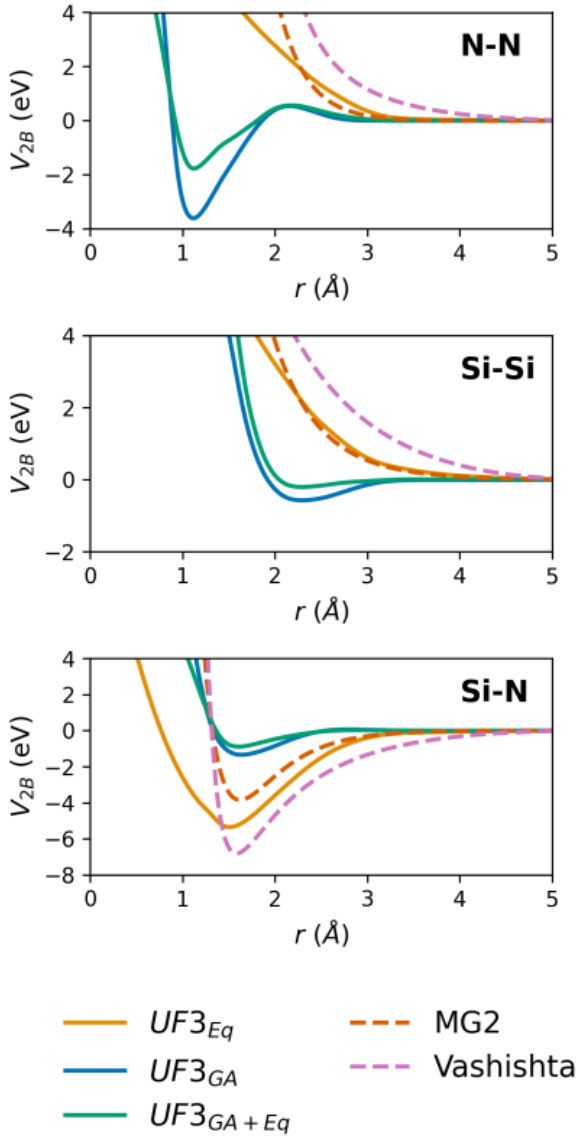
Training UF3

Empirical potentials (**MG2** & **Vashishta**) are trained using a finite set of near-equilibrium structures.

Using near-equilibrium training data (Eq) from *ab initio* Molecular Dynamics, **$UF3_{Eq}$** shows similar features to empirical models.

Training with non-3:4 structures generated by a genetic algorithm (GA) explores additional phase space in **$UF3_{GA}$**.

$UF3_{GA+Eq}$ combination of these training sets, retains equilibrium features while allowing investigation of phase space not previously possible.

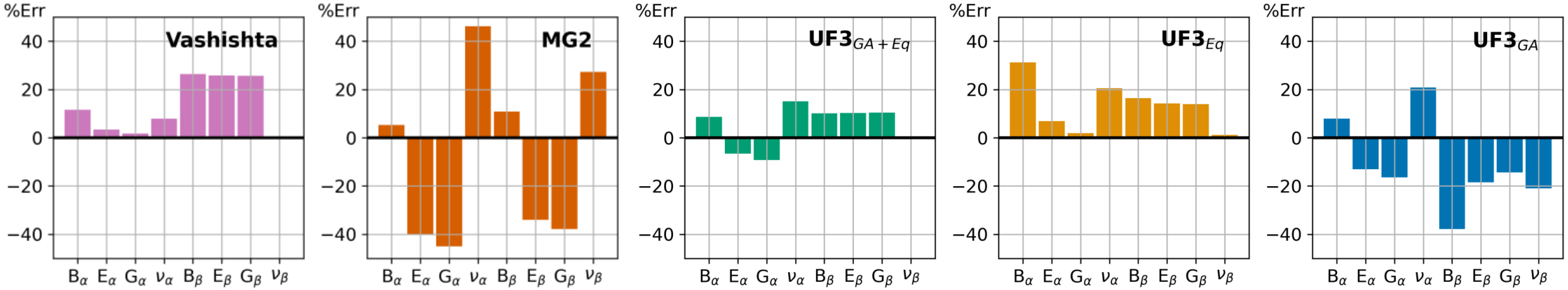


GA approach: J. Gibson, A. Hire and R. G. Hennig, *NPJ Comput. Mater.* **8**, 211 (2022)

