Ageing Resistance (12 years) of Hard and Oxidation Resistant **SiBCN** Coatings

Jiri Houska

Department of Physics and NTIS - European Centre of Excellence,
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DEPARTMENT OF PHYSICS

NTIS

Acknowledgment

Grant Agency of the Czech Republic through Project No. 15-00859Y

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in as-deposited state studied for years

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J. Houska et al.	J. Vac. Sci. Technol. A 25, 1411	2007	Bonding statistics and electronic structure of novel **Si-B-C-N** materials: ab-initio calculations and ...
J. Houska et al.	J. Phys.: Condens. Matter 19, 196228	2007	Effect of implanted argon on hardness of novel magnetron sputtered **Si-B-C-N** materials: ...
J. Cizek et al.	Thin Solid Films 516, 7286	2008	Mechanical and optical properties of quaternary **Si-B-C-N** films prepared by reactive magnetron sputtering
J. Vlcek et al.	J. Vac. Sci. Technol. A26, 1101	2008	Magnetron sputtered **Si-B-C-N** films with high oxidation resistance and thermal stability in ...
J. Capek et al.	Surf. Coat. Technol. 203, 466	2008	Effect of the gas mixture composition on high temperature behavior of magnetron suttered **Si-B-C-N** ...
J. Kalas et al.	Thin Solid Films 518, 174	2009	High-temperature stability of the mechanical and optical properties of **Si-B-C-N** films prepared by ...
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J.J. Gengler et al.	Surf. Coat. Technol. 206, 2030	2011	Thermal conductivity of high-temperature **Si-B-C-N** thin films
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J. Houska et al.	Ceram. Int. 41, 7921	2015	Ageing resistance of **SiBCN** ceramics
Other labs (examples)			
M.A. Rooke et al.	Chem. Mater. 9, 285	1997	Surface Studies of Potentially Oxidation Protective **Si-B-N-C** Films for Carbon Fibers
D. Hegemann et al.	Chem. Vap. Deposition 5, 61	1999	PACVD-Derived Thin Films in the System **Si-B-C-N**
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but rarely studied (also for obvious reasons)

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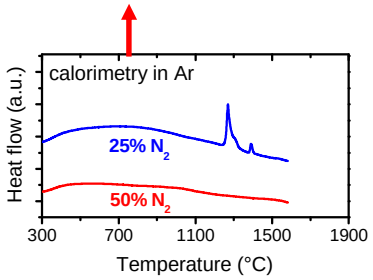
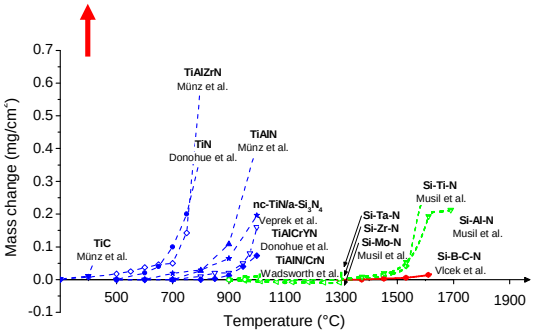
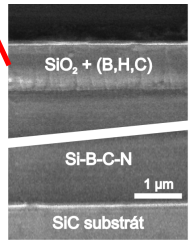
Motivation: examples of as-deposited propeties of SiBCN

Thermal stability and oxidation resistance up to ~1500 °C (thin surf. oxide at 1700 °C)







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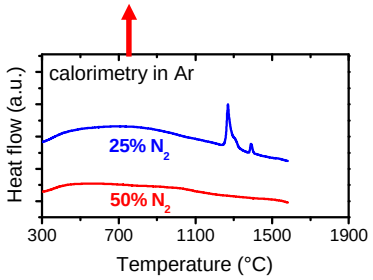
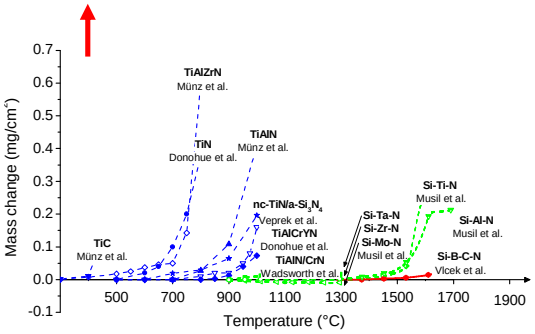
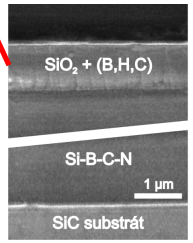
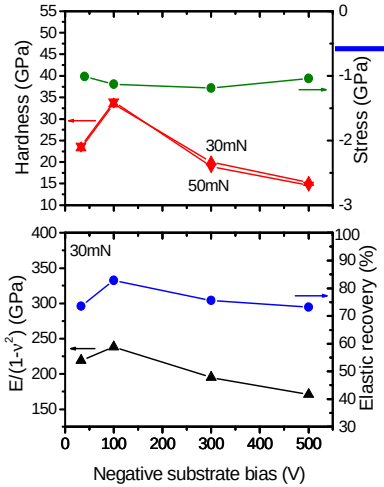


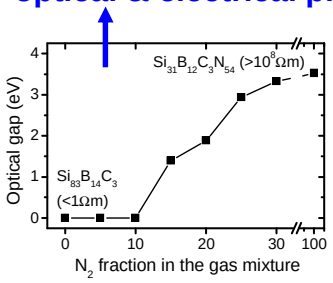






Tailored mechanical properties
(*H* up to ~35 GPa, *E* >300 GPa, ...)

Tailored electronic structure
⇒ optical & electrical prop.



