# Advanced modelling of structures and properties of crystalline, nanocrystalline and amorphous nitrogen-based materials

Jiri Houska

Department of Physics, University of West Bohemia, Czech Republic

FACULTY
OF APPLIED SCIENCES
UNIVERSITY
OF WEST BOHEMIA

DEPARTMENT
OF PHYSICS
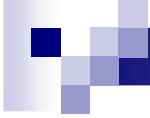
Objectives

- Review usefulness (range of phenomena captured) of various simulation techniques
  - different levels of theory
  - different simulation protocols used

- Show examples for different classes of novel materials
  - crystalline
 - nanocrystalline
  - amorphous
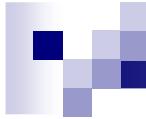
Outline

	DFT (Ab-initio)	Empirical potentials
Properties		
Liquid-quench		
Atom by atom dep.		

Outline

	DFT (Ab-initio)	Empirical potentials
Properties	3. crystalline (Ti/Cr)N+Si,C	
Liquid-quench	1. amorphous (dense) SiBCN	2. nanocomposite TiN+SiN
Atom by atom dep.		4. amorphous (voids) SiNH

1. Amorphous SiBCN

	DFT (Ab-initio)	**Empirical potentials**
Properties	3. crystalline (Ti/Cr)N+Si,C	
Liquid-quench	1. amorphous (dense) SiBCN	2. nanocomposite TiN+SiN
Atom by atom dep.		4. amorphous (voids) SiNH

Motivation (a-SiBCN)

- ## Superior high temperature behavior
  - amorphous structure stable up to a 1700 °C limit
  - extremely high oxidation resistance in air above 1500 °C

- ## Stable functional properties
  - high hardness (up to 35 GPa)
  - transparency ($k_{550nm} = 2 \times 10^{-4}$)
  - low thermal cond. (1.3 $Wm^{-1}K^{-1}$)
  - low compressive stress (1 GPa)

- ## Applications for high T
  - protective coatings
  - sensor components
  - microelectronics
  - fibres for composites

- ## See also
  - A1-2-7 (P.Zeman, Tuesday 15:30, Sunrise)
 - AP-3 (P.Steidl, Thursday poster)
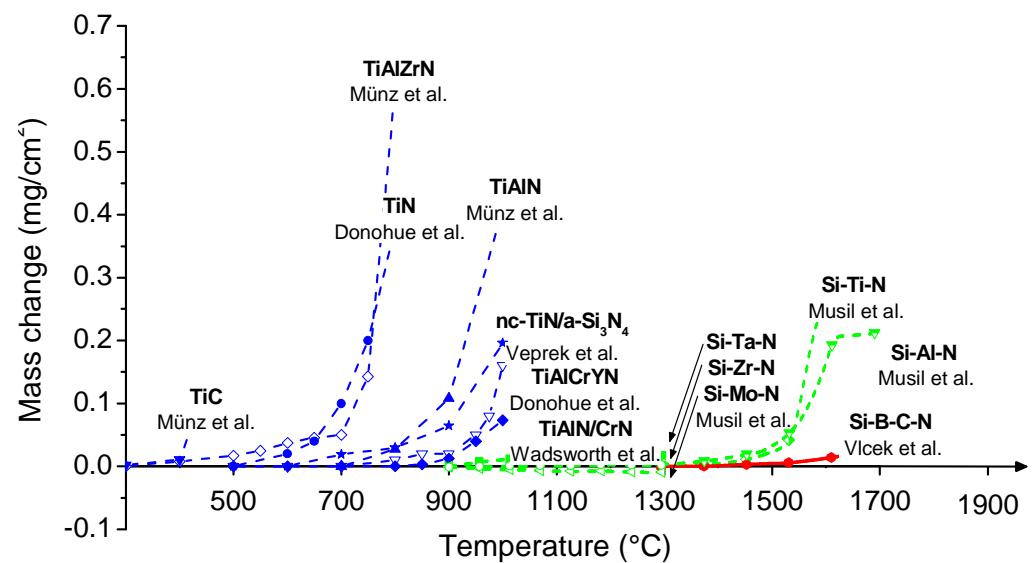
Methodology needed (a-SiBCN)

- **Energy ($\Rightarrow$ forces for molecular dynamics)**
  - <u>DFT</u>: implemented in the CPMD code
  - <u>atom cores and inner electron shells</u>: Goedecker-type pseudopotentials
  - <u>valence electrons wavefunction</u>: Kohn-Sham (Schrödinger-like) equations

- **Molecular-dynamics <u>simulation protocol</u> in order to predict material structure**
  - Liquid-quench algorithm captures material formation conditions arising from rapid cooling of the localized melt around sites of energetic ion impact
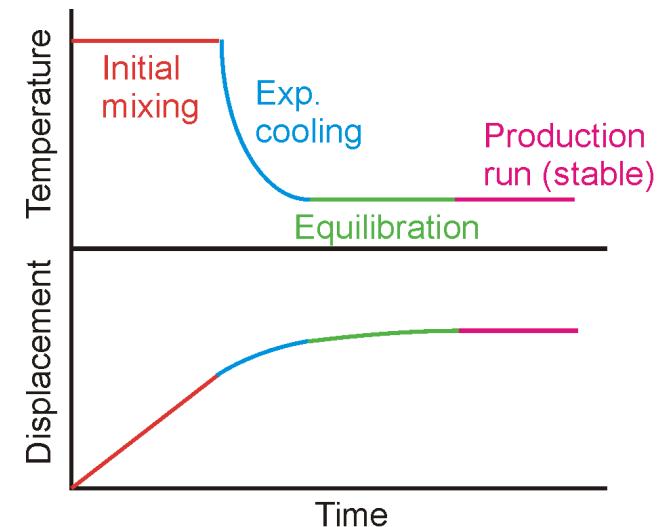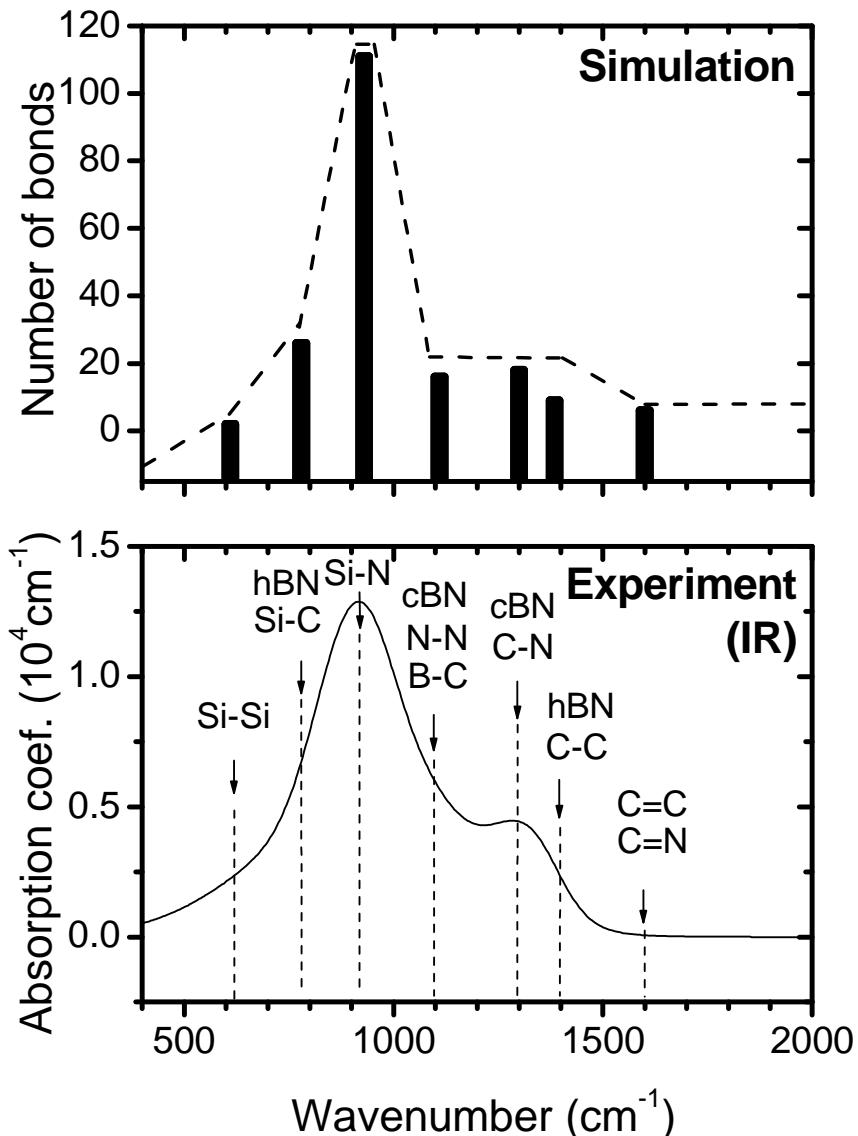
Bonding statistics of Si-B-C-N materials: experimental verification

Composition $Si_{32}B_8C_6N_{54}$ (Ar, H, O neglected)

- Example of hard, transparent, thermally stable composition

- Quantitative agreement with experiment
  (no oscillator strengths, single BN bonds in both c-BN and h-BN peaks)

[J. Houska et al., J. Vac. Sci. Technol. A 25, 1411 (2007)]
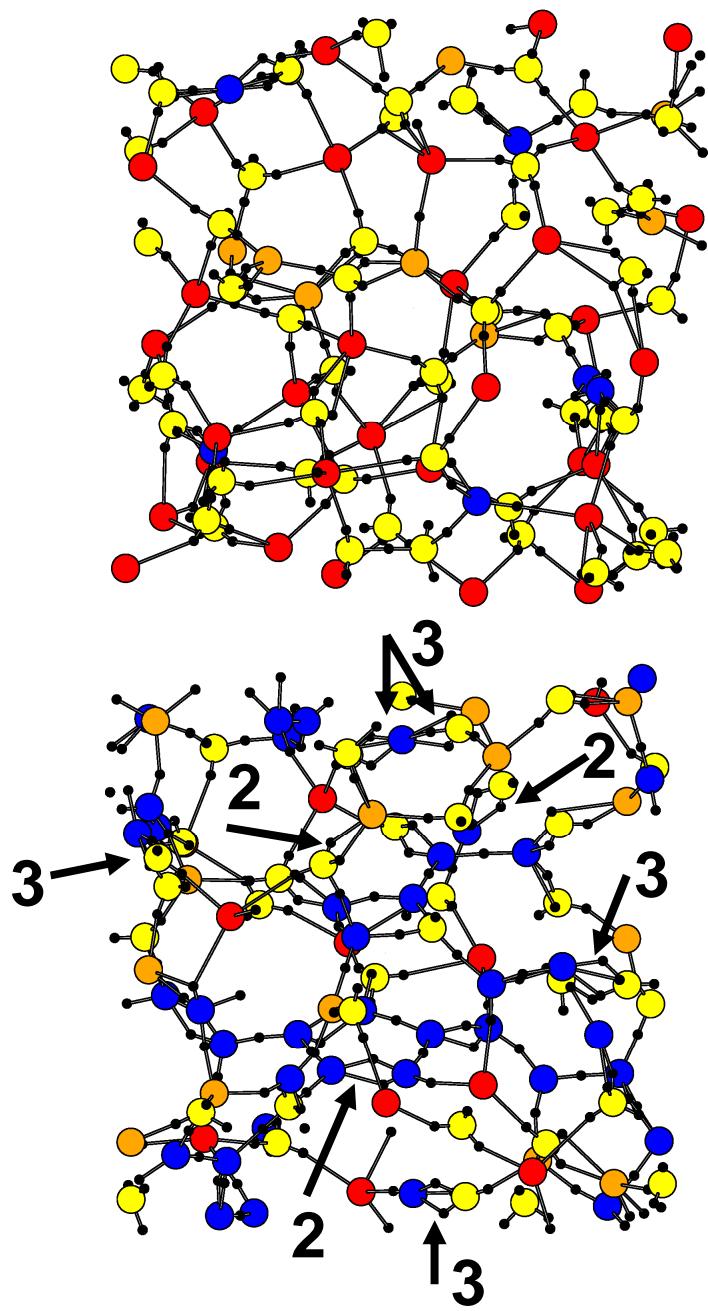
Bonding statistics of Si-B-C-N materials: effect of composition

