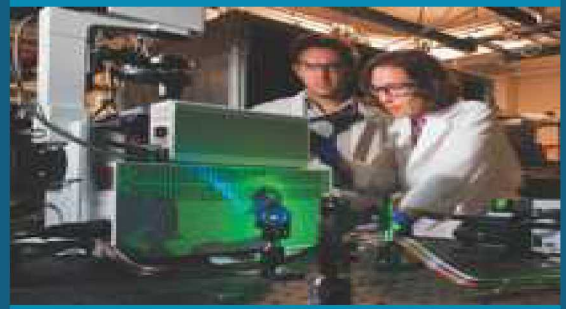
SAND2019-1057C

Role of Impurities on the Surface Properties of HfC



PRESENTED BY

Jessica M. Rimsza[1], Stephen Foiles[1], Joseph Michael[1], William Mackie[2], Kurt Larson[1]

1: Sandia National Laboratories, Albuquerque, NM 87123
2: Applied Physics Technologies (APTech), McMinnville, OR 97128

ICACC 2019, Daytona Beach FL, USA 2/1/2019

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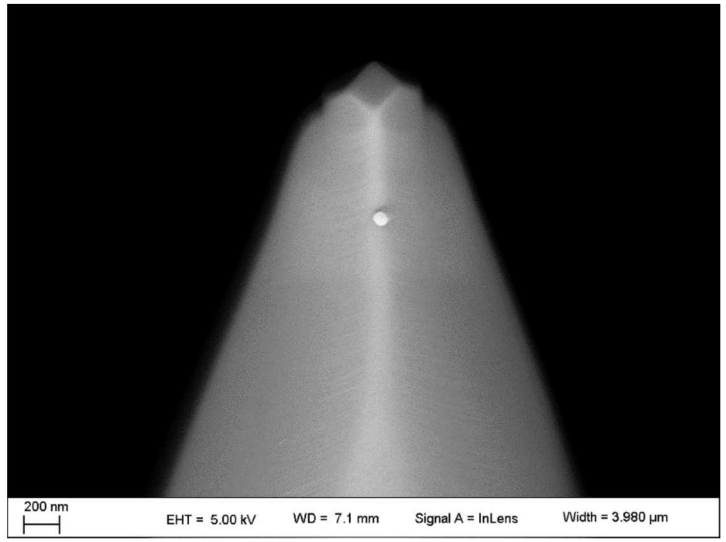
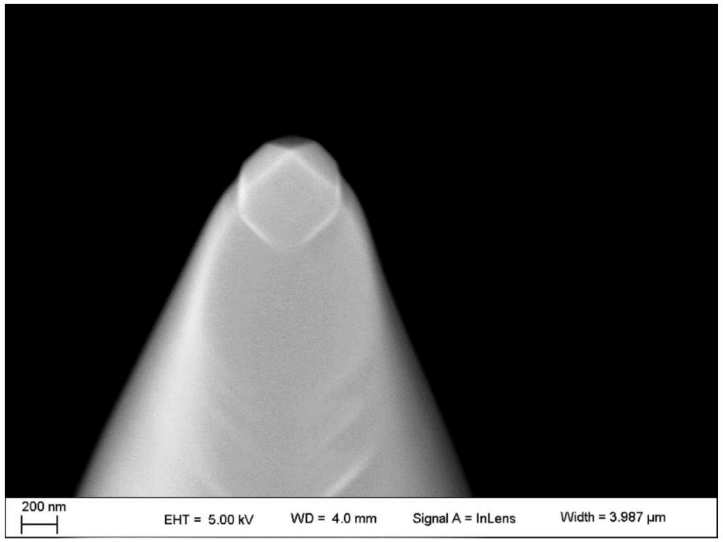
Background: Field Emission

- Field emission guns are used to produce a narrow electron beam for imaging samples
- Common electron emitters: W, LaB_6, Transition Metal Carbides (ZrC, TaC, TiC)
- Advantages of HfC: high temperature stability, low work function, high hardness
- HfC has been investigated for field emission starting in the early 1990s

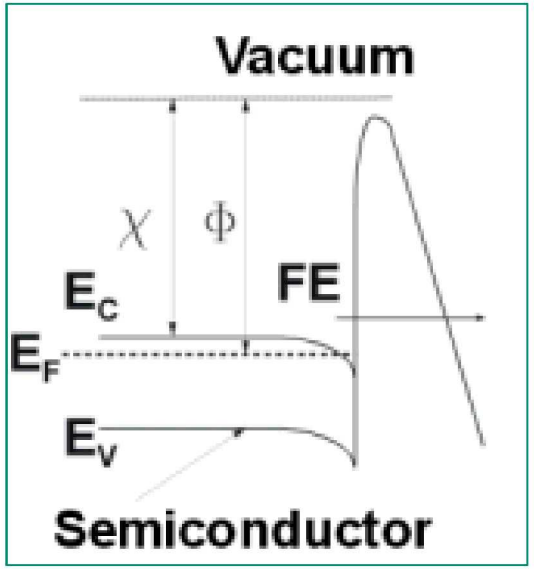
Mackie, W.A., et al. *JVST:A* (1992) Wei, Yi, et al. *JVST:B* (2001) Mackie, W. A., et al. JVST:B (1998)

During use the normally parabolic tip forms crystalline facets, along with degradation of emission properties



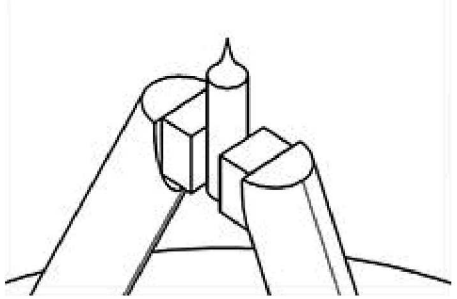


SEM images of faceted HfC field emission tips after use



Band diagram of a semiconductor field-emitter under loading.

