NEW Si-B-C-N COATINGS: AB-INITIO CALCULATIONS AND EXPERIMENTAL VERIFICATION

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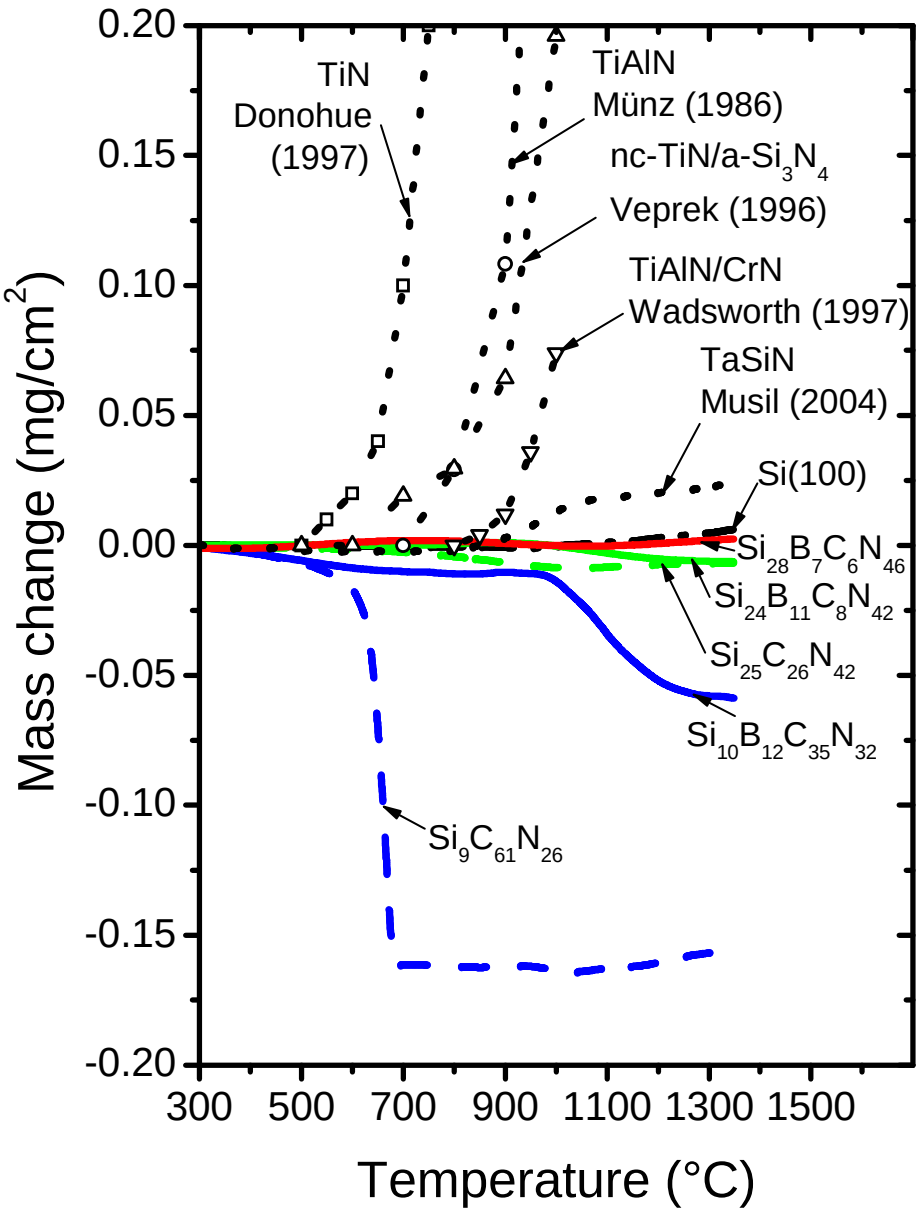


Motivation for new quaternary Si-B-C-N materials: exceptional oxidation resistance