Si: ●, B: ●, C: ●, N: ●,
2 valence electrons: ●

- $Si_{32}B_8C_6N_{54}$
  Single Si-N bonds
  $\Rightarrow$ high coordination

- $Si_{11}B_{14}C_{39}N_{36}$
  Double C=N, C=C and B=N, and triple C≡N bonds
  $\Rightarrow$ low coordination
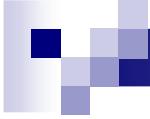
Methodology needed - thermal stability (a-SiBCN)

1) Temperature-dependence of formation of N_2 molecules

2) Temperature dependence of bond lifetimes

3) Bonding statistics (using known relative stability of various bond types)
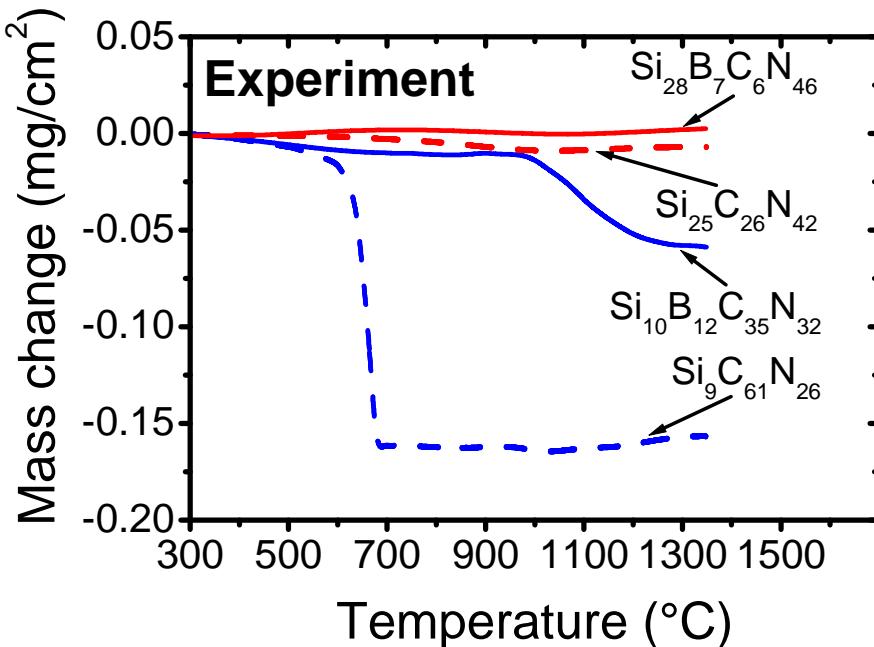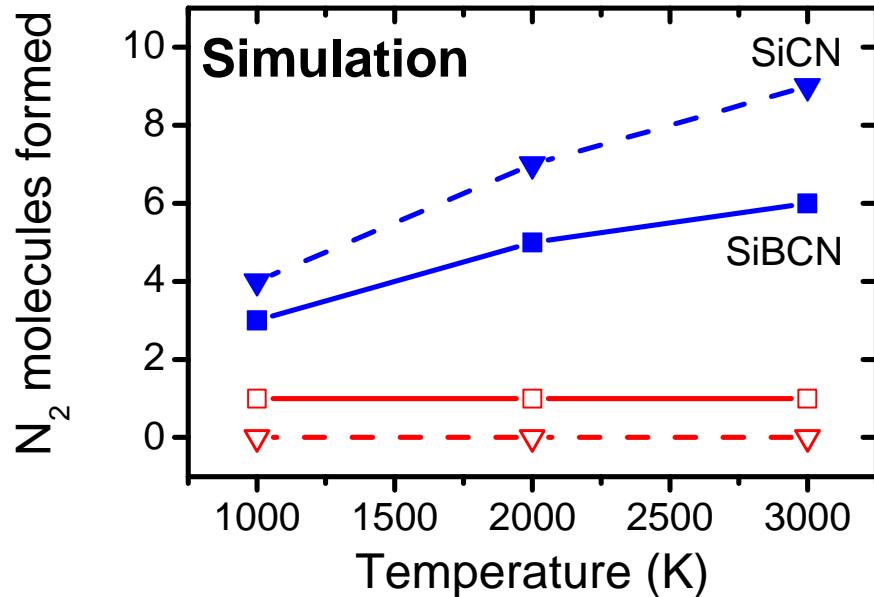
Temperature stability of Si-(B)-C-N materials: from N$_2$ formation

**Simulated compositions Si$_{39}$B$_{14}$C$_{11}$N$_{44}$, Si$_{53}$C$_{11}$N$_{44}$, Si$_{11}$B$_{14}$C$_{39}$N$_{44}$, Si$_{11}$C$_{53}$N$_{44}$**

- Decomposition reactions
  $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$
  and $Si_3N_4 \rightarrow 3Si + 2N_2$
  $\Rightarrow$ mass loss due to formation of N$_2$ molecules

- Less N$_2$ molecules formed at (1) higher **Si/C** ratio and (2) **B** addition

Simulation

| bond type	bond lifetime 1000 K (%)	bond lifetime 2400 K (%)
low Si/C ($Si_{11}B_{14}C_{39}N_{36}$)		
Si-N	46	33
B-N	53	45
C-N	48	40
high Si/C ($Si_{32}B_8C_6N_{54}$)		
Si-N	82	59
B-N	89	70
C-N	96	68
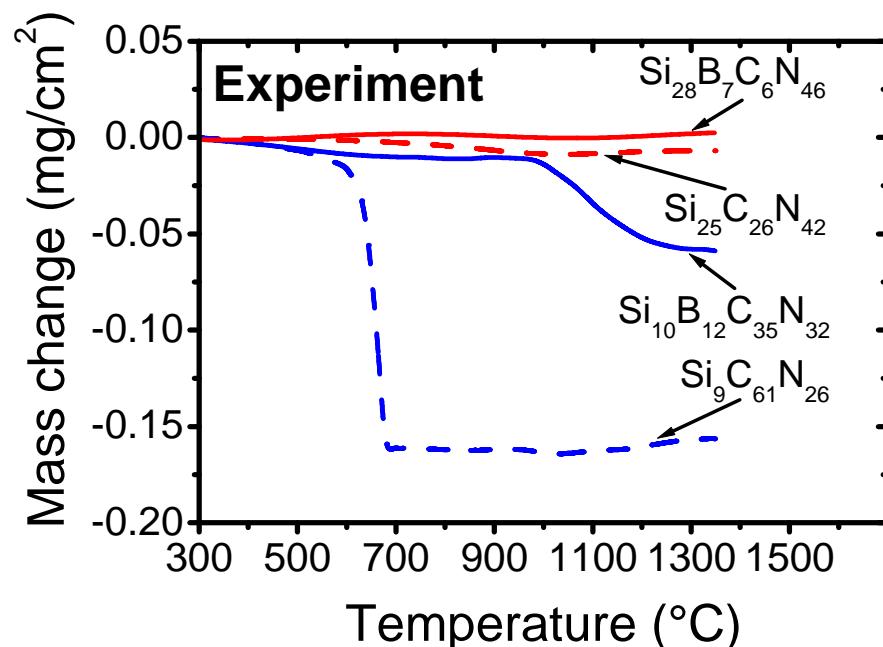
Temperature stability of Si-(B)-C-N materials: from bond lifetimes

Simulated compositions $Si_{32}B_8C_6N_{54}$, $Si_{11}B_{14}C_{39}N_{36}$

- Higher bond lifetimes in compositions with higher **Si/C** $\Rightarrow$ more stable network $\Rightarrow$ limited diffusion $\Rightarrow$ decomposition reactions shifted to higher T $\Rightarrow$ improved thermal stability


Experiment — Mass change (mg/cm^2) vs Temperature (°C): $Si_{28}B_7C_6N_{46}$, $Si_{25}C_{26}N_{42}$, $Si_{10}B_{12}C_{35}N_{32}$, $Si_9C_{61}N_{26}$

[J. Houska et al., Europhys. Lett. 76, 512 (2006)]
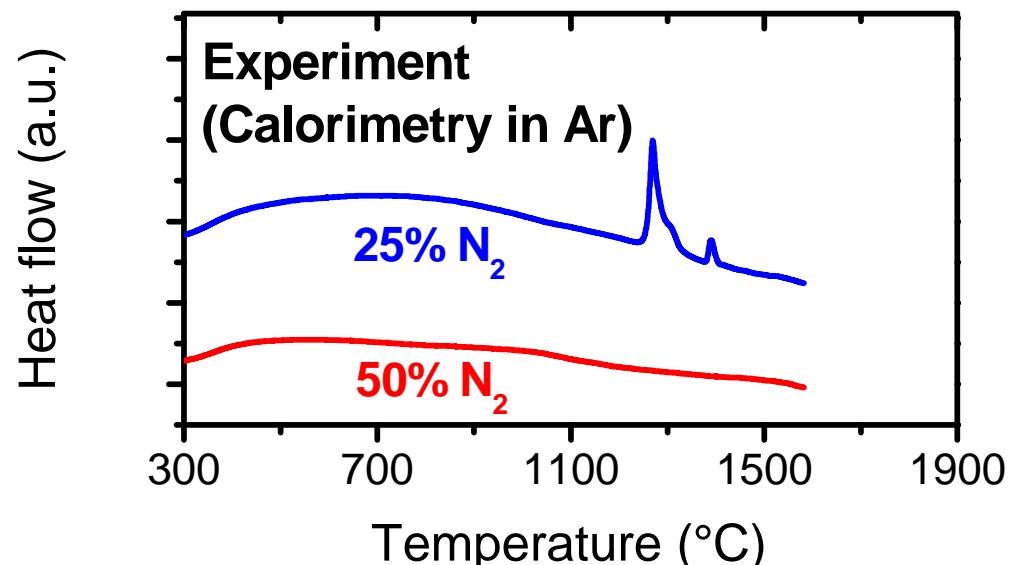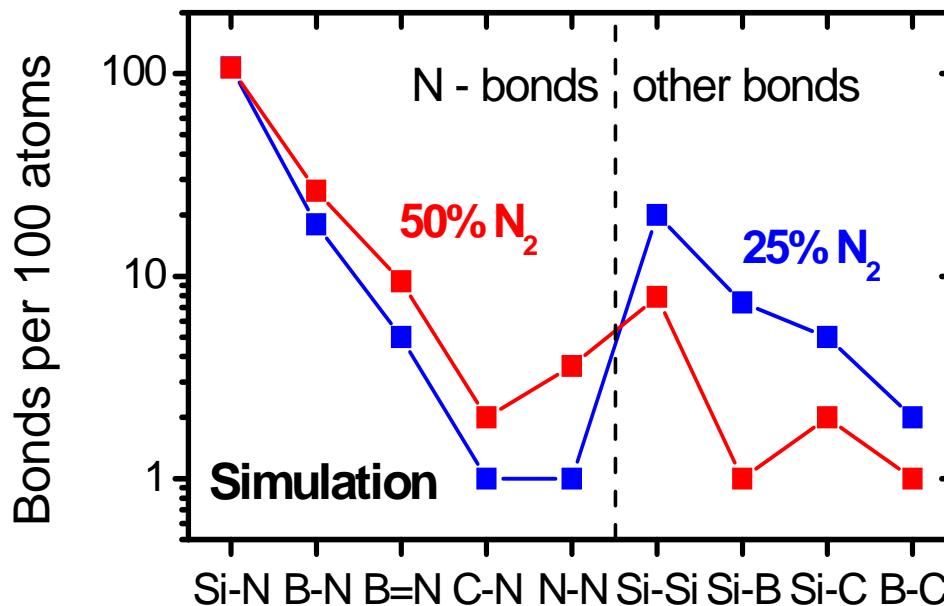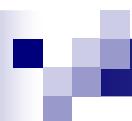
Temperature stability of Si-B-C-N materials: <u>**from bonding statistics**</u>

