Role of boron in amorphous SiBCN and nanocomposite MSiBCN

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- M. Bilek et al. *(Sydney)*, L. Martinu et al. *(Montreal)*, E.I. Meletis et al. *(Arlington)*

Predecessors and motivation

- **SiCN and BCN films** (1990's):
  - controllable properties of SiCN such as hardness or thermal stability, but not as good as after B incorporation
  - high compressive stress of BCN

- **SiBCN by pyrolysis**

  [R. Riedel et al., A silicoboron carbonitride ceramic stable to 2000 °C, Nature 382, 796 (1996)]

- **SiBCN films**

  [J. Vlcek et al., J. Vac. Sci. Technol. A 23, 1513 (2005)] : first paper on sputtered SiBCN

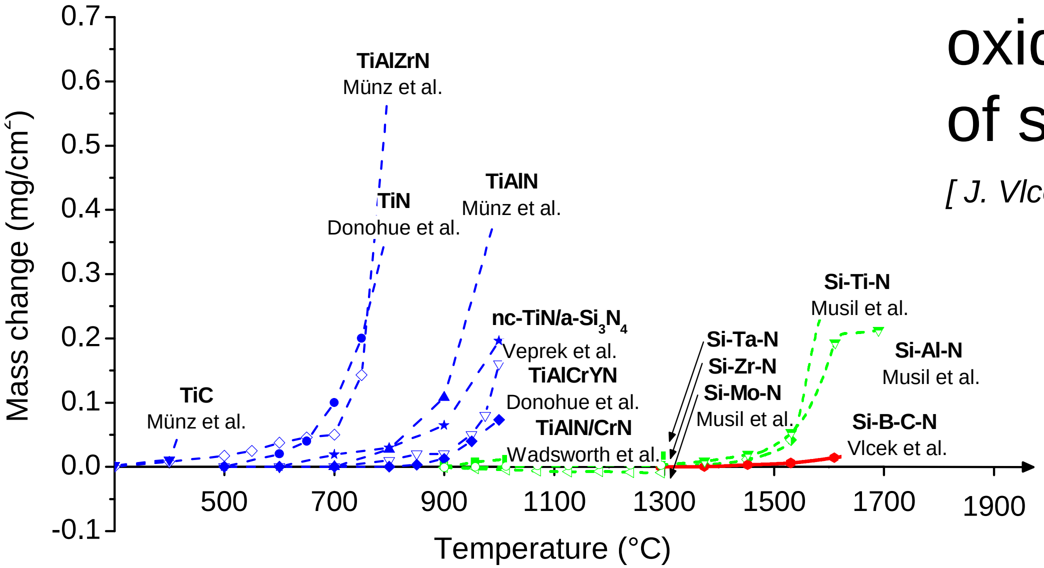
  [J. Houska, Ceram. Int. 41, 7921 (2015)] : includes recent overview on sputtered SiBCN
  - amorphous structure stable up to a 1700 °C limit
  - extremely high oxidation resistance in air above 1500 °C
  - high H up to 44 GPa and $E/(1-\nu^2)$ up to 240 GPa
  - controllable E_g = 0 to 3.5 eV ⇒ transparency ($k_{550nm} = 2\times10^{-4}$) or finite resistivity (~10^1 Ωm) depending on composition

- **MSiBCN films**

  [M. Zhang et al., Appl. Surf. Sci. 357, 1343 (2015)] : example for M = Hf

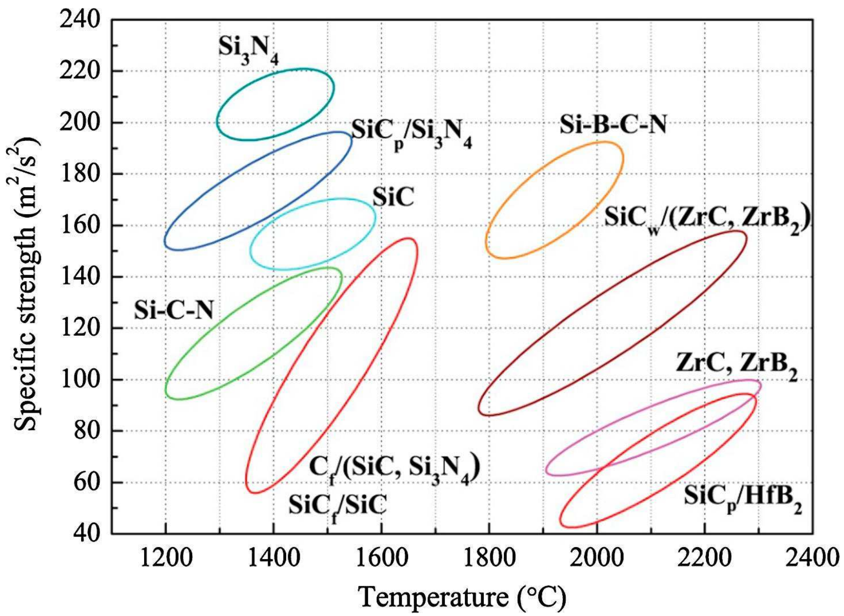
  [J. Houska et al., Ceram. Int. 42, 4361 (2016)] : example for M = Zr
  - wider range of structures, e.g. MB_2-based
  - wider range of properties, e.g. resistivity of "interesting" compositions
    SiBCN: from insulating to ~10^1 Ωm (SiBCN), ~10^{-1} Ωm (N-free SiBC)
    MSiBCN: from insulating to ~10^{-6} Ωm

Predecessors and motivation



oxidation resistance
of sputtered SiBCN

[J. Vlcek et al., J. Vac. Sci. Technol. A 23, 1513 (2005), etc.]



specific strength and working
temperature of SiBCN

[D. Jia et al., Prog. Mater. Sci. 98, 1 (2018)]

Boron-focused outline

Phenomena relevant for amorphous **SiBCN**
(including amorphous matrix of nanocomposite MSiBCN)

1-1 : effect of B content: thermal stability, hardness

1-2 : high compressive stress of BCN: how to decrease it

1-3 : homogeneous networks × formation of B-rich zones

1-4 : high-*T* oxidation: h-BN between bulk and surface oxide

1-5 : room-*T* oxidation: effect of B content on ageing resistance

Phenomena relevant only for **MSiBCN**

2-1 : crystalline phases obtained: h-MB_2, fcc-MB_xN_{1-x}

2-2 : effect of crystallinity: electrical and thermal conductivity

2-3 : high compressive stress of MB_2: how to decrease it

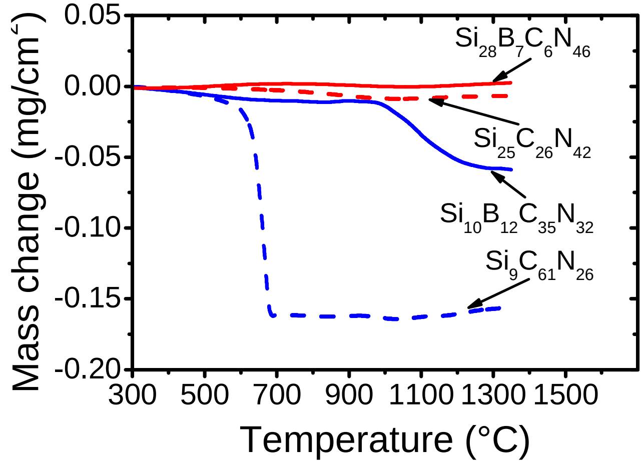
2-4 : M=Ti → M=Zr → M=Hf: effect on crystallinity