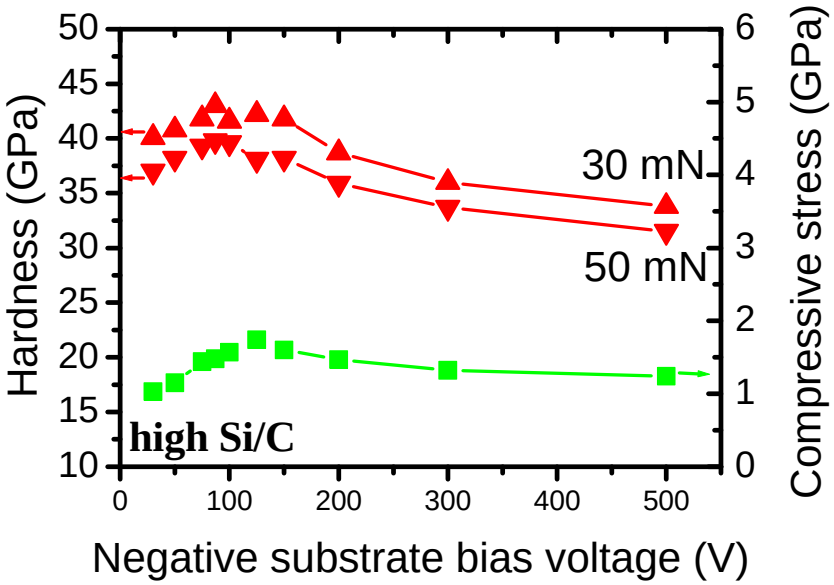
Solid: Si-B-C-N

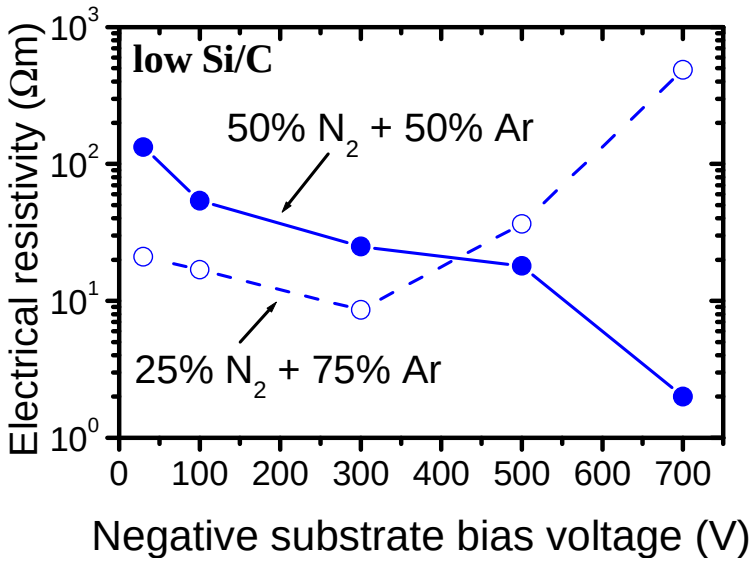
Dashed: Si-C-N

Dotted: other coatings

- Very high oxidation resistance (up to a 1350 °C substrate limit): important role of the Si/C ratio and the B content

