Introduction to Atomistic Modeling for Materials Characterization

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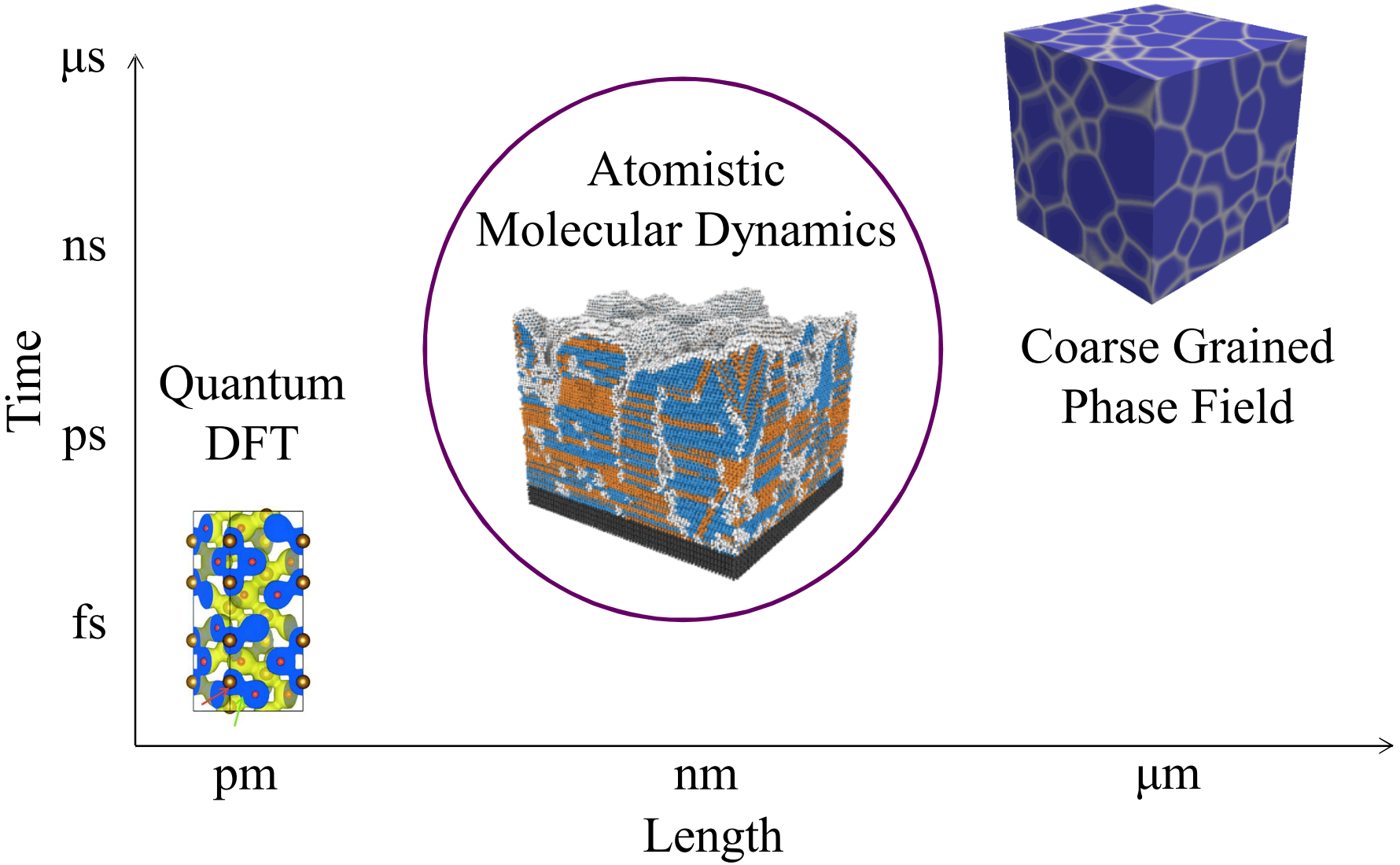
Overview

- Intro
  - Atomistic modeling?
  - What's it good for?
- MD Overview
  - Basic Implementation
  - Potentials
  - Pitfalls
- Applications
  - Metals
  - Semiconductors
  - CdTe Thin Films

Orders of Magnitude



Applications of Atomistic Modeling

- Experiments are great, but have limitations
- Atomistic simulation allows the fine resolution of the evolution of individual atomic positions and velocities
- Allows resolution of defects structures during the application of external stimuli and constraints and within bulk samples

