Transition metal based functional coatings: Effect of the choice of metal element

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DEPARTMENT
OF PHYSICS

+NTIS

Acknowledgment

Outline (materials discussed)

- MBCN *[J. Houska et al., Thin Solid Films 586, 22 (2015)]*

- reasons for Si incorporation

- MSiBCN *[J. Houska et al., Thin Solid Films 616, 359 (2016)]*

Motivation

- Combination of theoretical (calculated) and experimental data
- Capture the differences resulting from the M (Ti, Zr, Hf) choice
  - same theoretical and experimental techniques
  - same (calculations) / similar (experiment) M/B/C/N ratios
  - similar (low) compressive stress

Elemental composition choice

1) at this stage focus on MBCN (Si in second half of the presentation)

2) B/C ratio given by B_4C sputer target

3) not just nanocrystalline M(B,C,N) but nc-M(B,C,N)/a-BCN

$\Downarrow$

M content << 50 at. %

4) not hexagonal MB_2-based crystals but cubic MN-based crystals

$\Downarrow$

M/B ratio << 2

Compositions around $M_{41}B_{30}C_8N_{20}$

(except series with varied N content)

Experimental methodology

Reminder of the aim: thin films around $M_{41}B_{30}C_8N_{20}$

$M_{45}(B_4C)_{55}$ sputter target (M = Ti, Zr, Hf)

DC pulsed magnetron sputtering
- repetition frequency 10 kHz, duty cycle 85%
  ($\Rightarrow$ voltage pulse length 85 µs < $t_{krit} = \varepsilon_0 \varepsilon_r E_{br}/J_{it}$)
- substrate (Si, glass) temperature 450 °C
- substrates on floating potential around -40V

5% N_2 + 95% Ar plasma (except series with varied N content)

Bombardement of floating substrates
- by Ar^+ ions (overshoot voltage after switching off each pulse)
- by Ar neutrals reflected from sputter target (depends on M choice)

Adaptive discharge pressure at M = Ti, Zr, Hf

Ar reflected from target $\Rightarrow$ compressive stress in growing films

Fixed pressure (0.5 Pa), assume elastic head-on collisions of Ar^+ with M target, calculate energy of reflected Ar

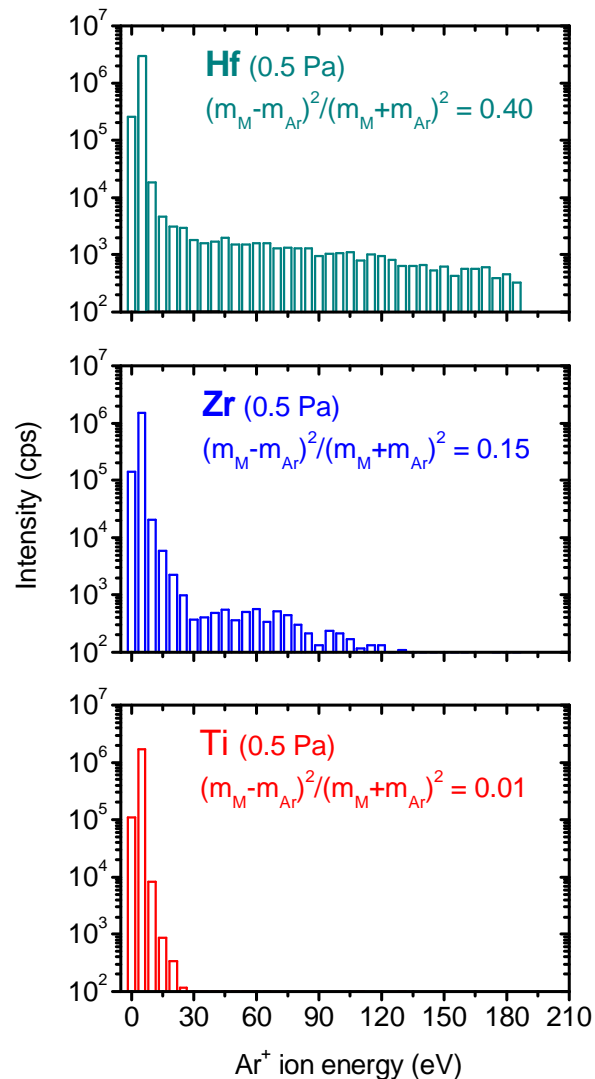M = Ti $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.01 \Rightarrow$ low (or tensile) stress

M = Zr $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.15 \Rightarrow$ medium stress

M = Hf $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.40 \Rightarrow$ high stress

(Monte Carlo simulations: same trend)

(Mass spectroscopy: same trend)

Adaptive discharge pressure at M = Ti, Zr, Hf

Hf (0.5 Pa)
$(m_M - m_{Ar})^2 / (m_M + m_{Ar})^2 = 0.40$

Zr (0.5 Pa)
$(m_M - m_{Ar})^2 / (m_M + m_{Ar})^2 = 0.15$

Ti (0.5 Pa)
$(m_M - m_{Ar})^2 / (m_M + m_{Ar})^2 = 0.01$

Intensity (cps)

Ar$^+$ ion energy (eV)

$\Rightarrow$ compressive stress in growing films

, assume elastic head-on collisions
ulate energy of reflected Ar

$+m_{Ar})^2 = 0.01 \Rightarrow$ low (or tensile) stress

$+m_{Ar})^2 = 0.15 \Rightarrow$ medium stress

$+m_{Ar})^2 = 0.40 \Rightarrow$ high stress

: same trend)

ne trend)

Adaptive discharge pressure at M = Ti, Zr, Hf

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Varied pressure in order to slow energetic Ar down by collisions

M = Ti $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.01 \Rightarrow$ **low stress at 0.35 Pa**

M = Zr $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.15 \Rightarrow$ **low stress at 0.5 Pa**

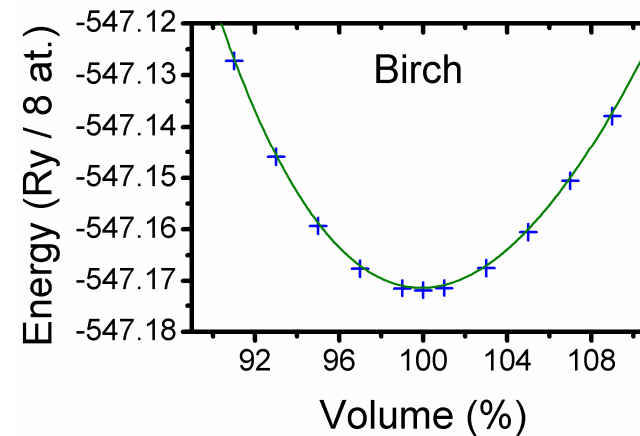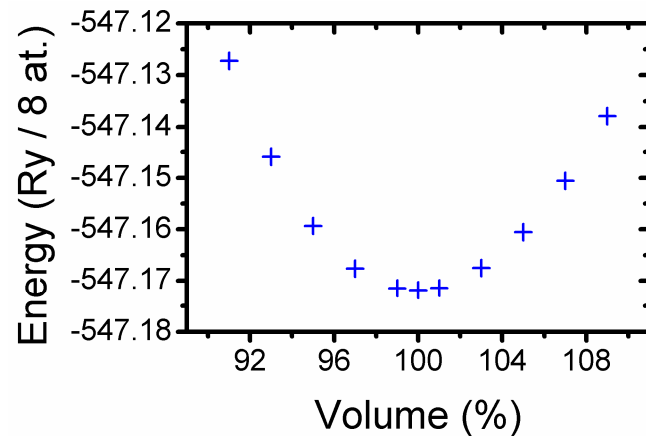M = Hf $\Rightarrow (m_M - m_{Ar})^2/(m_M + m_{Ar})^2 = 0.40 \Rightarrow$ **low stress at 1.7 Pa**

Support of experiment by ab-initio calculations

Motivation: calculate formation energies of fcc-$MB_xC_yN_{1-x-y}$
- with respect to fcc-MN + fcc-MC + MB_2 + M
  (stable constituent phases)
- with respect to fcc-MN + fcc-MC + fcc-MB
  (less stable but isostructural)

For each phase: calculate energy (E_0) from E(V) dependence

Birch eq. of state: $E = E_0 + 9/8\ B_0V_0([V_0/V]^{2/3}-1)^2 + 9/16\ B_0(B'-4)V_0([V_0/V]^{2/3}-1)^3$

Theoretical methodology

DFT as implemented in PWscf code
  - Atom cores + inner electron shells: Vanderbilt-type ultrasoft
    pseudopotentials
  - Valence electrons: plane wave basis, energy cutoff of 30 Ry
  - Exchange-correlation term: Perdew-Burke-Ernzerhof
    functional
  - Brillouin zone sampling $12\times12\times12$ k-points for 8 atoms

Periodical simulation cell
  - 8 atoms (uniform distribution of atoms in fcc-$MB_xC_yN_{1-x-y}$)
  - 48 atoms (cross-check using quasirandom distribution)