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





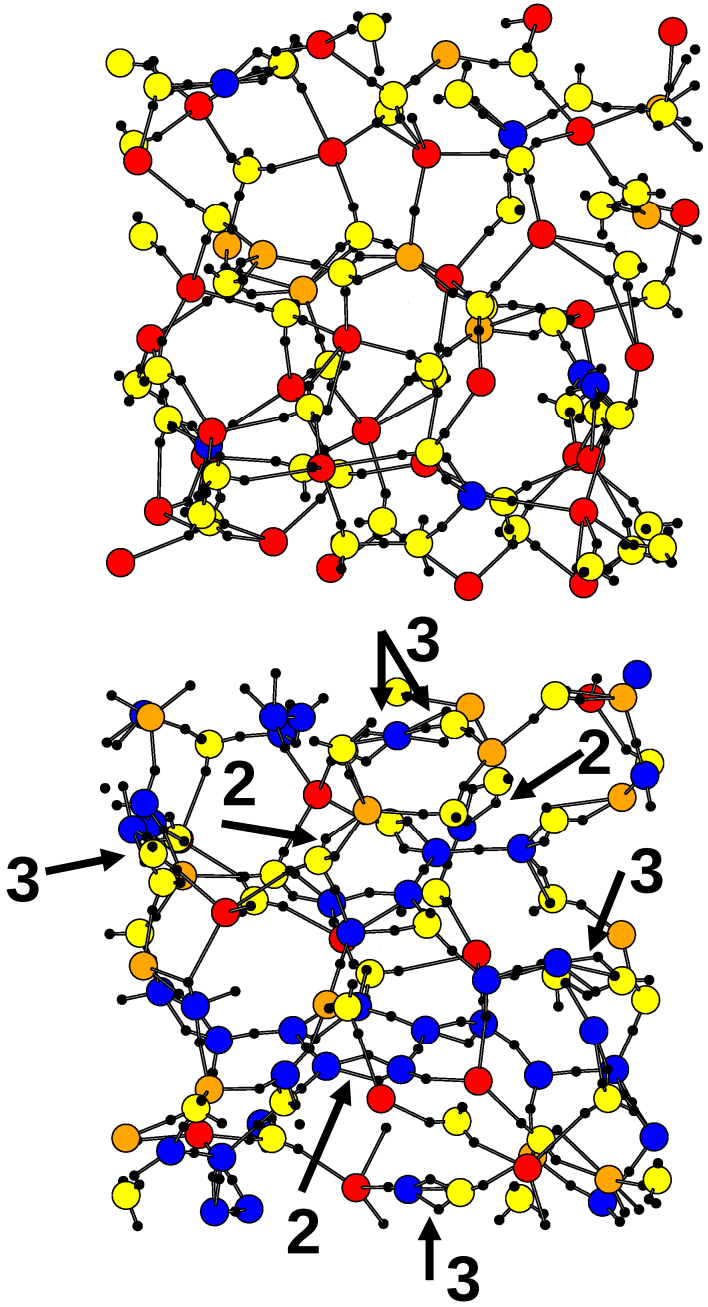
Controllable properties of sputtered Si-B-C-N materials - hardness, compressive stress, electrical conductivity

- Properties controlled by C-Si-B/B_4C-Si composed target composition, N_2-Ar gas mixture composition, negative rf substrate bias
- High hardness, very low stress, promising optical and electrical properties

[J. Houska et al., Diamond Relat. Mater. 16, 29 (2007)]

SUPPORT OF AN EXPERIMENT BY AB-INITIO SIMULATIONS

- **Density functional theory** (DFT) as implemented in the Car-Parrinello molecular dynamics (CPMD code)
- **Atom cores and inner electron shells** described by pseudopotentials (Goedecker type)
- **Valence electrons** described by Kohn-Sham (Schrödinger-like) equations expanded in a basis of plane-wave functions using BLYP functional
- **Liquid-quench algorithm** captures material formation conditions arising from rapid cooling of the localized melt around sites of energetic ion impact
- **3-dimensional periodical cubic cell** with ~100 atoms