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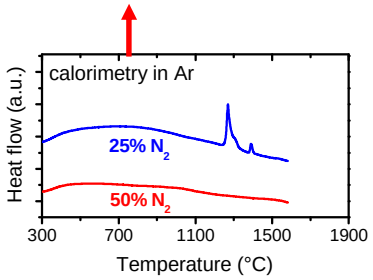

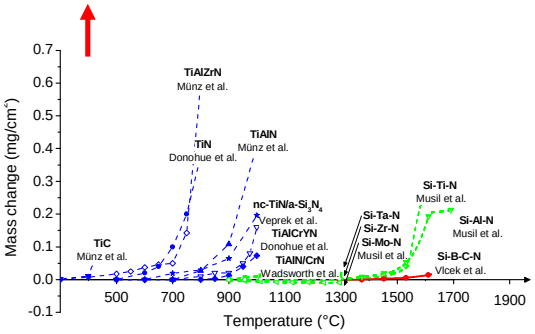

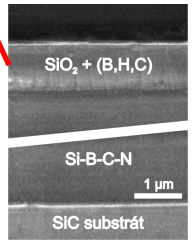

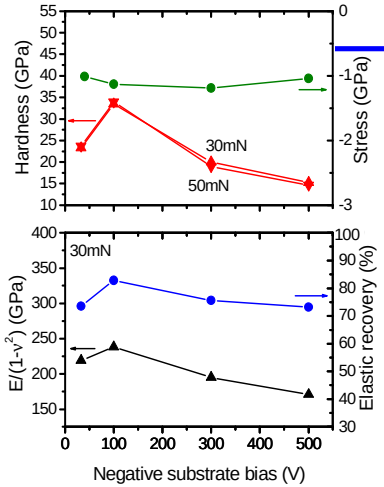

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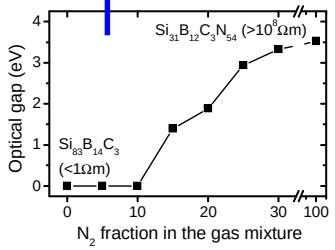

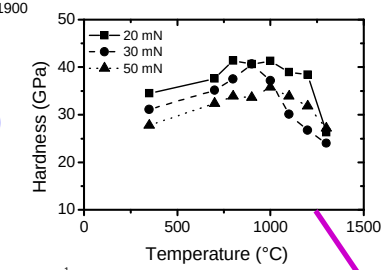

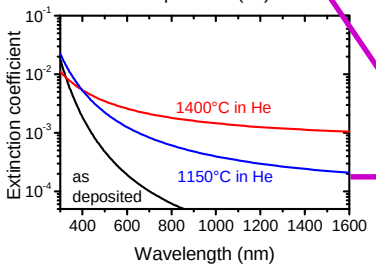

High-temperature stability of mechanical properties and optical properties

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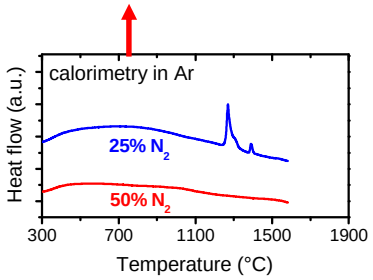
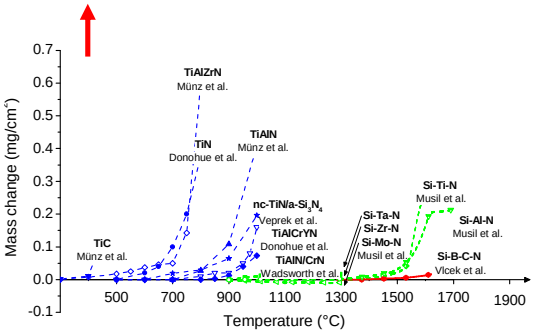
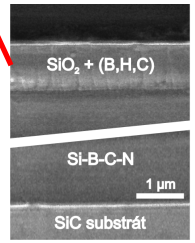
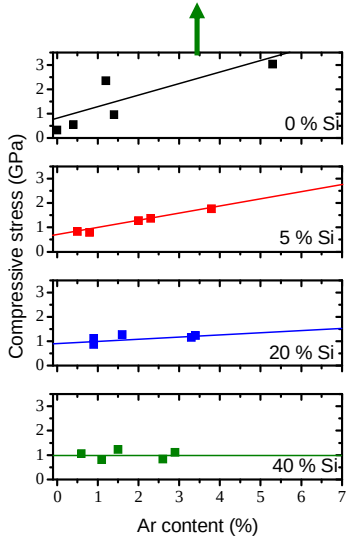
Thermal stability and oxidation resistance up to ~1500 °C (thin surf. oxide at 1700 °C)

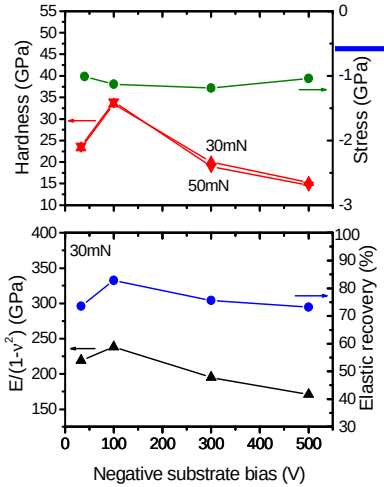






Si relaxes stress caused (in BCN) by implanted Ar





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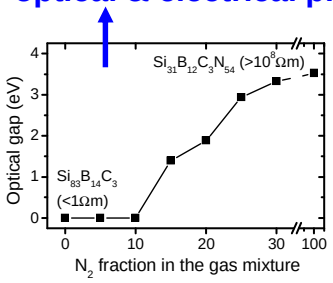

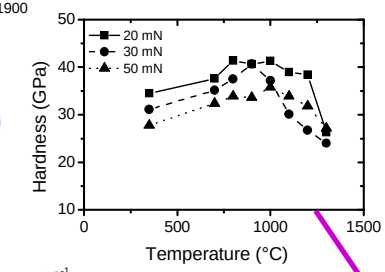

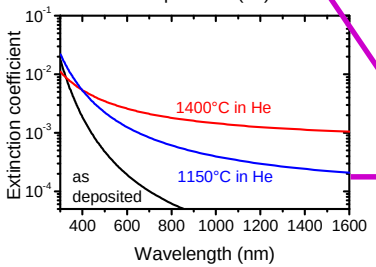

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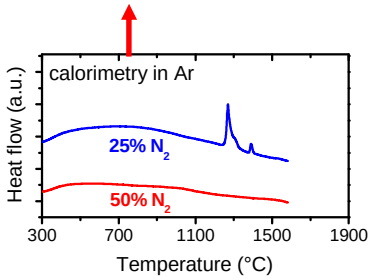