Effect of M choice on structure of $M_{41}B_{30}C_8N_{20}$

M = Ti: X-ray amorphous

M = Zr: ZrN-like crystals, shift of 111 peak towards e.g. ZrB

M = Hf: HfN-like crystals, shift of all peaks towards e.g. HfB
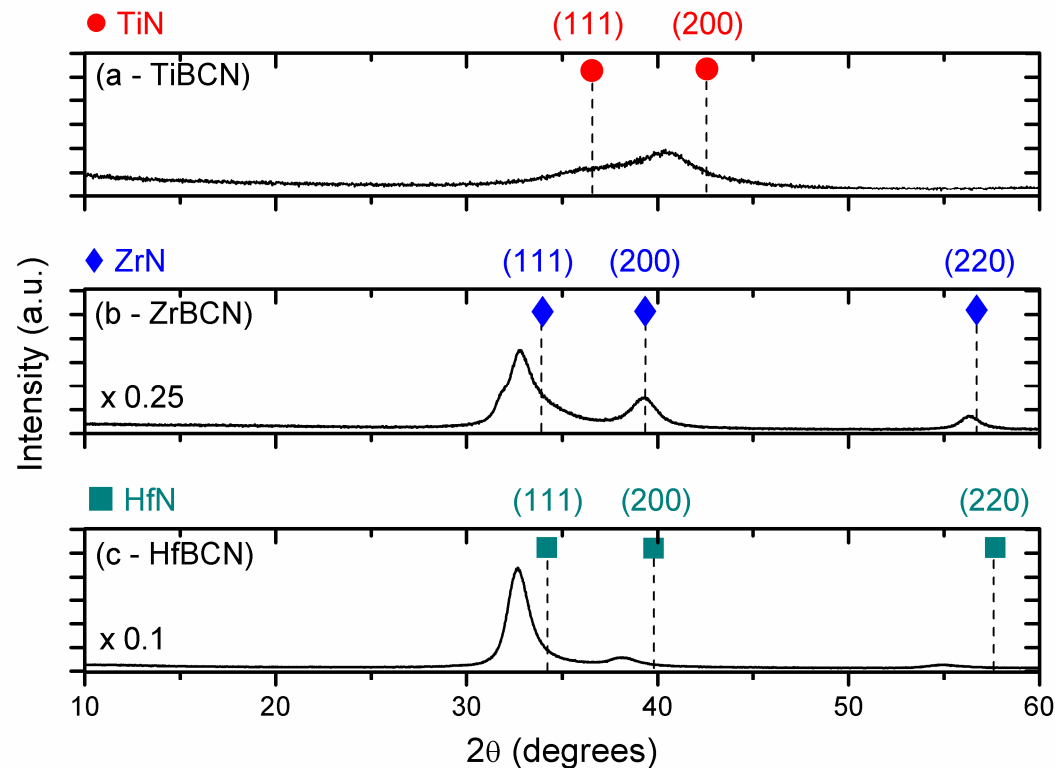
Transition from M = Ti through Zr to Hf $\Rightarrow$
decreasing formation energy ($\Rightarrow$ more likely formation)
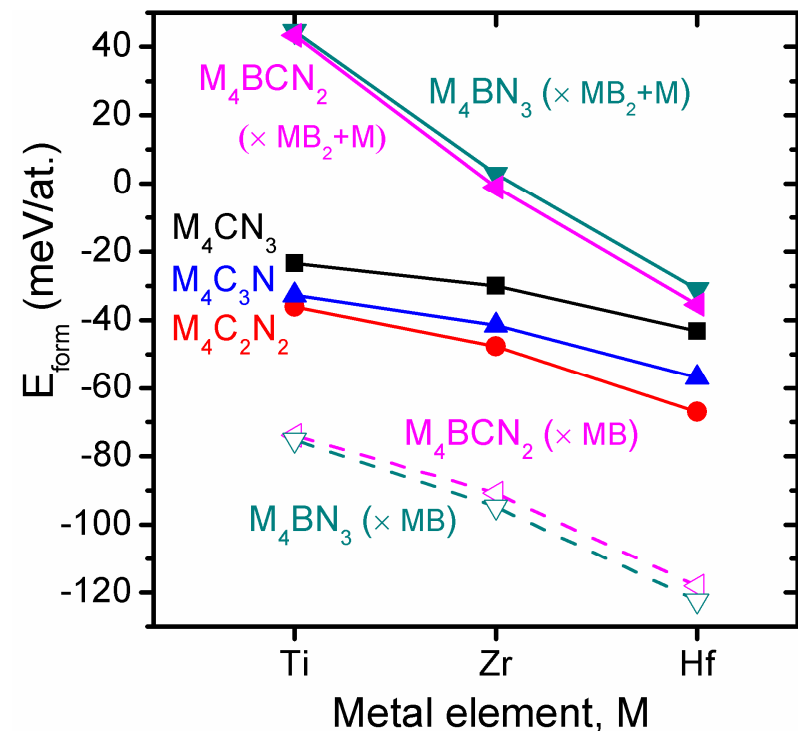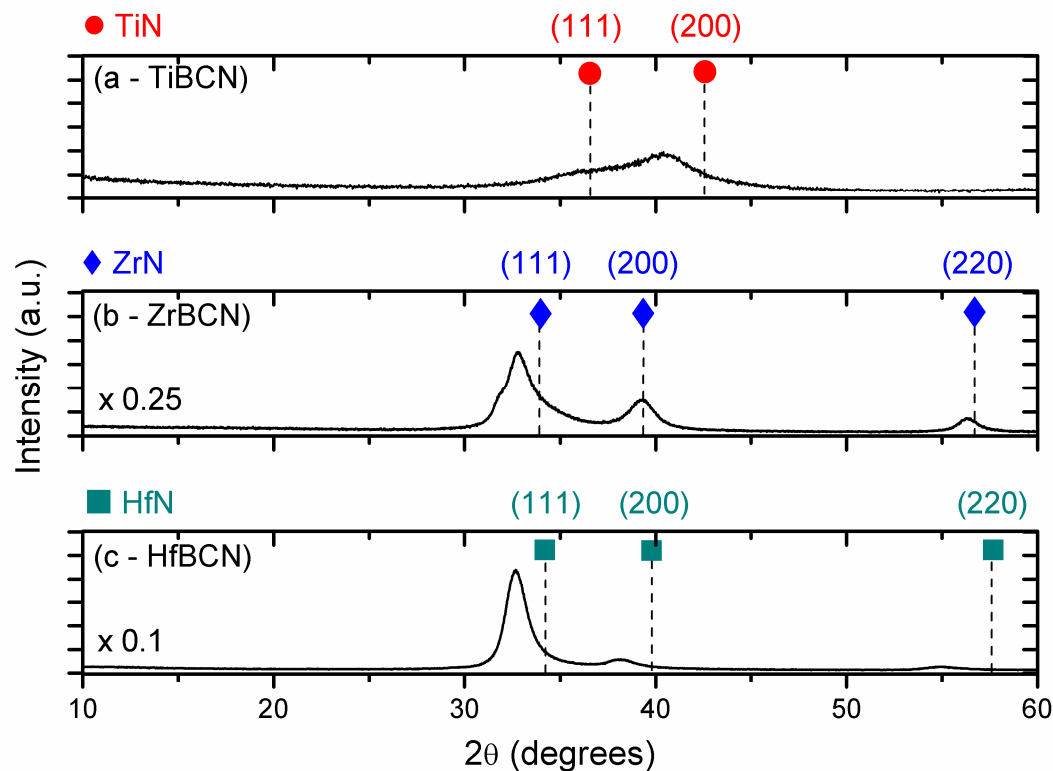of all $MB_xC_yN_{1-x-y}$ solid solutions considered
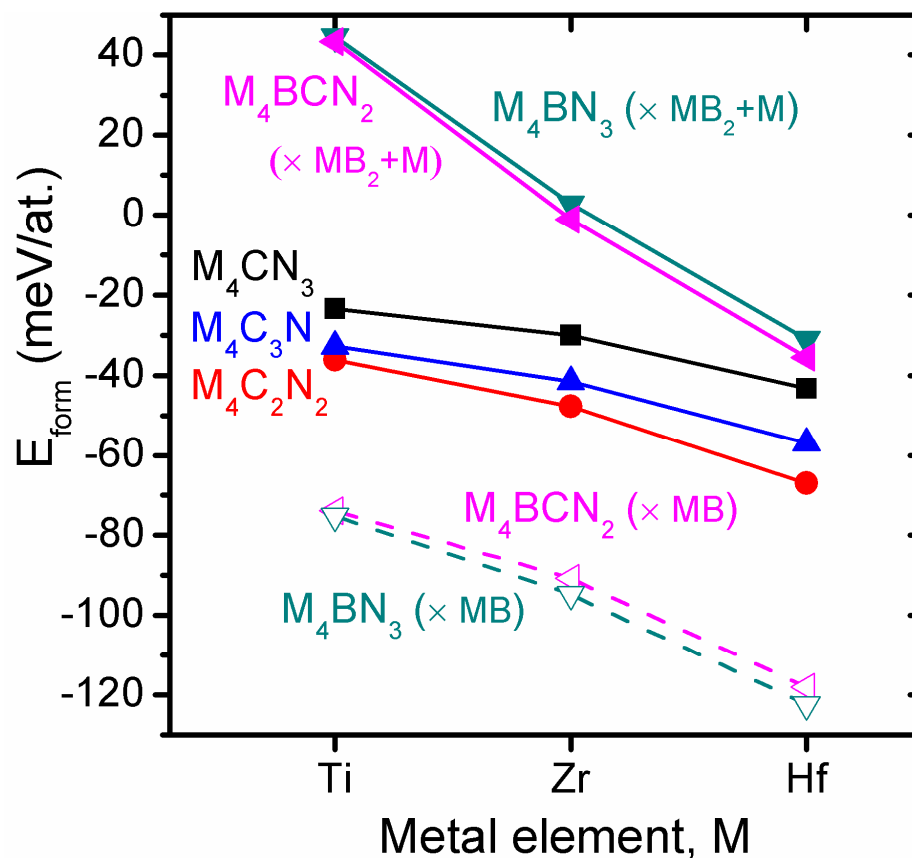
M = Ti: x-ray amorphous