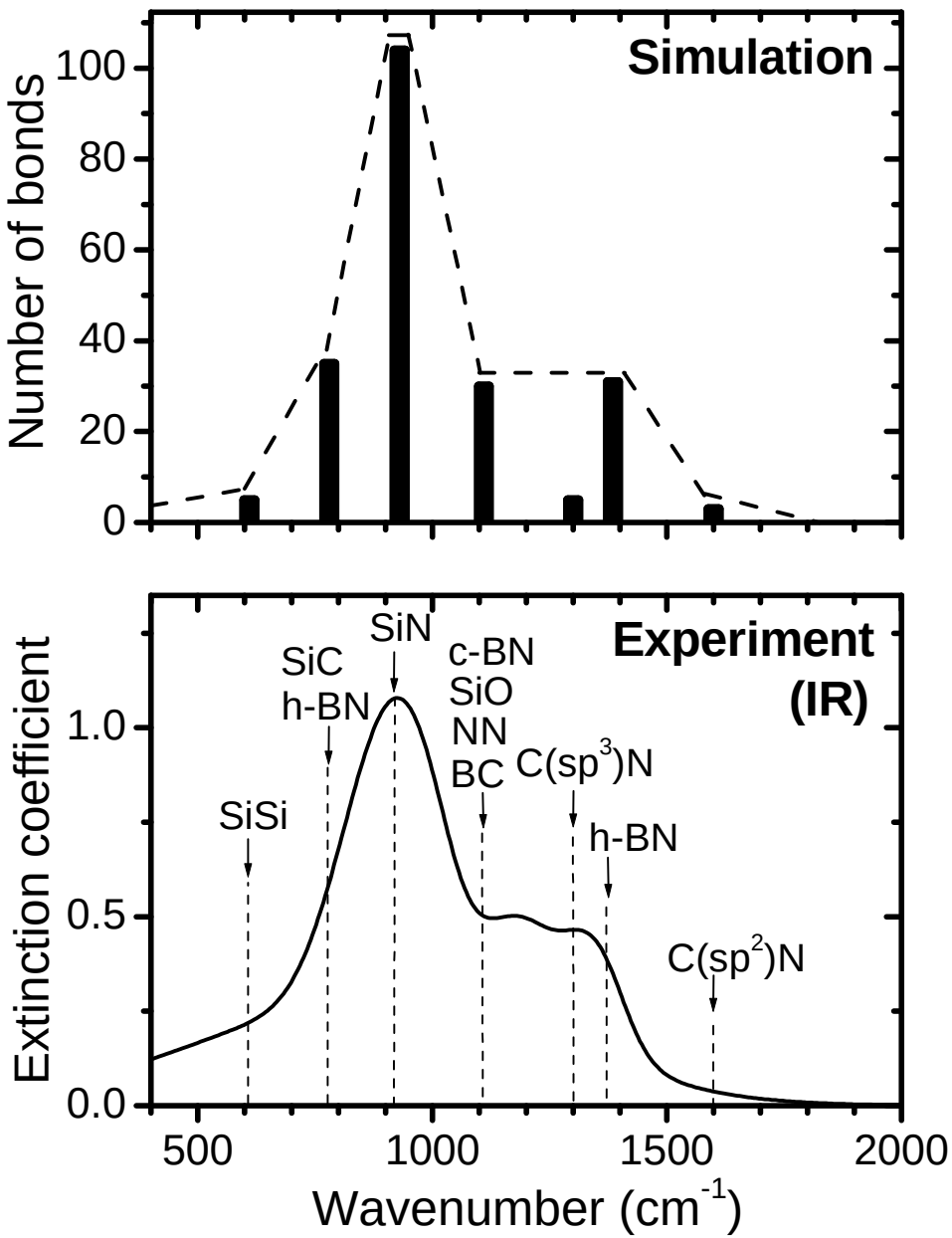


Molecular-dynamics simulations of Si-B-C-N materials

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

- $Si_{32}B_8C_6N_{54}$ [75% Si]
  Single Si-N bonds
  $\Rightarrow$ high coordination