Crystal Properties

Bulk Modulus, $B = -V\frac{dP}{dV}$ Young's Modulus, $E = \frac{\sigma}{\epsilon_{axial}}$ Shear Modulus, $G = \frac{\tau_{xy}}{\gamma_{xy}}$ Poisson Ratio, $\nu = -\frac{d\epsilon_{transverse}}{d\epsilon_{axial}}$

versus DFT, 0K



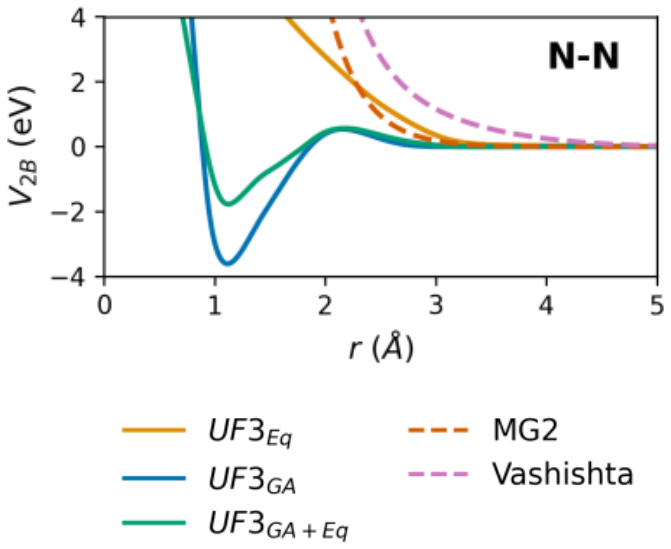
$UF3_{GA+Eq}$ outperforms other models in reproducing mechanical crystal properties.

Structural Properties

Empirical model amorphous structures are generated using a melt-quench approach.

$UF3_{GA+Eq}$ (like experiment) forms N2 at high temperatures. Gentle relaxation is required.

Melt-quench in MG2 to 2000K → Relax via DFT → Relax in UF3 at 1800K → Quench in UF3 to target temperature



	T_m (K)	α Crystal, 300K (g/cm^3)	Amorphous, 300K (g/cm^3)	$\frac{\rho_{amorphous}}{\rho_{\alpha-crystal}}$
MG2	2439(10)	3.157(6)	3.065(1)	0.97
Vashishta	2890(10)	3.176(6)	2.643(1)	0.83
$UF3_{GA+Eq}$	--	3.225(2)	3.090(1)	0.96
Ref	**--**	**3.1719[1]**	**3.0(1)[2]**	**0.95**

[1] Expt: P. Yang, H.-K. Fun, I. A. Rahman, and M. I. Saleh. *Ceram. Int.* **21** (1995) 137
[2] Expt: Mastrangelo, Carlos H., Yu-Chong Tai, and Richard S. Muller. *Sens. and Actuator A Phys.* **23** (1990) 856-860. (agrees with our experiment)

$UF3_{GA+Eq}$ retains high-temperature dissociation behavior
…and reproduces structure well for **both** crystal and amorphous