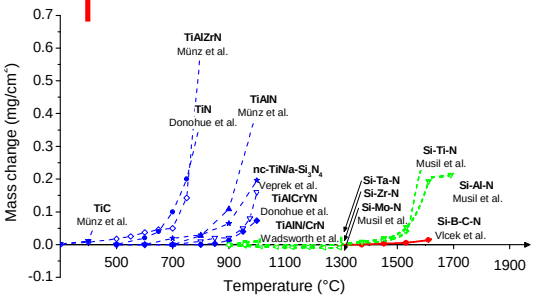

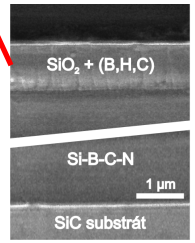

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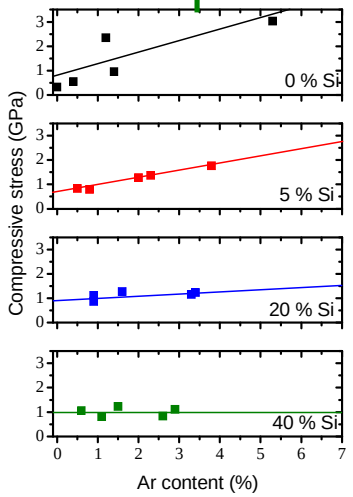

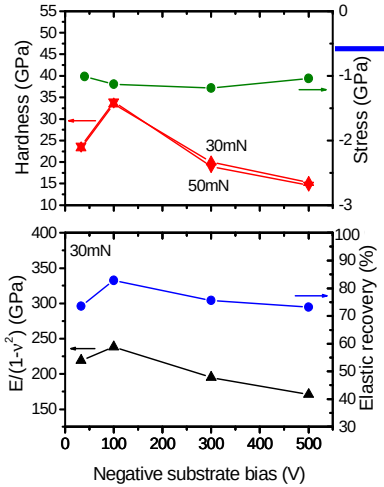

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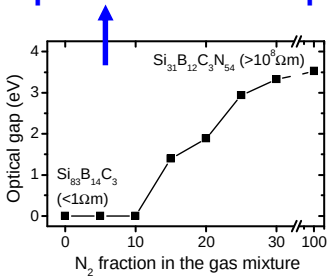
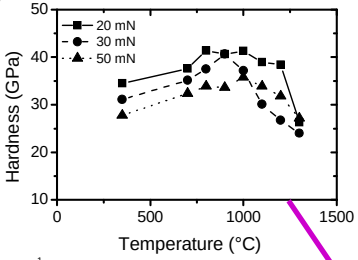
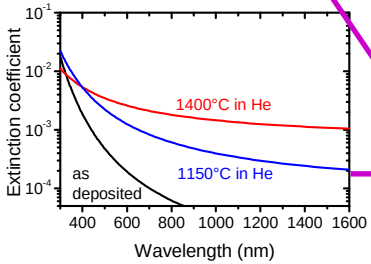


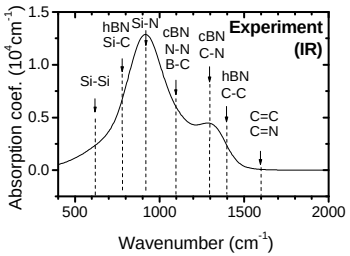


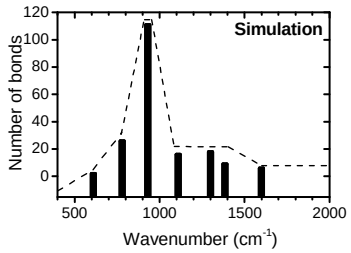


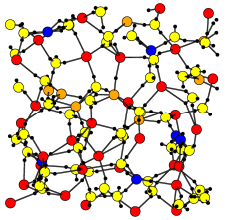
High-temperature stability of mechanical properties and optical properties

Explanations by ab-initio calculation of structures and electronic structures

(clustering of Si around Ar, doping role of C atoms and CC bonds, ...)





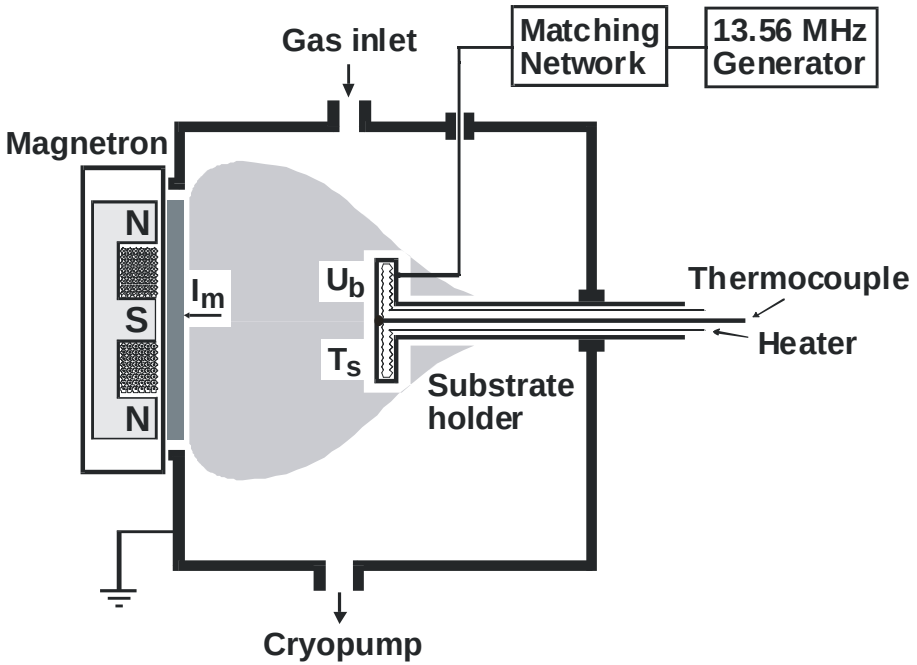


Deposition technique

DC magnetron sputtering of $Si_x(B_4C)_{1-x}$ in N_2+Ar at 350 °C
(selected compositions: cross-check using dc pulsed magnetron sputtering)