- largely positive E_{form} of all B-containing crystals
- formation of B-free TiC_yN_{1-y} is thermodynamically OK, but kinetically difficult (low C+N content; low E of bombarding Ar)
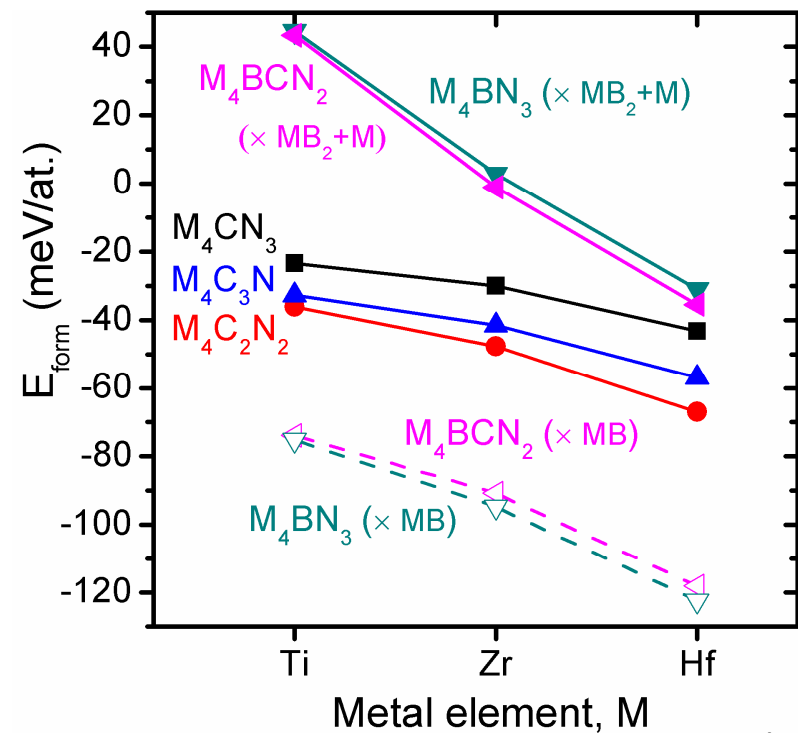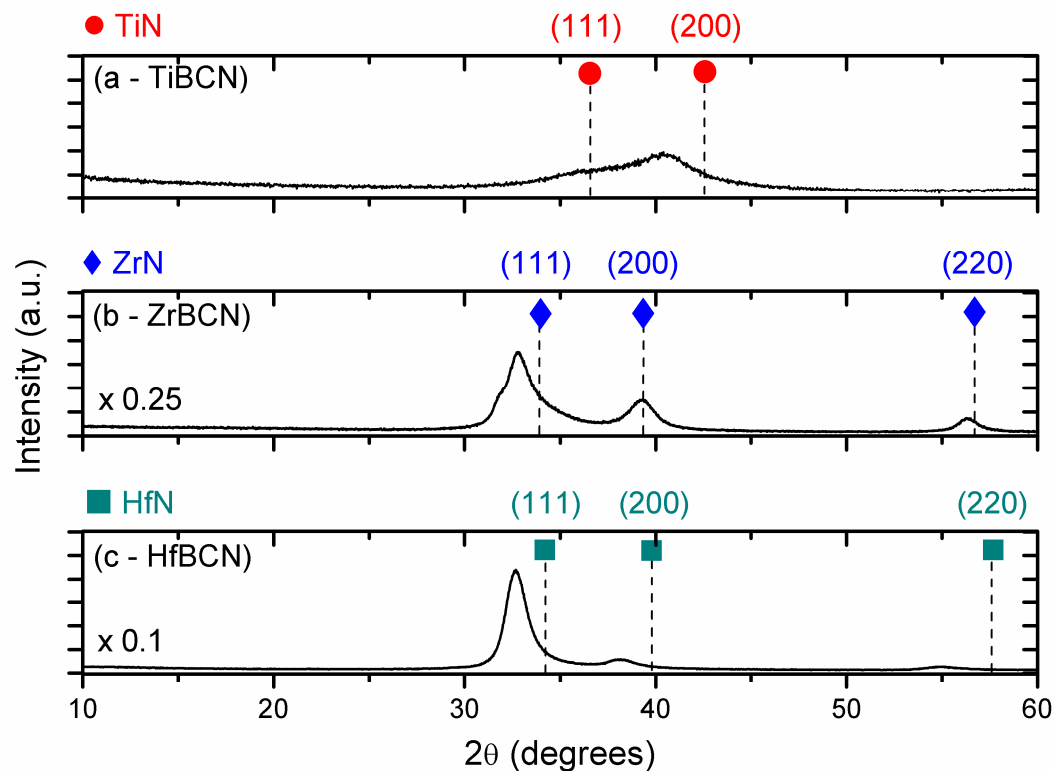
M = Zr: ZrN-like crystals, shift of 111 peak towards ZrB

- at least 111 crystals are fcc-$ZrB_xC_yN_{1-x-y}$ solid solutions; explained by E_{form} ~0 for $ZrB_{0.25}C_{0.25}N_{0.50}$ or $ZrB_{0.25}N_{0.75}$
- consistent lattice constant differences from pure ZrN (3.1% from XRD, e.g. 2.1% calculated for $ZrB_{0.25}C_{0.25}N_{0.50}$)

M = Hf: HfN-like crystals, shift of all peaks towards HfB

- all crystals are fcc-$HfB_xC_yN_{1-x-y}$ solid solutions; explained by even lower E_{form} values (compared to M = Zr)
- more pronounced texture/crystallinity (XRD peaks scaled down) and 111 preference (compared to M = Zr)
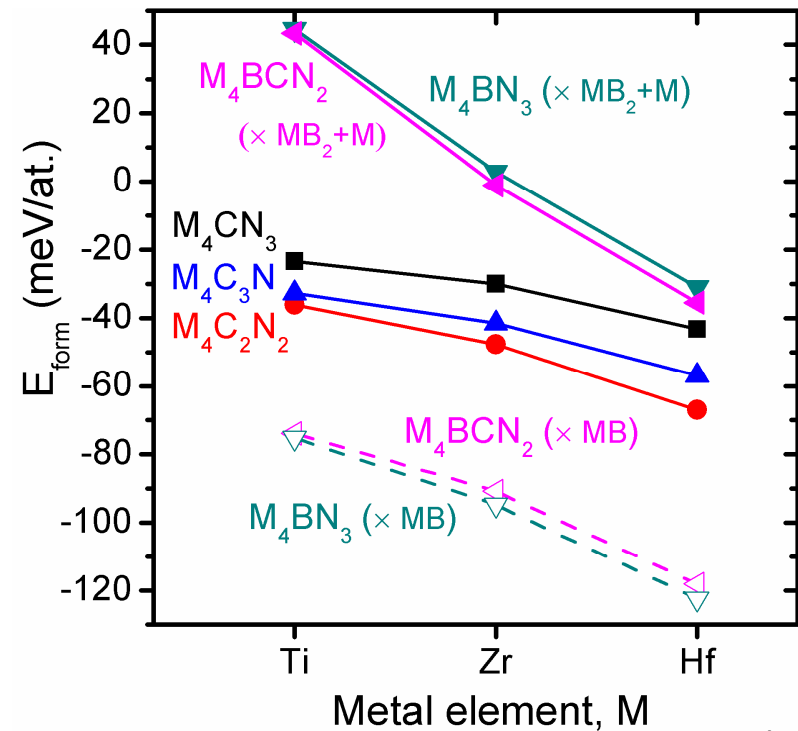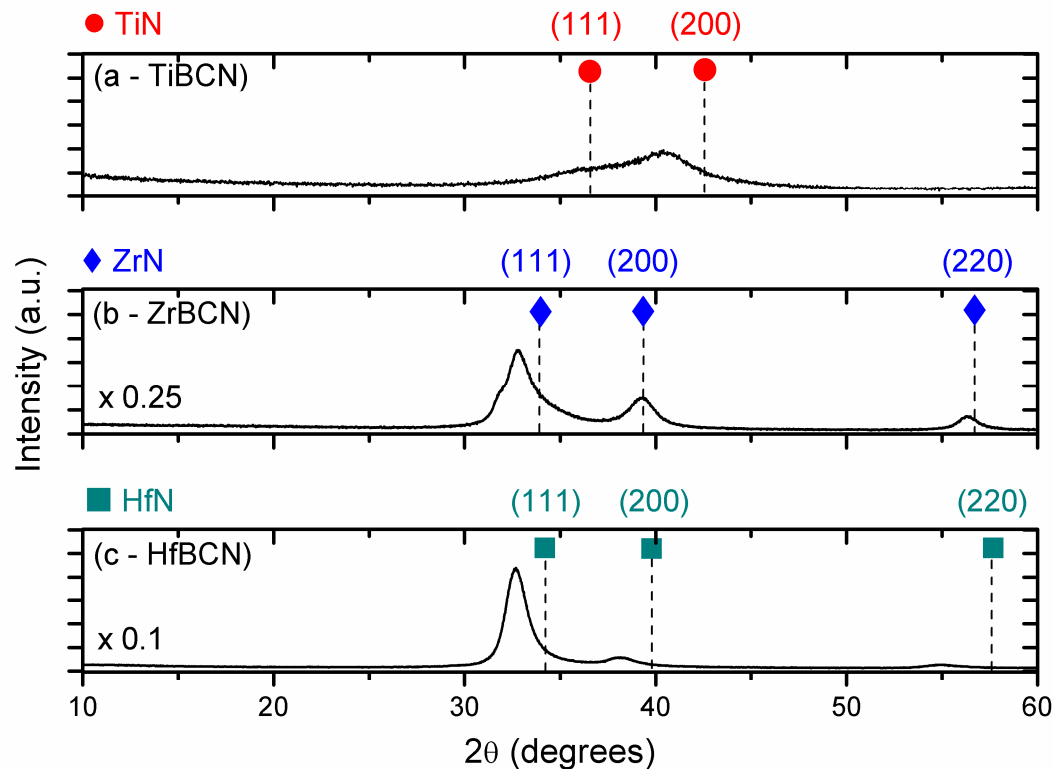
Effect of M choice on structure of $M_{41}B_{30}C_8N_{20}$