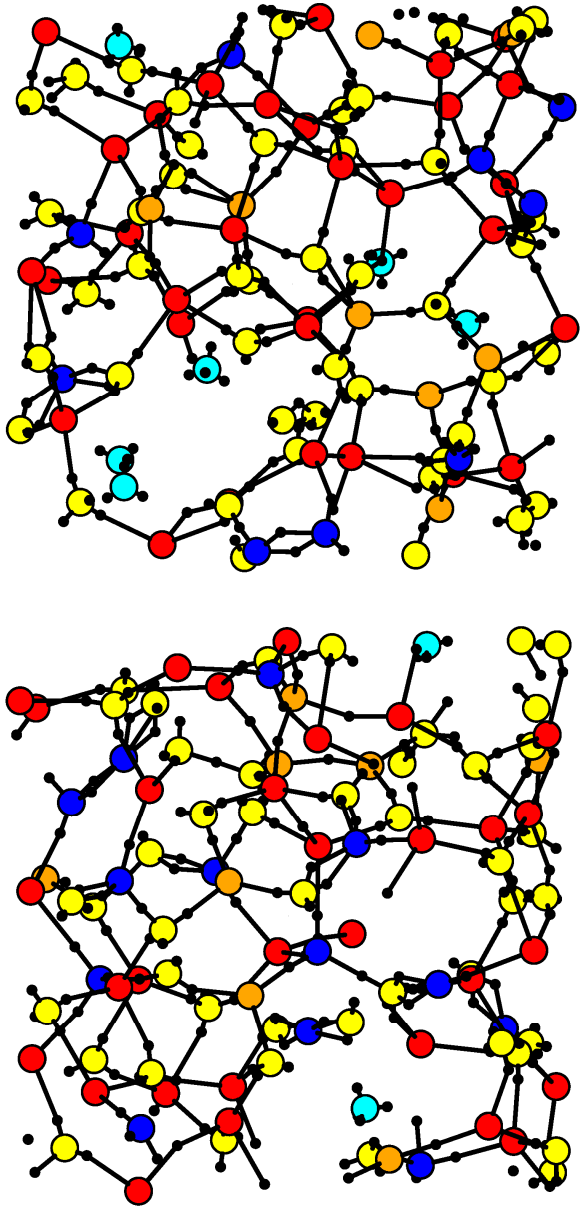
- $Si_{11}B_{14}C_{39}N_{36}$ [5% Si]
  Double C=N, C=C and B=N, and triple C≡N bonds
  $\Rightarrow$ low coordination



Calculated bonding statistics and experimental verification

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

- Example of hard, transparent, thermally stable composition
- Comparison of bonding statistics with IR spectra (no oscillator strengths, single BN bonds in both c-BN and h-BN peaks)