2-5 : M=Ti → M=Zr → M=Hf: effect on properties

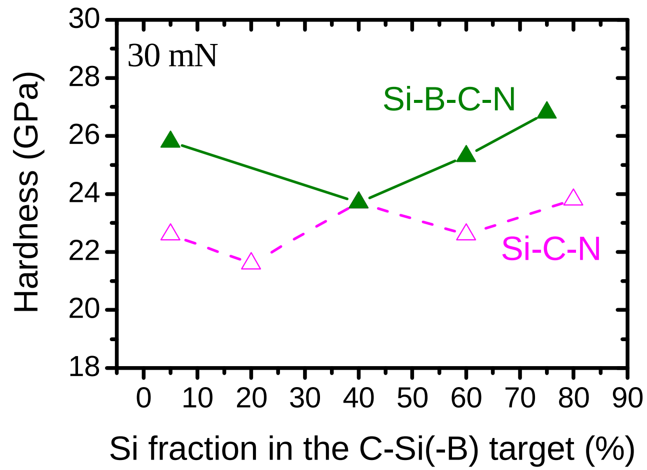
Phenomenon 1-1 (SiBCN): effect of B content

B incorporation into SiCN (at high Si/C or low Si/C):

- better thermal stability



- higher hardness

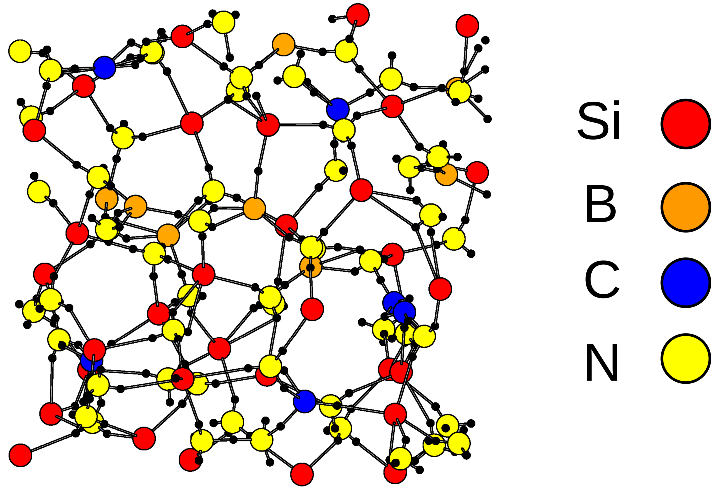


[J. Houska et al., Europhys. Lett. 76, 512 (2006)]

Phenomenon 1-1 (SiBCN): effect of B content

Explanation of hardness and stability after B incorporation:

- structures predicted by liquid-quench ab-initio simulations



- high affinity of B to N

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some N electrons are lonepairs in SiCN, but bonding el. in SiBCN

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higher N coordination in SiBCN

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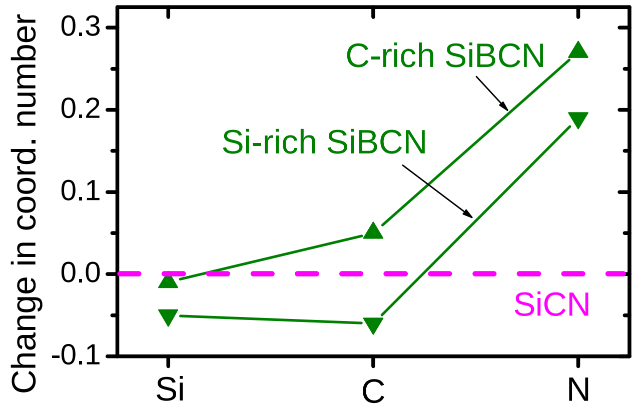
lower rate of N_2 formation, longer bond lifetimes (not shown)



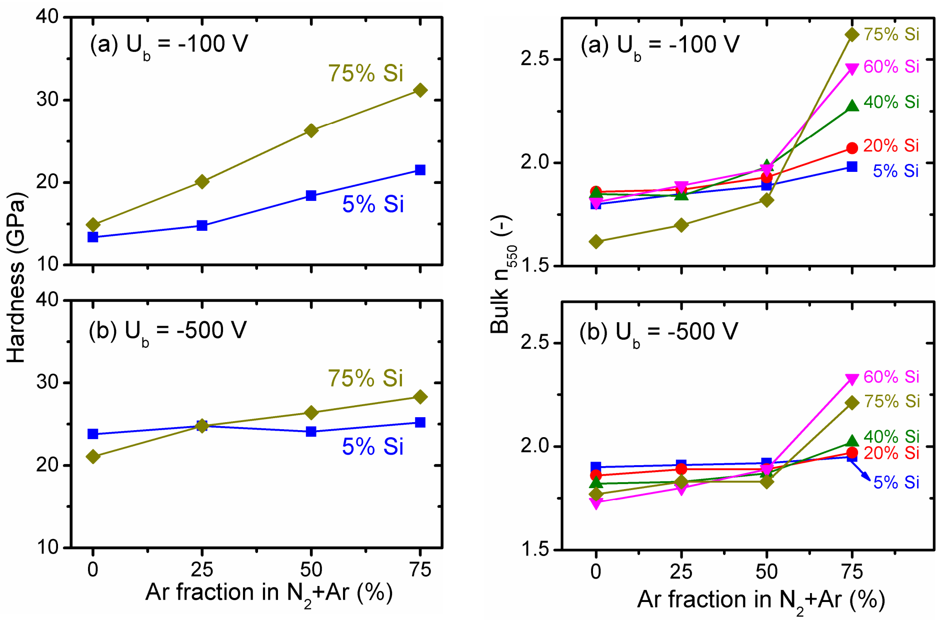
[J. Houska et al., Europhys. Lett. 76, 512 (2006)]

Phenomenon 1-1 (SiBCN): effect of B content

Sputtering of $Si_x(B_4C)_{1-x}$ targets: **densification** (hardness, refractive index) is different for **B_4C-rich** and **Si-rich** films