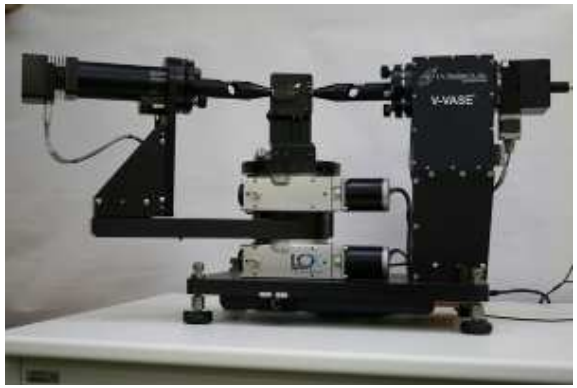
Three main control parameters

- sputter target composition
- discharge gas mixture compositon
- substrate bias voltage

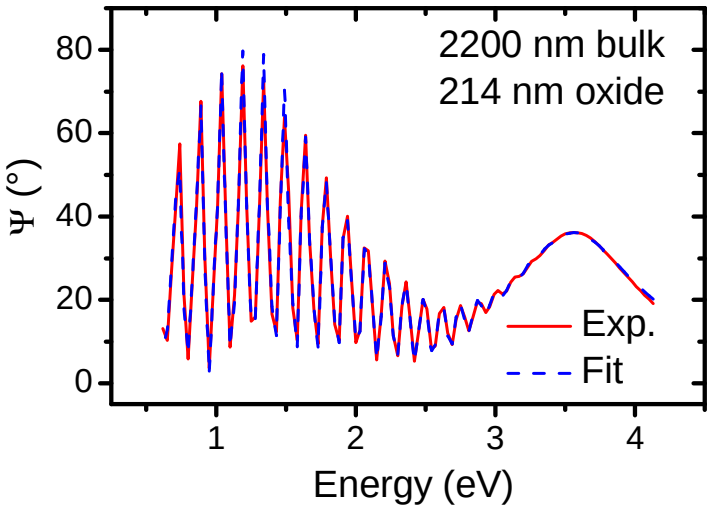


Main characterization technique

Ageing resistance expressed in terms of the thickness of the surface oxide layer measured by **spectroscopic ellipsometry**



Example of measured and fitted raw ellipsometric data:
(change of light polarization after its reflection from the coating)
clear optical boundary between thin surface oxide (low *n*) and thick bulk nitride (high *n*)



SiBCN coatings studied

5 $Si_x(B_4C)_{1-x}$ sputter target comp.
$[Si_{target}]$ = 5, 20, 40, 60, 75%

×

4 N_2+Ar gas mixture comp.
$[Ar_{plasma}]$ = 0, 25, 50, 75%

×

2 substrate bias values
U_b = -100 or -500 V

×

2 storage conditions (open air or in polyethylene bags)

⇓

80 coatings studied

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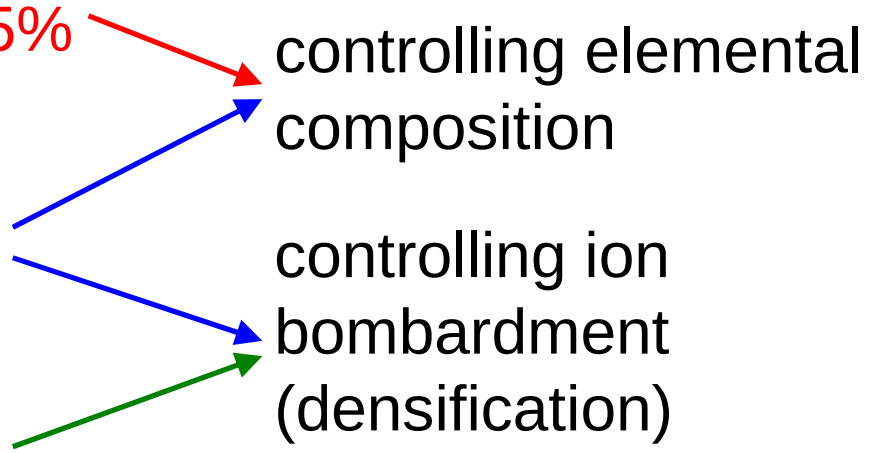