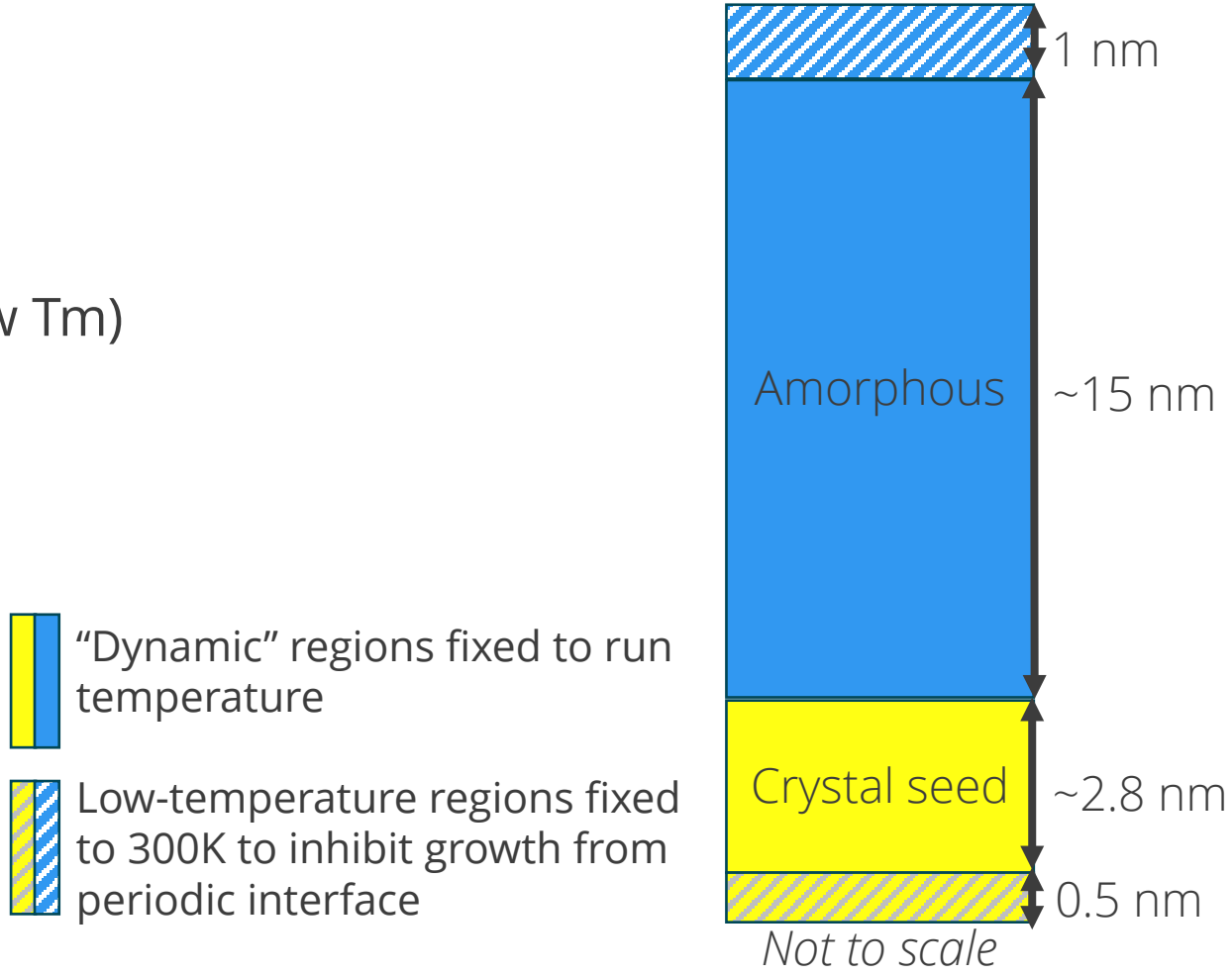
Crystallization Simulations in LAMMPS

Seeded growth from α-Si_3N_4

Growth from [0 0 1] and [0 1 0]

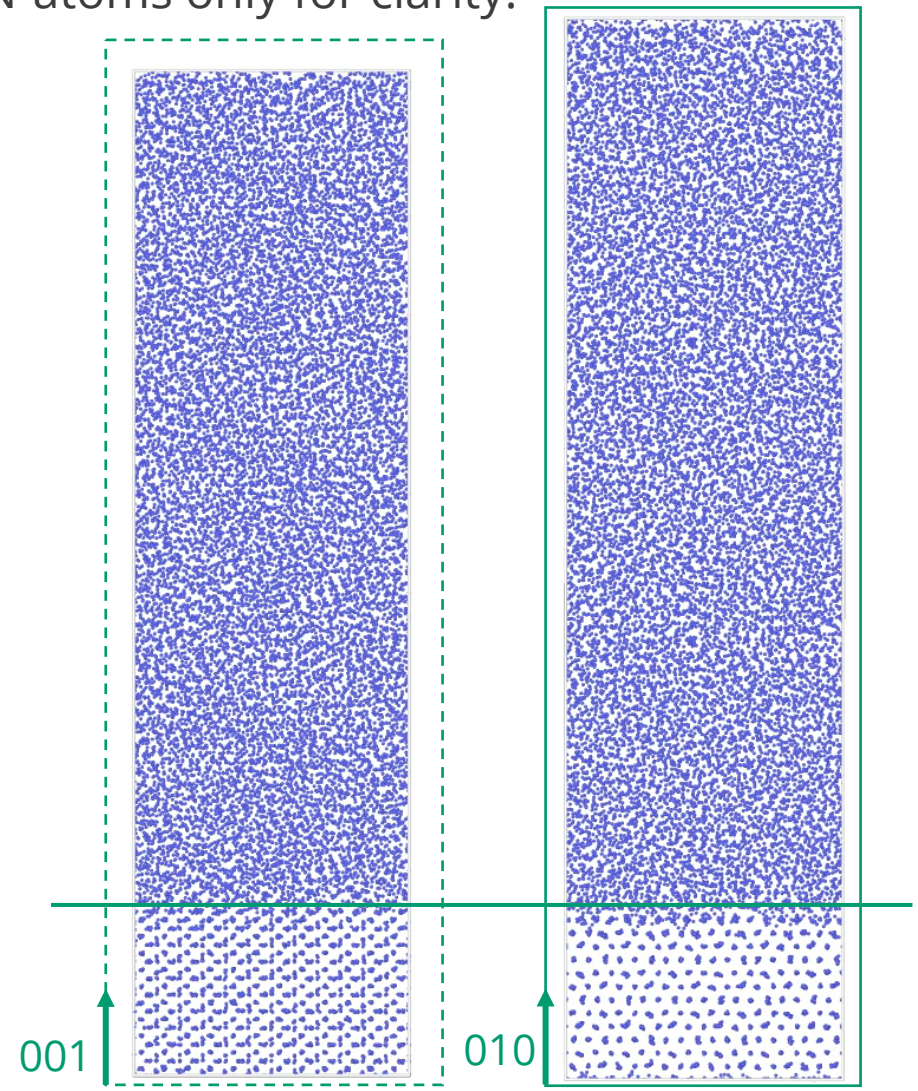
Potential-dependent for extrapolation (below Tm)
(1700K, 1750K, 1800K for UF3)