Simulated compositions

$Si_{32}B_{12}C_3N_{53}$ prepared in 50% N_2+50% Ar, N/(Si+B+C) = <u>1.13</u>

$Si_{42}B_{11}C_2N_{45}$ prepared in 25% N_2+75% Ar, N/(Si+B+C) = <u>0.82</u>

- A low abundance of less thermally stable Si-Si bonds at **N/(Si+B+C) > 1** $\Rightarrow$ maintenance of the amorphous state at higher temperatures

[*J. Capek et al., Surf. Coat. Technol. 203, 466 (2008)*]
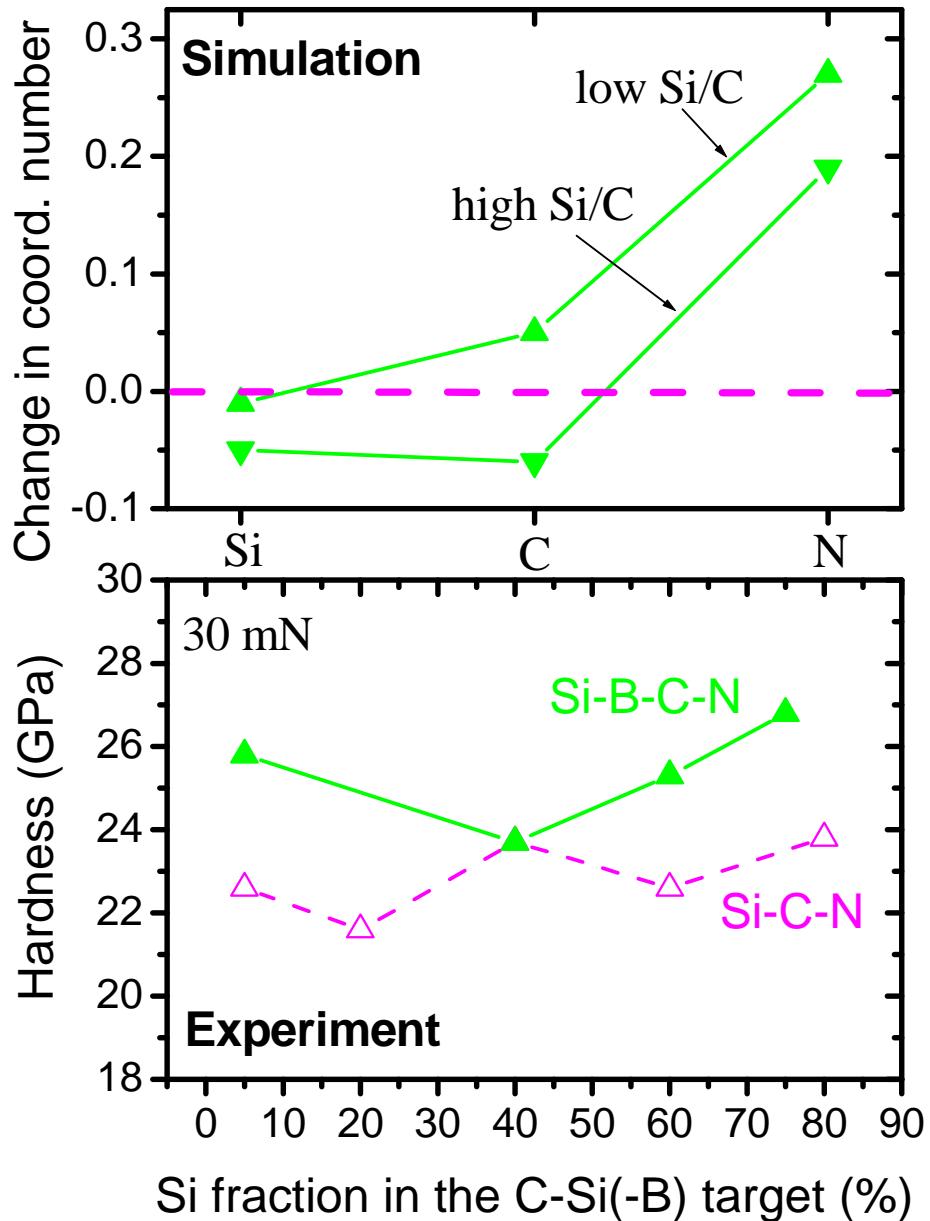
Role of B - comparing of Si-C-N and Si-B-C-N (experiment and molecular dynamics)

- Preferential bonding of B to N ⇒ **converting of some N lonepairs to bonding electrons** ⇒ higher N coordination
- Improved mechanical properties and thermal stability

2. Nanocrystalline TiSiN

|	DFT (Ab-initio)	Empirical potentials
Properties	3. crystalline (Ti/Cr)N+Si,C	
Liquid-quench	1. amorphous (dense) SiBCN	2. nanocomposite TiN+SiN
Atom by atom dep.		4. amorphous (voids) SiNH

Motivation (nc-TiSiN)
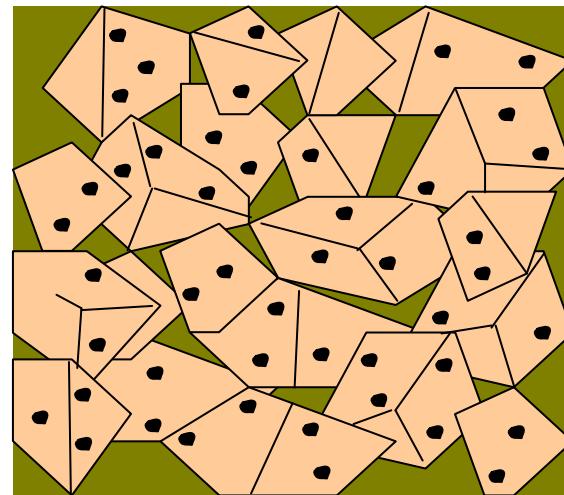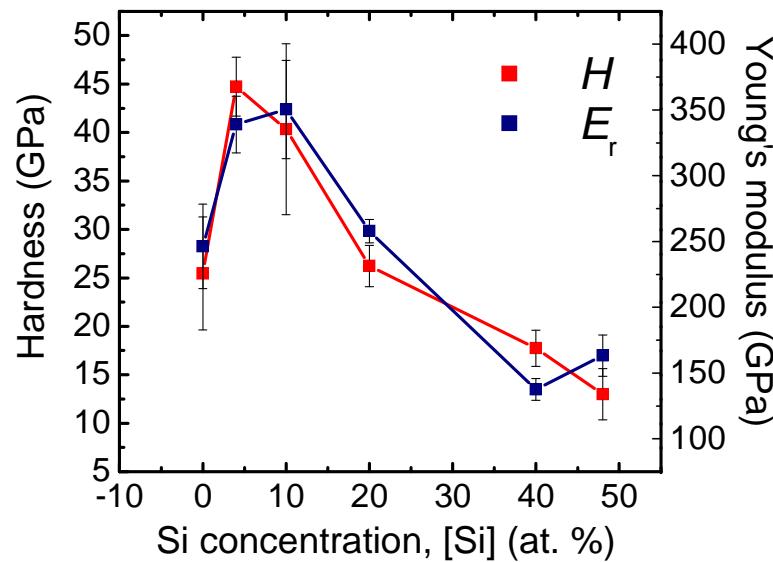
- Enhanced hardness of TiSi(C)N at [Si] = 5-10 % ⇔ nanopaticles (with impurities) in an amorphous matrix
- Predict crystal size distribution, amorphous phase thickness, maximal impurities concentration, etc.

Methodology needed (nc-TiSiN)

- ## Empirical <u>interaction potential</u>
  - fitted using DFT (ab-initio) energies calculated for various fcc-Ti(Si)N configurations
  - DL POLY code

○ Ti

● Si

○ N
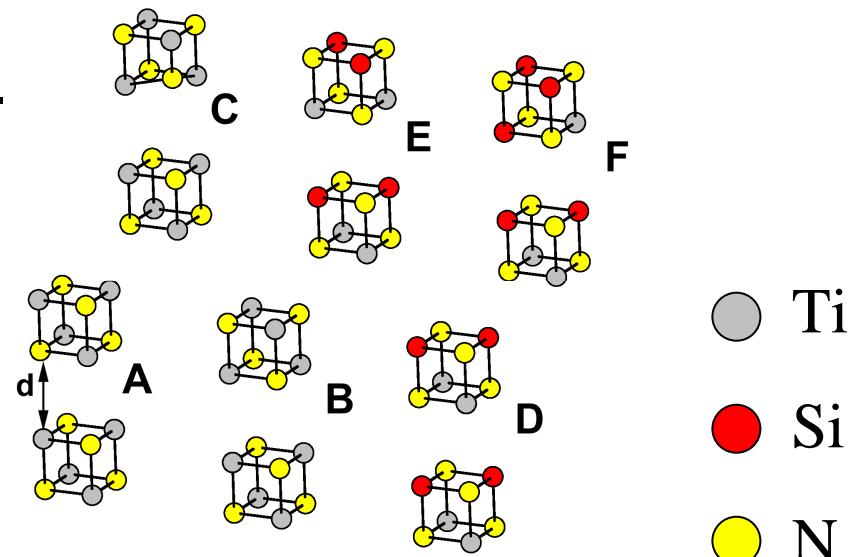
- ## Molecular-dynamics <u>simulation protocol</u> in order to predict preferred nanocrystalline structures
 - liquid-quench as in the a-SiBCN case:
    - → amorphous structures independent of the cooling time after $\sim 10^{-12}$ s
    - → nanocryst. structures independent of the cooling time after $\sim 10^{-9}$ s
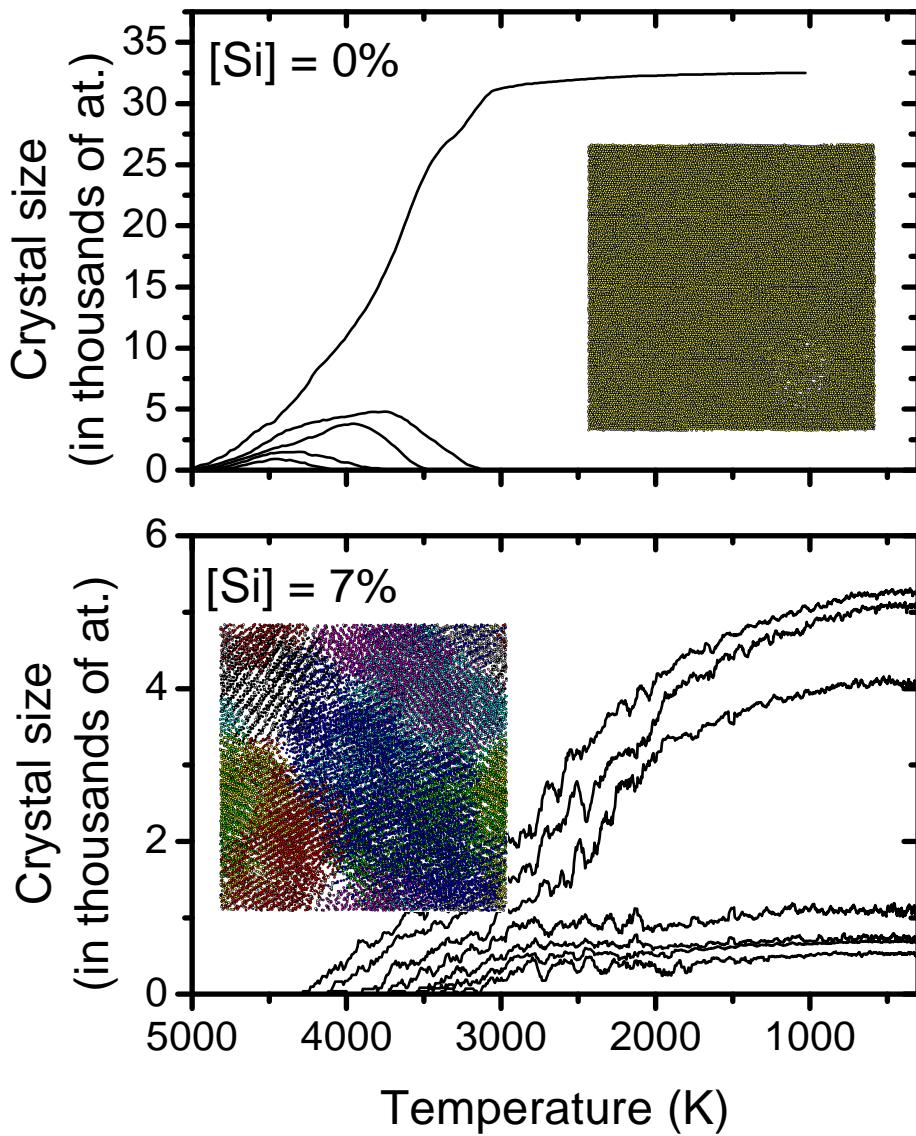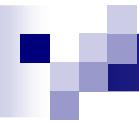
**Searching for preferred structure by exponential cool down:**

dependence on [Si]