- B_4C-rich SiBCN:
  best densification by high-energy (500 eV) nitrogen ions

- Si-rich SiBCN:
  best densification by medium-energy (100 eV) argon ions



- Related also to the Si role during Ar^+ implantation (next slide)

[J. Houska, Ceram. Int. 41, 7921 (2015)]

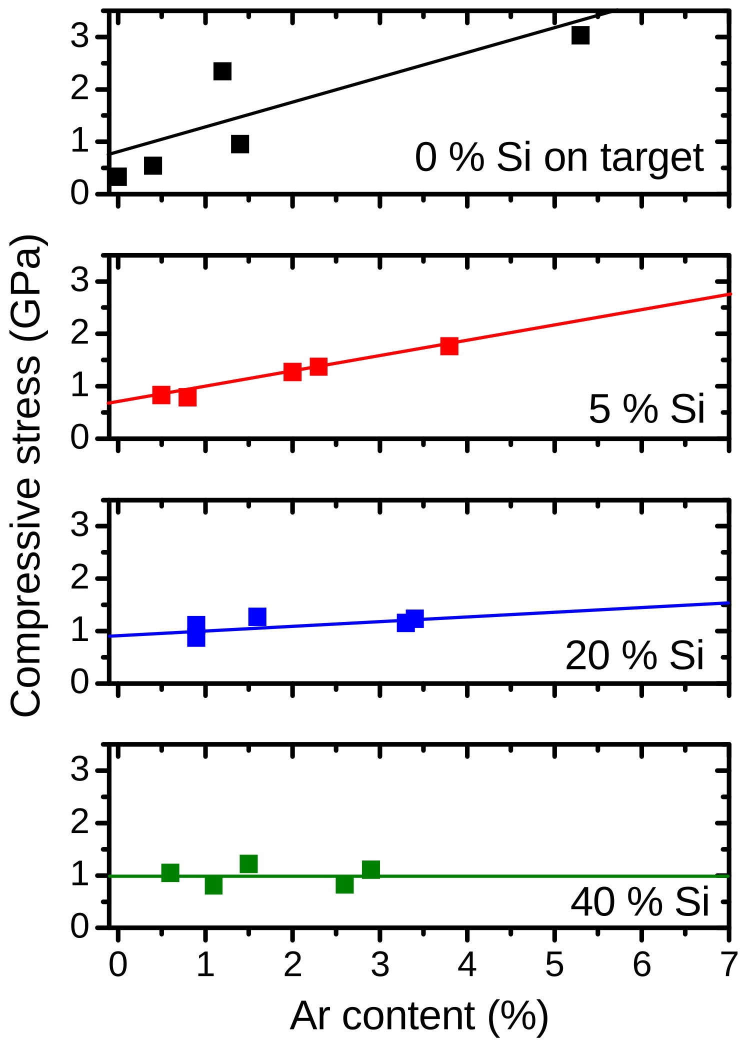
Phenomenon 1-2 (SiBCN): compressive stress

BCN sputtered in N_2+Ar:

- high compressive stress due to implanted Ar^+

Increasing Si content:

- stress relaxation (decreasing slope of the stress-Ar content dependence)

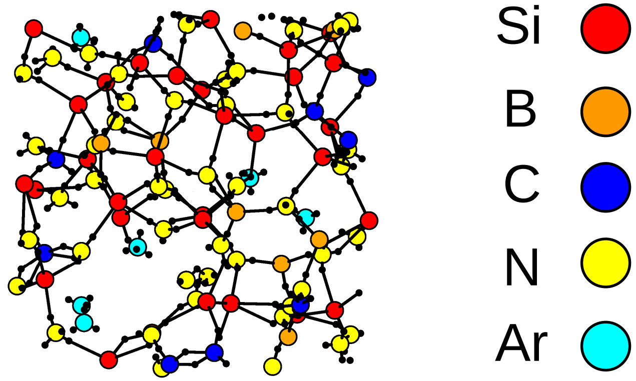


[J. Houska et al., J. Phys.: Condens. Matter 18, 2337 (2006)]

Phenomenon 1-2 (SiBCN): compressive stress

Explanation of stress relaxation after Si incorporation:

- again, structures predicted by ab-initio simulations



- short B/C/N bonds × long Si bonds

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  surrounding the Ar-containing voids by longer and more flexible Si bonds leads to lower energy penalty

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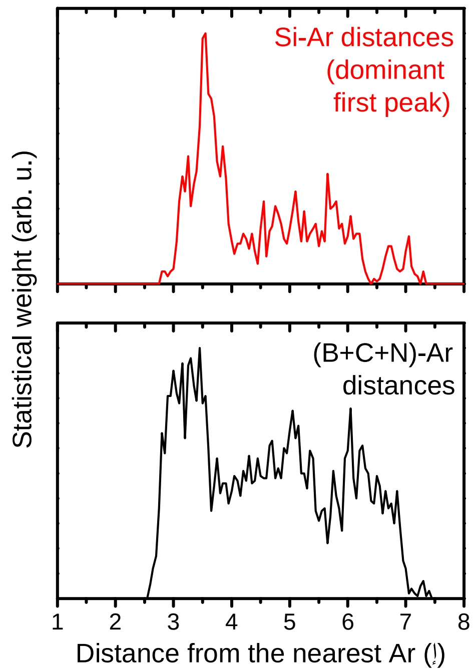
  low-stress networks with **Si-rich zones segregated around Ar**

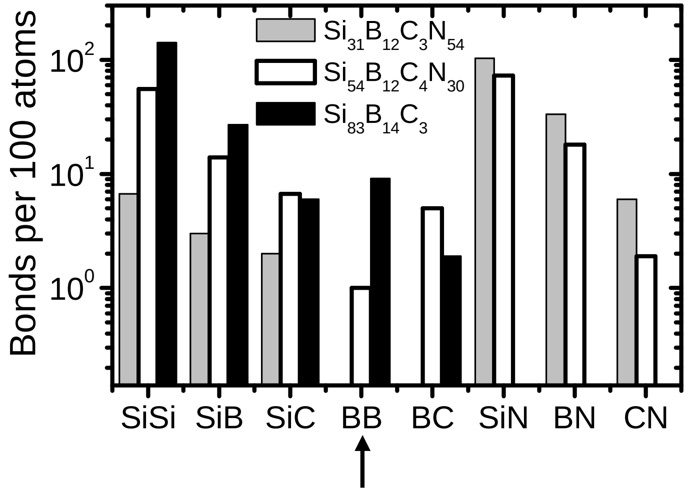


[J. Houska et al., J. Phys.: Condens. Matter 18, 2337 (2006)]