Summary of this part

M = Ti: x-ray amorphous

- high E_{form} of solid solutions
- low E of Ar reflected from sputter target

M = Zr: nanocomposite containing

- $ZrB_xC_yN_{1-x-y}$ (x $\geq$ 0.25)
- ZrC_yN_{1-y}
- amorphous phase (reminder: M content well below 50 at. %)
- HRTEM: the amorphous phase is around "nanoneedles"

   [M. Zhang et al., Acta Materialia 77, 212 (2014)]

M = Hf: nanocomposite containing

- $HfB_xC_yN_{1-x-y}$ (higher x compared to M = Zr)
- amorphous phase (reminder: M content well below 50 at. %)

Observation: preferred orientation of MBCN solid solution is 111
$\times$ preferred orientation of B-free Zr(C)N is 200

Explanation: lower diffusion rate on 111 surface (3 "backbonds")
(part of)   Growth of non-segregated solid solutions requires
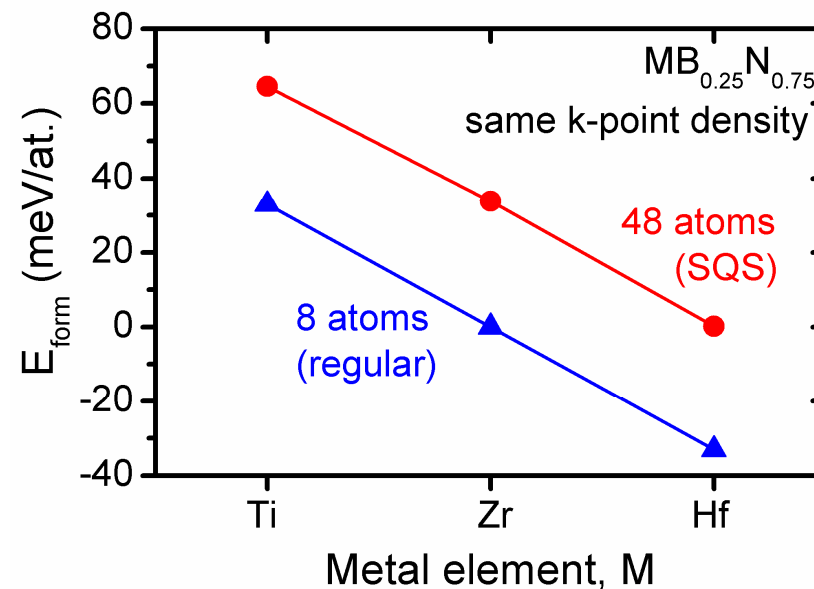less diffusion $\Rightarrow$ 111 relatively more likely.
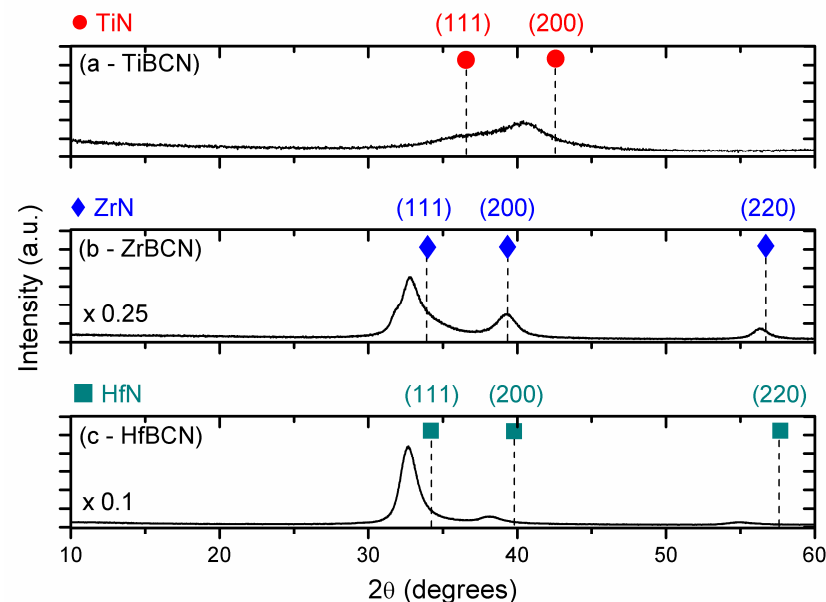
Two more remarks (ii) On the distribution of B,C,N atoms

8 atoms (M_4BN_3) $\Rightarrow$ regular distribution of atoms: lower E_{form}
 - thermodynamically (not kinetically) more preferred
 - used in the rest of this presentation

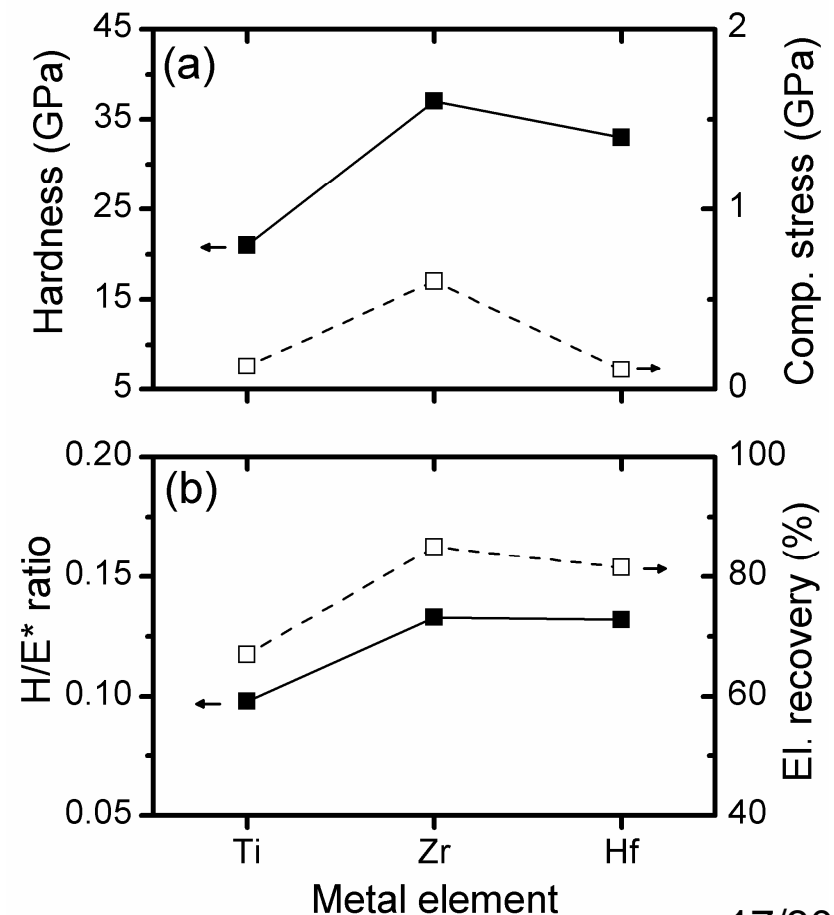48 atoms ($M_{24}B_6N_{18}$), quasirandom SQS cell: higher E_{form}

same trends of E_{form} along Ti→Zr→Hf, same lattice constants

Effect of M choice on mechanical properties

Transition from amorphous TiBCN to nanocomposite ZrBCN and HfBCN improves

- hardness (21 → 33-37 GPa)

- el. recovery (67 → 82-85%)

- H/E* ratio (0.098 → 0.132-0.133)

Effect of M choice on electrical resistivity

Varied N content ($\Rightarrow$ leaving the $M_{41}B_{30}C_8N_{20}$ composition)