- **0% Si**: monocrystal
  (up to 8 crystals; 1 survived)
- **7% Si**: nanocomposite
 (up to 10 crystals; 8 survived)
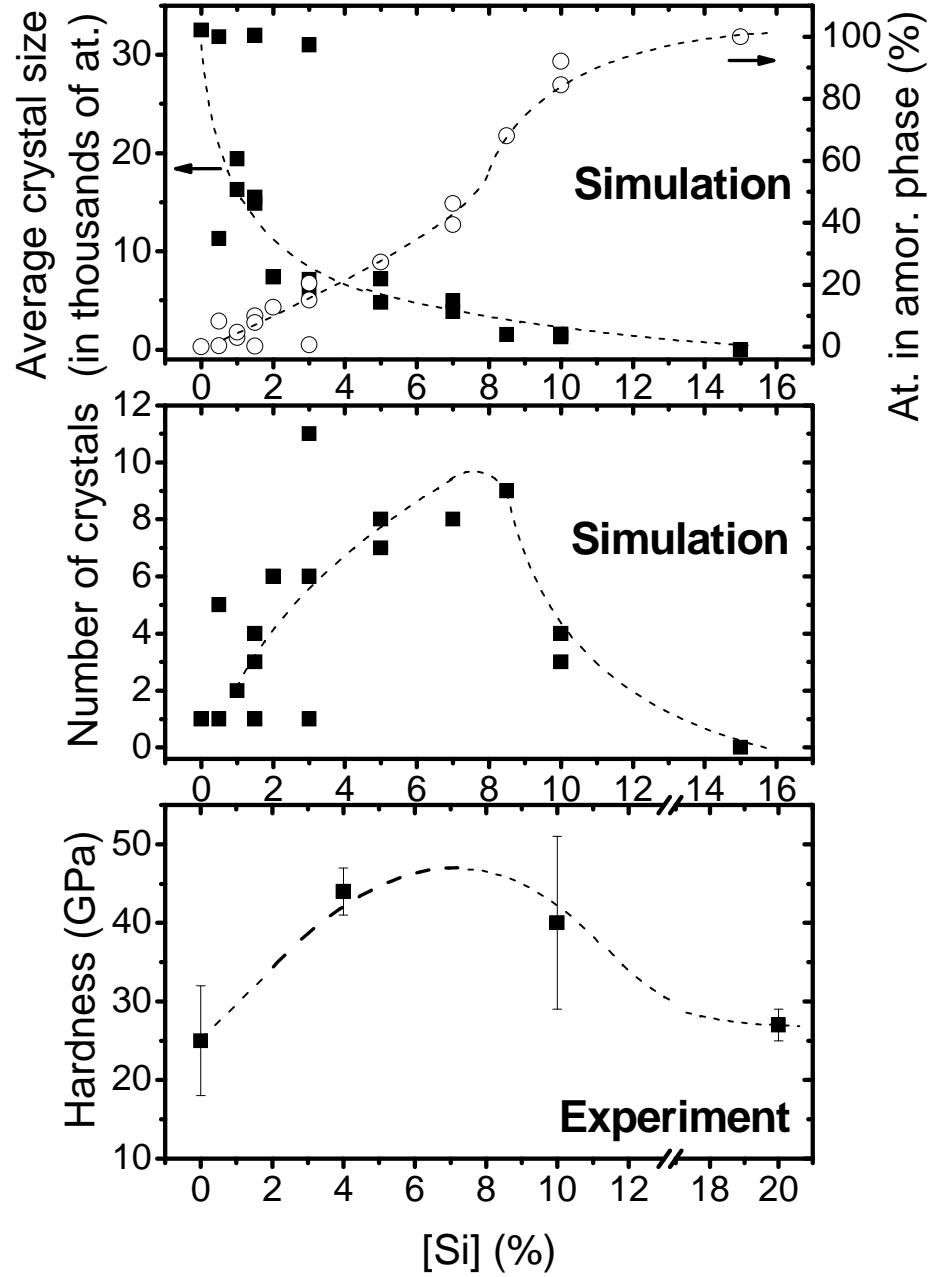
Structures formed: dependence on [Si]

- [Si] ≤3%: monocrystals

  [Si] <8.5%: increasing number of crystals, *N*

  highest N: crystals of 4-7000 at. (**3-6 nm**)

  [Si] >8.5%: decreasing N

  [Si] ≥15%: amorphous

- Experiment: e.g. ≤**4-5nm** in S. Veprek *et al.*, *Nanostruct. Mater. 10, 679 (1998)*
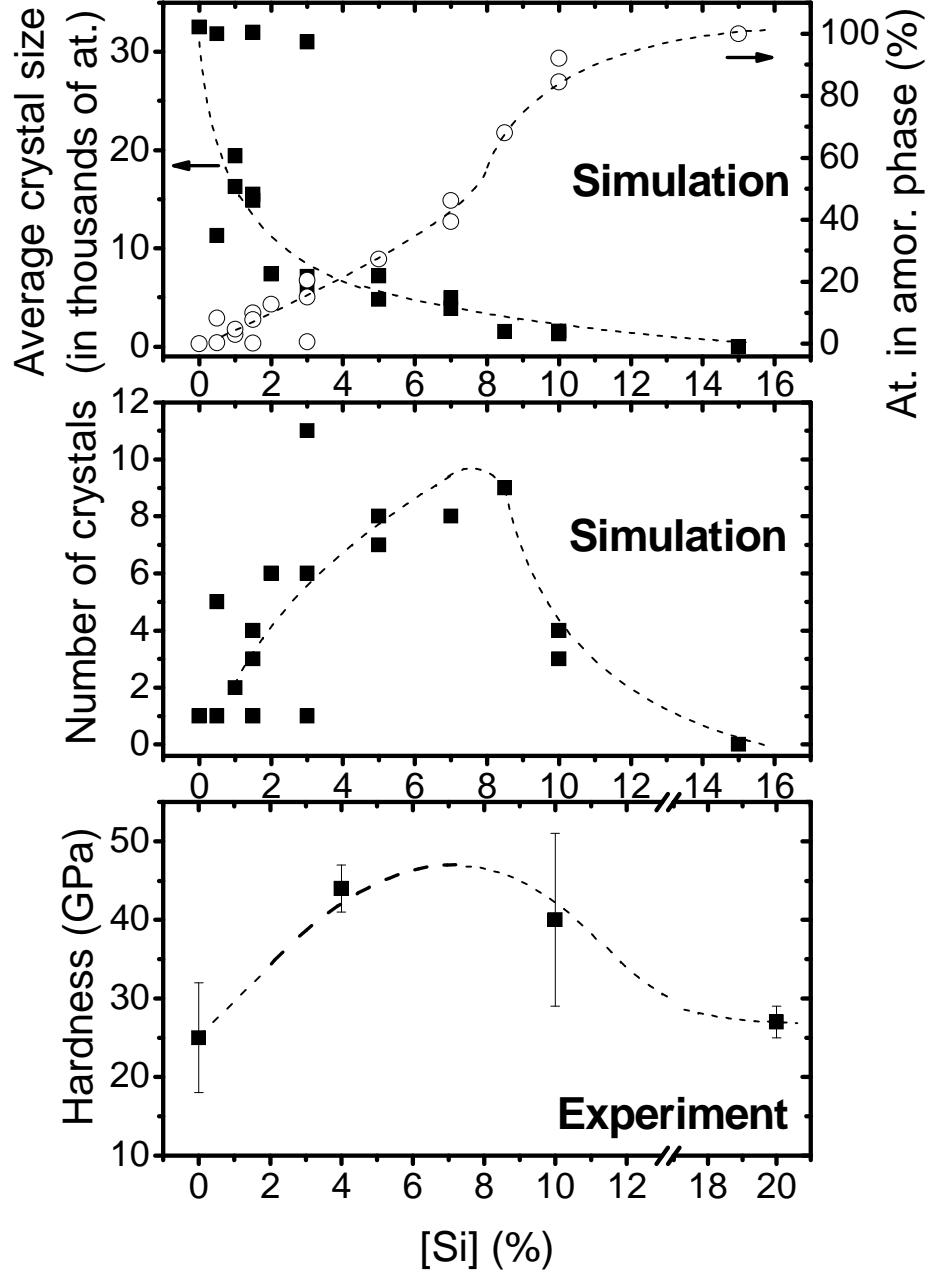
Structures formed: dependence on [Si]

- **[Si]** $\leq$**3%**: monocrystals

  [Si] <8.5%: increasing number of crystals, *N*

  highest N: crystals of 4-7000 at. (3-6 nm)

  [Si] >8.5%: decreasing N

  [Si] $\geq$**15%**: amorphous

- Experiment: e.g. **8.9%** and **15.5%** in *J.H. Jeon et al., Surf. Coat. Technol. 188, 415 (2004)*
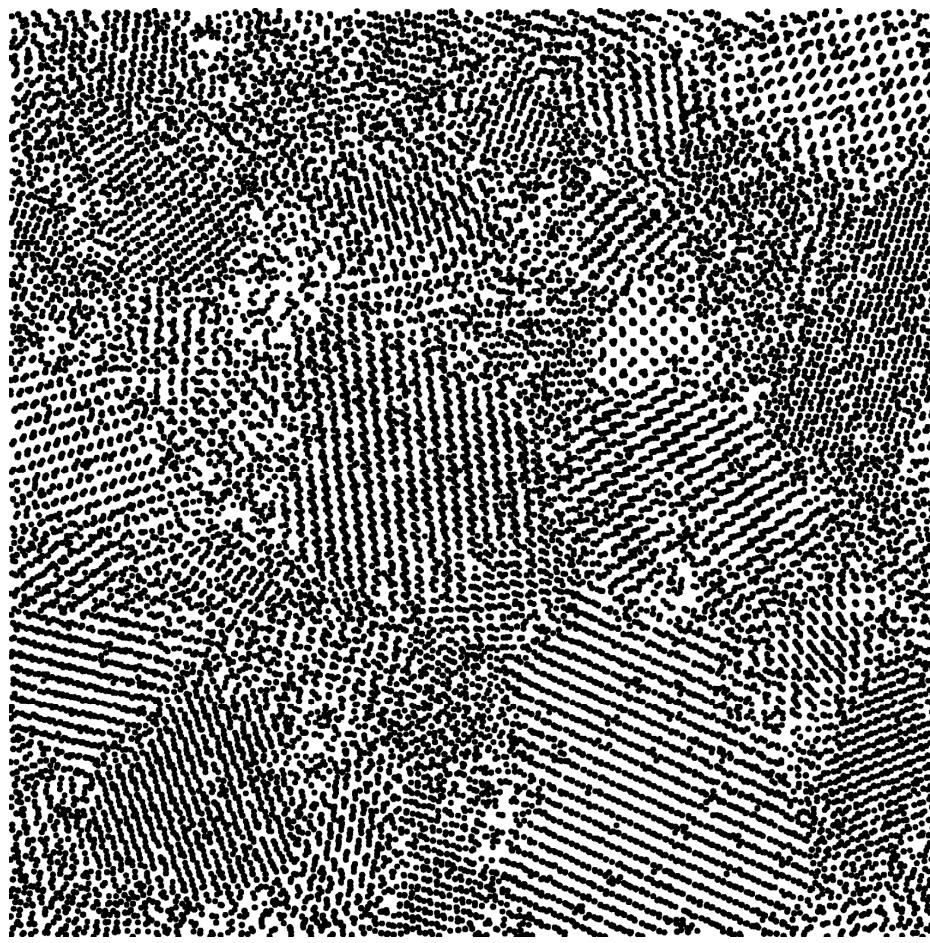
Fine nanostructures formed at [Si] ~ 7%:

thin slice of a final structure

- Crystals of various orientations
- Occasionally not separated by the amorphous phase, but directly touch each other