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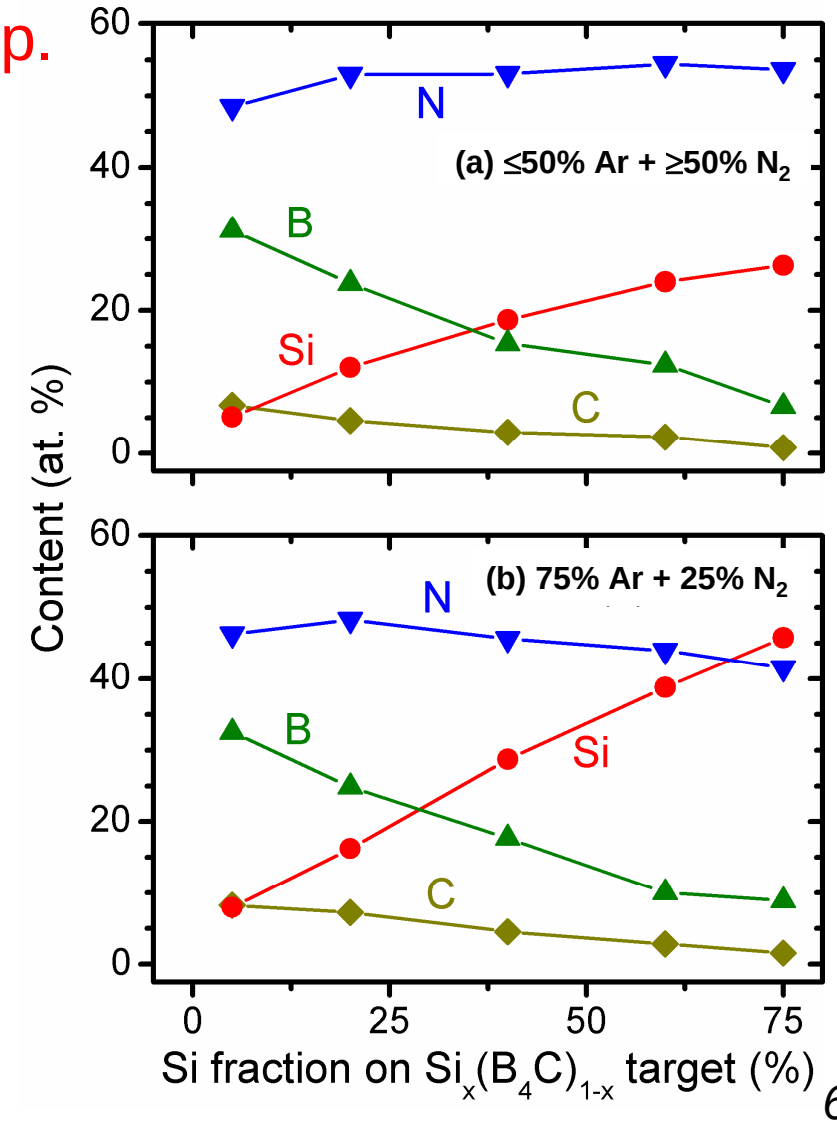
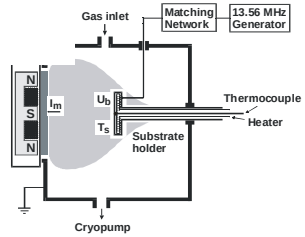


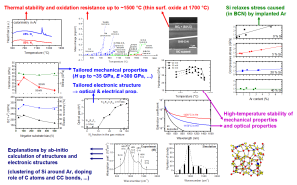
SiBCN coatings studied

2002-2003 : 80 coatings deposited,
as-deposited properties measured



↓

2005+ : as-deposited properties published

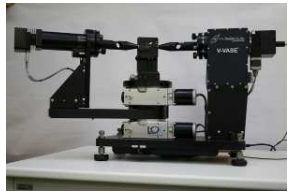


↓

2003-2015 : storage of 40 coatings under
open air + 40 coatings in polyethylene bags

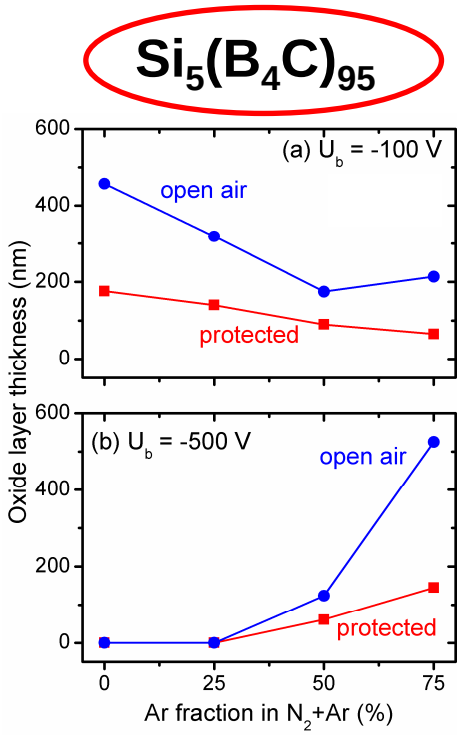
↓

**2015 : ageing resistance (surface
oxide thickness) studied**



Ageing resistance for $Si_5(B_4C)_{95}$ target

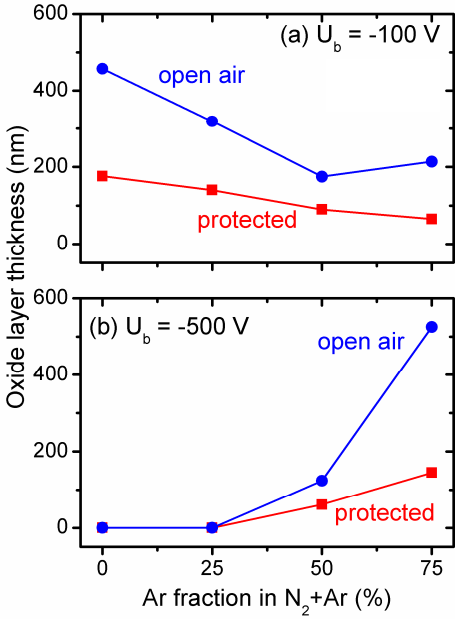
- oxidation barrier formed in all cases
- effect of gas mixture composition qualitatively depends on U_b
- perfect ageing resistance at high $|U_b|$ and low $[Ar_{plasma}]$



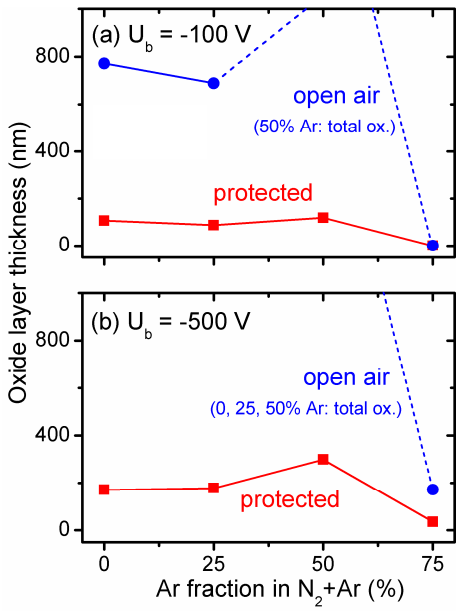
Ageing resistance for $Si_{20}(B_4C)_{80}$ target

- least optimum target composition: frequent complete oxidation down to a substrate
- ageing resistance at strong Ar^+ bomb. (highest [Ar_{plasma}])