1 bar pressure



UF3 Crystal Growth (Preliminary)

N-atoms only for clarity:

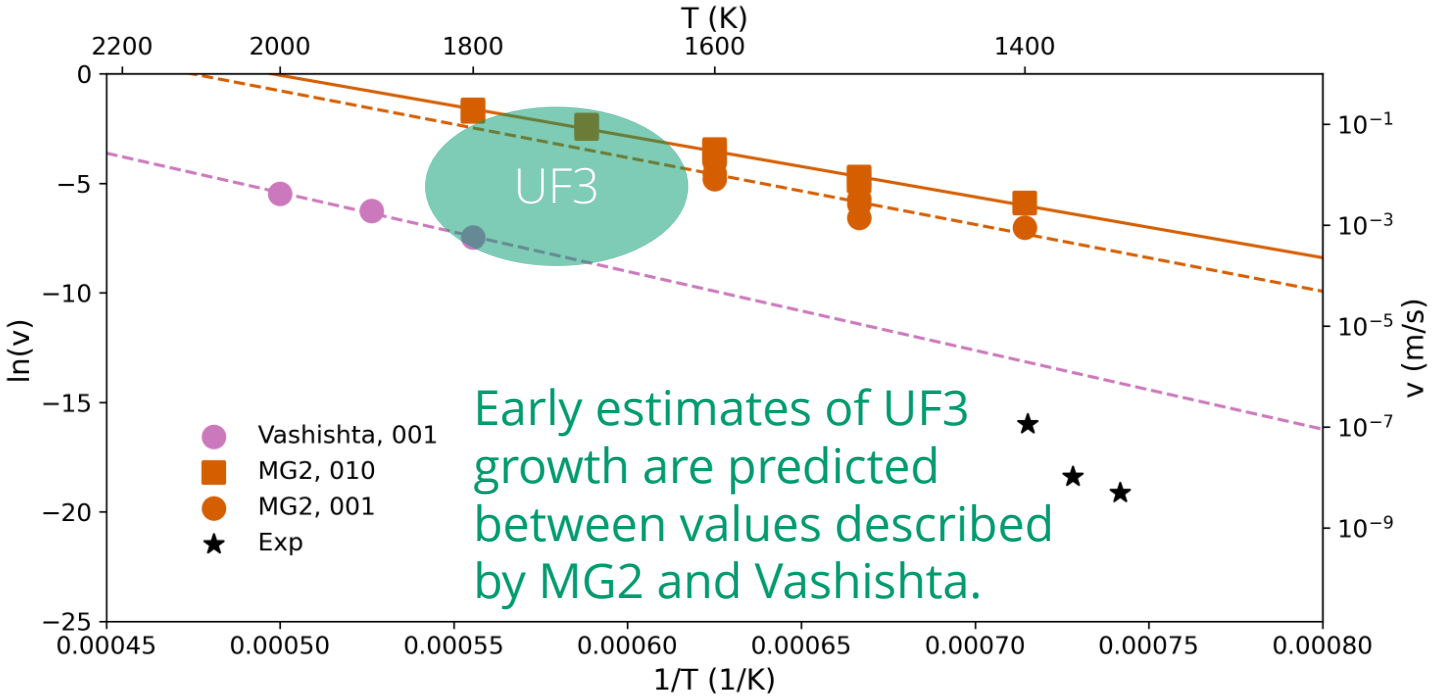


1800K; 100ns simulation time : 1s playback

✓UF3 can model crystallization.