14 nm (262.000 atoms)

[J. Houska et al., Surf. Coat. Technol. 203, 3348 (2009)]
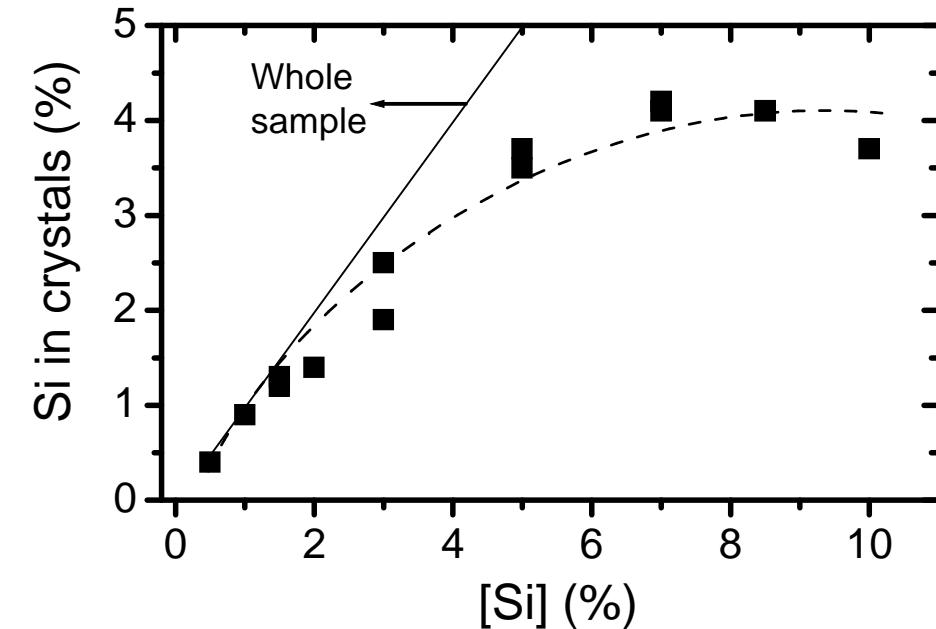
Si defects in crystals

- Up to **4%** Si trapped in TiN crystals ($\Rightarrow Ti_{0.92}Si_{0.08}N$)

- Experiment (at low mobility of atoms - low T, E_{ion}): e.g. **4.5%** in *A. Flink et al., J. Mat. Res. 24, 2483 (2009)*
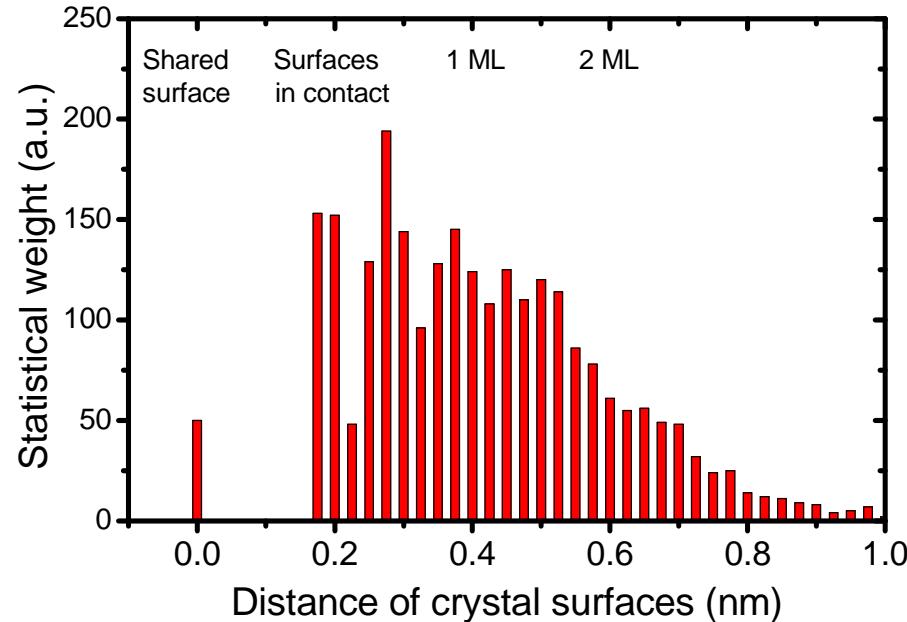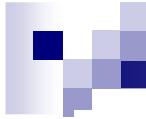
Thickness of the amorphous phase

- Distribution of distances to the nearest surface atom of another crystal
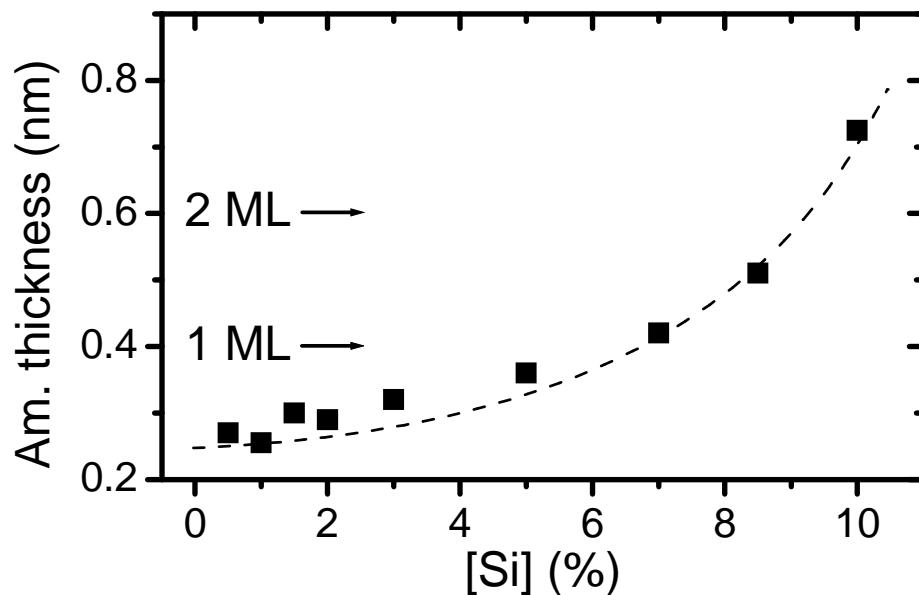
- Weighted average of the distances: **1 monolayer at [Si] = 7%**

3. Characteristics of fcc-MSiCN

	DFT (Ab-initio)	Empirical potentials
Properties	3. crystalline (Ti/Cr)N+Si,C	
Liquid-quench	1. amorphous (dense) SiBCN	2. nanocomposite TiN+SiN
Atom by atom dep.		4. amorphous (voids) SiNH

Motivation (fcc-MSiCN)

TiN   ## CrN

- high hardness   x   oxidation resistance
- nonmagnetic   x   magnetic
- metallic-like   x   semiconductive
- cubic   x   low-T AFM configuration
   => shear ($\alpha < 90°$)
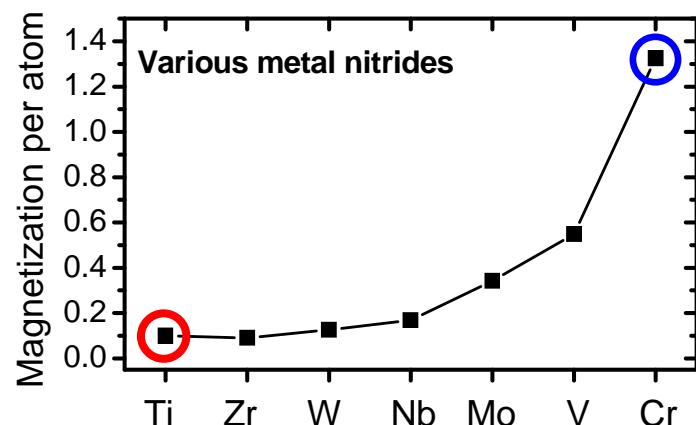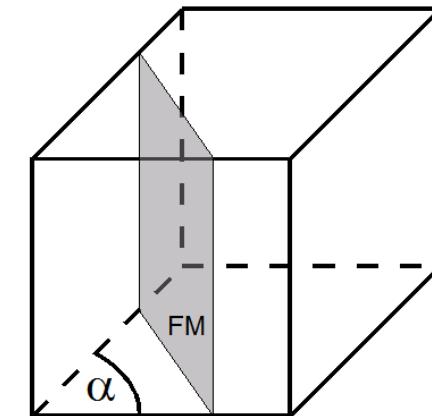
- Phenomena specific for CrN
- Different effect of Si and C in CrN and TiN

Methodology needed (fcc-MSiCN)

- **Electronic structure and energy of a crystal from given composition and deformation applied**

    - DFT: implemented in the PWSCF code
    - atom cores and inner electron shells: Vanderbilt-type pseudopotentials
    - valence electrons wavefunction: Kohn-Sham (Schrödinger-like) equations

- **Material characteristics from the energy-deformation dependencies calculated**

    - B and a_0: by changing of cell volume
    - C_{ij}: by applying volume-conserving shear and strain
    - E,G,ν for polycrystalline material: from C_{ij}
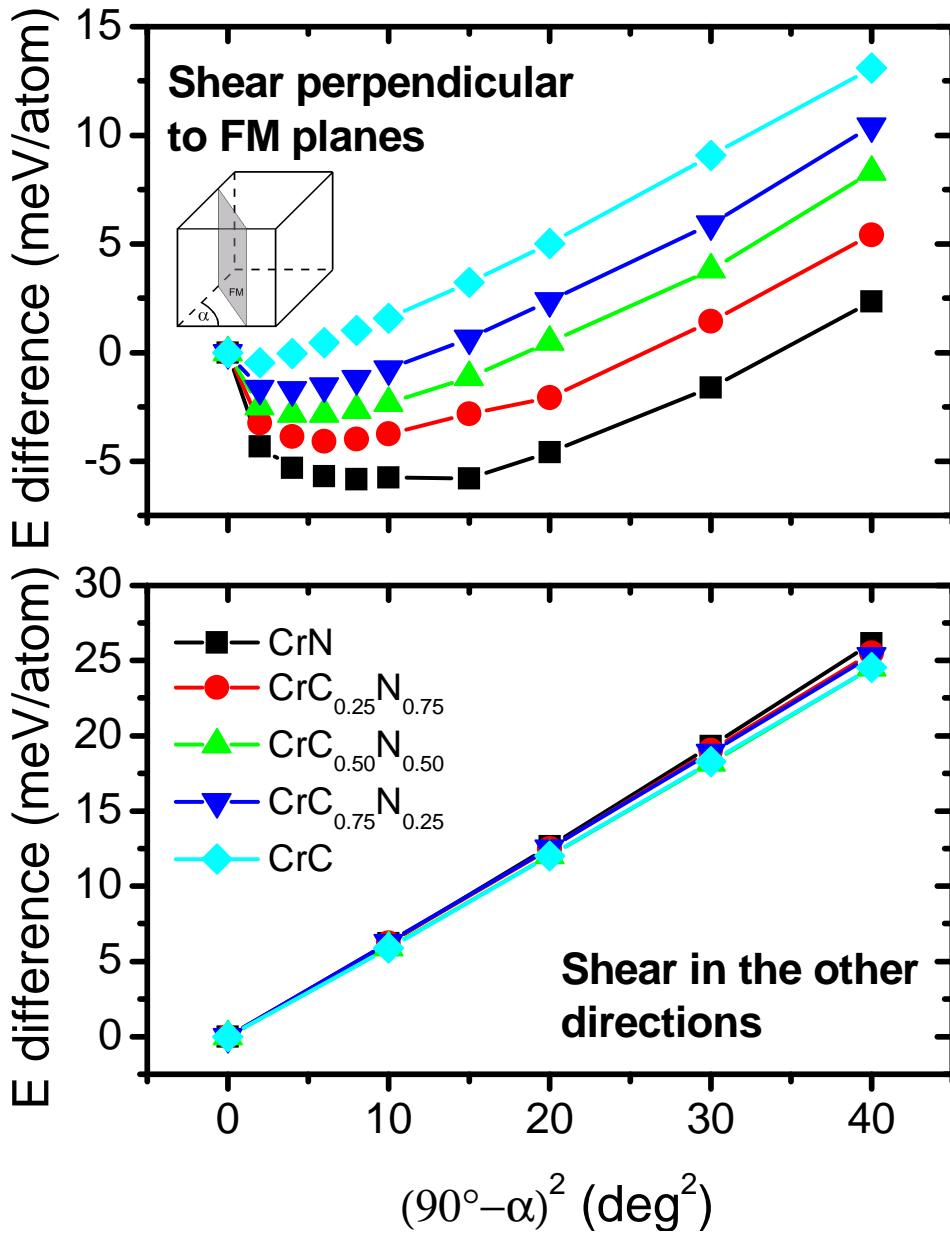
Effect of magnetization on preferred low-T structure (110 FM planes)