MD Overview

INPUTS

Geometry
- Size
- Boundary

Particles
- Number
- Type
- Position
- Velocity

Interaction
- Interatomic Potential

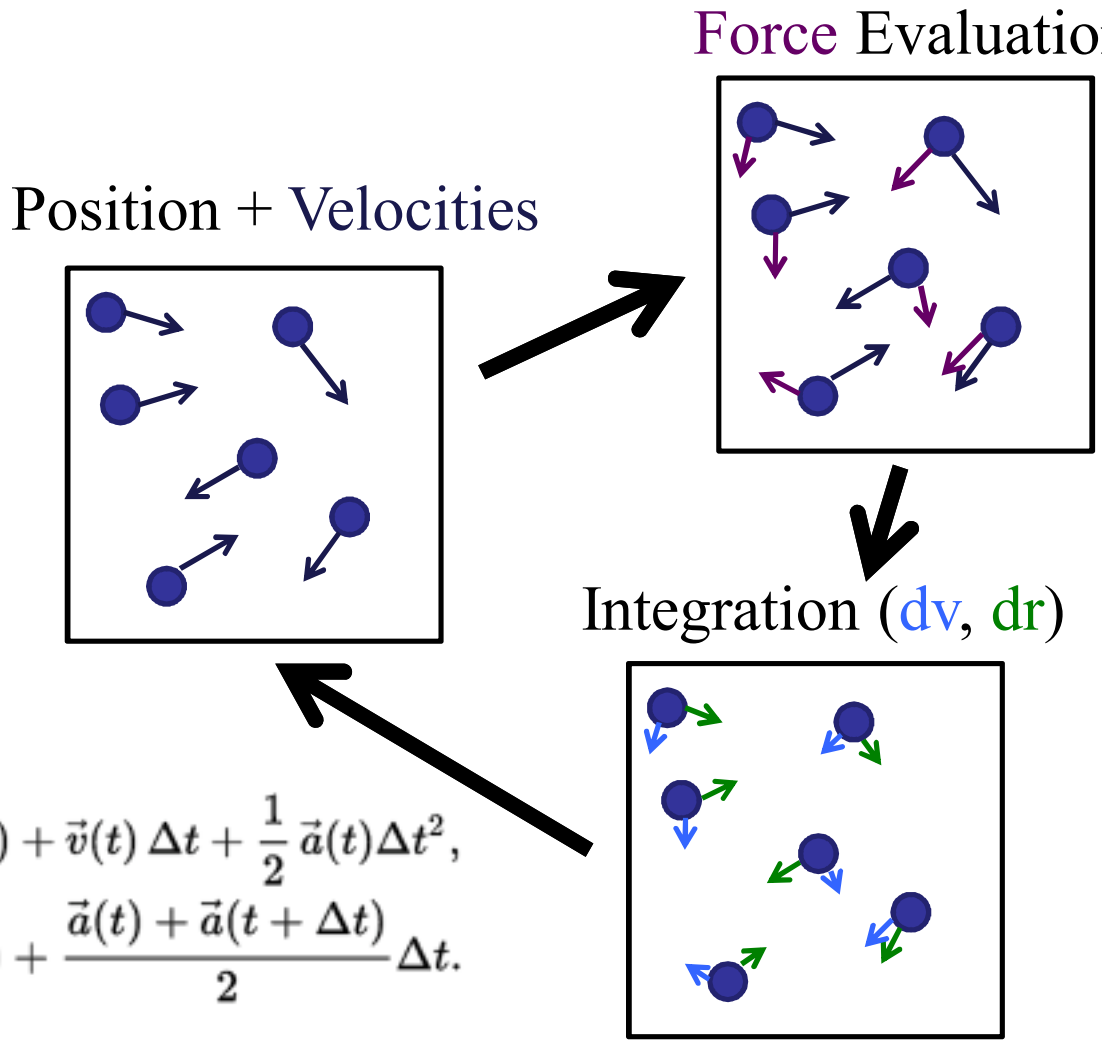
Environment
- Thermodynamic Ensemble

Geometry Evolution
Environment Evolution
Arbitrary Constraints

Outputs

Particle Properties
- Position
- Velocity
- Arbitrary Functions

Algorithm Overview

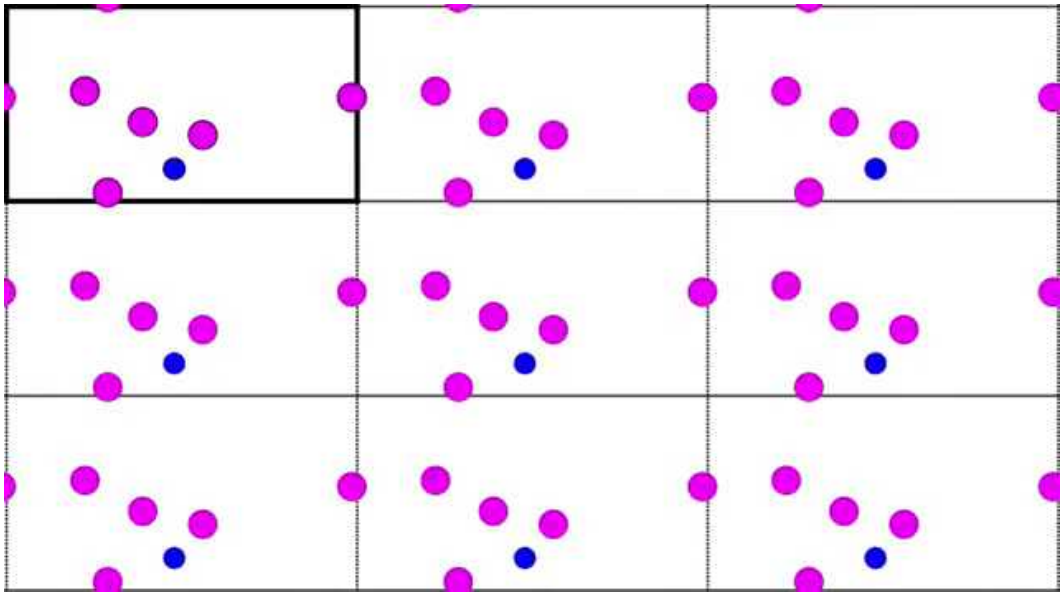


$$\vec{x}(t+\Delta t) = \vec{x}(t) + \vec{v}(t)\,\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2,$$

$$\vec{v}(t+\Delta t) = \vec{v}(t) + \frac{\vec{a}(t) + \vec{a}(t+\Delta t)}{2}\Delta t.$$

Boundary Conditions

- Periodic



- Free Surface

Potential Overview

- Interatomic potential defines total energy of particles as a function of position
- Most models define a finite interaction radius for efficiency
- Garbage in → Garbage out
  - Potential quality is central to extraction of valid trends

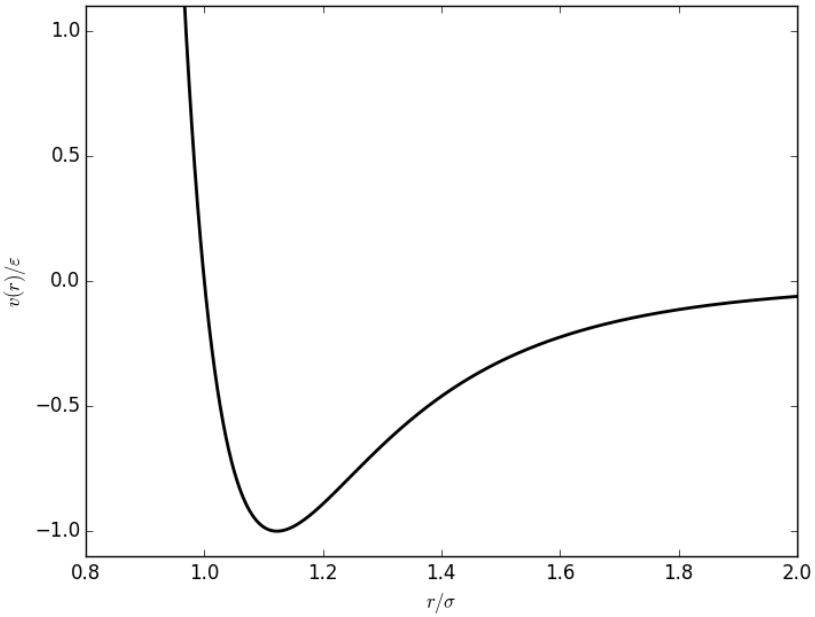
Pair Potentials – Lennard-Jones

$$V(r_i) = \sum_{i \neq j} v(\|r_{ij}\|)$$

- Lennard-Jones pair potential
  - Van Der Waals bonding
    - Noble gasses
    - Polymers
    - Layered systems

$$v(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]$$

- Morse pair potential



Many Body Potentials

- Pair potentials cannot capture all real materials, e.g. those with angular dependent bonding or complex interactions
  - Semiconductors
    - Often exhibit mixed character bonding with strong angular dependence
  - Metals
    - Electron delocalization