- first impression: Ti$\rightarrow$Zr$\rightarrow$Hf enhances N incorporation

- RBS shows metal-independent N contents: any other (calculations-based) explanation of different resistivities?
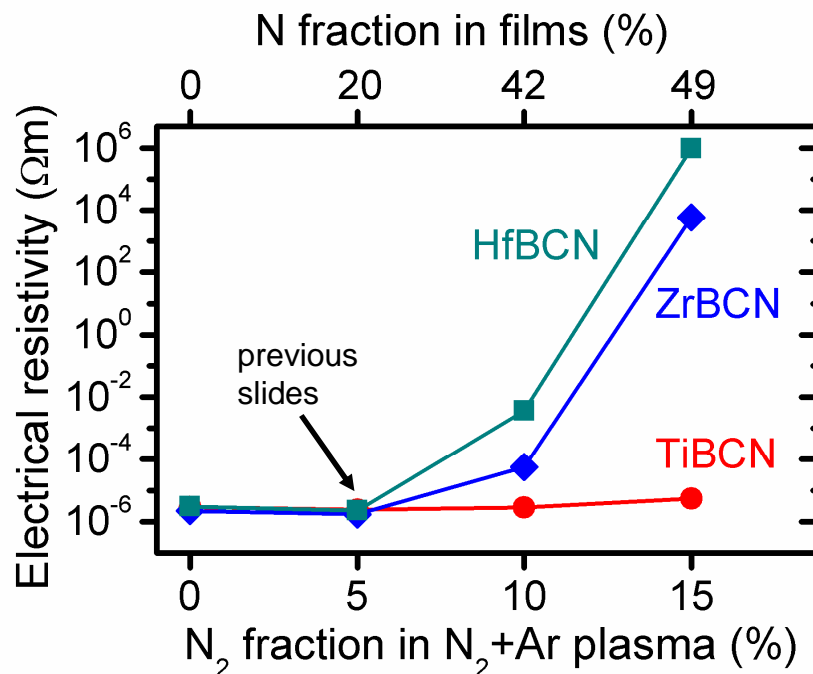
15% N_2 in N_2+Ar

M = Ti : $\rho \sim 10^{-6}$ Ωm

M = Zr : $\rho \sim 10^3$ Ωm

M = Hf : $\rho \sim 10^6$ Ωm

# Effect of M choice on electrical resistivity

Varied N content ($\Rightarrow$ leaving the $M_{41}B_{30}C_8N_{20}$ composition)

M = Ti: homogenous M-containing conductive material

M = Zr: M segregated into conductive nanocrystals, separated by insulating a-BCN (BN: band gap $\geq$ 5.2 eV)

M = Hf: even lower E_{form} of nanocrystals $\Rightarrow$ trend continues
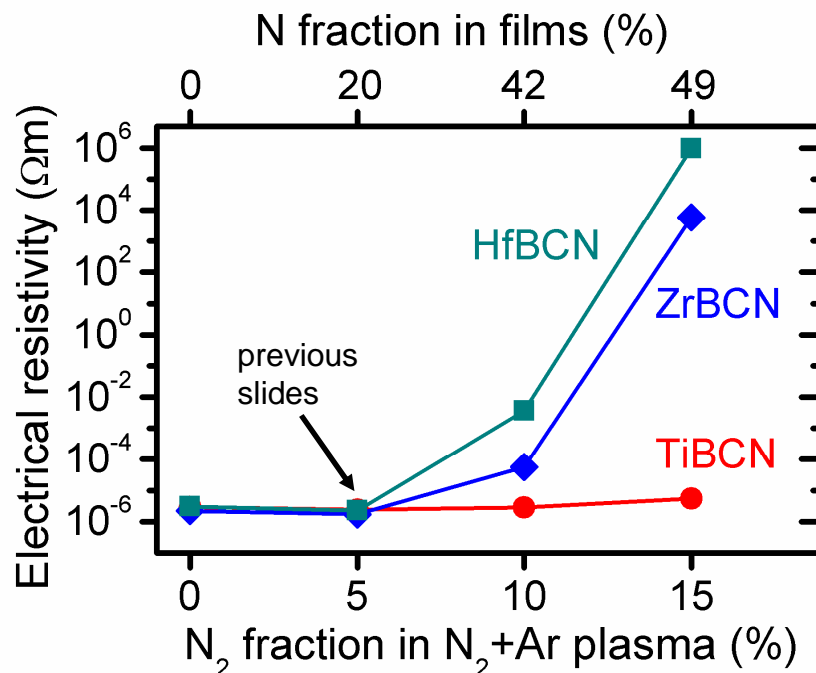
15% N_2 in N_2+Ar

M = Ti : $\rho \sim 10^{-6}$ Ωm

M = Zr : $\rho \sim 10^3$ Ωm

M = Hf : $\rho \sim 10^6$ Ωm

Effect of M choice on optical transparency

Shown for N-rich compositions (15% N_2 in N_2+Ar plasma)

M = Ti: homogenous M-containing opaque material

M = Zr: M segregated into opaque nanocrystals, separated by transparent a-BCN (BN: band gap $\geq$ 5.2 eV)

M = Hf: even lower E_{form} of nanocrystals $\Rightarrow$ trend continues
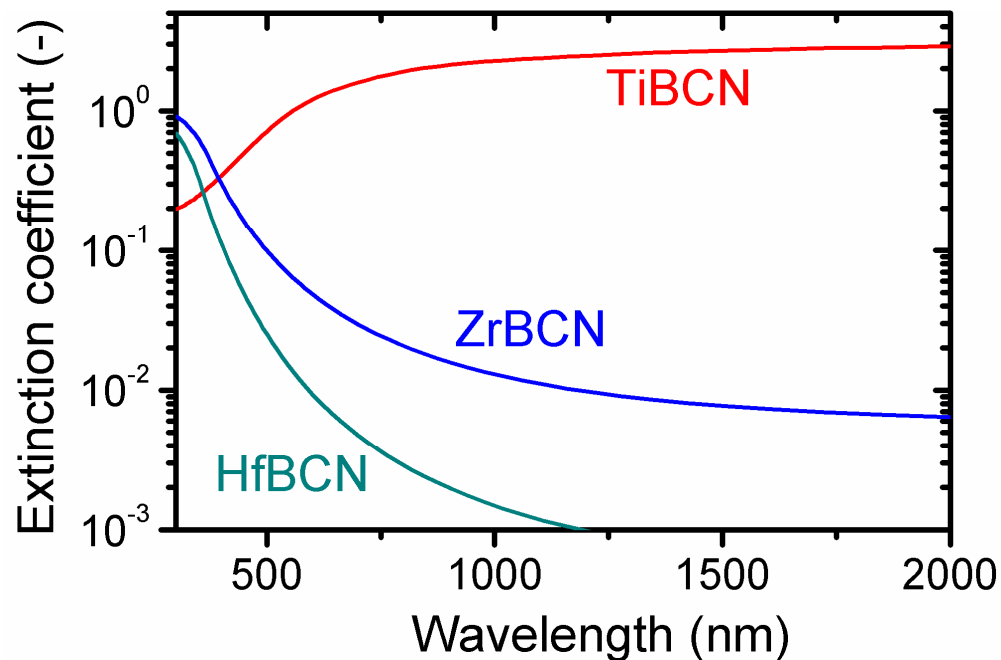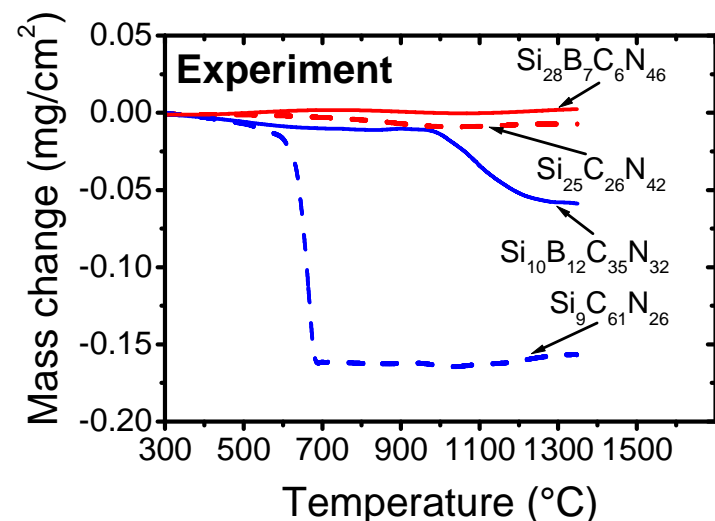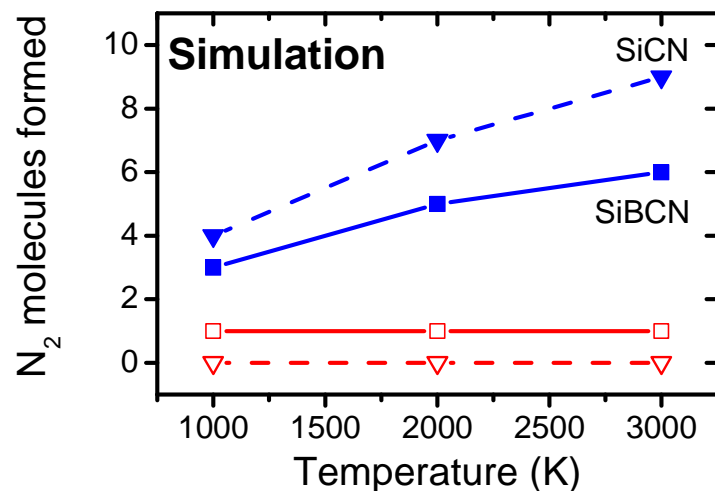

15% N_2 in N_2+Ar
M = Ti : k_{550} = 0.98
M = Zr : k_{550} = 0.06
M = Hf : k_{550} = 0.014

Thermal stability and oxidation resistance is improved by Si

- Thermal stability by MD simulations of $\underline{N_2 \text{ formation}}$

  a-$Si_{39}B_{14}C_{11}N_{44}$, a-$Si_{53}C_{11}N_{44}$, a-$Si_{11}B_{14}C_{39}N_{44}$, a-$Si_{11}C_{53}N_{44}$