$Si_5(B_4C)_{95}$



$Si_{20}(B_4C)_{80}$

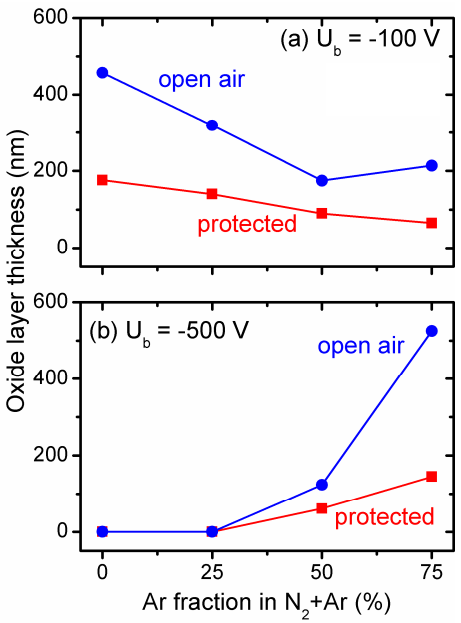


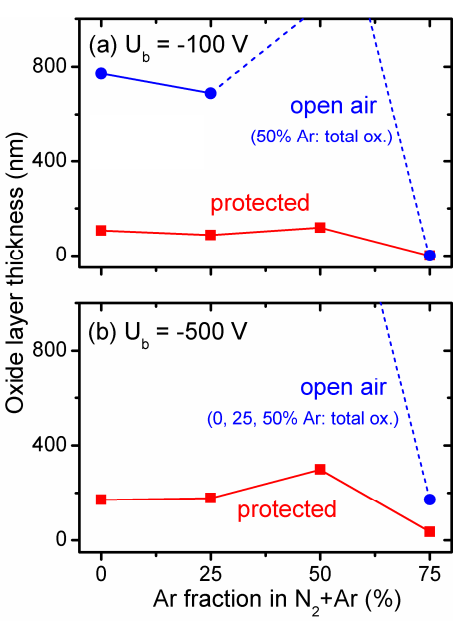
: complete oxidation (down to substrate)

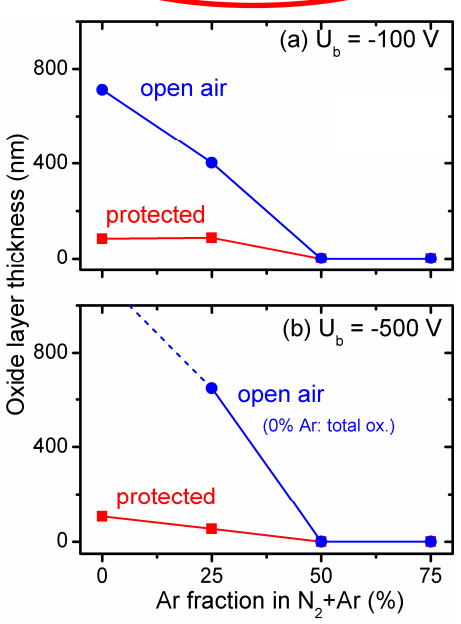
Ageing resistance for $Si_{40}(B_4C)_{60}$ target

- overall improvement compared to $Si_{20}(B_4C)_{80}$ target
- perfect ageing resistance at high [Ar_{plasma}]
- even higher Si content: even better (only resistant samples)

$Si_5(B_4C)_{95}$ | $Si_{20}(B_4C)_{80}$ | **$Si_{40}(B_4C)_{60}$** | **$Si_{60\text{-}75}(B_4C)_{25\text{-}40}$**







resistant

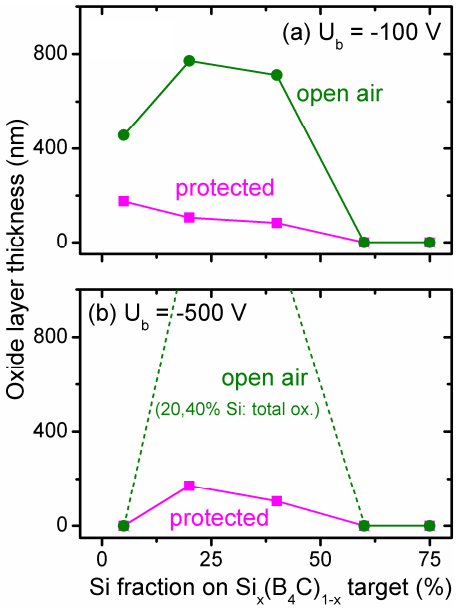
(no oxidation beyond surf. roughness)

: complete oxidation (down to substrate)

Ageing resistance for 100% N_2 + 0% Ar plasma
($\Rightarrow$ "saturation" N content in SiBCN)

- ageing at medium [Si_{target}] = 20-40%
- stronger dependence on [Si_{target}] at high $|U_b|$ = 500 V

100% N_2 + 0% Ar



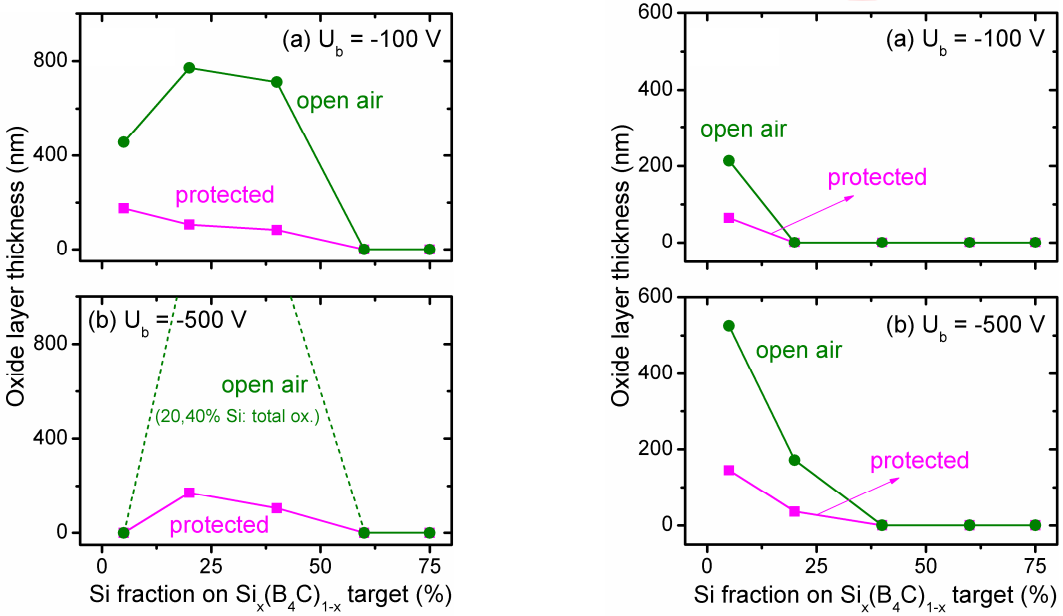
------ : complete oxidation (down to substrate)