Stillinger-Weber Potential

- Enforces minimum energy with tetrahedral coordination

$$V = \frac{1}{2}\sum_{ij}\phi(r_{ij}) + \sum_{ijk} g(r_{ij})g(r_{ik})\left(\cos\theta_{jik} + \frac{1}{3}\right)^2$$

Pair | Spatial Decay | Angular Dependence

- Can capture elastic properties of Si, III-V
- Often fails to properly capture behavior of configurations far from equilibrium
  - Surfaces
  - Point defects
  - Dislocations

Tersoff Potential

- Bonding is angularly dependent but weakens with increasing coordination

$$V = \frac{1}{2}\sum_{ij}\phi_R(r_{ij}) + +\frac{1}{2}\sum_{ij}B_{ij}\phi_A(r_{ij}) \qquad B_{ij} = B(G_{ij})$$

$$G_{ij} = \sum_k f_c(r_{ik})g(\theta_{jik})f(r_{ij} - r_{ik})$$

Repulsion (pair)

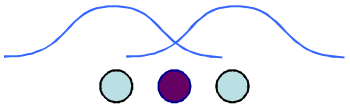
Attraction (3-body)

Coordination Dependence

- More realistic, expensive than Stillinger-Weber
- Expensive to optimize

Embedded Atom Model

$$E_{\text{coh}} = \underbrace{\sum_i F_i(\rho_i)}_{\text{Embedding energy}} + \underbrace{\frac{1}{2}\sum_i \sum_{j \neq i} V(R_{ij})}_{\text{Pair potential}} \qquad \rho_i = \sum_{i \neq j} f(R_{ij})$$



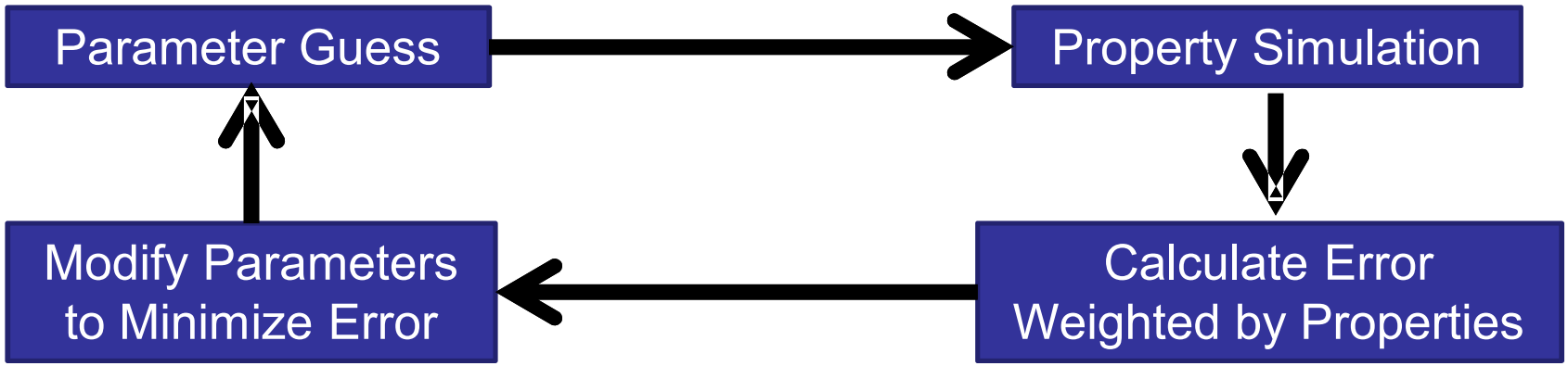
- Functional form of F(ρ) and ρ(r) is unknown
  - Typically chosen as splines
- V(r) usually chosen from well-defined pair potentials e.g. LJ or Morse

Advanced Potentials

- AIREBO (Adaptive Interatomic Reactive Empirical Bond Order)
  - Combination Van der Waals and covalent potential for hydrocarbons
- ReaxFF (Reactive Force Field)
  - General purpose bond order potential
  - Applicable to many materials systems with varying results
- COMB (Charge-Optimized Many Body)
  - Tersoff + long range coulombic interactions
  - Ionic Materials

Potential Optimization

- All models include unknown parameters
- Parameters optimized by an iterative process



Properties
- Cohesive Energy
- Bulk Modulus
- Elastic Constants
- Surface Energies
- Defect Energies

Challenges
- Big, Weird Space
- Expensive
- DFT Often Unreliable
- Incompatible Properties
- Weighting of Errors

Applications and Examples

- Dislocation motion and nucleation
- Irradiation and point defect classification
- Semiconductor film growth
- CdTe thin films

Dislocation Motion and Nucleation

- Motivation
  - Proof of concept showing the fine resolution of atomistics for mechanics
- Setup
  - Ni (EAM), Si (SW)
  - Pre-constructed dislocation dipole
  - Imposed shear strain

Dislocation Motion

Dislocation Motion Video Placeholder (Ni)

Dislocation Motion Video Placeholder (Si)

Single Radiation Event Simulation

- Observe the residual defects left after a radiation induced collision cascade

- Setup
  - Ni (EAM-ZBL), Si (SW-ZBL)
  - Single Crystal
  - Impart KE to single atom
  - Variable time-step

Radiation Cascade

Radiation Cascade Video Placeholder (Ni)

Radiation Cascade Video Placeholder (Si)

Point Defect Identification

- Cascade → Residual Defects
- What are they?

- Post-processing algorithms can be used to identify both individual defects and clusters

- Evolution of defects can be tracked with time

Defect Diffusion Coefficients

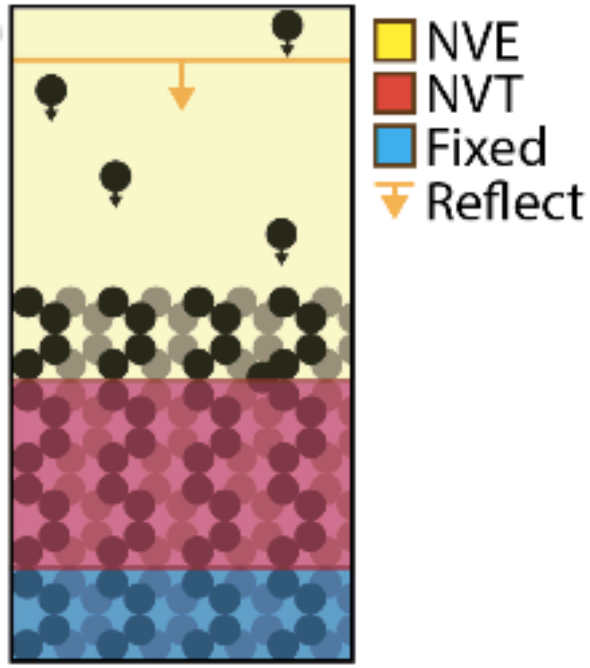
- Setup
  - Si (SW)
  - Single Crystal, seeded with vacancies
  - Large time-step