- Decomposition reactions $Si_3N_4 + 3C \Rightarrow 3SiC + 2N_2$ and $Si_3N_4 \Rightarrow 3Si + 2N_2$ $\Rightarrow$ mass loss due to N_2

- Less N_2 molecules formed at (1) higher **Si/C** ratio and (2) **B** addition

Thermal stability and oxidation resistance is improved by Si

- Thermal stability by MD simulations of $\underline{N_2}$ formation

  a-$Si_{39}B_{14}C_{11}N_{44}$, a-$Si_{53}C_{11}N_{44}$, a-$Si_{11}B_{14}C_{39}N_{44}$, a-$Si_{11}C_{53}N_{44}$

  Si-rich   C-rich

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

[J. Houska et al., Europhys. Lett. 76, 512 (2006)]
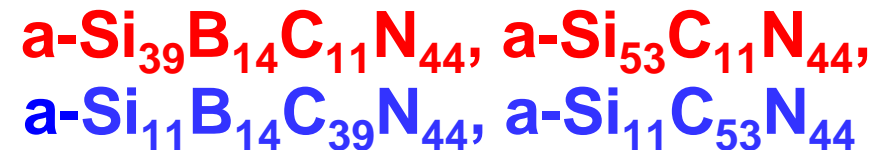
Moving to oxidation resistance $\Rightarrow$ moving to MSiBCN

Thermal stability and oxidation resistance is improved by Si

- Thermal stability by MD simulations of N$_2$ formation
  a-Si$_{39}$B$_{14}$C$_{11}$N$_{44}$, a-Si$_{53}$C$_{11}$N$_{44}$, a-Si$_{11}$B$_{14}$C$_{39}$N$_{44}$, a-Si$_{11}$C$_{53}$N$_{44}$
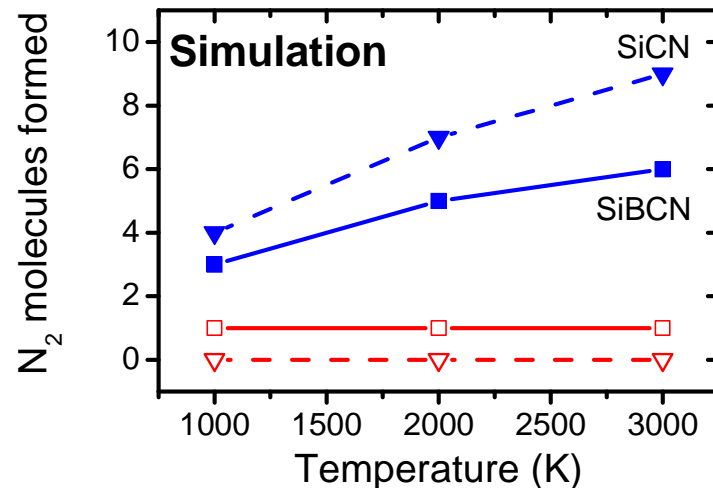
$\Rightarrow$ moving from **MBCN** [M$_{45}$(B$_4$C)$_{55}$ sputter target]
              to **MSiBCN** [M$_{15}$(B$_4$C)$_{65}$Si$_{20}$ sputter target]

Effect of M choice on oxidation resistance (experiment)

- $M_{15}(B_4C)_{65}Si_{20}$ sputter target
- **Oxide layer thickness** (measured by spectroscopic ellipsometry) after annealing in air up to 1000 and 1300 °C
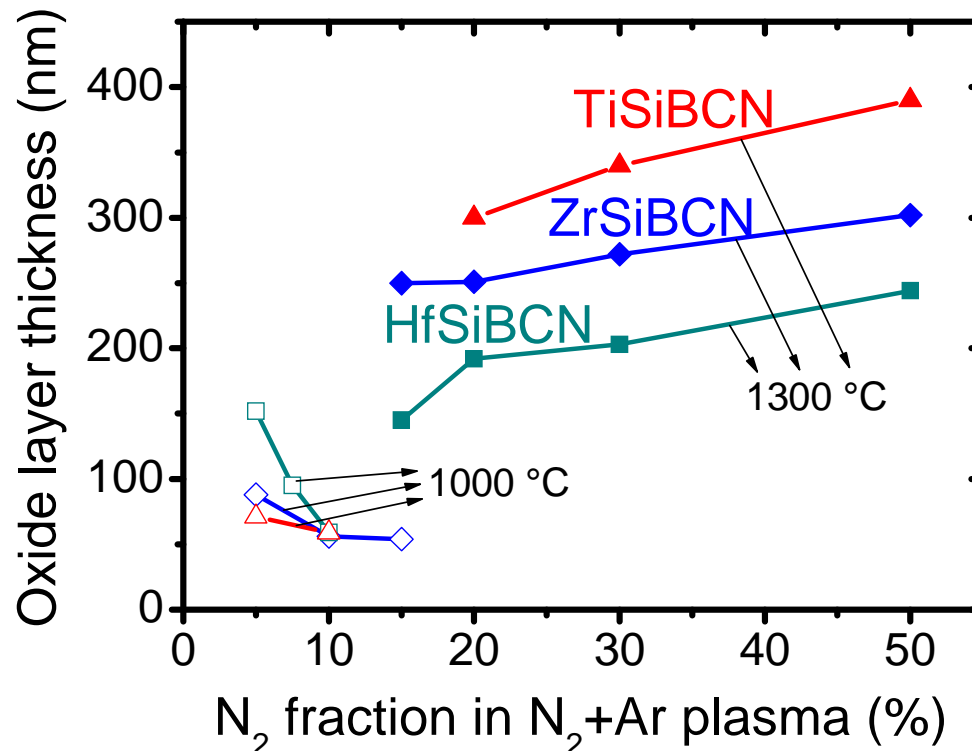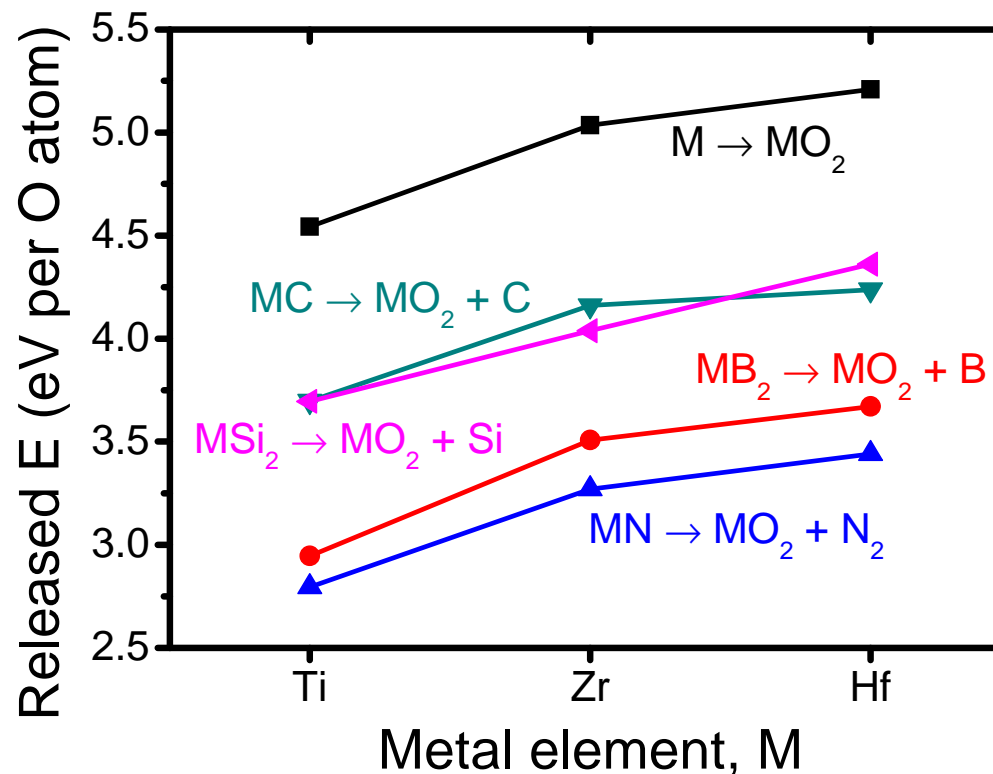
N-poor ($\Rightarrow$ higher M content) at 1000 °C

best Ti → Zr → worst Hf

N-rich ($\Rightarrow$ lower M content) at 1300 °C

worst Ti → Zr → best Hf

Effect of M choice on oxidation resistance:
Calculations relevant for M-rich crystalline compositions
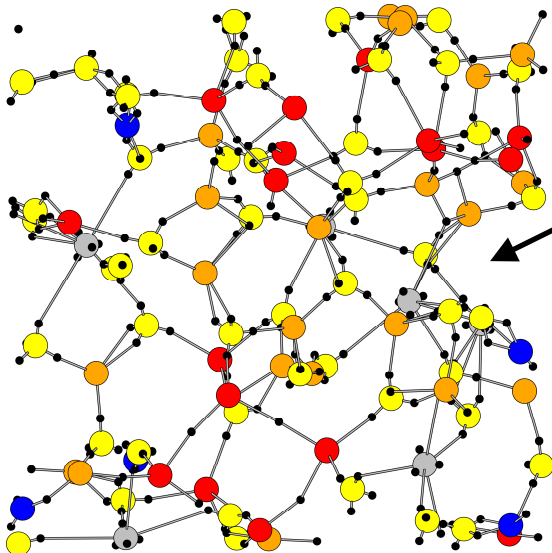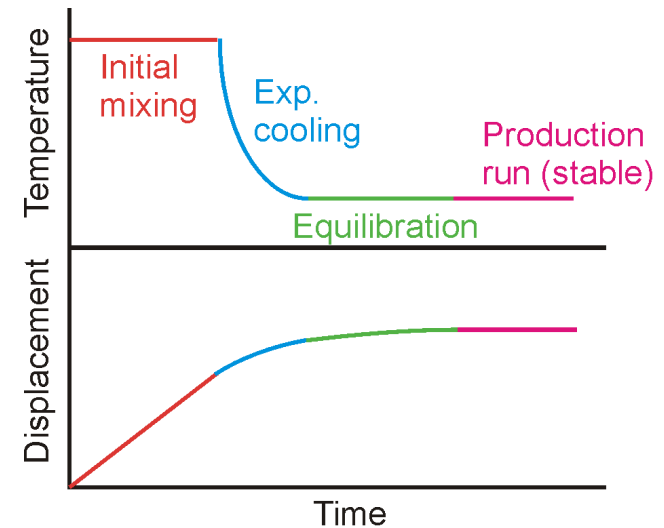(E_{form} of crystals and molecules)