Phenomenon 1-3 (SiBCN): formation of B-rich zones

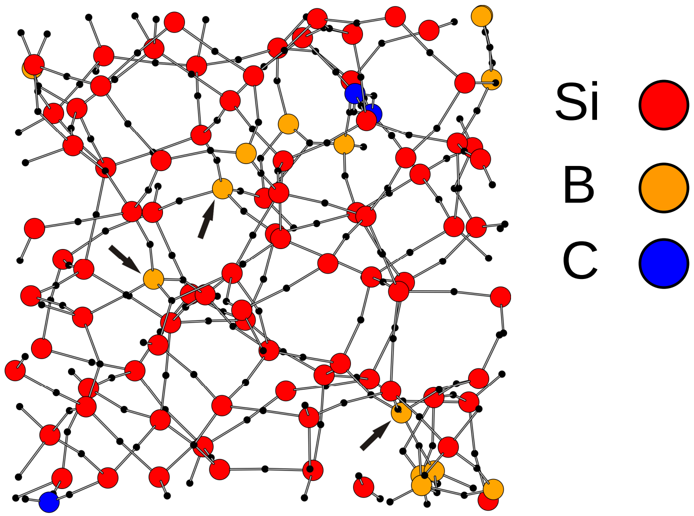
N-rich SiBCN:

- homogeneous
  (SiN, BN, CN bonds)



Replacement of N by Si:

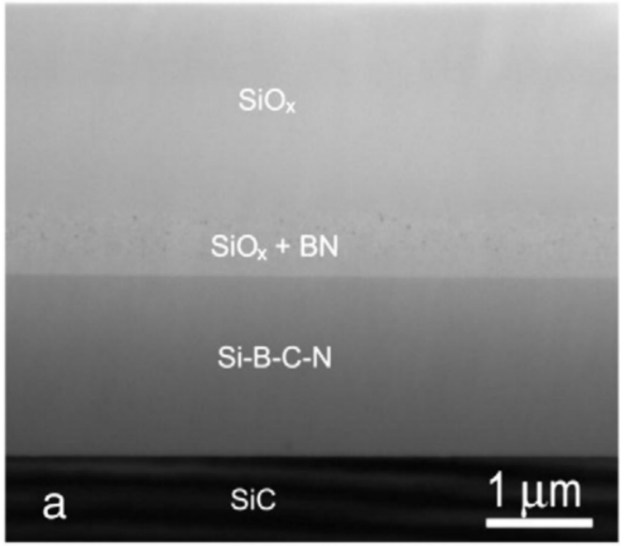
- steeply increasing number of BB bonds
- B atoms nevertheless trapped
  in a-Si have coordination of 4
  (similarly to B dopants in c-Si)



[V. Petrman et al., Acta Mater. 59, 2341 (2011)]

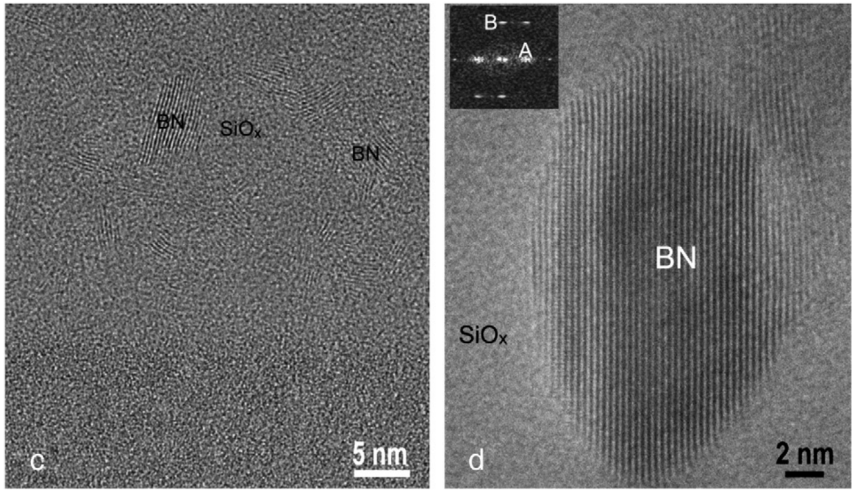
Phenomenon 1-4 (SiBCN): high-*T* oxidation

SiBCN annealed in air up to 1700 °C:



- amorphous SiO_2-based top layer
  +
  transition layer with **BN nanocrystals** in amorphous SiO_2-based matrix
  +
  original bulk layer of SiBCN (on SiC)

- BN-rich transition layer is another barrier for O_2 diffusion
  $\Downarrow$
  higher oxidation resistance of SiBCN compared to SiCN



[J. He et al., Thin Solid Films 542, 167 (2013)]

Phenomenon 1-5 (SiBCN): room-*T* oxidation

80 SiBCN coatings oxidizing at room-*T* for 12 years

two information in one box: effect of substrate bias

- bottom: B_2O_3 layer can protect bulk material
- top: SiO_2 layer can protect bulk material
- medium compositions: $Si_xB_yO_z$ (B constitutes impurities, not oxide in its own right) can NOT protect bulk material

$Si_x(B_4C)_{1-x}$ sputter target composition	0% Ar	25% Ar	50% Ar	75% Ar
75% Si	resistant	resistant	resistant	resistant
60% Si	resistant	resistant	resistant	resistant
40% Si	ox. barrier / complete ox.	oxidation barrier	resistant	resistant
20% Si	ox. barrier / complete ox.	ox. barrier / complete ox.	complete oxidation	resistant / ox. barrier
5% Si	resistant / ox. barrier	resistant / ox. barrier	oxidation barrier	oxidation barrier

N_2+Ar discharge gas mixture composition

[J. Houska, Ceram. Int. 41, 7921 (2015)]

Phenomenon 1-5 (SiBCN): room-*T* oxidation

Bias voltage leading to better ageing resistance

- corelation with growth conditions leading to best densification (Phenomenon 1-1):

  bombardment of B_4C-rich SiBCN by 500 eV $N_{(2)}^{+}$

  bombardment of Si-rich SiBCN by 100 eV Ar^{+}

$Si_x(B_4C)_{1-x}$ sputter target composition	0% Ar	25% Ar	50% Ar	75% Ar
75% Si	any U_b	any U_b	any U_b	any U_b
60% Si	any U_b	any U_b	any U_b	any U_b
40% Si	-100 V	-100 V	any U_b	any U_b
20% Si	-100 V	-100 V	-100 V	-100 V
5% Si	-500 V	-500 V	-500 V	-100 V

N_2+Ar discharge gas mixture composition

[J. Houska, Ceram. Int. 41, 7921 (2015)]

Phenomenon 2-1 (MSiBCN): crystalline phases obtained

ZrBCN deposited in a wide range of $Zr_x(B_4C)_{1-x}$ target compositions and N_2+Ar gas mixture compositions

- medium Zr content : **h-ZrB_2** based nanocomposites
- high Zr content : **fcc-ZrN** based nanocomposites
- N is amorphizer (seriously: ZrN-like crystals are more likely at zero N content than at too high N content)
- Si is amorphizer (not shown)