Molecular-dynamics simulations of Si-B-C-N-Ar materials

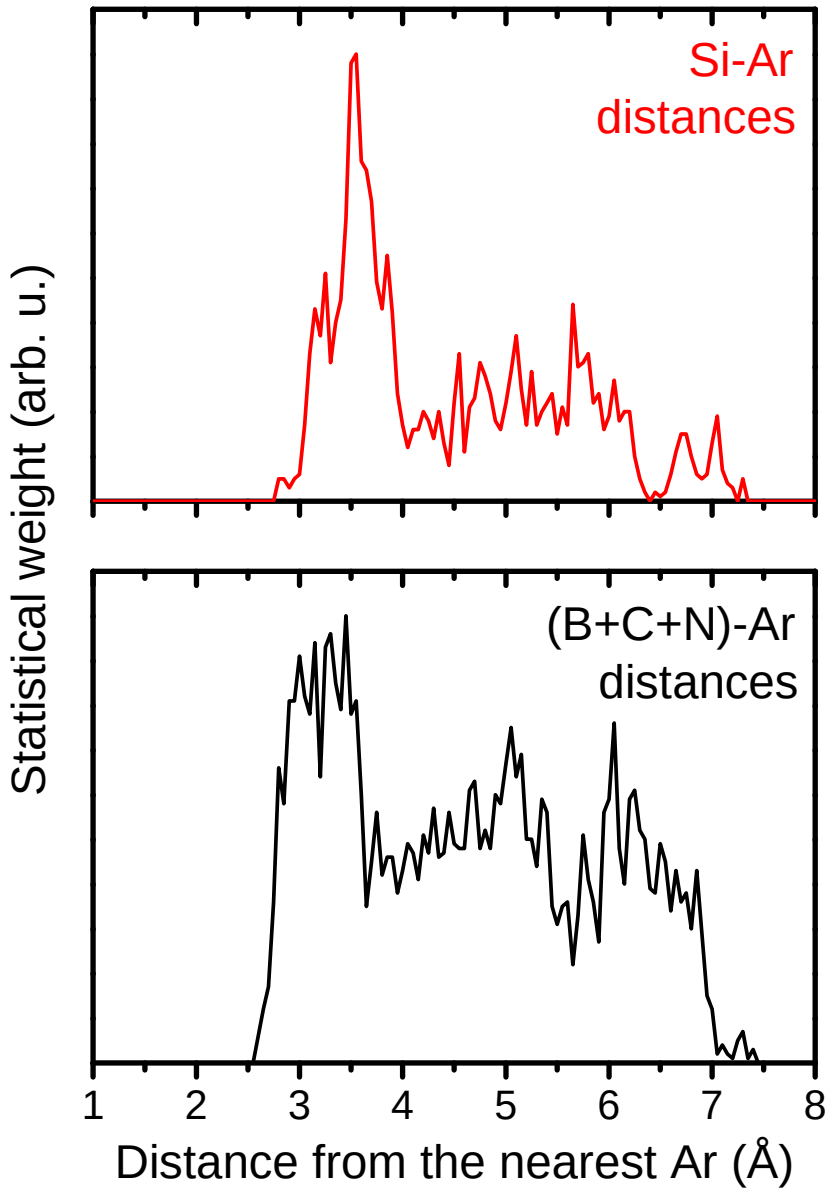
Si: ●, B: ●, C: ●, N: ●, Ar: ●

2 valence electrons: ●—●

- $Si_{31}B_8C_9N_{46}Ar_6$ [high $|U_b|$]
  $Si_{31}B_8C_{13}N_{46}Ar_2$ [low $|U_b|$]
  : formation of cavities with isolated Ar atoms

- Experimentally known effect of Ar content on material characteristics

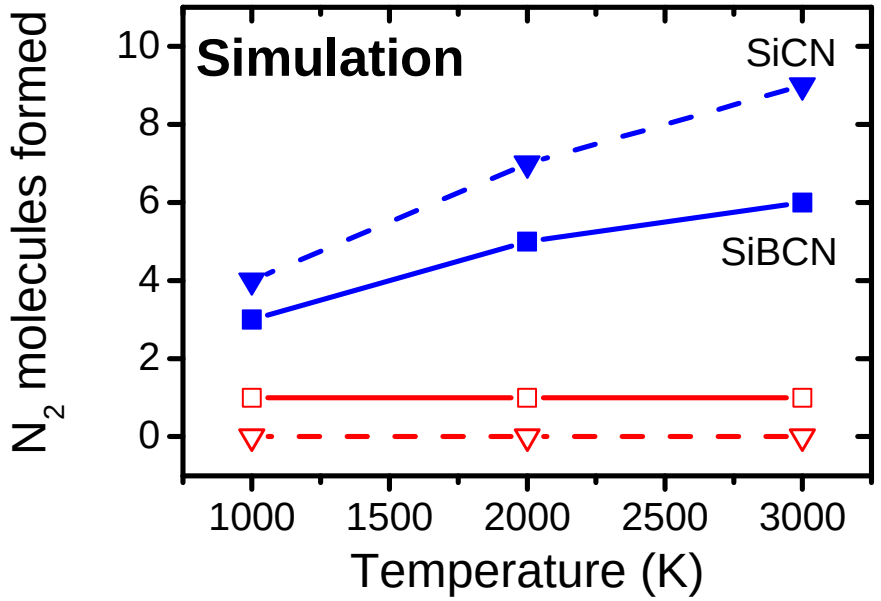
[J. Houska et al., J. Phys.: Condens. Matter 18, 2337 (2006)]