Vacancy Diffusion Video Placeholder (Si)

Semiconductor Film Growth

- Understand how growth defects form under variable conditions

- Setup
  - Si
  - Variable temperature
  - Complex thermo. ensemble
  - Randomly generated adatoms



Semiconductor Film Growth

Film Growth Low T
Placeholder

Film Growth High T
Placeholder

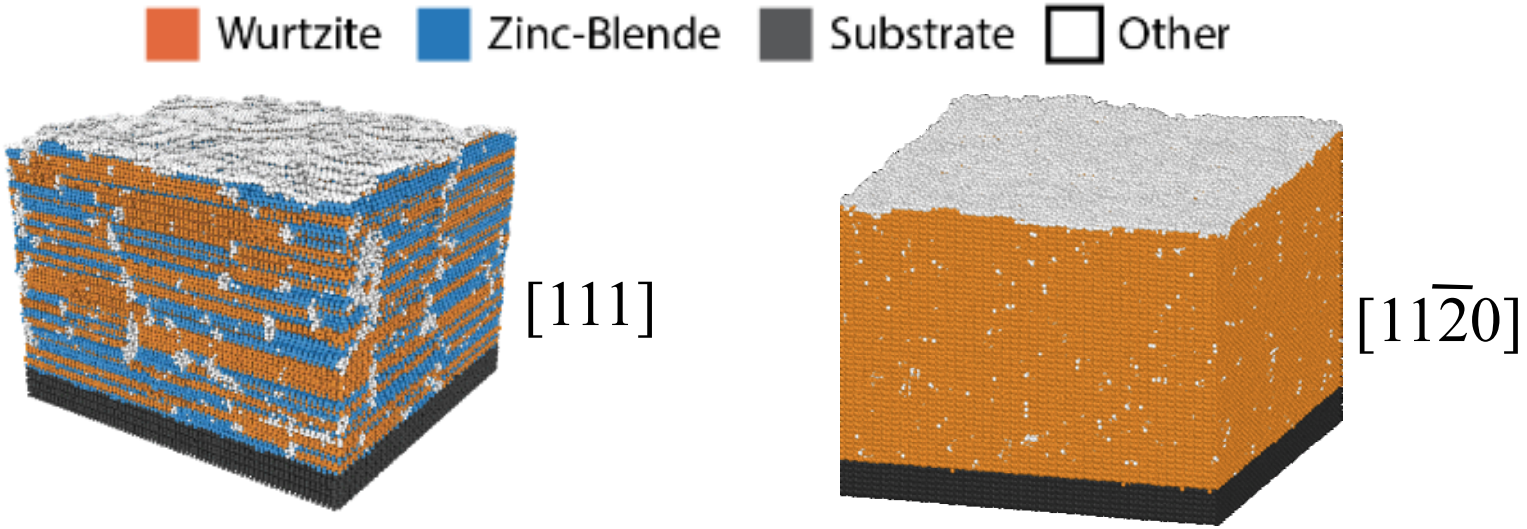
Film Characterization

- Surface roughness
  - Either approximated or using simulated probe
- Defect concentrations
  - Can be spatially resolved to identify substrate effects
  - Point defects and dislocations can be resolved using various algorithms
- Grain/Domain Size

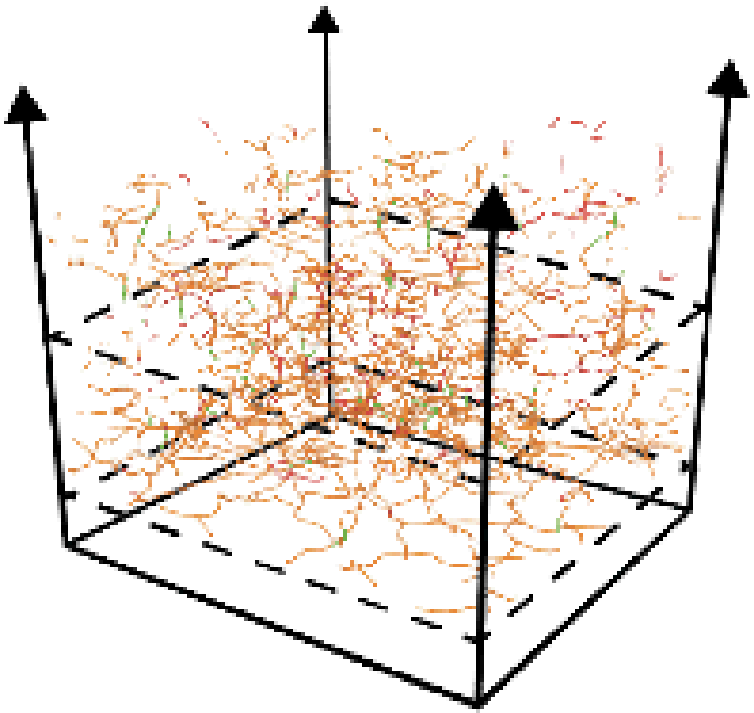
Effect of Potential on Growth

- Potential choice matters significantly for semiconductor growth

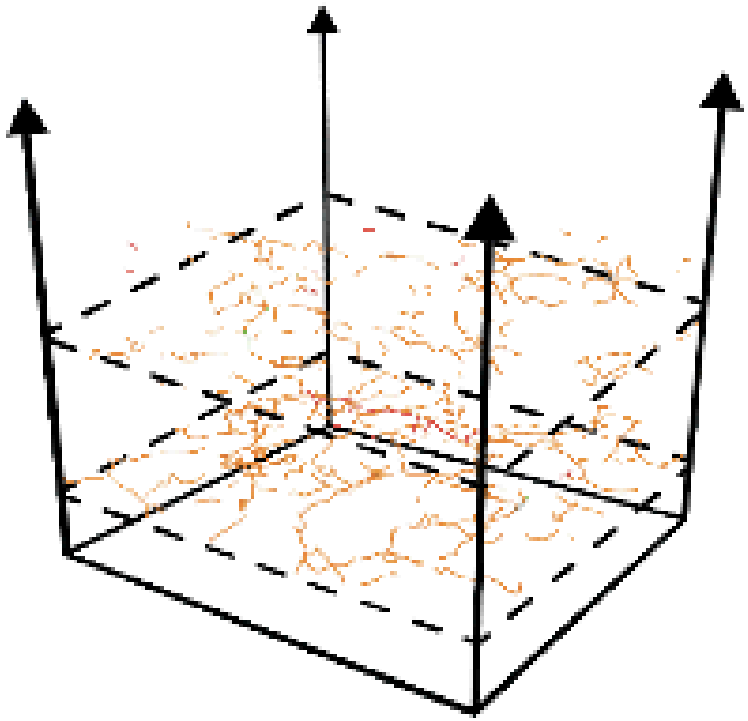
- SW model is limited: wurtzite and zinc blende are degenerate in some growth directions