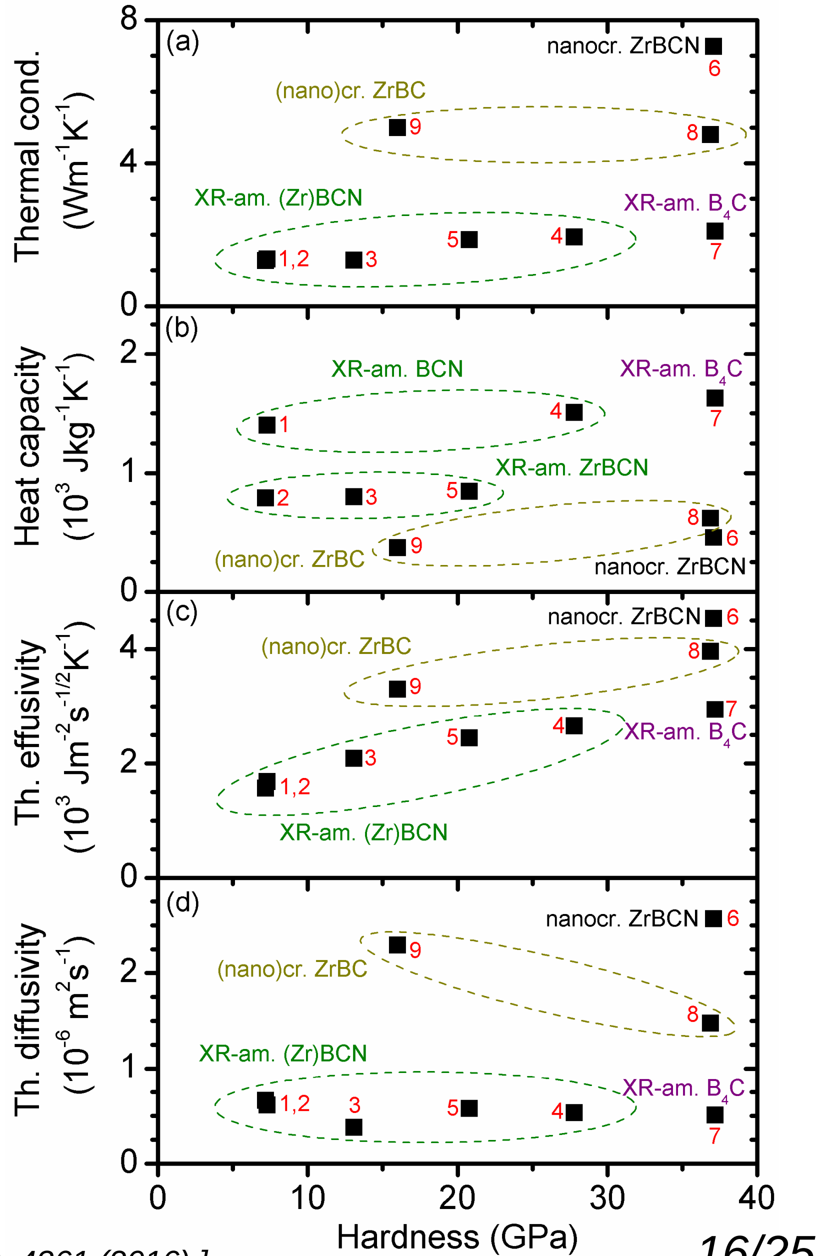
	0% Zr	**15% Zr**	**45% Zr**
50% N_2	$B_{44}C_{11}N_{42}$ XR-am. (1)	$Zr_6B_{37}C_5N_{47}$ XR-am. (2)	$Zr_{19}B_{24}C_3N_{52}$ XR-am. (3)
5% N_2	$B_{69}C_{16}N_{13}$ XR-am. (4)	$Zr_{14}B_{50}C_{13}N_{22}$ XR-am. (5)	$Zr_{41}B_{30}C_8N_{20}$ nanocr. cubic (6)
0% N_2	$B_{81}C_{17}$ XR-am. (7)	$Zr_{25}B_{57}C_{14}$ cr. hexagonal (8)	$Zr_{61}B_{27}C_6$ nanocr. cubic (9)

[J. Houska et al., Ceram. Int. 42, 4361 (2016)]

Phenomenon 2-2 (MSiBCN): effect of crystallinity

Nine (Zr)BC(N) films of various structures from the previous slide

- Thermal conductivity & diffusivity & effusivity depend mostly on structure
- Heat capacity depends mostly on composition
- High hardness achieved for (i) crystalline compositions, and (ii) B_4C-rich amorphous compositions



[J. Houska et al., Ceram. Int. 42, 4361 (2016)]

Phenomenon 2-2 (MSiBCN): effect of crystallinity

Nine (Zr)BC(N) films of various structures

- Electrical conductivity is high at
  sufficiently high Zr content and sufficiently low N content
  (seriously: ZrN is conductive, but N makes ZrBC insulating)

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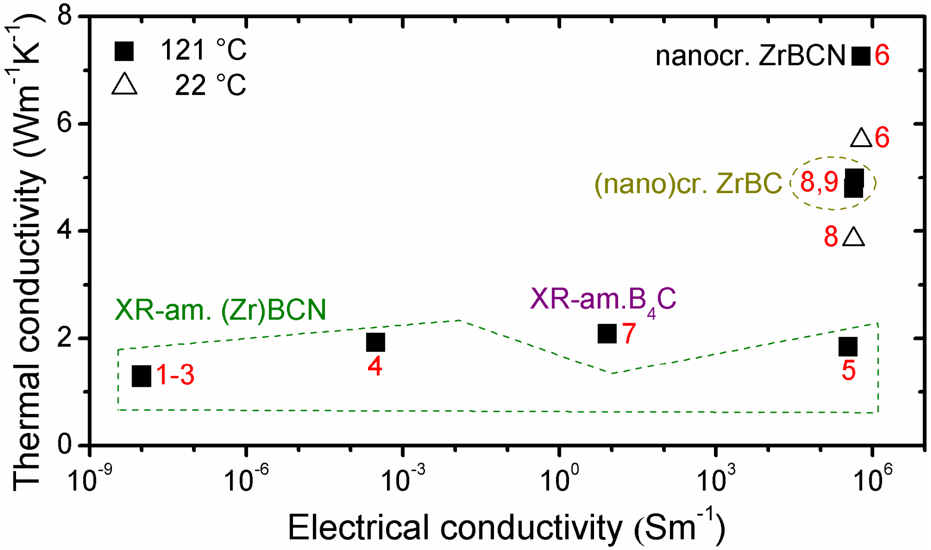
  for the same compositions which are crystalline

- Difference between thermal conductivities is due to the electronic contribution (well corresponds to the Wiedemann-Franz law)