- **CrN:** xy shear
- **C or Si addition:**
  (C replaces N, Si replaces Cr)
  lower total mag. $\Rightarrow$ higher cubic preference

Characteristics of pure metal nitrides

Material	Configuration	a_0 (Å)	B (GPa)	G (GPa)	E (GPa)	ν
TiN	Nonmagnetic	4.249	274	191	464	0.22
CrN	Magnetic	4.156	241	153	379	0.24
CrN	Mag., relaxation of at.pos.	4.141	240	151	375	0.24
CrN	Nonmagnetic	4.050	322			

- TiN crosscheck: Agreement with previously calculated data, but large spread of experimental data especially for E

- Low-T spin ordering of CrN $\Rightarrow$ decrease of a_0
  (4.156 → 4.141)

- Lower B of CrN compared to what would result from valence electron density (*magnetization penalty*)

[J. Houska et al., J. Phys.: Condens. Matter (2009)]

Changes of MN characteristics: effect of C incorporation
## effect of Si incorporation

Ti(Si)(C)N

Cr(Si)(C)N
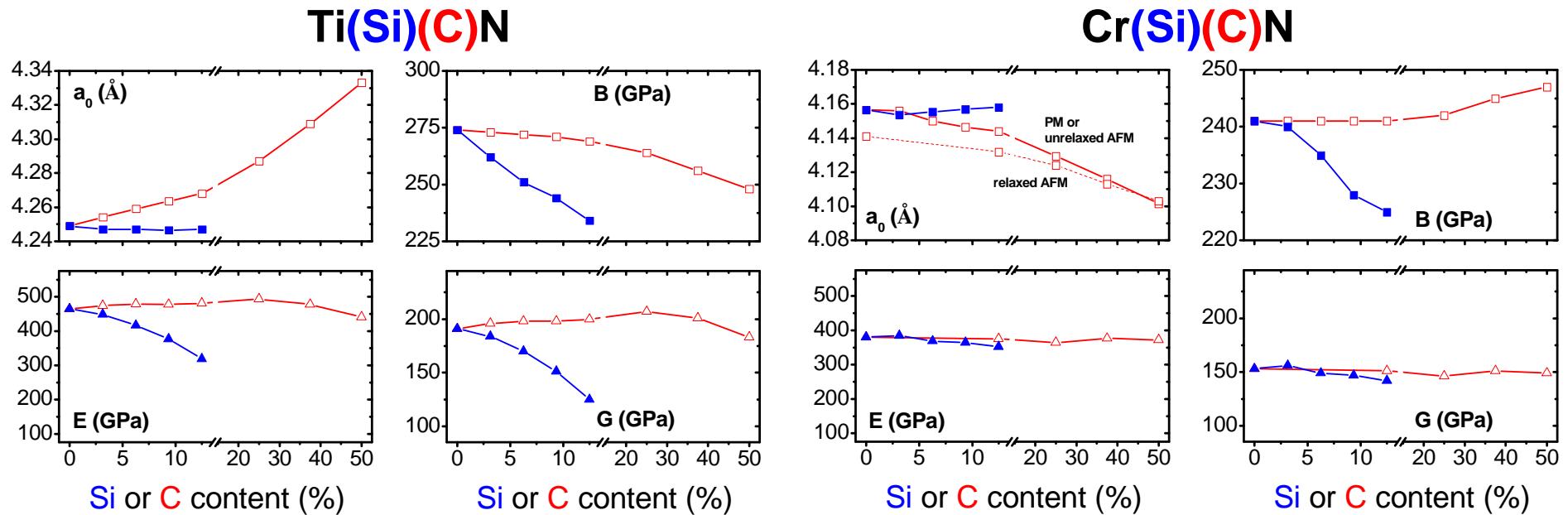
- Decreasing TiN moduli x constant / increasing CrN moduli
  (disappearing "magnetization penalty")

- E,G maxima for TiCN x no extramal behavior for CrCN
  (shear-resistant orbitals filled for all compositions)
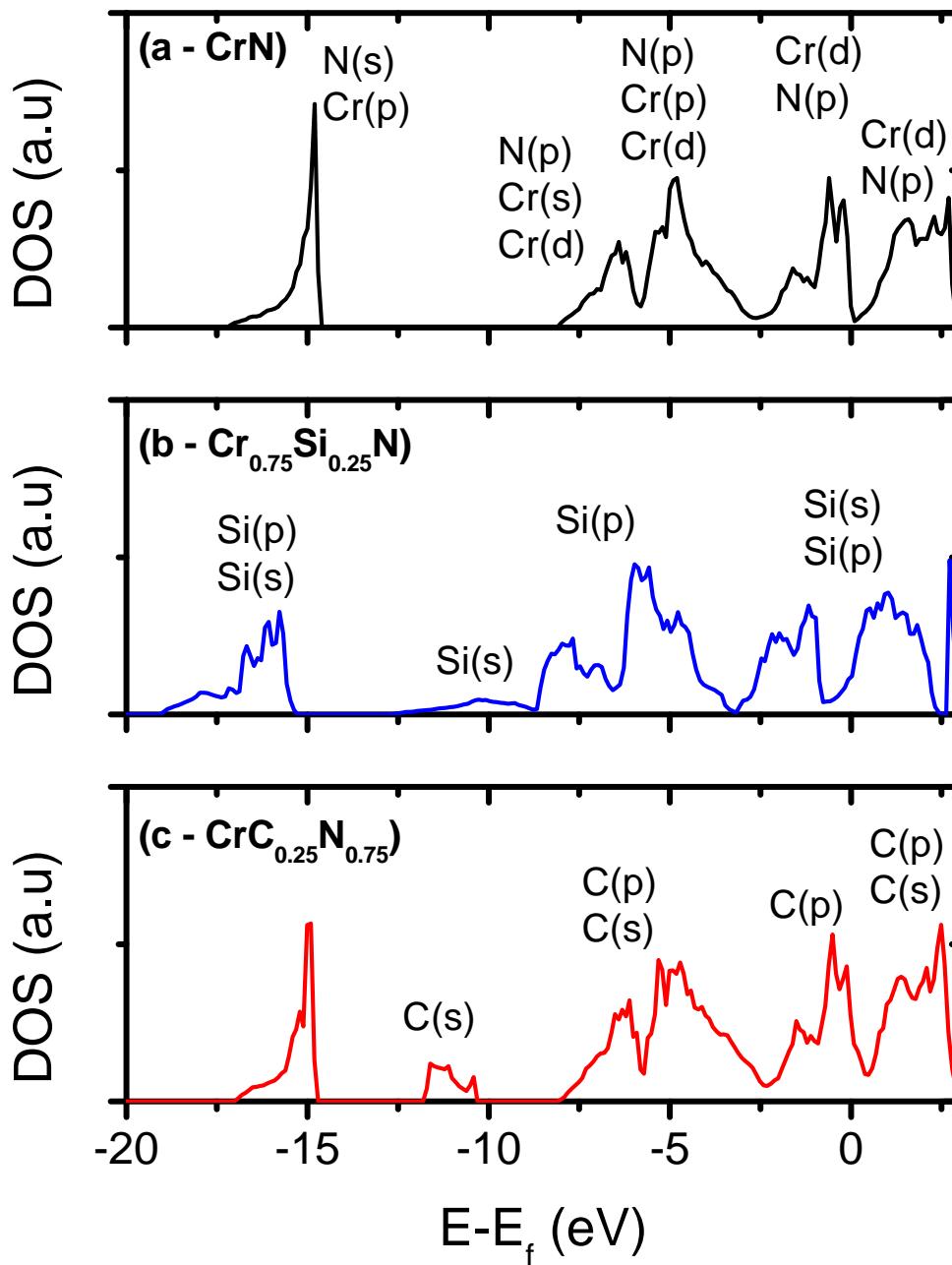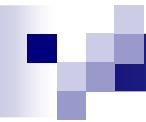
Density of states (DOS) for AFM CrN

- Narrow (pseudo)gap at the Fermi energy (E_f) for pure CrN
- Si and C addition
  - $\Rightarrow$ shift of the gap position
  - $\Rightarrow$ the gap itself becomes less pronounced

4. Voids-containing SiNH

	DFT (Ab-initio)	Empirical potentials
Properties	3. crystalline (Ti/Cr)N+Si,C	
Liquid-quench	1. amorphous (dense) SiBCN	2. nanocomposite TiN+SiN
Atom by atom dep.		4. amorphous (voids) SiNH

Motivation (a-SiNH)

- **SiNH for single-material inhomogeneous optical filters** (controlled fraction of voids $\Rightarrow$ controlled n)

- **Reproduce PECVD in a mixture of SiH$_4$/N$_2$** (main precursors: SiH$_{x \leq 3}$ and N radicals)
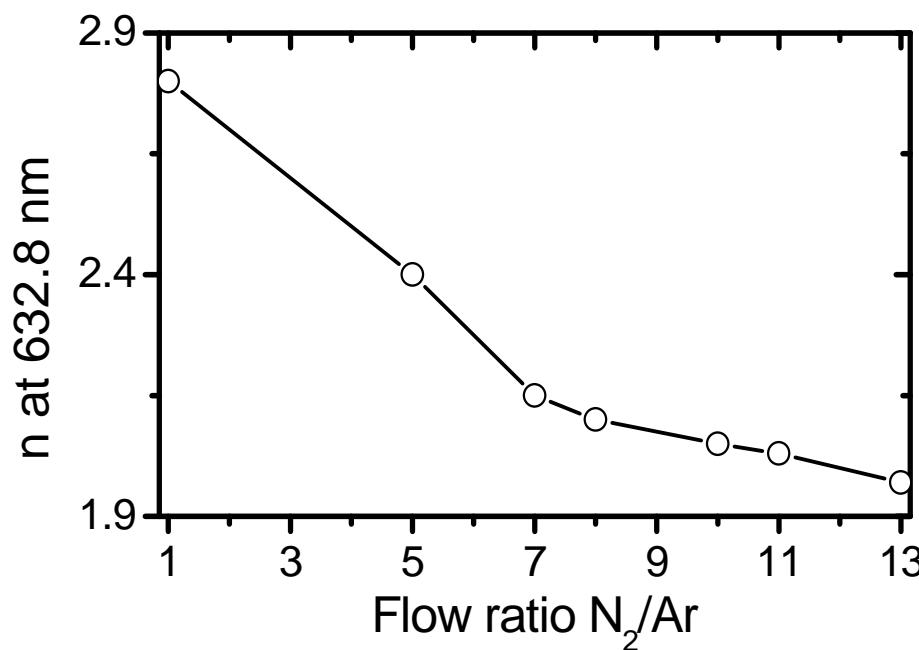
Methodology needed (a-SiNH)

