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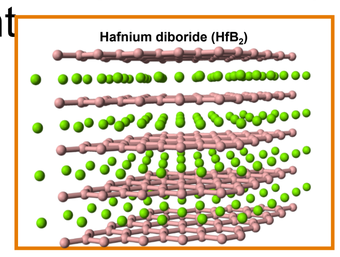
Development of Metal Boride/Carbide Precursors for CVD Applications

Problem:

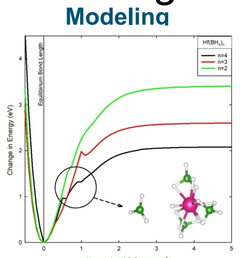
- Vapor deposition processing of high temperature resistant metal borides & metal carbides onto/into different supports are critically needed to protect components.
- Limited metal-boron containing precursors that can convert stoichiometric metal boride materials prevents rapid thermal protective materials development



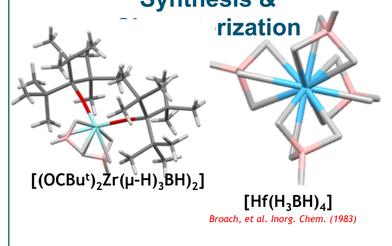
Approach:

Develop tailored precursors that will produce intercalated thermal protective coatings of Metal Boride or Metal Carbide using MOCVD processes. Guided by molecular modeling, precursor will be synthesized and evaluated under vapor processing conditions.

Molecular Modeling



Precursor Synthesis & Characterization



MOCVD Processing & Materials Characterization

Results:

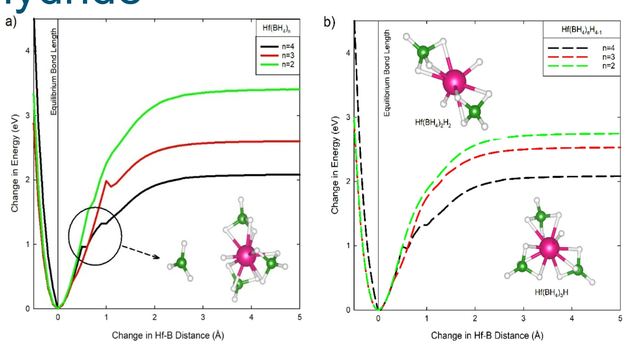
DFT simulation results illustrate potential intermediate for the hafnium borohydride $[Hf(BH_4)_4]$ precursor

Molecule	Hf-B Dist. (Å)	E_D (eV)		IP (eV)	EA (eV)
		BH_3+H*	BH_4^		
$Hf(BH_4)_4$	2.278	2.07	4.26	10.108	-0.912
$Hf(BH_4)_3$	2.257	2.58	4.59	7.395	-0.919
$Hf(BH_4)_2$	2.203	3.52	5.68	7.607	-0.929

*H atom remains to coordinate the central Hf atom and removal of BH_3, ^Complete removal of -BH_4

Potential energy surface (PES) scans, disassociation energies (E_D), ionization potential (IP), and electron affinity (EA) used to determine stable precursors.

Preliminary efforts indicate the release of a proton from the BH_4 ligand to stabilize the $[Hf(BH_4)_3H]$ intermediate.



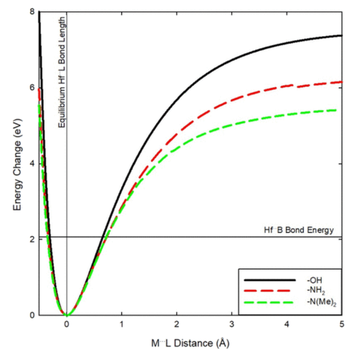
Energy and snapshots of (a) $[Hf(BH_4)_n]$ (n = 4–2) PES scans, and the inset shows the intermediate state of $[Hf(BH_4)_3(H)]$ and BH_3 and (b) energy and snapshots of $[Hf(BH_4)_nH_{4-n}]$ (n = 4–2) and insets of $Hf(BH_4)_3H$ and $Hf(BH_4)_2H_2$. Atom colors: Hf (pink), B (green), and H (white).

Does the same mechanism exist in other candidate precursors?

DFT simulation of $[Hf(BH_4)_2L_2]$ candidate precursors to examine stability of intermediate as ligand changes

Ligand	Hf-L Dist. (Å)	E_D (eV)	IP (eV)	EA (eV)
-BH_4	**2.278**	**2.07***	**10.108**	**-0.912**
-Br	2.468	0.95	10.114	4.485
-OH	1.901	12.44	10.554	0.161
-OMe	1.890	11.02	9.442	0.262
-O-tBu	1.889	11.28	8.906	0.236
-NH_2	2.008	11.87	8.364	0.103
-N=C=O	2.008	9.37	10.22	-0.955
-$N(Me)_2$	2.0165	19.85	7.220	0.050

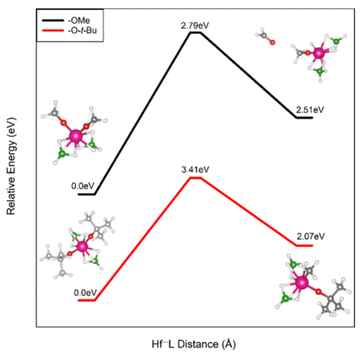
Candidate precursors with $Hf(BH_4)_2L_2$ compositions simulated + halide (Br), hydroxides (OH), alkoxide (OMe, OBu^t), amide (NH_2, NEt_2) isocyanate (N=C=O), Lewis bases (NC_5H_5 (py)), pyridimium (H-py).