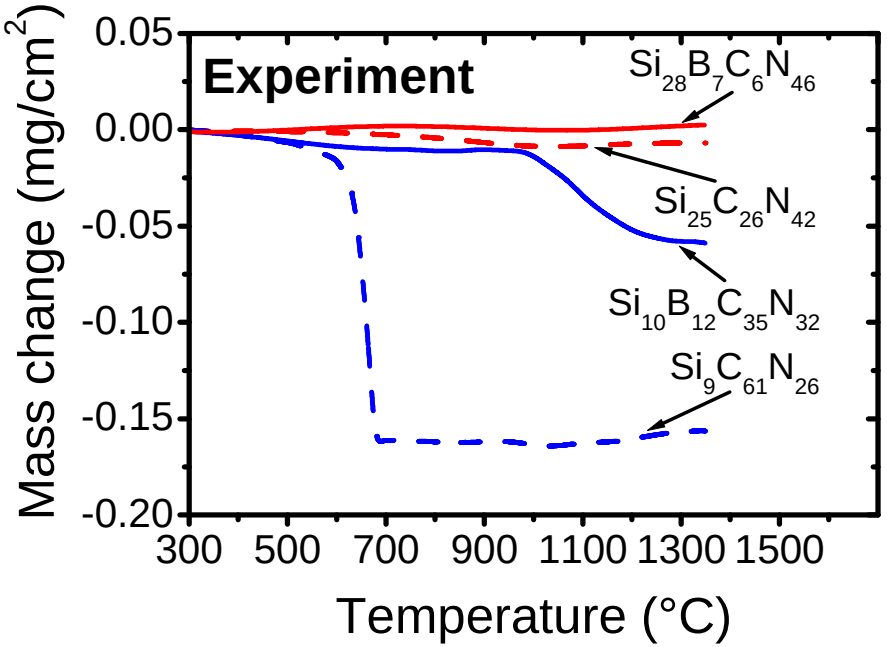


Effect of implanted Ar on Si-B-C-N materials (molecular dynamics)

Simulated composition $Si_{31}B_8C_{13}N_{46}Ar_2$

- Segregation of Si around Ar-cavities (long flexible bonds) ⇒ low energy penalty ⇒ **low stress**
- Formation of a two phase close-to-Ar (37% Si) and far-from-Ar (28 % Si) material ⇒ **enhanced extrinsic hardness**





Temperature stability of Si-(B)-C-N materials (molecular dynamics)

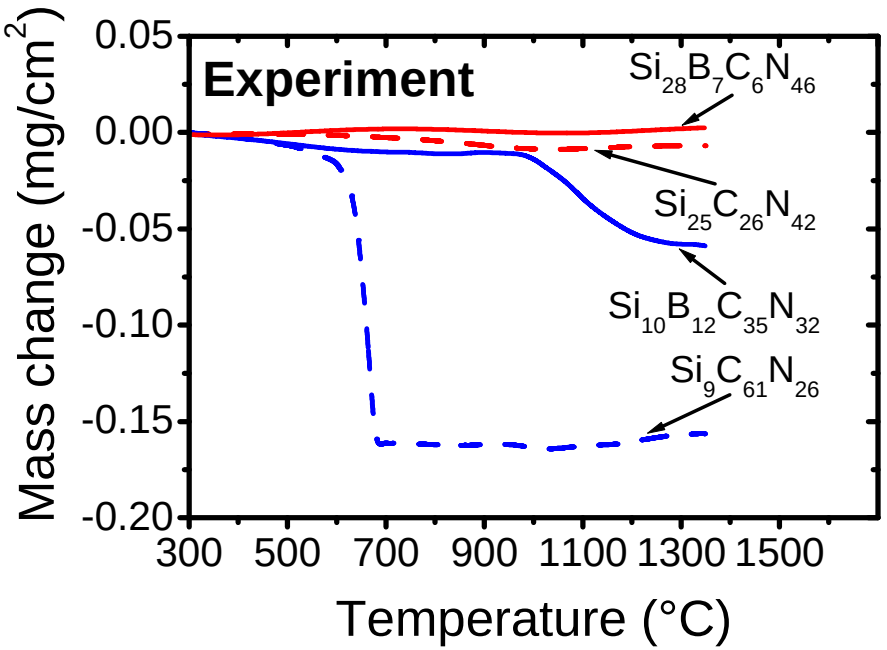
Simulated compositions

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

- Decomposition reactions $Si_3N_4 + 3C \rightarrow 3SiC + 2N_2$ and $Si_3N_4 \rightarrow 3Si + 2N_2$ => 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