Ageing resistance for 25% N_2 + 75% Ar plasma
(⇒ "sub-saturation" N content in SiBCN)

- better - or even perfect - ageing resistance at higher [Si_{target}]
- again, stronger dependence on [Si_{target}] at high $|U_b|$ = 500 V

100% N_2 + 0% Ar

25% N_2 + 75% Ar



: complete oxidation (down to substrate)

SiBCN ageing resistance map

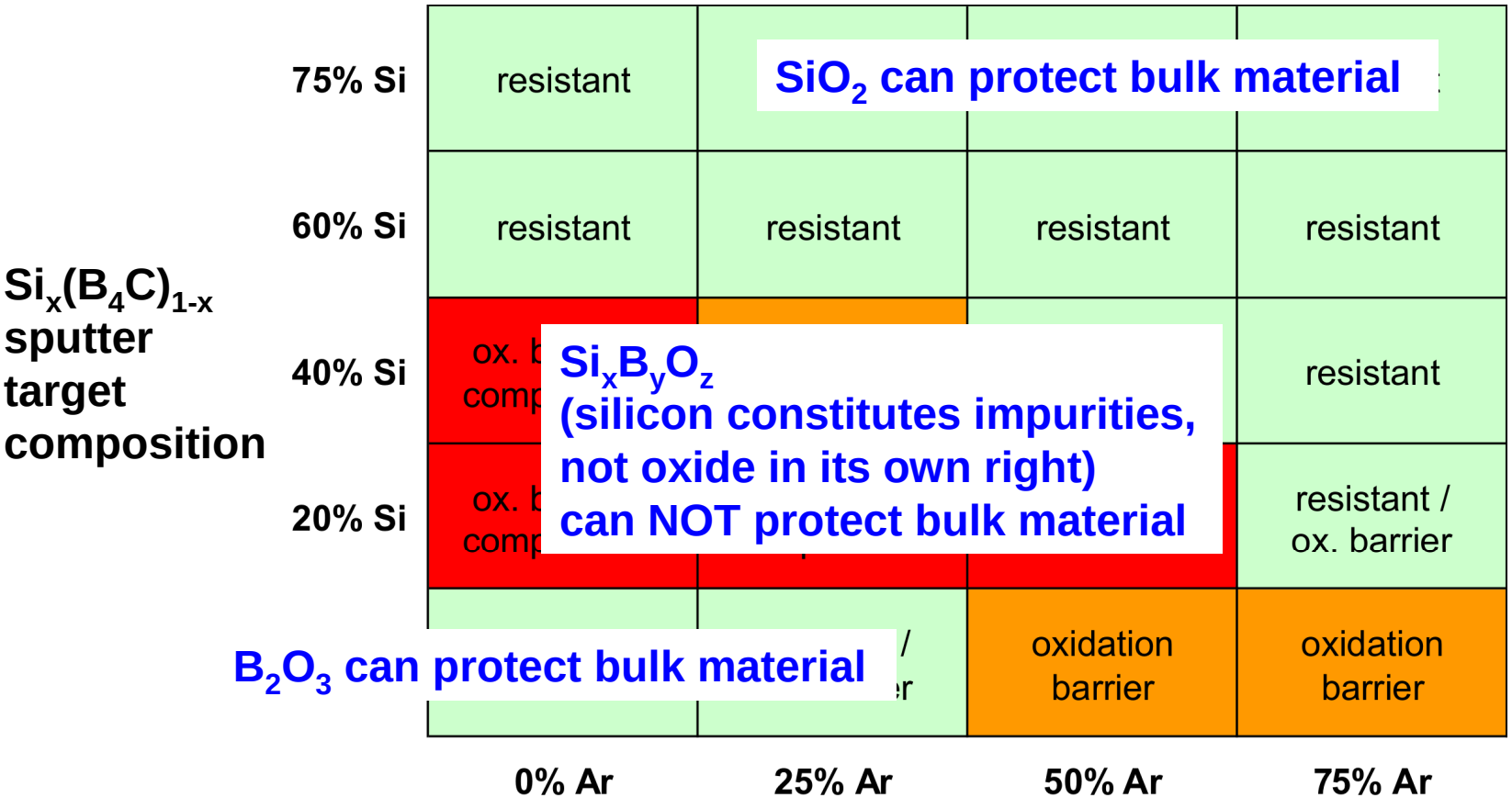
two information in one box: effect of substrate bias