- **Empirical (Tersoff-type) <u>interaction potential</u>**

  - atoms i,j,k and elements I,J,K: $V_{ij} = f_{ij}^{IJ} [A_{ij}\exp(-\lambda^{IJ}r_{ij}) - b_{ij}^{IJ}B^{IJ}\exp(-\mu^{IJ}r_{ij})]$
  dependence on distance, bonding angle, bond order (coordination numbers):
  $b_{ij}^{IJ} = f(\chi^{IJ}, \beta^I, \beta^J, n^I, n^J, c^I, c^J, d^I, d^J, h^I, h^J, r_{ik}, r_{jk}, \theta_{jik}$ over all k)

- **Recursive atom-by-atom <u>simulation protocol</u>**

  1) new <u>SiH$_x$ and N particles</u> (x, SiH$_x$/N, ion fraction F$_i$, ion energy E$_i$, flux angle)
  2) <u>fixed-energy run</u>: particle collisions and energy dissipation
  3) <u>fixed-temperature run</u>: reestablish the deposition T
  4) <u>removal</u> of resputtered/desorbed particles


- Si
- N
- H

former substrate

all atoms

4 eV

10 eV

20 eV

50 eV
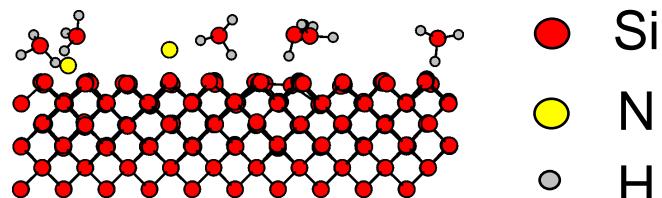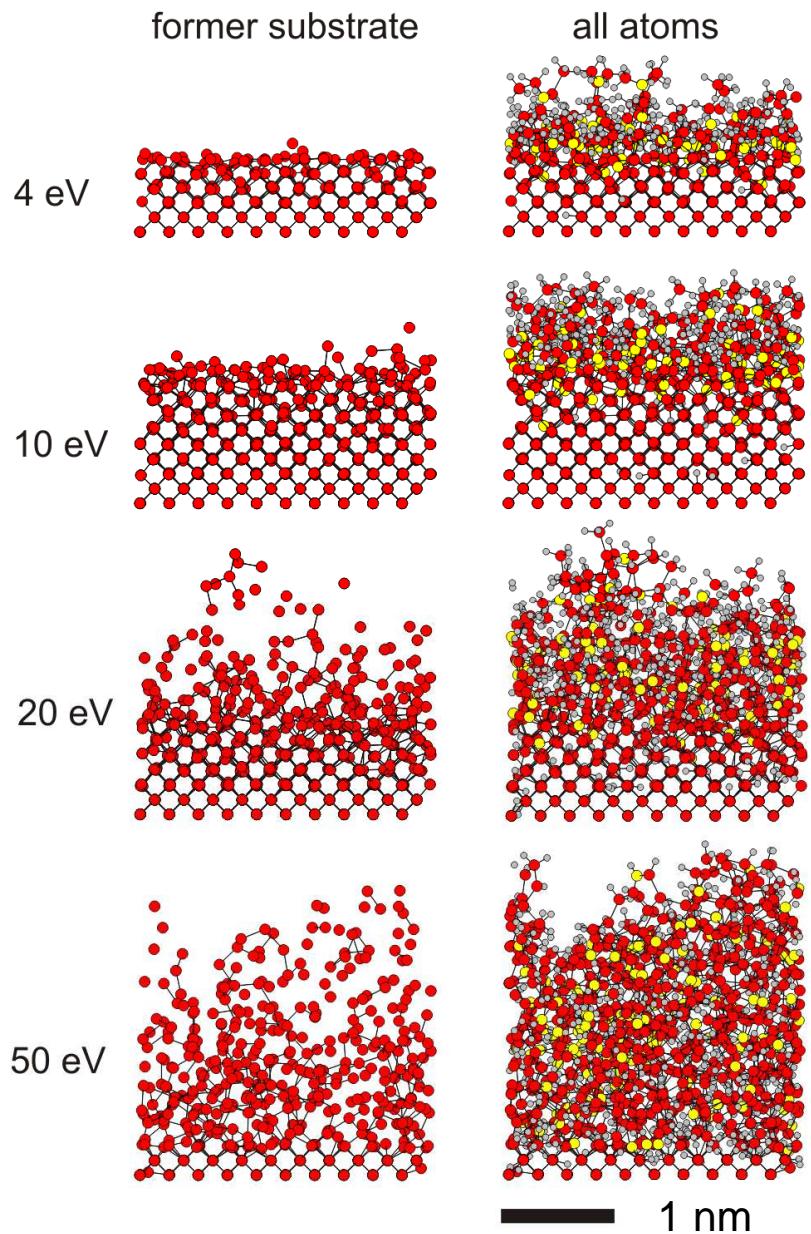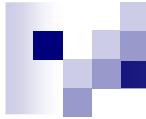
Mechanism of SiNH growth from SiH$_3$ and N: mixed zone formation

Si/N deposited ratio = 52/25, 25% ion fraction

- Surface layer of SiH$_3$ (dissociated by energetic particles)

- Formation of mixed zone (damage layer) on the substrate-film interface

● Si

● N

● H

1 nm
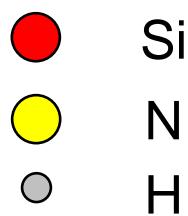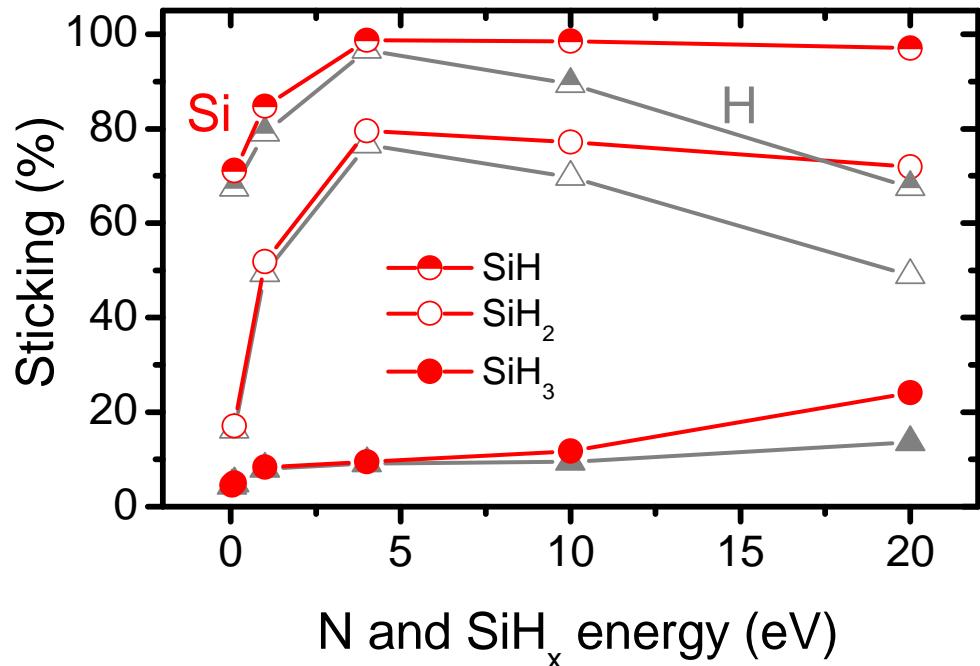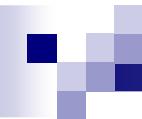
Mechanism of SiNH growth from SiH_3 and N: SiH_x dissociation

same E of all particles, 90° angle, Si/N deposited ratio = 52/25

- Much higher Si sticking at x=2 (or 1) compared to x=3

- H/Si ratio is lower

  - for higher energy per particle

  - if same total energy is distributed among less particles (not shown)

  - at flux angle <90° - only "well dissociated" SiH_3 stick (not shown)
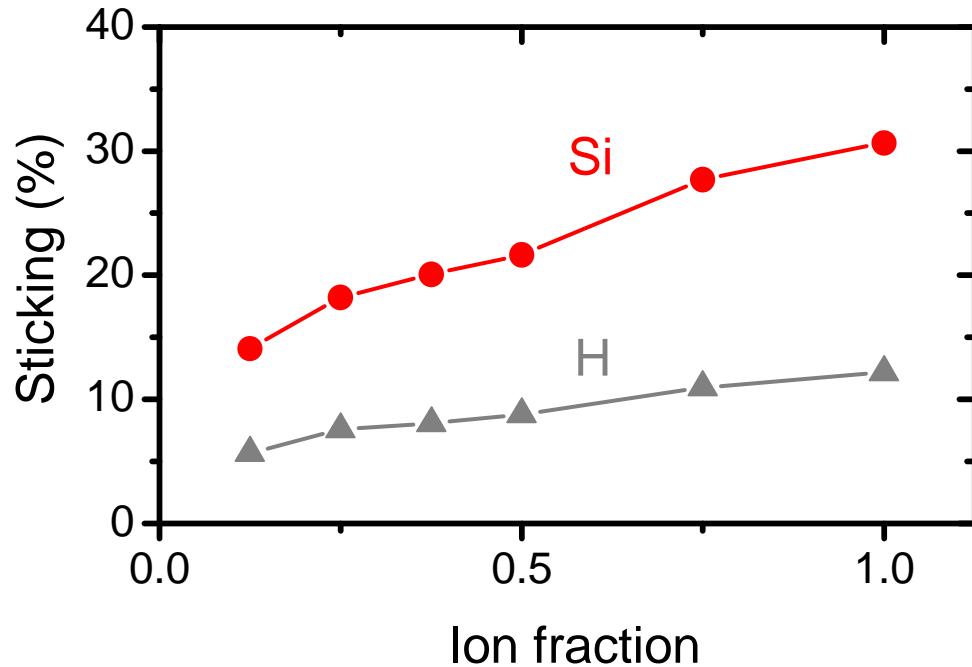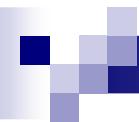
Effect of ion fraction, F_i, on dep. char.

E_i = 20 eV, SiH_3/N flux ratio 1/1

- Increasing $F_i \Rightarrow$ linearly increasing Si (and H) sticking coef.