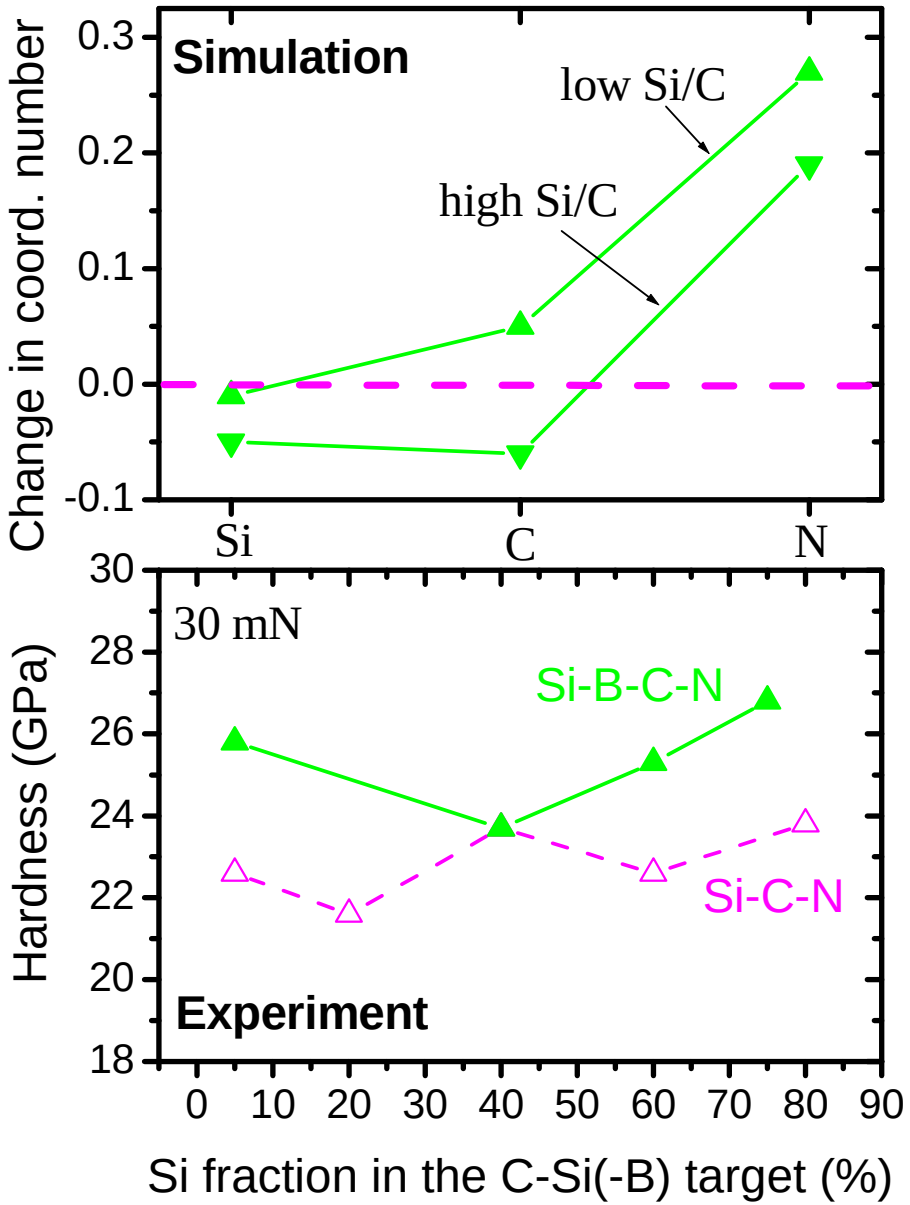


Temperature stability of Si-(B)-C-N materials (molecular dynamics)

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 => more stable network => limited diffusion => decomposition reactions shifted to higher T => improved thermal stability

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



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 nitrogen coordination
- Improved mechanical properties and thermal stability

CONCLUDING REMARKS

- **A complex quaternary system Si-B-C-N**: chemical bonding structure, electronic structure, high-temperature behaviour, role of energy, Si, B, C and implanted Ar
- **Support of an experiment by simulations**: providing information on atomic scale inaccessible experimentally
- **Difference between Si-based and C-based networks**: single Si bonds, many double and triple C bonds
- **Role of implanted Ar atoms**: segregation of Si around Ar-cavities $\Rightarrow$ low stress, enhanced extrinsic hardness
- **High-temperature stability:** longer bond lifetimes at higher Si/C, lower rate of N_2 formation at higher Si/C and after addition of B