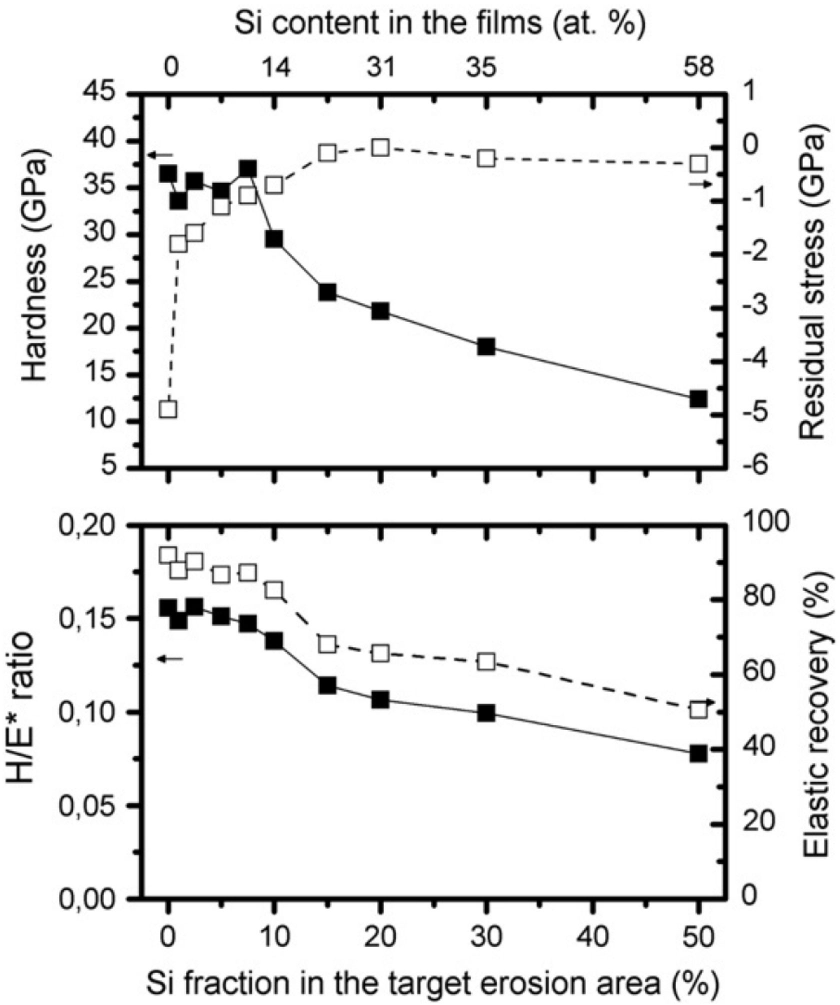


[J. Houska et al., Ceram. Int. 42, 4361 (2016)]

Phenomenon 2-3 (MSiBCN): compressive stress

HfB_2-based HfSiBC with a wide range of Si contents

- Si-free HfBC : huge compressive stress of 5 GPa
- Si content of 1-10% : stress relaxation to 2 GPa and then 1 GPa at preserved hardness



[J. Kohout et al., Surf. Coat. Technol. 257, 301 (2014)]
[M. Zhang et al., Appl. Surf. Sci. 357, 1343 (2015)]

Phenomenon 2-3 (MSiBCN): compressive stress

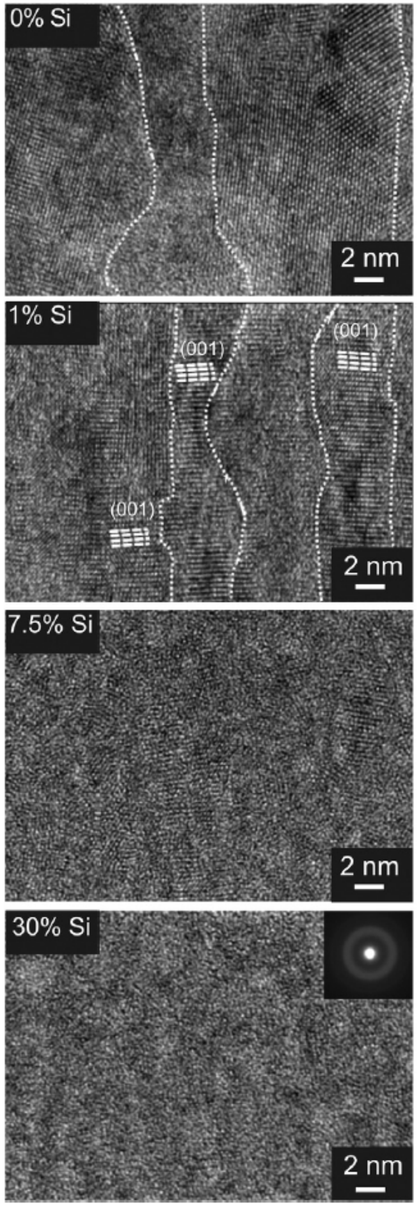
Explanation of stress relaxation by HRTEM

0% Si on target: wide HfB_2 nanocolumns

1% Si on target: narrow HfB_2 nanocolumns (at a lower stress and preserved *H*)

7.5% Si on target: isotropic MB_2 nanocrystals (at even lower stress and still preserved *H*)

30% Si on target: almost amorphous

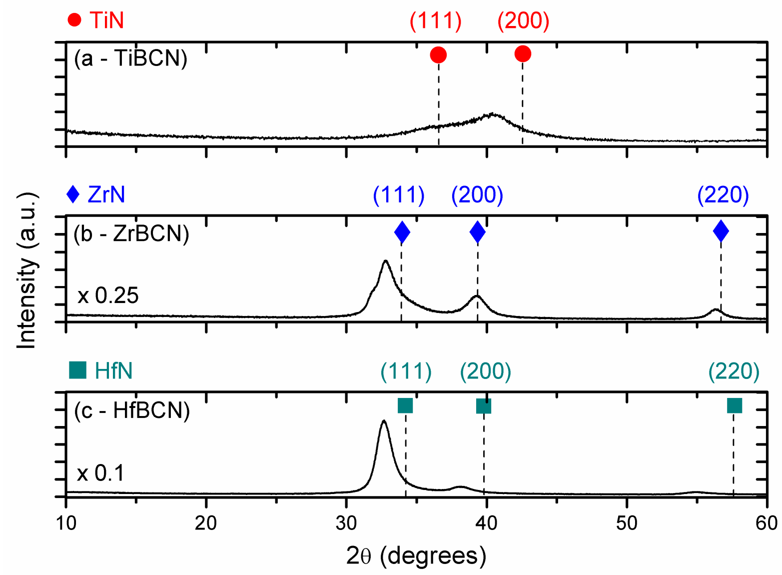


[J. Kohout et al., Surf. Coat. Technol. 257, 301 (2014)]
[M. Zhang et al., Appl. Surf. Sci. 357, 1343 (2015)]