- Model of *"growth from ions"*: on the average, an ion dissociates the same number of SiH_3 at any F_i

[J. Houska et al., J. Appl. Phys. 107, 083501 (2010)]

Effect of E_i and flux comp. on dep. char. (ion fraction $F_i = 0.25$)
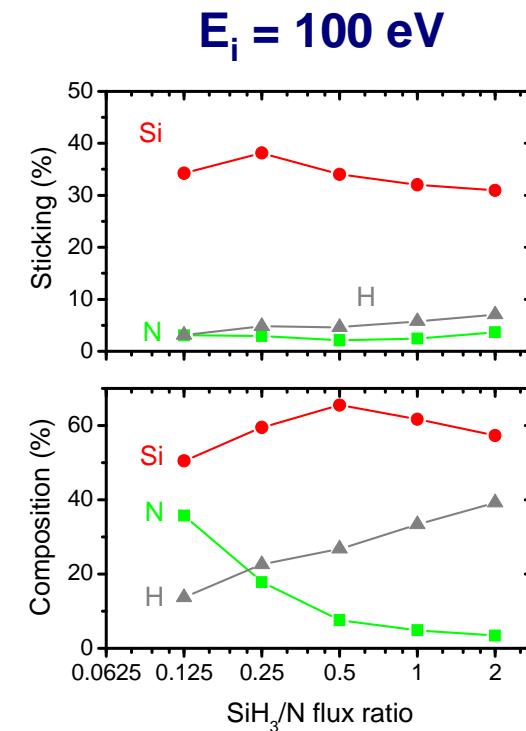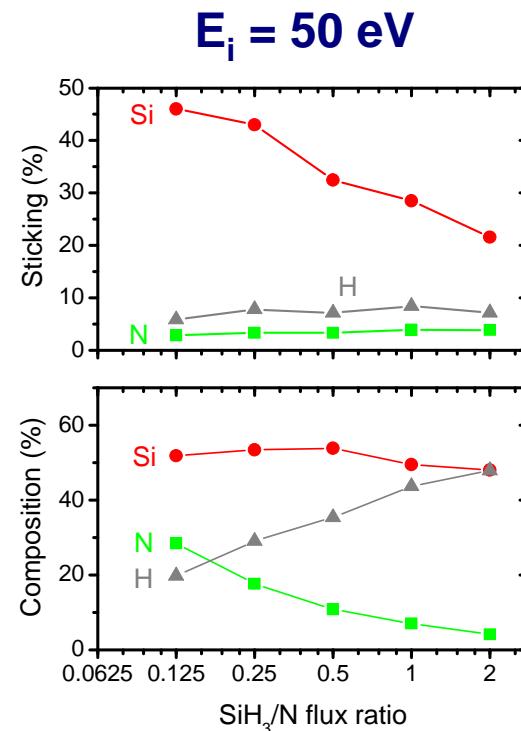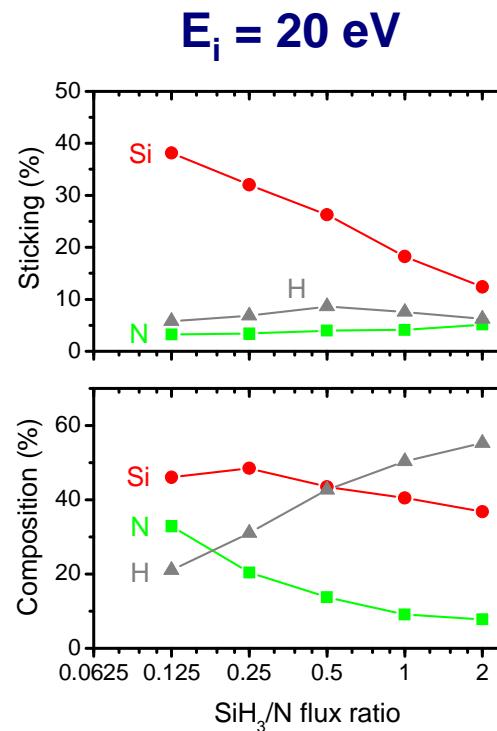

- Dependence of the Si sticking coefficient on the SiH_3 + N flux composition is more significant at lower E_i
  (SiH_3 is dissociated by both SiH_3^+ and N^+)

- H/Si ratio systematically increases with increasing SiH_3/N
  (H delivered only by SiH_3, but resputtered by both SiH_3^+ and N^+)
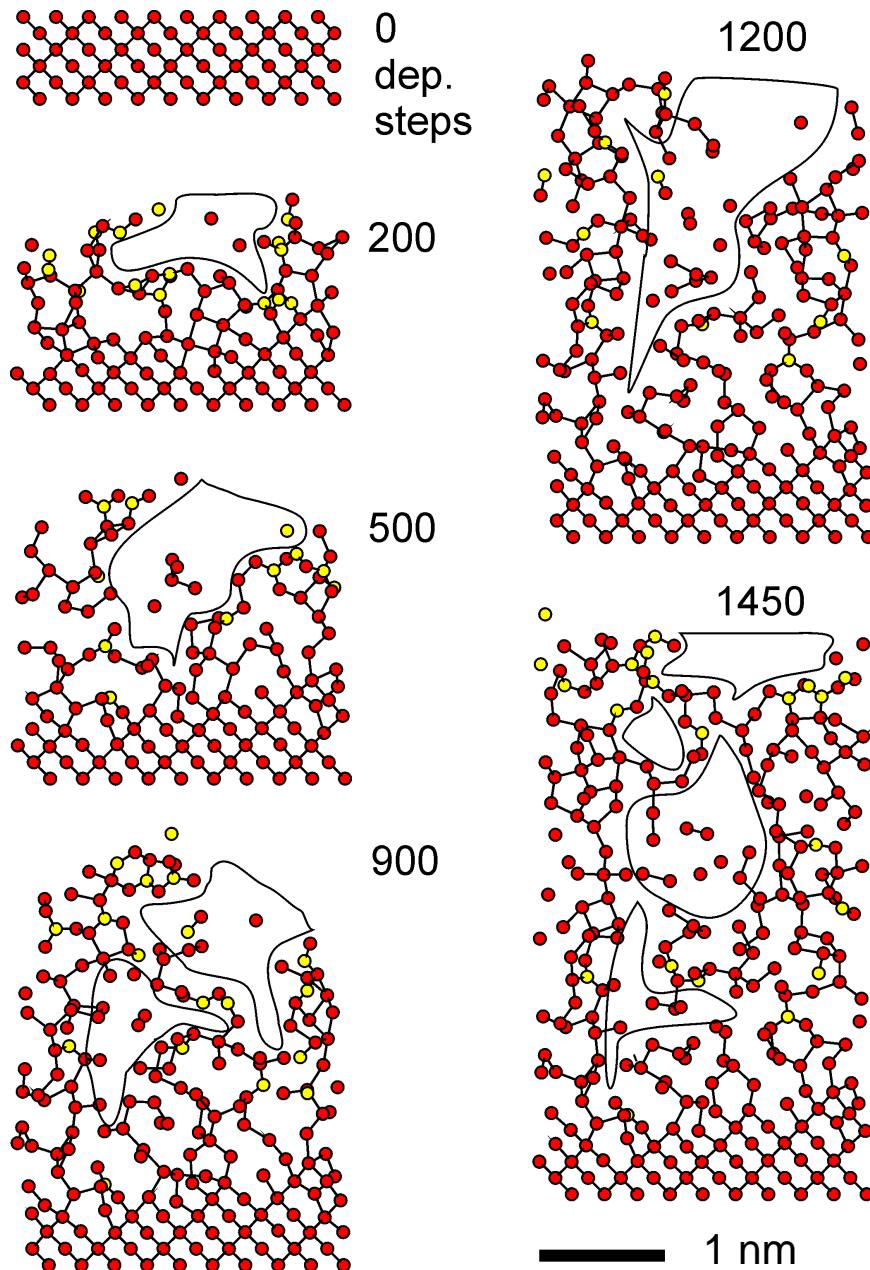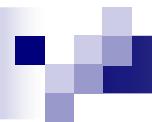
Example of growth of voids-containing SiNH

25% ion fraction, low E_i of 20 eV, medium SiH_3/N flux ratio of 1:1

- 0.5 nm thick slices, H not shown
- 1-2 nm (non-spheric) voids

0 dep. steps

200

500

900

1200

1450

● Si

● N

—— 1 nm
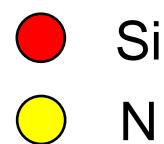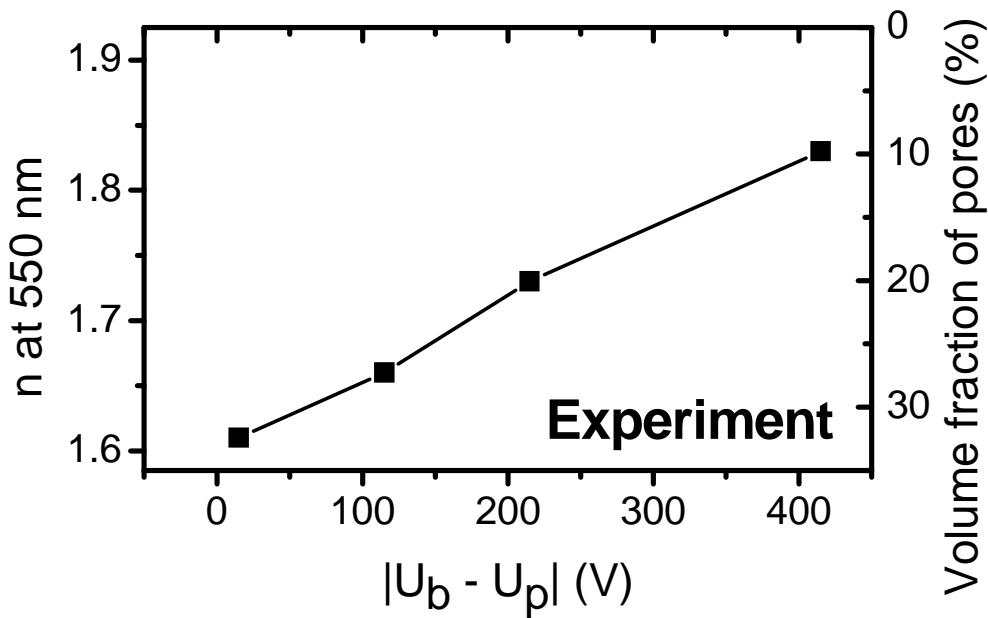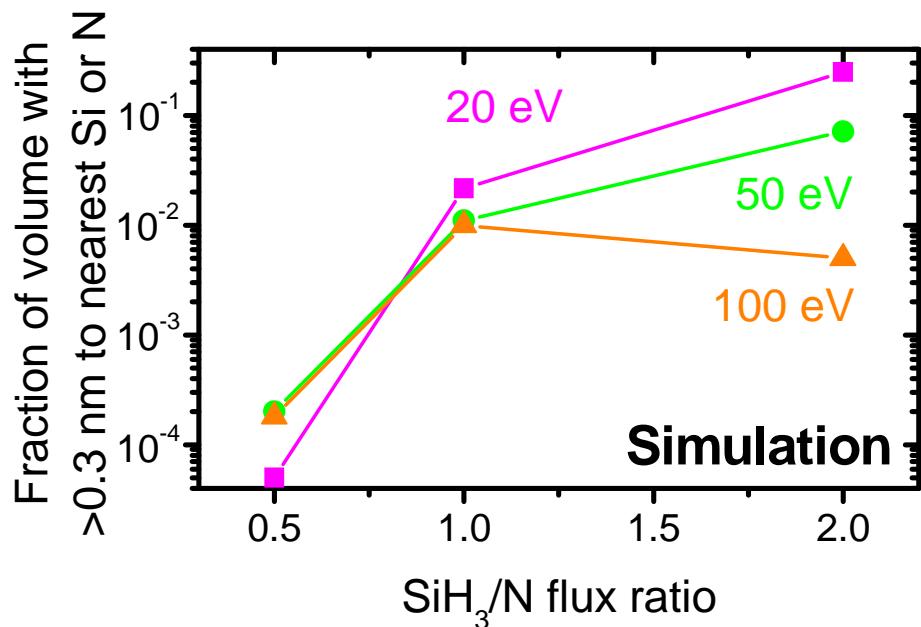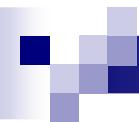
Size of voids

fractional volume of empty spheres with diameter > 0.6 nm

25 % ions, various E_i and flux composition

- Only lower bound of non-spheric voids size shown
- Higher voids volume for
  - lower E_i (exp. lower $|U_b-U_p|$)
  - higher SiH_3/N flux ratio

Conclusions (data calculated)

- **Deposition characteristics**
  (sticking coefficients, dissociation of molecules)

- **Material structures on nm scale**
  (distribution of crystal sizes, voids)

- **Material structures on atomic scale**
  (bonding statistics, coordination numbers)

- **Material properties**
  (formation E, electronic structure, band gap, magnetization)

- **Temperature-dependent characteristics**
  (bond lifetimes, gas molecules formation)

Acknowledgements