$$\ln(v) = \ln(v_o) - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

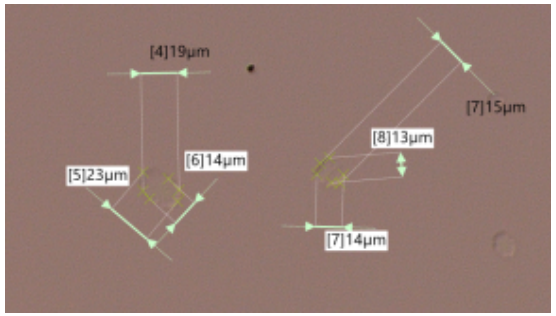
T : temperature
v : velocity
E_a : activation ener



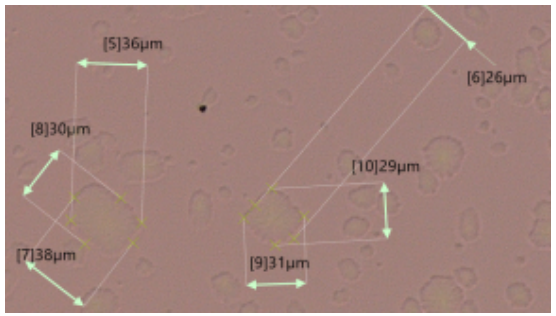
Early estimates of UF3 growth are predicted between values described by MG2 and Vashishta.