Phenomenon 2-4 (MSiBCN): M choice ↔ crystallinity

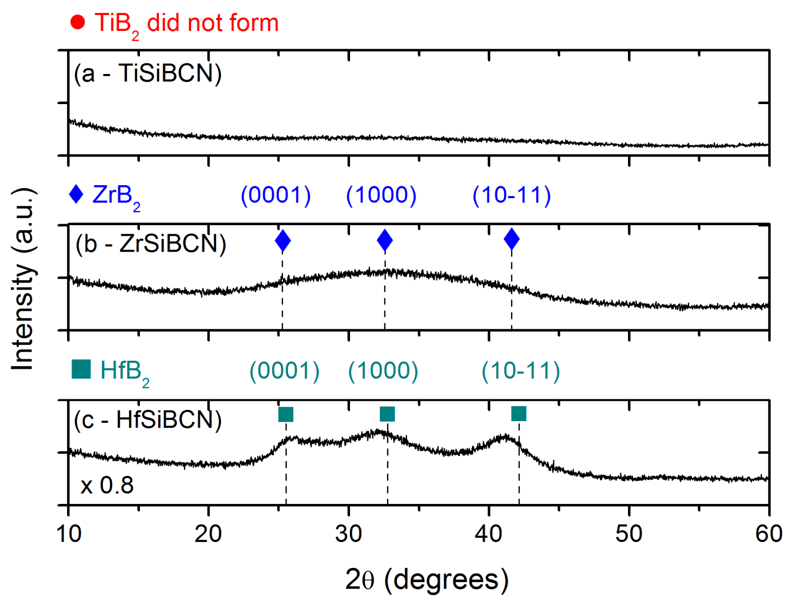
- Sputtering of $M_{0.45}(B_4C)_{0.55}$ in 5% N_2 + 95% Ar :

  M=Ti → M=Zr → M=Hf leads to **stronger MN peaks** (incl. shifted: solid solutions)



- Sputtering of $M_{15}Si_{20}(B_4C)_{65}$ in 5% N_2 + 95% Ar

  M=Ti → M=Zr → M=Hf leads to **stronger MB_2 peaks**



[J. Houska et al., Thin Solid Films 586, 22 (2015)]
[J. Houska et al., Thin Solid Films 616, 359 (2016)]

Phenomenon 2-4 (MSiBCN): M choice ↔ crystallinity

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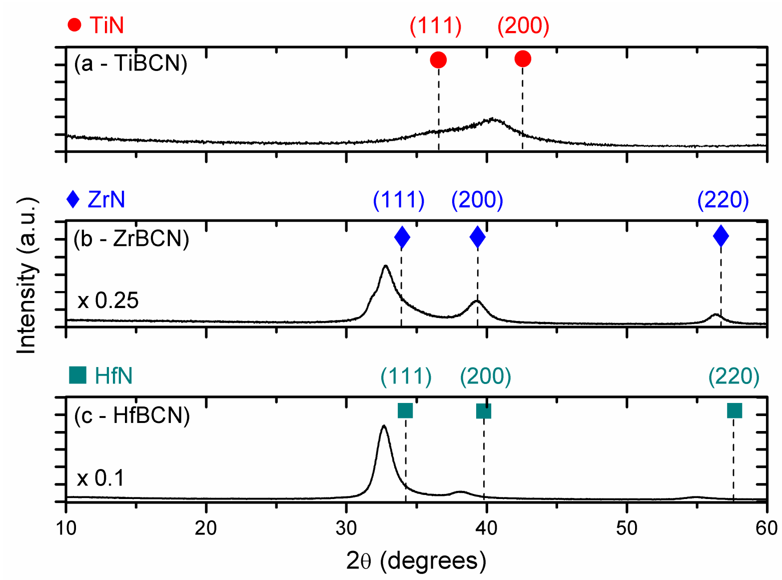

- **Explanation by ab-initio calculations**:

  M=Ti → M=Zr → M=Hf
  leads to decreasing formation energy of the corresponding solid solutions

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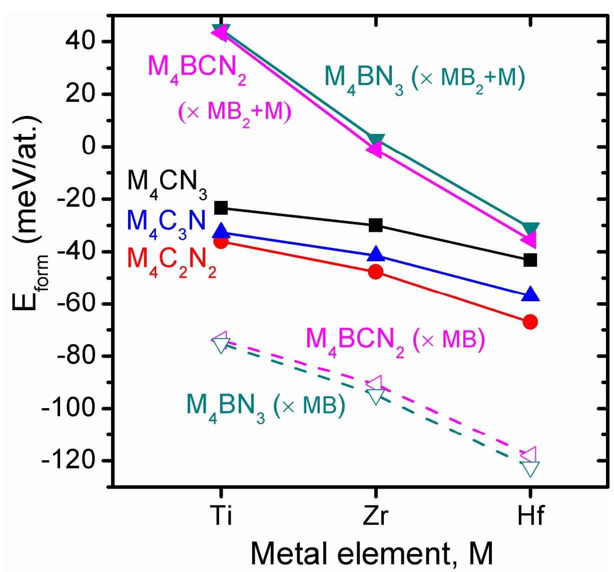
  crystallization does not need (so much) segregation

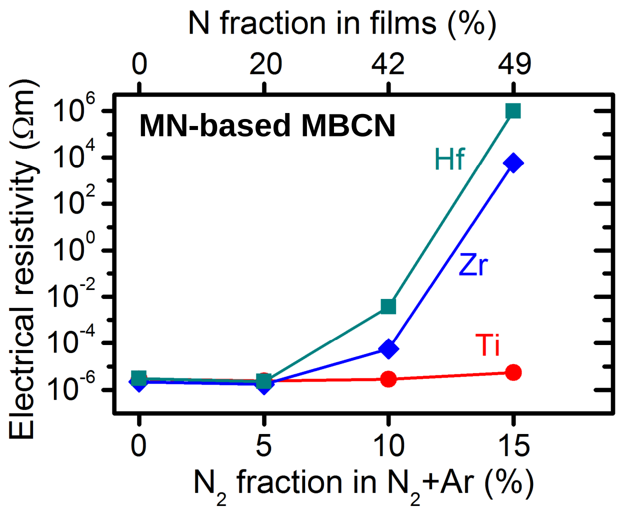


[J. Houska et al., Thin Solid Films 586, 22 (2015)]
[J. Houska et al., Thin Solid Films 616, 359 (2016)]