PES scan of $[Hf(BH_4)_2L_2]$ with L = −OH, $-NH_2$, and $-NMe_2$.

L = -OH, -Br, $-NH_2$, $-N(Me)_2$

Did not exhibit an intermediate states and disassociation energies too high to be viable replacements.



Energy and snapshots of $[Hf(BH_4)_2(OMe)_2]$ and $[Hf(BH_4)_2(O\text{-}t\text{-}Bu)_2]$ PES scan. Colors: Hf (pink), B (green), H (white), O (red), and C (gray).

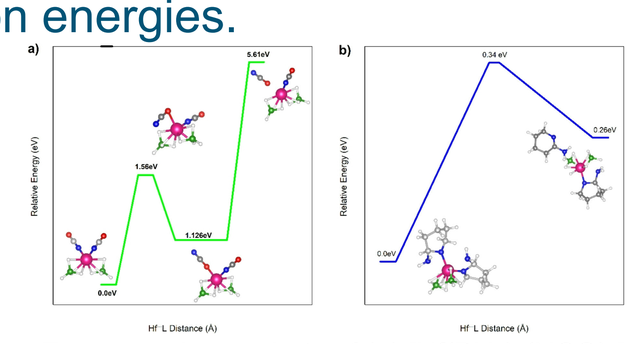
DFT Simulation of $Hf(BH_4)_2L_2$ candidate precursors indicate larger ligands lower dissociation energies.

Ligand	Hf-L Dist. (Å)	E_D (eV)	IP (eV)	EA (eV)
-BH_4	**2.278**	**2.07***	**10.108**	**-0.912**
-Pip2A	2.073	0.34*	6.389	0.537

*H atom remains to coordinate the central Hf atom

L = $N(CH_2)_5NH_2$ (1-piperidin-2-amine referred to as Pip2A)

- Low E_D (0.34 eV) due to H atom remaining to coordinate the Hf atom
- Same mechanism seen in $Hf(BH_4)_4$ molecule for lowering E_D values

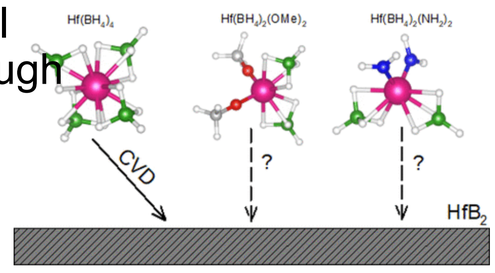


Energy and snapshots of (a) $[Hf(BH_4)_2(NCO)_2]$ and (b) $[Hf(BH_4)_2(Pip2A)_2]$ PES scan. Colors: Hf (pink), B (green), H (white), O (red), C (gray), and N (blue).

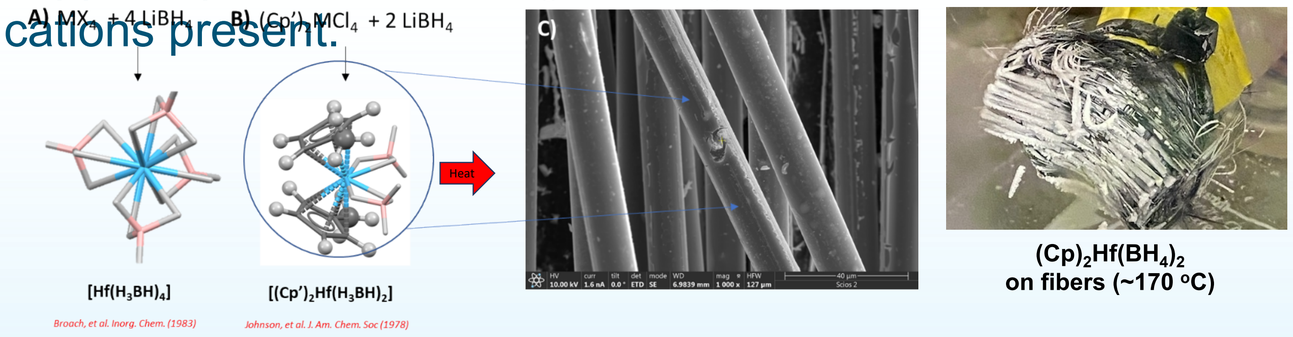
Recommendations for candidate precursors: larger ligands with loosely bound hydrogens or methyls to lower disassociation energies

Summary

- Alternative candidate precursors to hafnium borohydride and potential intermediates were identified through Density Functional Theory simulations.
- Preliminary results from vapor processing of precursors indicate coatings contain hafnium oxides, optimization needed to avoid oxide production.



Preliminary vapor processing of precursors onto fiber supports produces coatings. Analysis identified hafnium cations present.



$(Cp)_2Hf(BH_4)_2$ on fibers (~170 °C)

Precursors of A) hafnium borohydride $[Hf(H_3BH)_4]$ and B) bis-cyclopentadienyl hafnium borohydride $[(Cp')_2Hf(H_3BH)_2]$ were synthesized. C) Scanning electron microscope image of Hf_xB_y coating on fiber supports. XRF and EDS identified Hf was present on coating.

Acknowledgements:

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