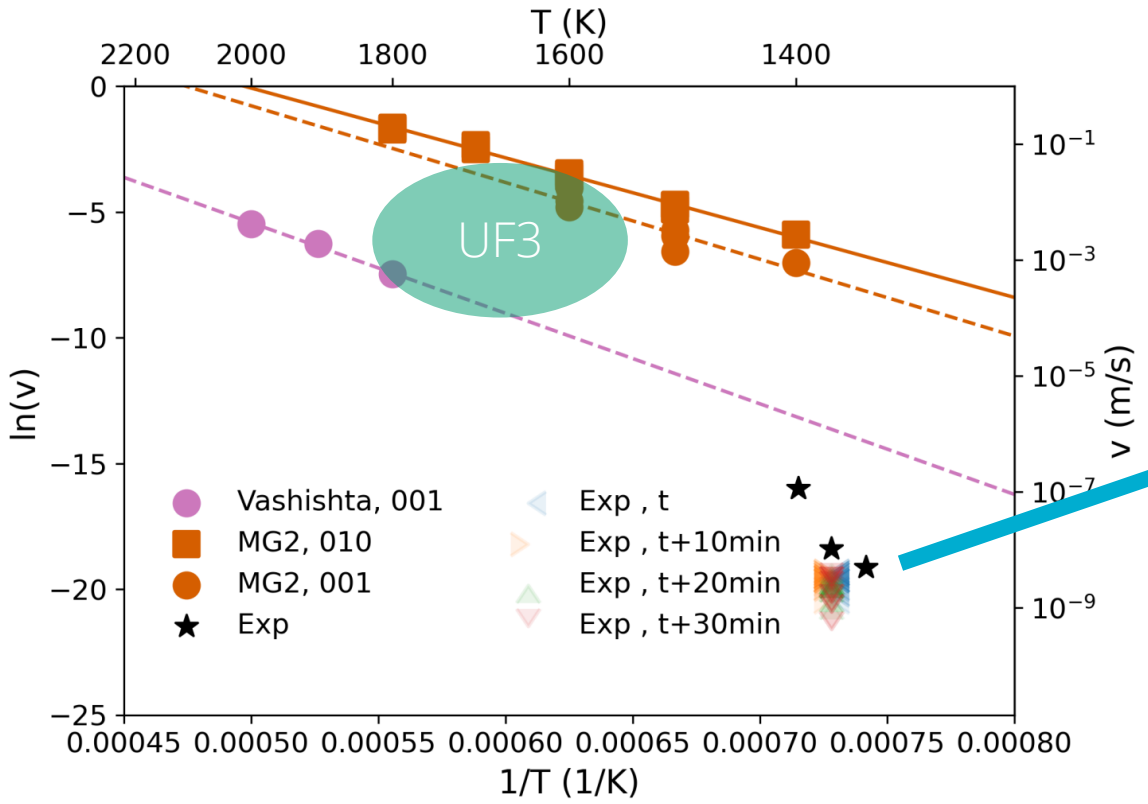
Experimental Comparison Ongoing

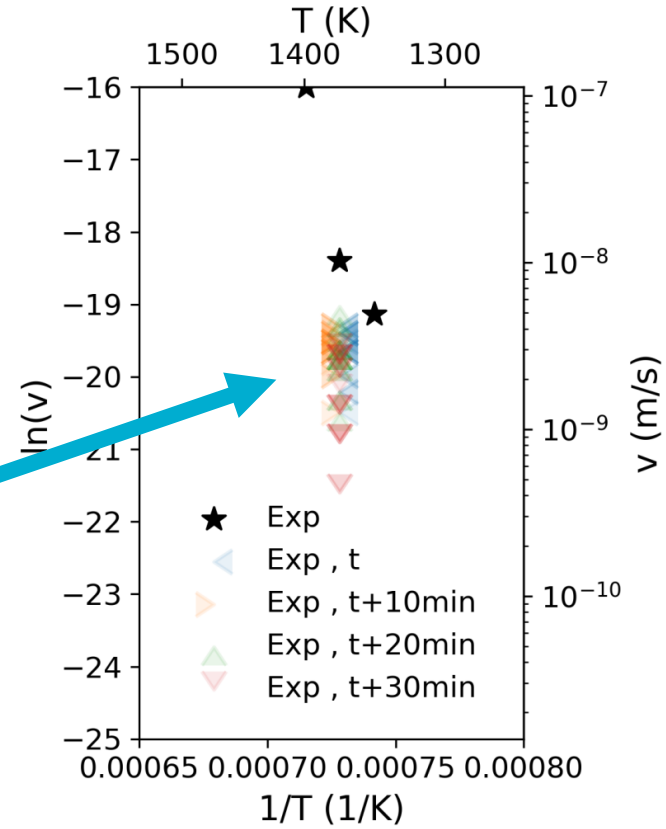
New experiments indicate both orientational and time dependence in growth.



50 minutes, 1373K



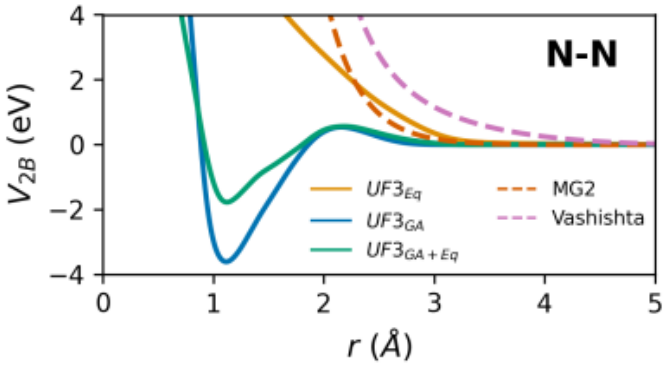




Qualitative orientational dependence is reproduced in our models.
Additional characterization is ongoing to assign growth facets to experimental images.

CONCLUSIONS

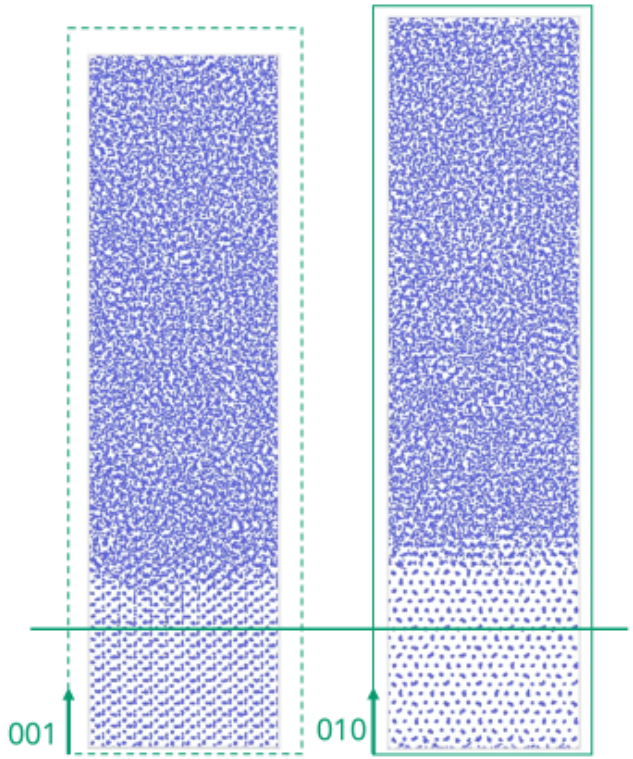
Accurately model structural properties in silicon nitride