Dislocation Concentrations



Low T

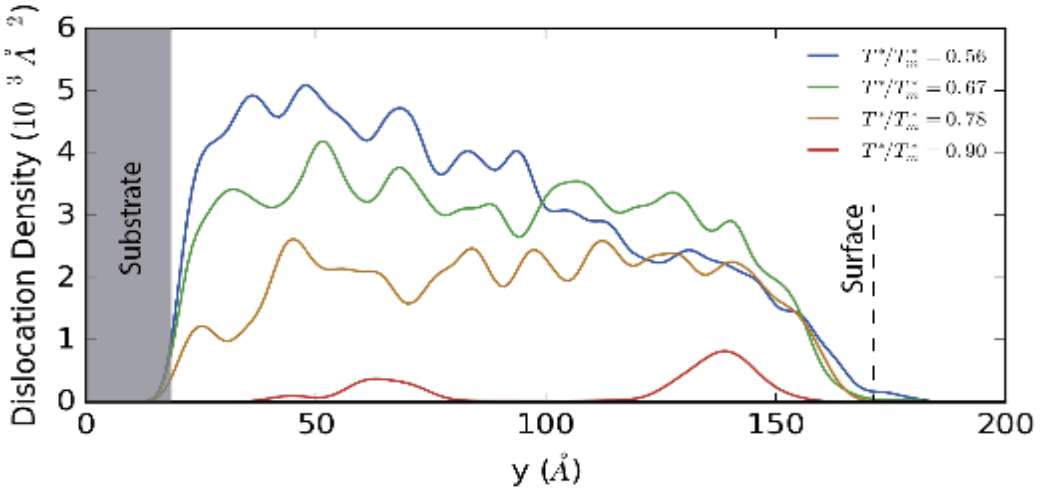


High T

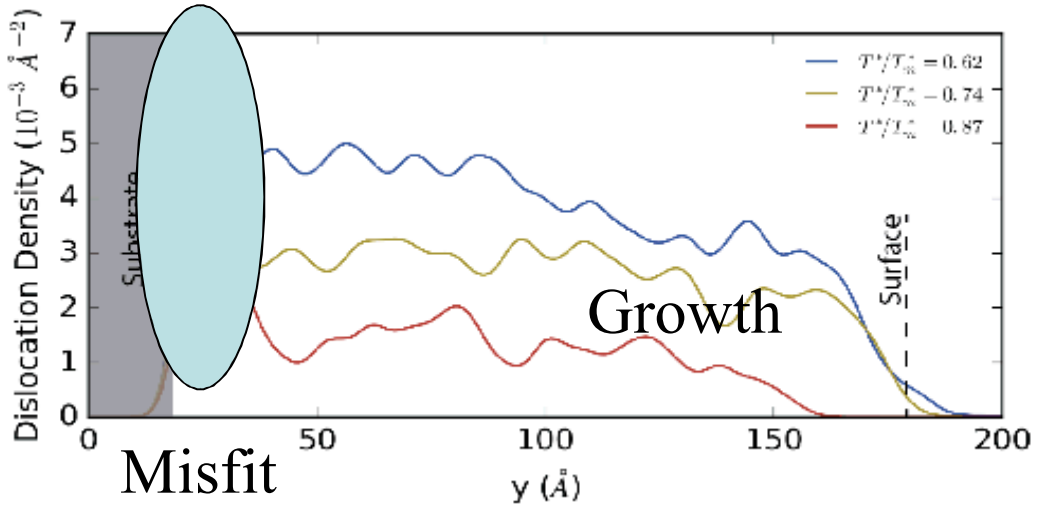
Dislocations are kinetically trapped!

Misfit Dislocation Identification

GaN/GaN

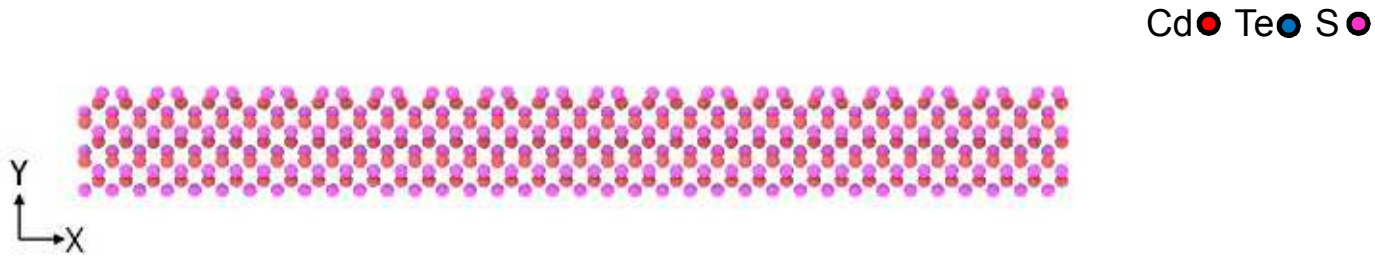


InGaN/GaN



CdTe Thin Films

- CdTe/CdS solar cells are hindered by a high defect density:
  -Grain boundaries, dislocations, point defects
- MD can help understand defect formation mechanisms, inform experiments
- LAMMPS[1] MD code
- Stillinger-Weber potential[2] for II-VI compounds: Cd, Te, Zn, Se, Hg, and S (Cu coming soon)