$Si_x(B_4C)_{1-x}$ 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

SiBCN ageing resistance map

two information in one box: effect of substrate bias



SiBCN ageing resistance map

two information in one box: effect of substrate bias

$Si_x(B_4C)_{1-x}$ sputter target composition	0% Ar	25% Ar	50% Ar	75% Ar
75% Si	resistant	resistant	resi	
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

best high-temperature (~1500 °C) stability and oxidation resistance

N_2+Ar discharge gas mixture composition

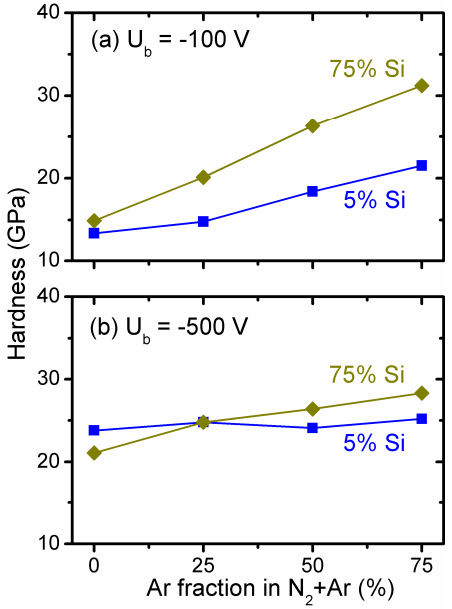
SiBCN ageing resistance map

substrate bias leading to better performance

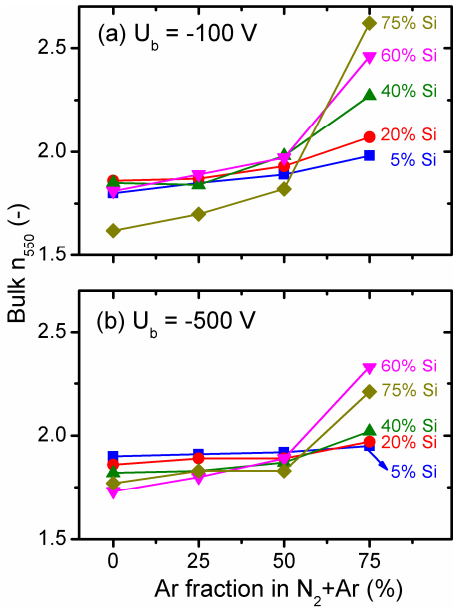
$Si_x(B_4C)_{1-x}$ sputter target composition	0% Ar	25% Ar	50% Ar	75% Ar
75% Si	any U_b	any U_b	any U_b	any U_b
60% Si	any U_b	any U_b	any U_b	any U_b
40% Si	-100 V	-100 V	any U_b	any U_b
20% Si	-100 V	-100 V	-100 V	-100 V
5% Si	-500 V	-500 V	-500 V	-100 V

N_2+Ar discharge gas mixture composition

Explanation of some trends shown: densification



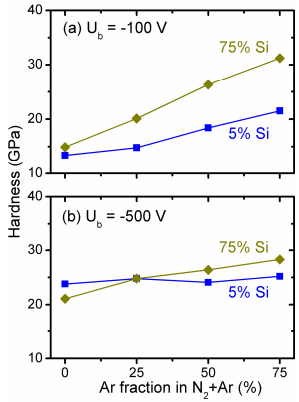
Densification expressed
(despite compositional changes with $[Ar_{plasma}]$)
in terms of hardness
in terms of refractive index

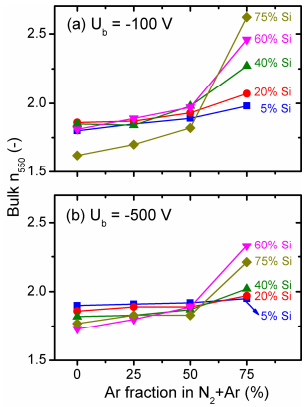


- Higher $[Ar_{plasma}]$: densification of SiBCN coatings (steeper trends at higher $[Si_{target}]$ and lower $|U_b|$)
- Other words: transition from U_b = -500 V to -100 V is more beneficial / less harmful at higher $[Ar_{plasma}]$
- Yet other words: do not combine high $|U_b|$ + high $[Ar_{plasma}]$

Explanation of some trends shown: densification

	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





ageing resistance

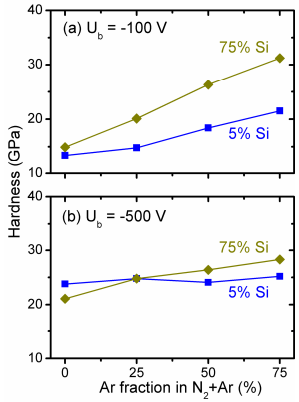
(densification in terms of) hardness

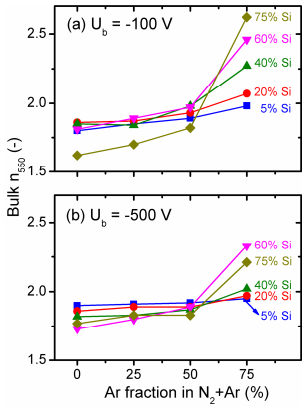
(densification in terms of) refractive index

Performance of Si-rich films
- steeply dependent on [Ar_{plasma}]
- the best at high [Ar_{plasma}] and low $|U_b|$

Explanation of some trends shown: densification

	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





ageing resistance

(densification in terms of) hardness

(densification in terms of) refractive index

Performance of Si-rich films
- steeply dependent on [Ar_{plasma}]
- the best at high [Ar_{plasma}] and low $|U_b|$

Performance of Si-poor films
- more weakly dependent on [Ar_{plasma}]
- the best at low [Ar_{plasma}] and high $|U_b|$

Conclusions

SiBCN coatings prepared in a wide range of compositions (⇒ properties)

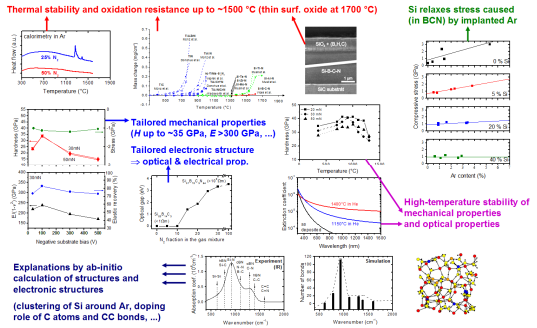
Ageing expressed in terms of surface oxide thickness (ellipsometry) after 12 yr

Optimization of process parameters for each composition ⇒ ageing resistance (and densification)

Si-rich compositions resistant, prefered preparation in Ar-rich plasma at low $|U_b|$

B_4C-rich compositions resistant, prefered preparation in Ar-poor plasma at high $|U_b|$

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



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5% Si	resistant / ox. barrier	resistant / ox. barrier	oxidation barrier	oxidation barrier

	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