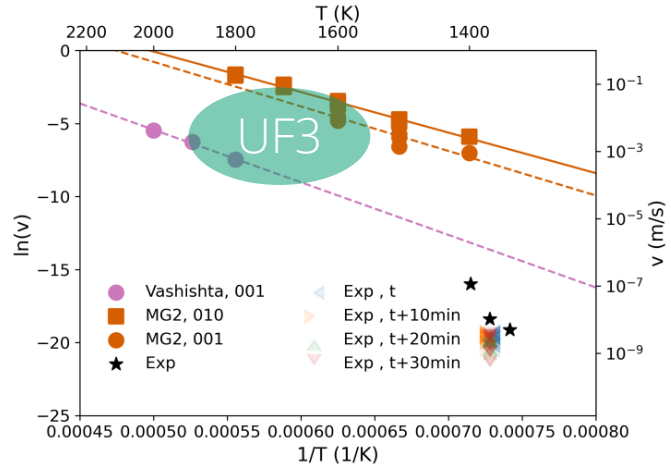
Incorporation of broad training structures enables exploration of physical phase space not possible for existing empirical models.

Show that we can reproduce experimental growth behaviors

Orientational growth rate dependence *qualitatively* agrees with experiment.



Extract mechanistic details where possible

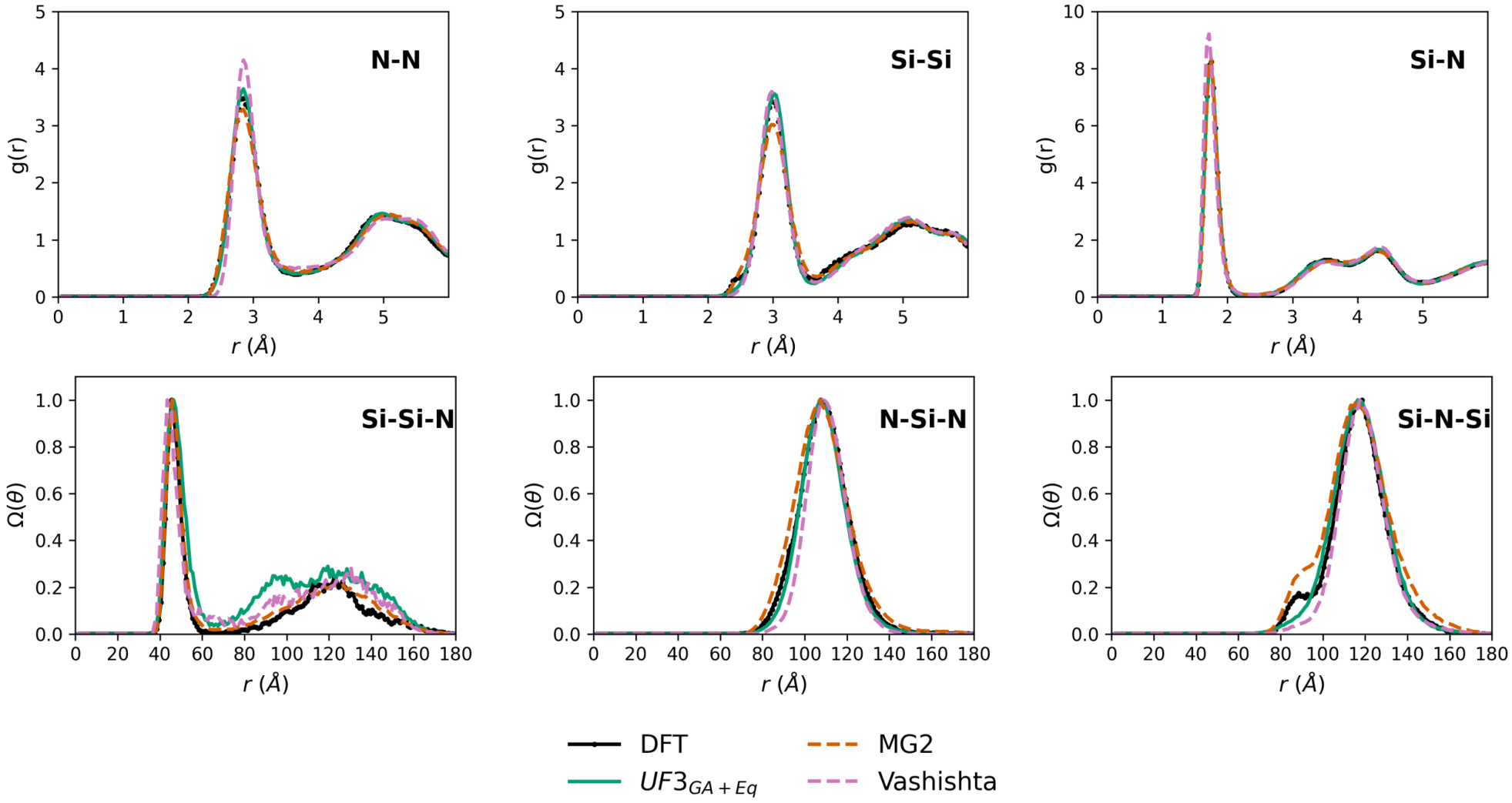


Quantification of growth mechanism is ongoing.

Future work:

- Add stress, impurities