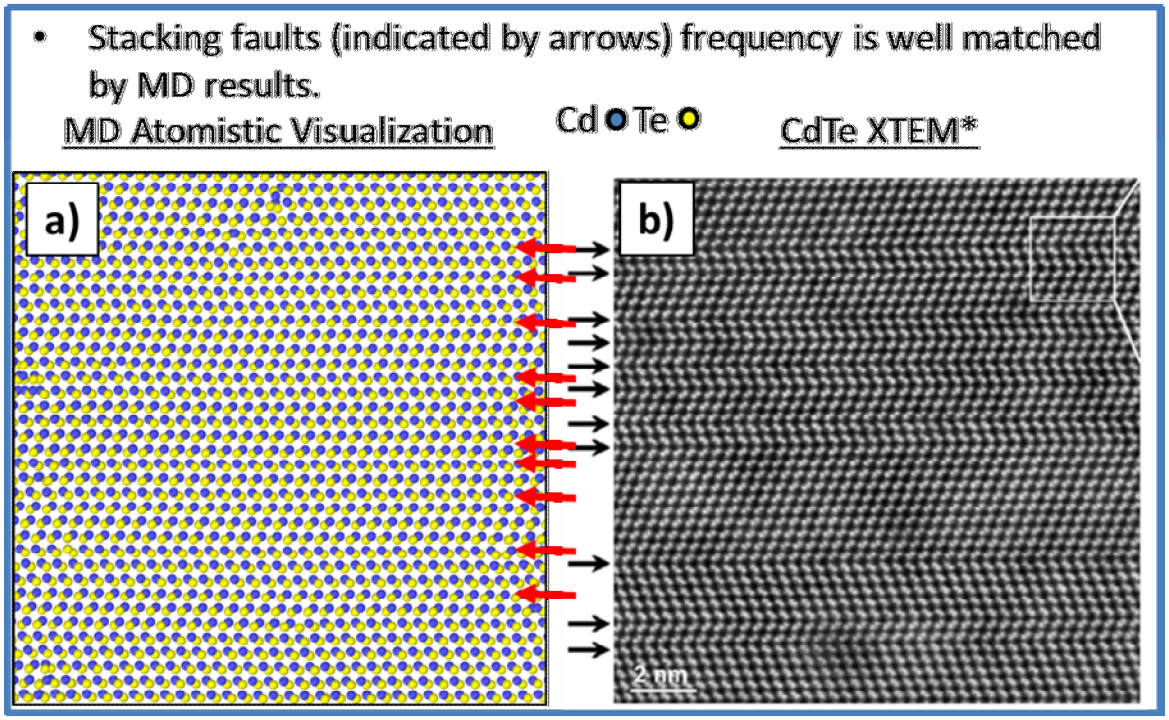


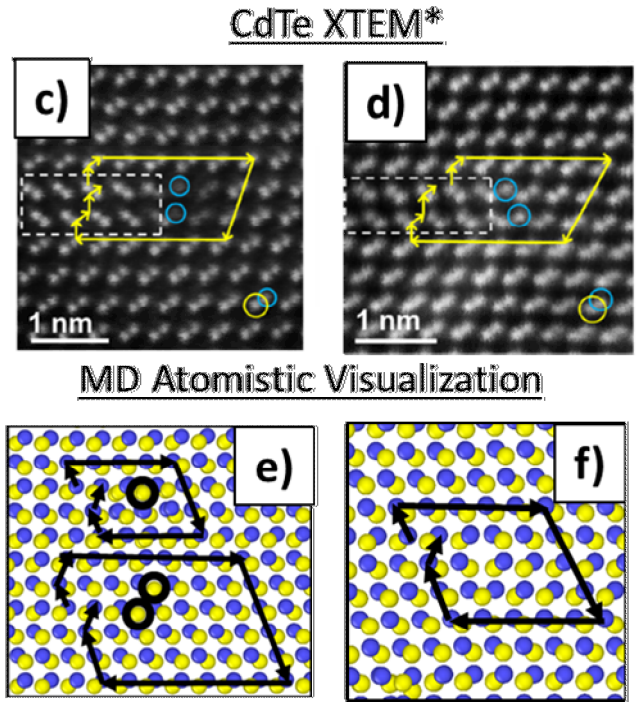
[1]S. Plimpton, *J. Comput. Phys,* pp. 1-19, 1995

[2]X. W. Zhou, et. al., *Phys. Rev. B,* 88, 2013

Predicted Defect Structure Validation

- CdTe epilayers and defect structures observed in MD match well with results published in literature
- Dislocation core structures in literature are found in MD in addition to others that are difficult to observe in experiments



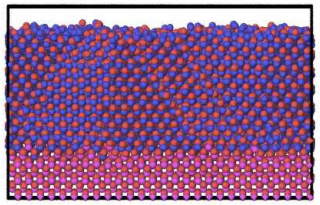


*C. Li, et al, *Ultramicroscopy*, 134, 113-125, 2013

Software Analysis Tools

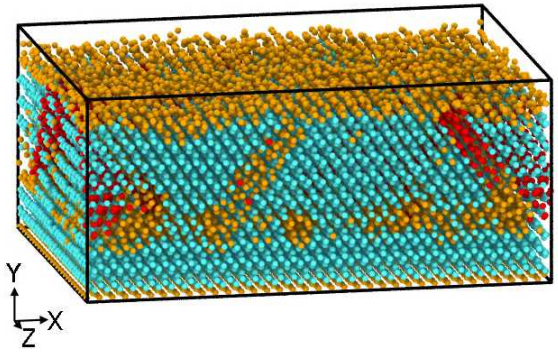
- Visualization & Analysis: OVITO[1]
  - Common neighbor analysis[1]
    -detection of lattice structures and distorted atoms
  - Dislocation extraction algorithm[2]
    -linear defect identification, total length, Burgers vector

Atomistic visualization



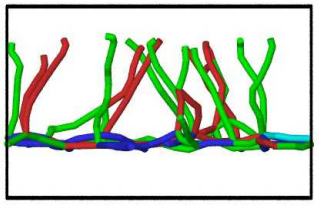
Cd Te S

Lattice structure analysis



zinc blende wurtzite
unmatched

Dislocation analysis



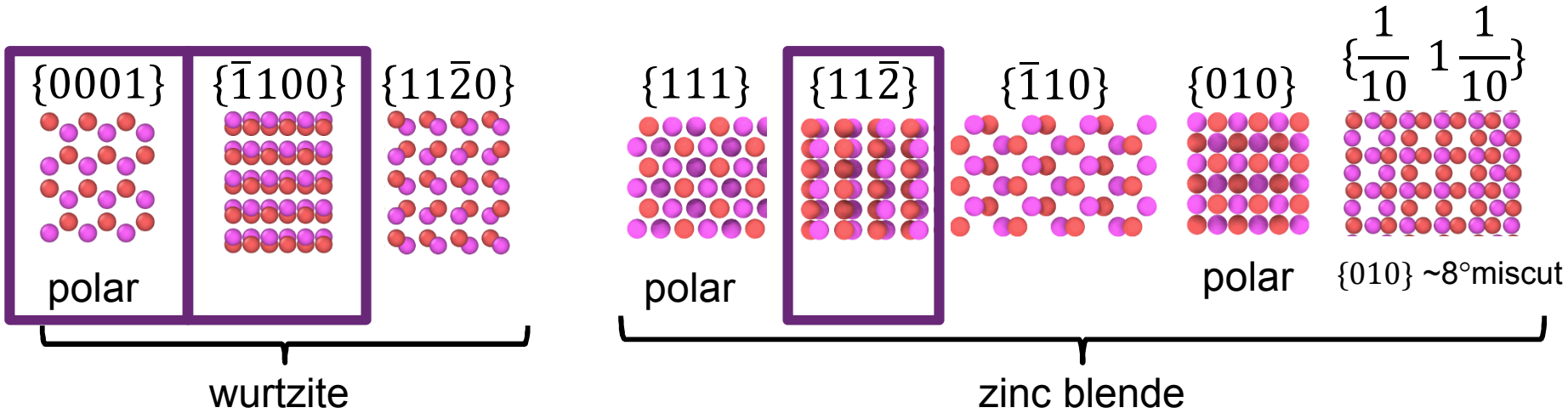
½<110> (full dislocation)
1/6<112> (Shockley partial)
1/6<110> partial
1/3<111> partial
other