Energy released during oxidation increases from M = Ti through Zr to Hf

Effect of M choice on oxidation resistance (calculation)
Calculations relevant for M-poor (N-rich) compositions
(bonding preferences in amorphous networks)

Liquid-quench algorithm captures material formation conditions arising from rapid cooling of the localized melt around sites of ion impact

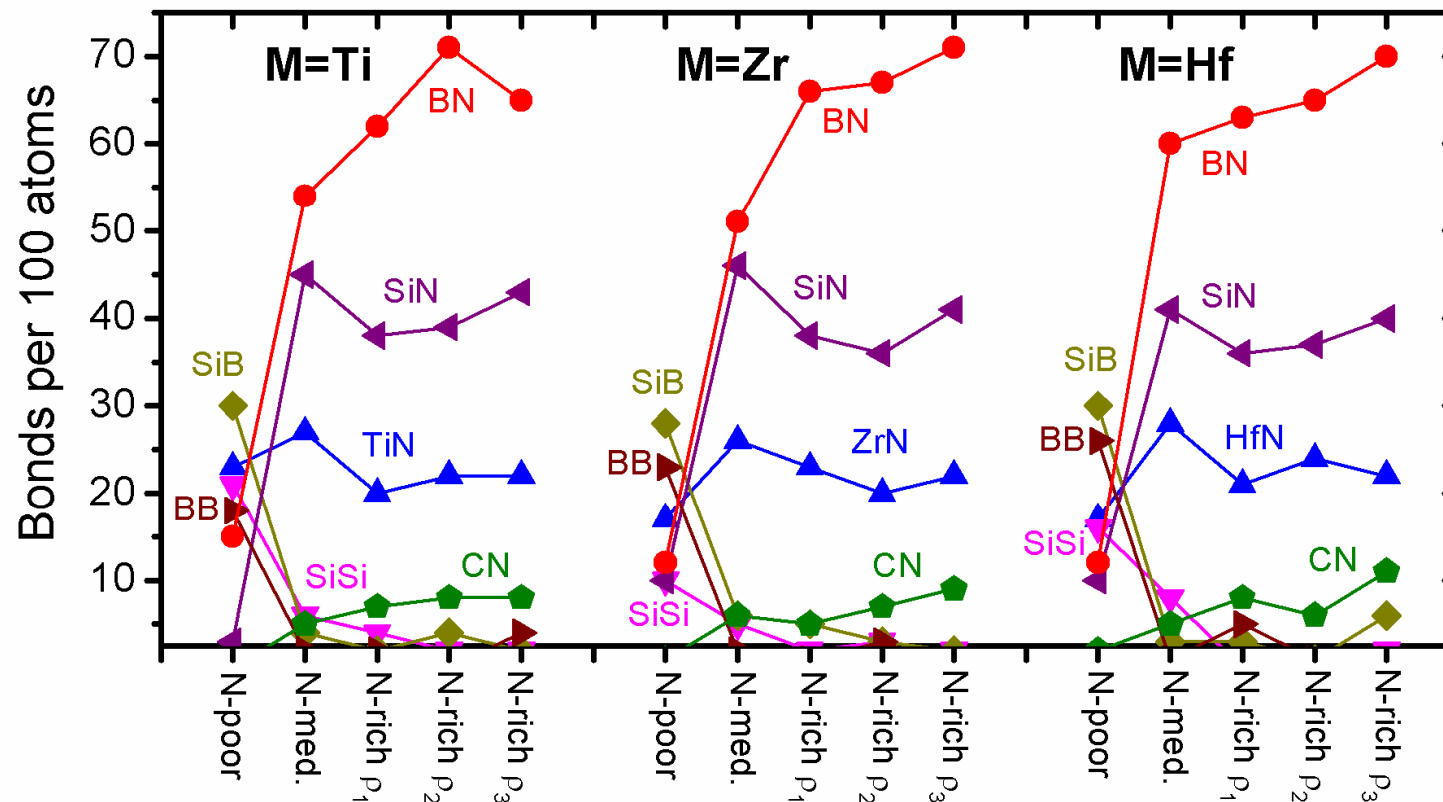example shown for $Hf_6Si_{17}B_{22}C_5N_{50}$

Si: 🔴, B: 🟠, C: 🔵, N: 🟡, Hf: ⚪
2 valence electrons: ━━●━━

Effect of M choice on oxidation resistance (calculation)
Calculations relevant for M-poor (N-rich) compositions
(bonding preferences in amorphous networks)

3 compositions ($M_{16}Si_{27}B_{36}C_9N_{12}$, $M_6Si_{17}B_{22}C_5N_{50}$, $M_5Si_{13}B_{26}C_6N_{50}$),
3 densities for the last composition ... but **no real differences**

Effect of M choice on oxidation resistance
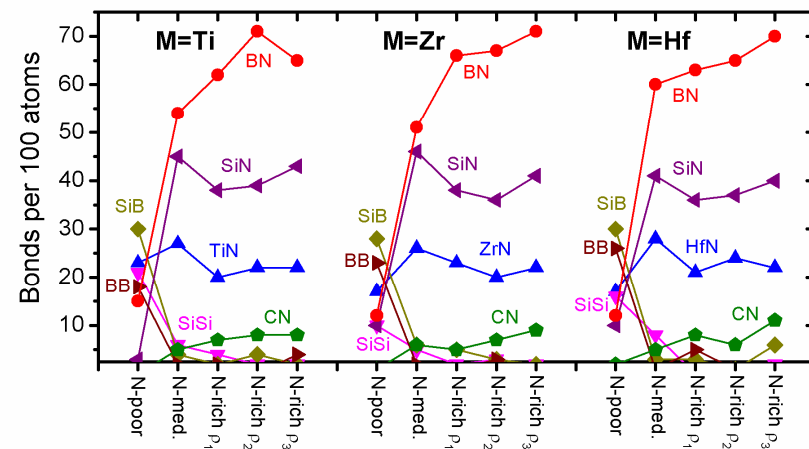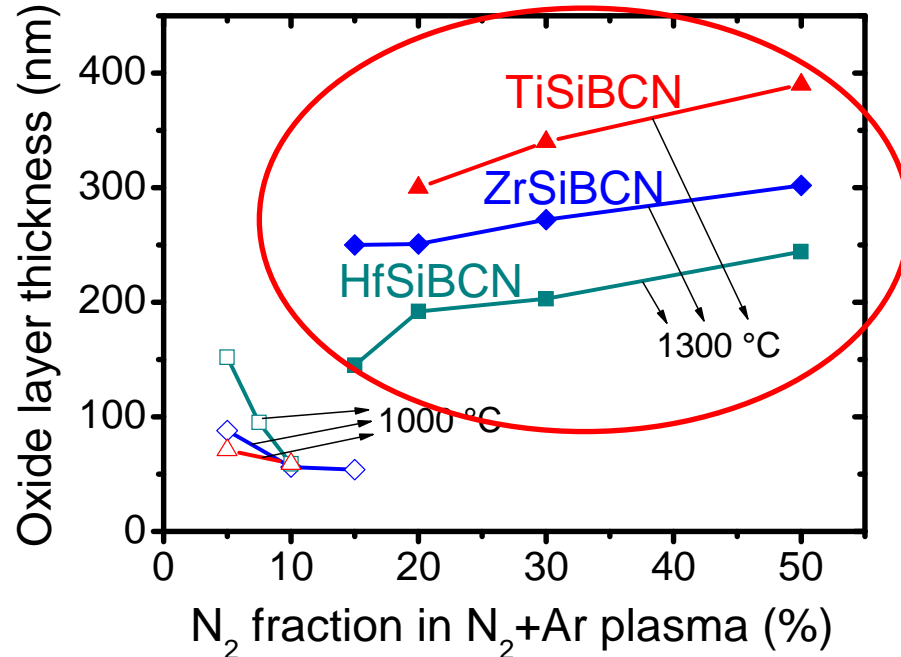## explanation for M-rich ($\Leftrightarrow$ N-poor) MSiBCN