- Incorporate defects

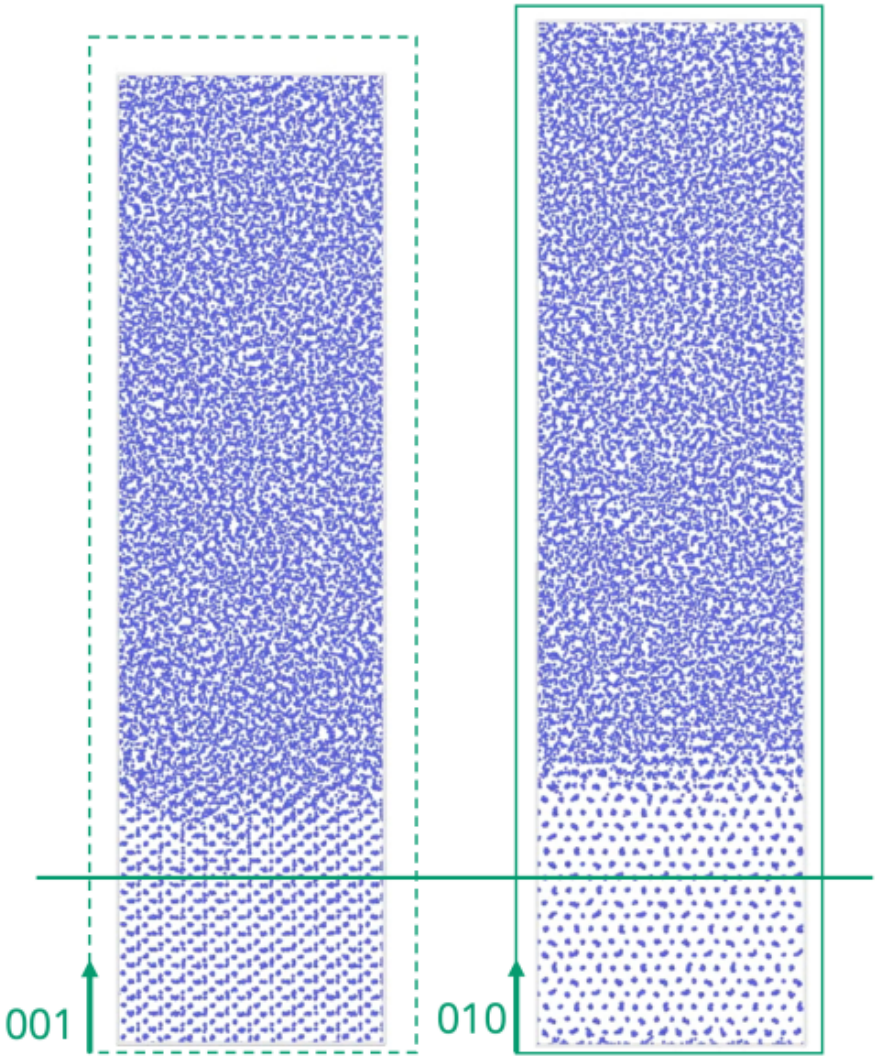
Additional Amorphous Structural Properties



All models reproduce amorphous distributions well; MG2 and UF3 perform slightly better in low-angle Si-N-Si angle values.

UF3 Crystal Growth (Preliminary)

N-atoms only for clarity:



✓ UF3 can model crystallization.

Quantifying growth rates enables experimental comparison

Interfaces are defined as a transition in the potential energy profile along the direction of growth.