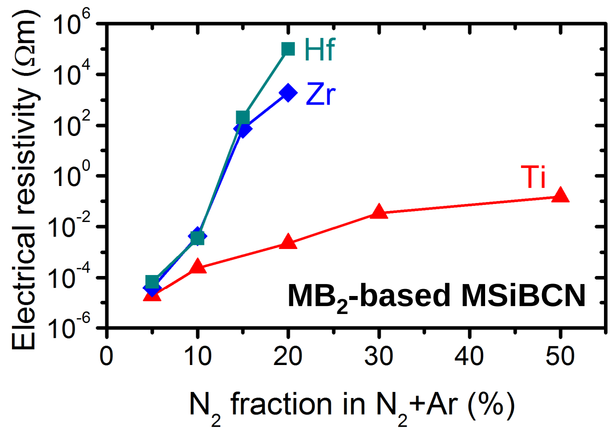
Phenomenon 2-5 (MSiBCN): M choice ↔ properties

High N content
(high importance of M-free amorphous matrix, if there is any):

- M=Ti → M=Zr → M=Hf
  leads to **increasing resistivity of MN-based MBCN**
  (better crystallinity shown above ⇒ conductive crystals encapsulated by insulating amorphous matrix)



- M=Ti → M=Zr → M=Hf
  leads to **increasing resistivity of MB_2-based MSiBCN**
  (same reason)

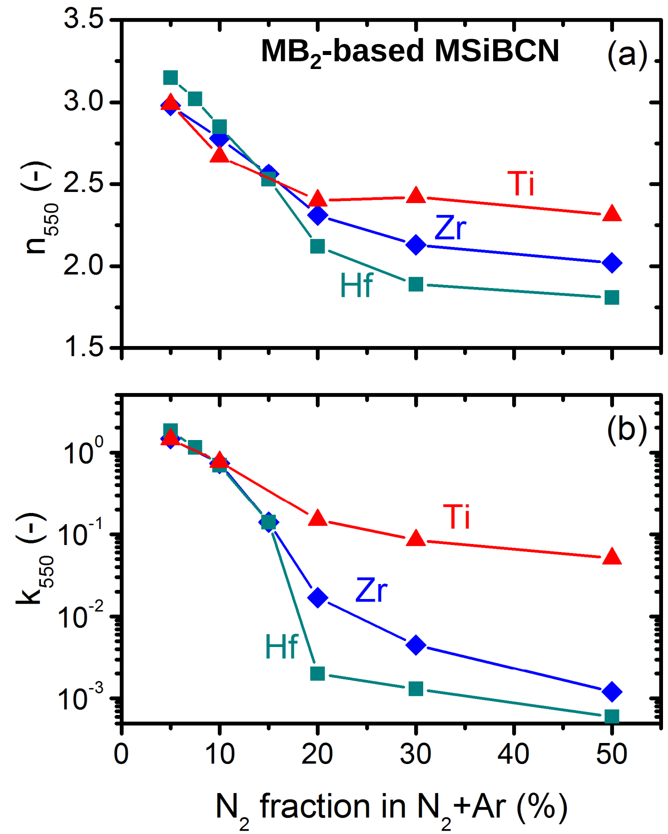


[J. Houska et al., Thin Solid Films 586, 22 (2015)]
[J. Houska et al., Thin Solid Films 616, 359 (2016)]

Phenomenon 2-5 (MSiBCN): M choice ↔ properties

High N content
(high importance of M-free amorphous matrix, if there is any):

- M=Ti → M=Zr → M=Hf
  leads to **decreasing refractive index and extinction coefficient of MB_2-based MSiBCN**
  (complementary to the resistivity shown above: more conductive material is less transparent)

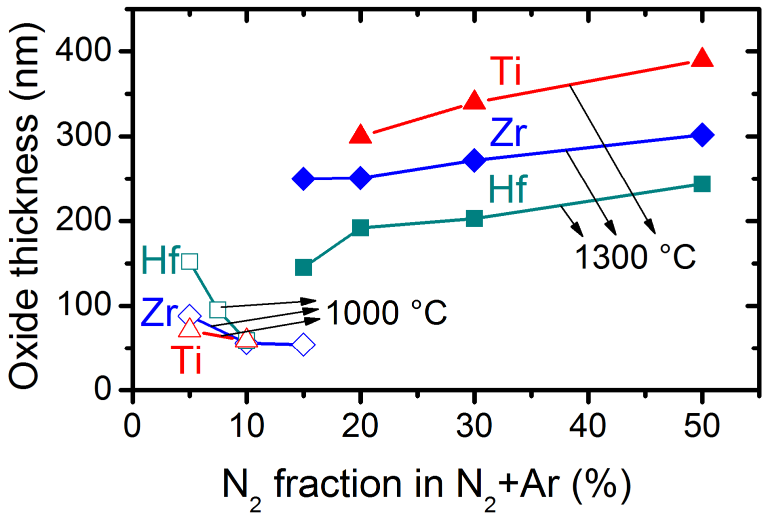


[J. Houska et al., Thin Solid Films 586, 22 (2015)]
[J. Houska et al., Thin Solid Films 616, 359 (2016)]

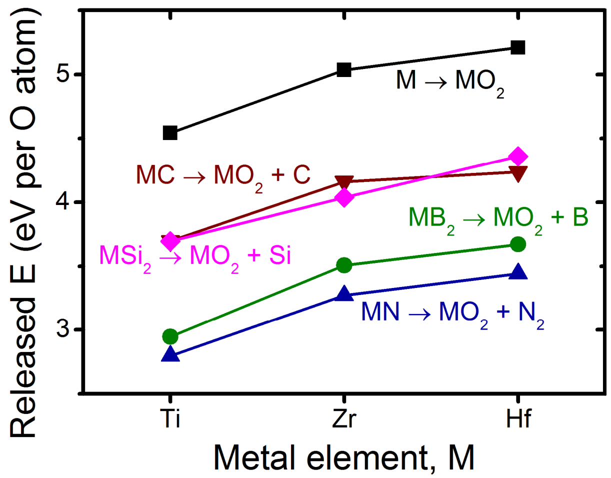
Phenomenon 2-5 (MSiBCN): M choice ↔ properties

- M=Ti → M=Zr → M=Hf leads to **worse oxidation resistance of M-rich N-poor** MB_2-based MSiBCN

  (in agreement with ab-initio calculations: motivation to oxidize M-based phases)



- M=Ti → M=Zr → M=Hf leads to **better oxidation resistance of M-poor N-rich** MB_2-based MSiBCN



[J. Houska et al., Thin Solid Films 586, 22 (2015)]
[J. Houska et al., Thin Solid Films 616, 359 (2016)]

Conclusions

- **amorphous SiBCN**:
  thermal stability (1700 °C), oxidation resistance (1500 °C), hardness (44 GPa), transparency ($k_{550nm} = 2\times10^{-4}$), resistivity (from insulating to 10^{1} Ωm), etc.
- **amorphous or MB_2-based or MN-based MSiBCN**:
  wider range of resistivity (from insulating to 10^{-6} Ωm), etc.
- effect of B and MB_2 on materials properties explained
- compressive stress relaxation in SiBCN or MB_2 explained
- effect of Ti/Zr/Hf choice on structure and properties explained