[1]A. Stukowski, *Modelling Simil. Mater. Sci. Eng.*, vol. 18, no. 015012, 2012

[2]A. Stukowski, et al, *Modelling Simil. Mater. Sci. Eng.*, vol. 20, no. 085007, p. 16, 2012

Effect of Substrate Orientation

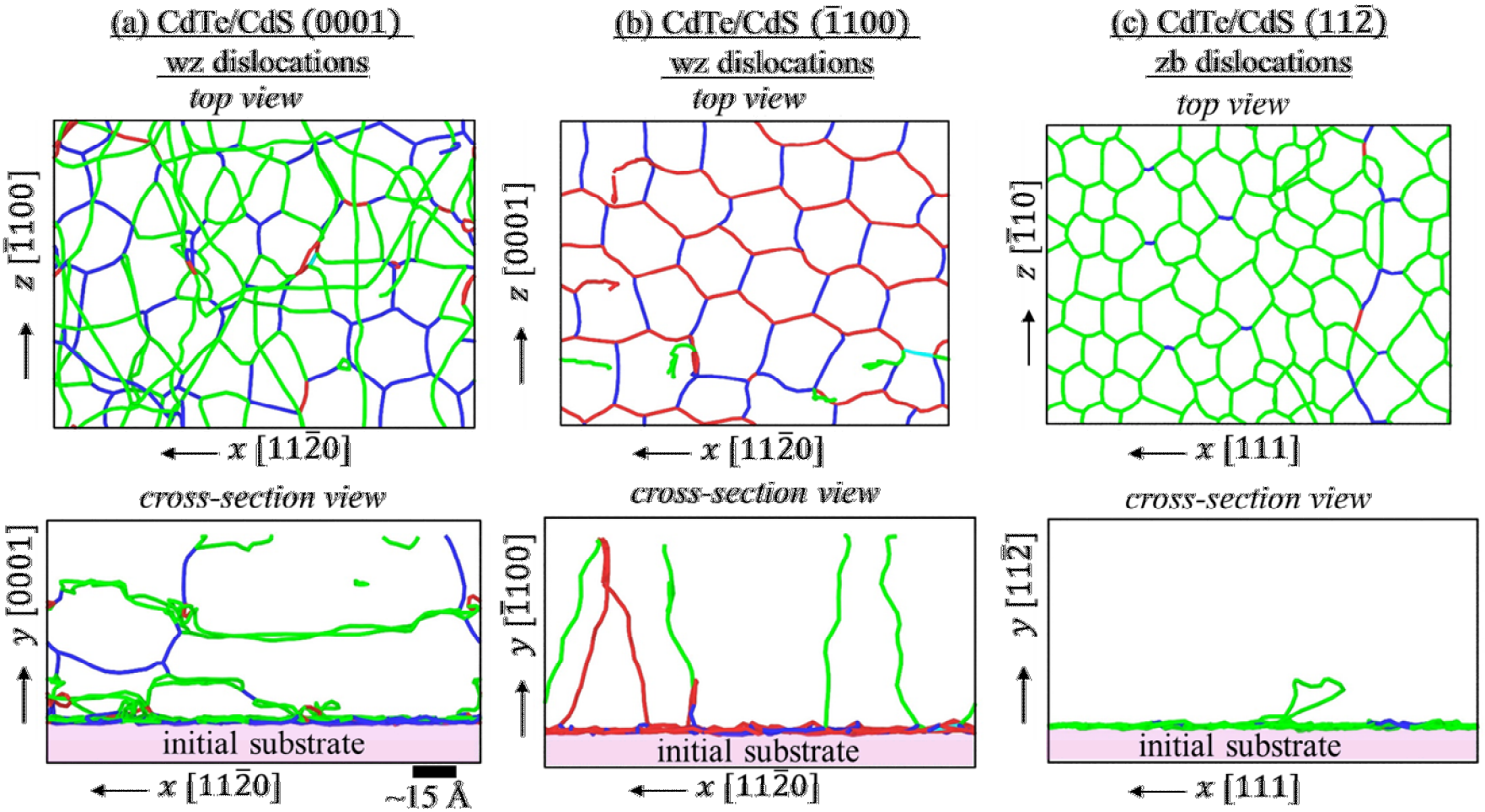
- CdTe films were grown on eight different CdS surfaces:



- Results indicate that fewer epilayer defects are formed when substrate surface:
  - Has a low symmetry
  - It is nonpolar to avoid significant reconstructions
- This data agrees with a DFT study by NREL*