- decreasing oxidation resistance from Ti through Zr to Hf
- explained by **calculated energies of M-based compounds**
  (Ti$\rightarrow$Zr$\rightarrow$Hf $\Rightarrow$ higher driving force towards oxidation)
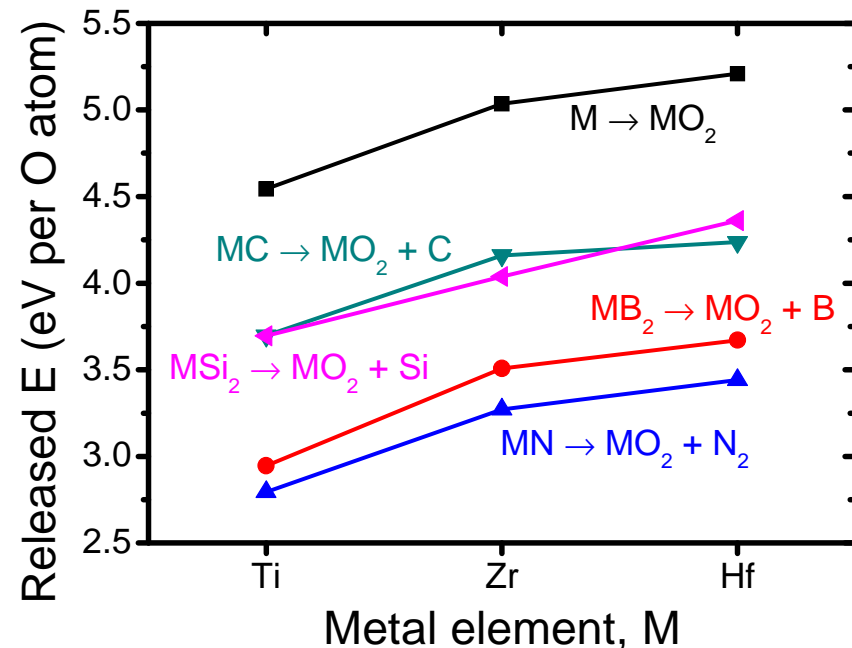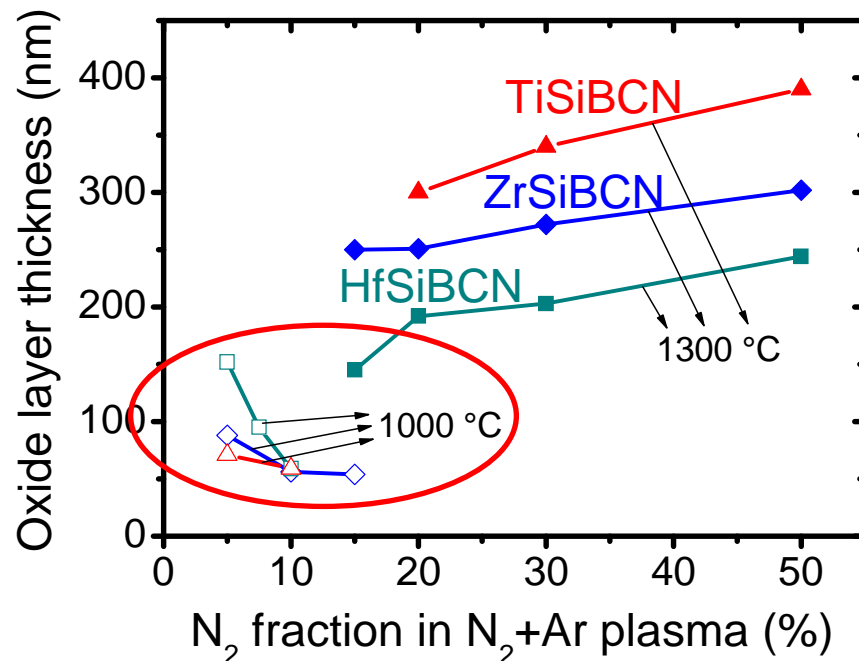
Effect of M choice on oxidation resistance
explanation for M-poor ($\Leftrightarrow$ N-rich) amorphous MSiBCN

- increasing oxidation resistance from Ti through Zr to Hf
- not explained by calculated bonding statistics
- above: Ti/Zr/Hf-based MBCN are not "equally amorphous"
- here: Ti/Zr/Hf-based MSiBCN are not equally amorphous either

Effect of M choice on oxidation resistance
explanation for M-poor (⟺ N-rich) amorphous MSiBCN

- increasing oxidation resistance from Ti through Zr to Hf
- above: Ti→Zr→Hf decreases k of MBCN (calculated E_{form} !)
- here: Ti→Zr→Hf decreases k of MSiBCN as well
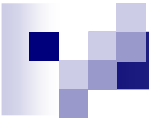 ⟺ (once again) slight **segregation** or slightly higher N content
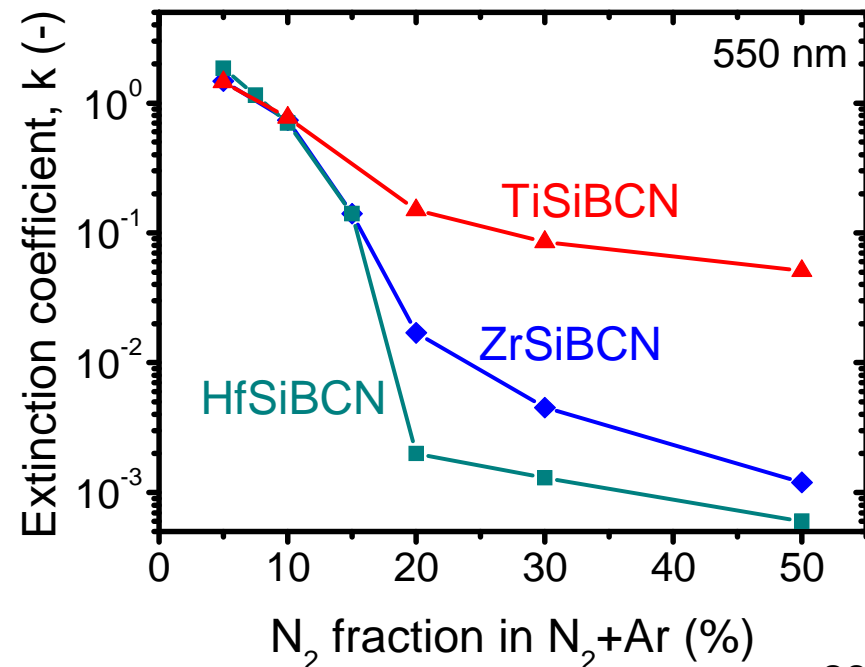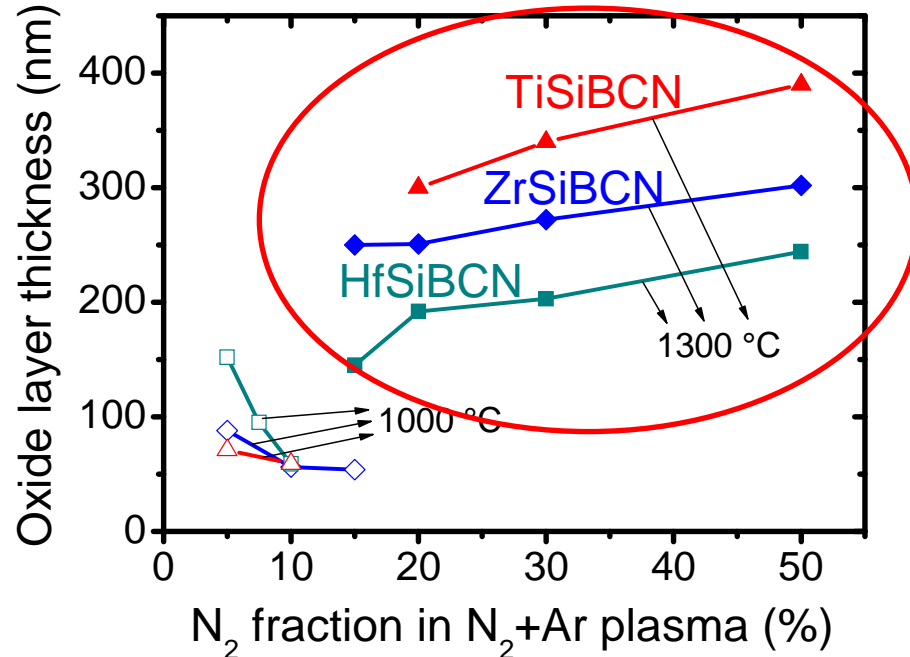
Conclusions 1/2 - fundamental differences

Experiment: Ti→Zr→Hf leads to

- Increasing E of reflected Ar
  (suppressed by varied pressure)

- Possibly easier N incorporation
  (not measurable directly, but can explain better transparency)

Calculations: Ti→Zr→Hf leads to

- Decreasing E_{form} of cubic (MN-like) solid solution crystals
- Increasing energy relieved after oxidation of M-based crystals
- Same bonding preferences in amorphous networks

Conclusions 2/2 - consequences

Low (~20 at. %) N content: Ti→Zr→Hf leads to

- Transition from a-TiBCN through nanocomposite $ZrB_xC_yN_{1-x-y}/ZrC_yN_{1-y}/a$-(Zr)BCN to $HfB_xC_yN_{1-x-y}/a$-BCN
- Consequently enhanced hardness, eastic recovery, H/E[*]
- Worse oxidation resistance (at 1000 °C) of MSiBCN

High (~50 at. %) N content: Ti→Zr→Hf leads to

- Increasing electrical resistivity
- Decreasing extinction coefficient (better trasparency)
  - of M-rich MBCN
  - of M-poor MSiBCN
- Better oxidation resistance (at 1300 °C) of MSiBCN