*W. Yin, et al, *Appl. Phys. Lett.* 107, 141607, 2015

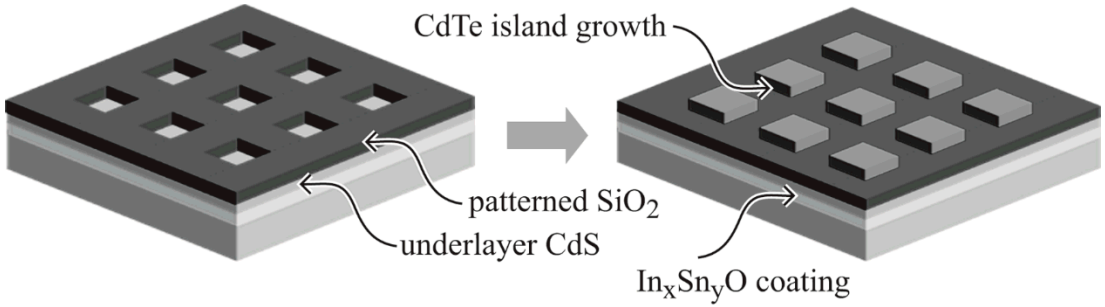
Dislocation Line Distribution

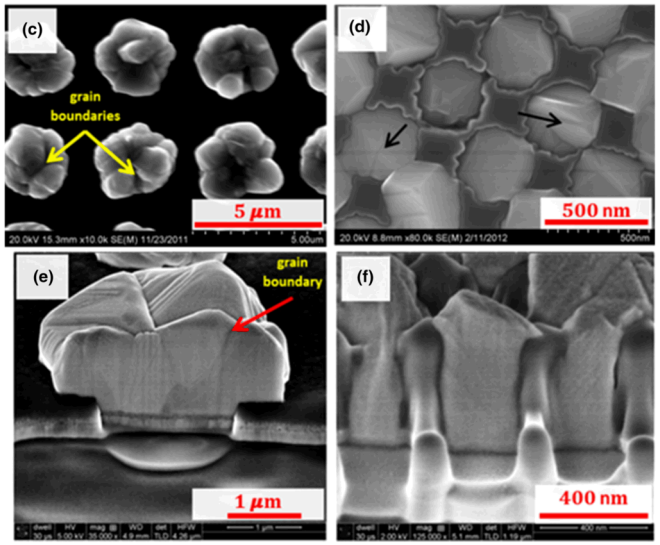


*J. Chavez, et al, *J. Mater. Sci. Res.*, Vol. 5, No. 3, 2016

Island Growth

- Selectively grown island structures can suppress the formation of lattice mismatch defects[1]
  - Three dimensional strain relief
  - Strain partitioning between the film and substrate
- Island structure enables the study of isolated defects





[1]D. Zubia and S. D. Hersee, *J. App. Phys.,* vol. 85, 1999

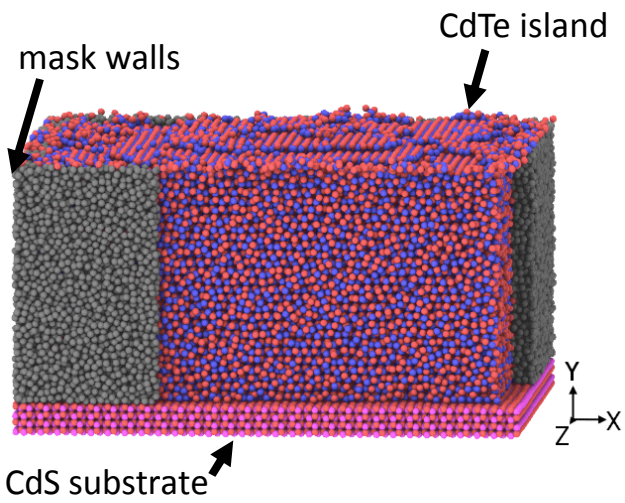
[2]X. Zhou, et al, (2016) *Advanced Characterization Techniques for Thin Film Solar Cells.2nd ed.*

[3]B.Aguirre, et al, *J. Electron. Mater.,* Vol. 43, No. 7, 2014

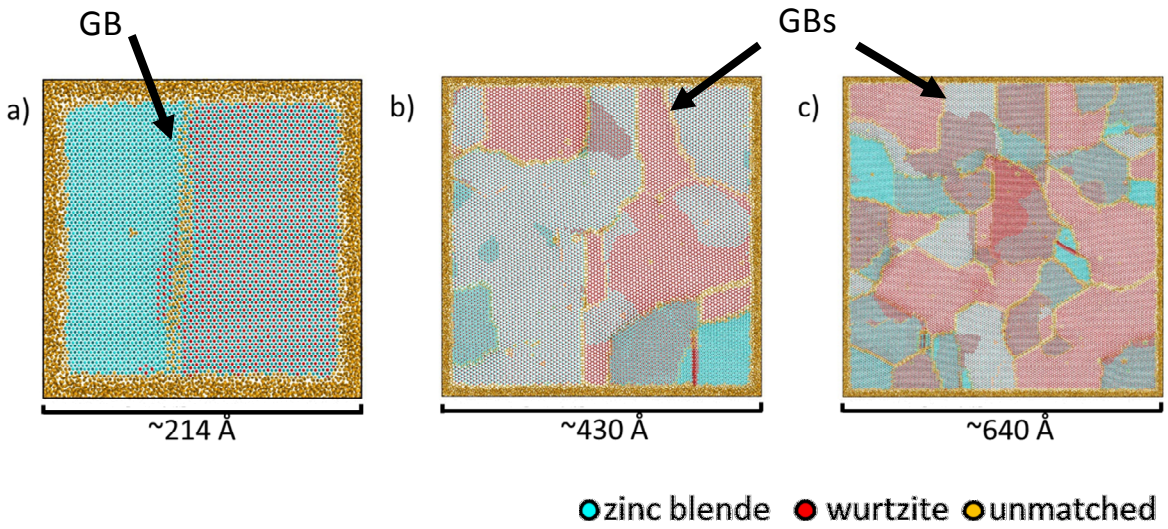
MD Island Growth

- MD growth for three different island sizes
- The microstructure study shows improved film crystallinity for small islands:
  - The number of grains and grain boundaries (GBs) decreased

MD heteroepitaxy island



Top view: island lattice structure maps



*X. Zhou, et al, (2016) *Advanced Characterization Techniques for Thin Film Solar Cells.2nd ed.*

Conclusion

- Atomistic simulation is a valuable tool for
  - Length/time scales beyond DFT
  - Fine resolution of defect structures
  - Mechanical and kinetic properties

- Atomistic simulation is limited by
  - Cost and quality of available potentials
  - Cost of large systems

Recommended Resources

Overview of MD methods

- Cai W., Li J., and Yip S. (2012) Molecular Dynamics. In: Konings R.J.M., (ed.) Comprehensive Nuclear Materials, volume 1, pp. 249-265 Amsterdam: Elsevier.
- Rapaport D.C. (2004) The Art of Molecular Dynamics. 2nd Ed. Cambridge University Press.

MD thin film growth and interatomic potentials

- X. Zhou, et al, *Phys. Rev. B.*, 88, 085309, 2013
- X. Zhou, et al, *Phys. Rev. B.*, 85, 245302, 2012
- D. Ward, et al, *Phys. Rev. B.*, 85, 115206, 2012

Molecular simulators

- LAMMPS, http://lammps.sandia.gov/
- Many more options! (https://en.wikipedia.org/wiki/Comparison_of_software_for_molecular_mechanics_modeling)

Visualization and crystal lattice structure analysis algorithms

- A. Stukowski, *Modell. Simul. Mater. Sci. Eng.*, 18, 015012, 2012 (http://ovito.org/)
- L. Duo, et al, *Sci. China. Phys. Mech. Astron.*, 57, 2177, 2014

High performance computing for new and advanced users: access, tutorials, scholarships, technical support

- https://www.xsede.org/home (USA), http://www.prace-ri.eu/ (EU), https://www.computecanada.ca/ (Canada), http://www.riken.jp/en/ (Japan)