Eng et al. III-V-Halbleiter Feldemissions-Sensoren und Mikrowellenquellen



Schematic of a field emission source in a holder

AP Tech Applied Physics Technologies

What is causing the HfC faceting?

We propose two factors that contributed to HfC faceting:

1. High temperature application (2050K-2250K)
2. Carbon deficient structures (HfC_x, $0.56 < x < 1.0$)

Theories to limit the impact of carbon deficient structures:

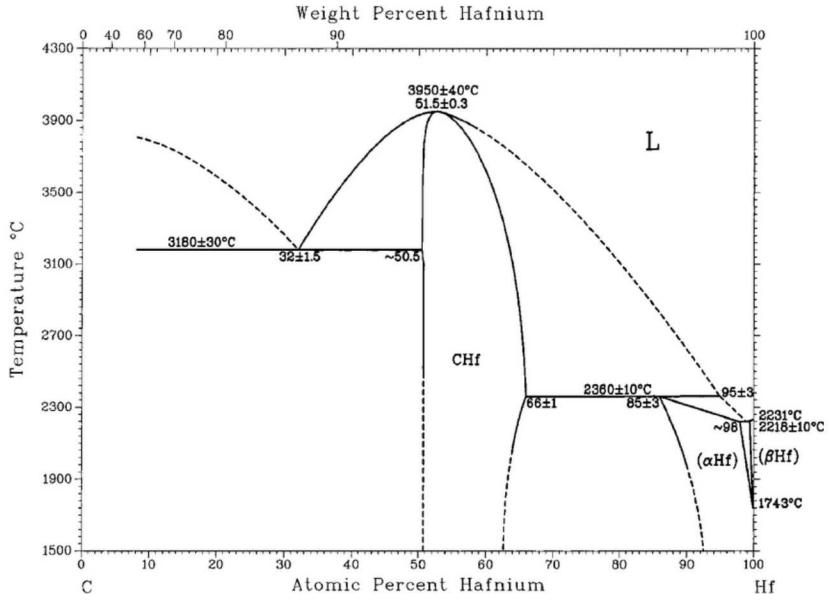
1. Increase the melting temperature to stabilize the structure
2. Introduce other elements to fill carbon vacancies

Candidate impurities: Ta, N

- Found to increase the melting temperature of HfC and are also components of low work function carbides or nitrides
  - TaC work function: 3.17eV, 3.84eV, 4.38eV, 5.0eV

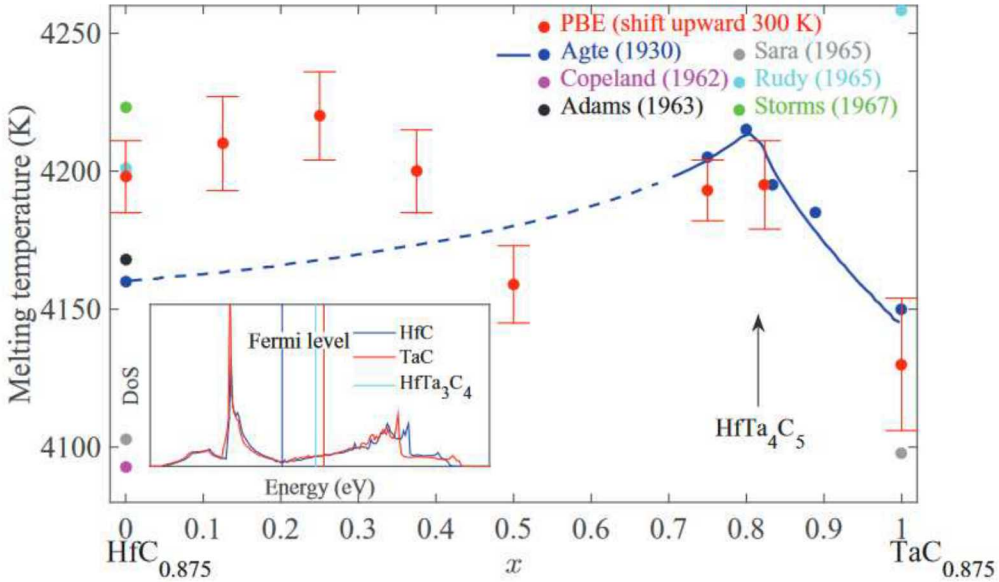
    Echstein and Forman, J. Appl. Phys (1962), Price et al. Phys Rev B. (1993), Gotoh et al. JVSTB (2003)
  - HfN work function: 4.5eV, 4.6eV, 4.9eV

    Tsai et al. J. Alloy Comp. (2009), Gotoh et al. JVSTB (2003)



The Hf-C Phase Diagram

Bandyopadkyat et al. J. Phase Equil. 2012



Melting temperature of $Ta_xHf_{1-x}C_{0.875}$ as a function of x

Hong and van de Walle Phys Rev B (2015)

Computational Methodology

Electronic Structure Calculation

- Vienna Ab inito Simulation Package (VASP)
- GGA PBE Functional
- 216 atoms (100) surfaces, 208 atoms (111) surfaces

Surface Energy: $\gamma = \frac{E_{tot}[surf] - E_{tot}[bulk]}{2A}$

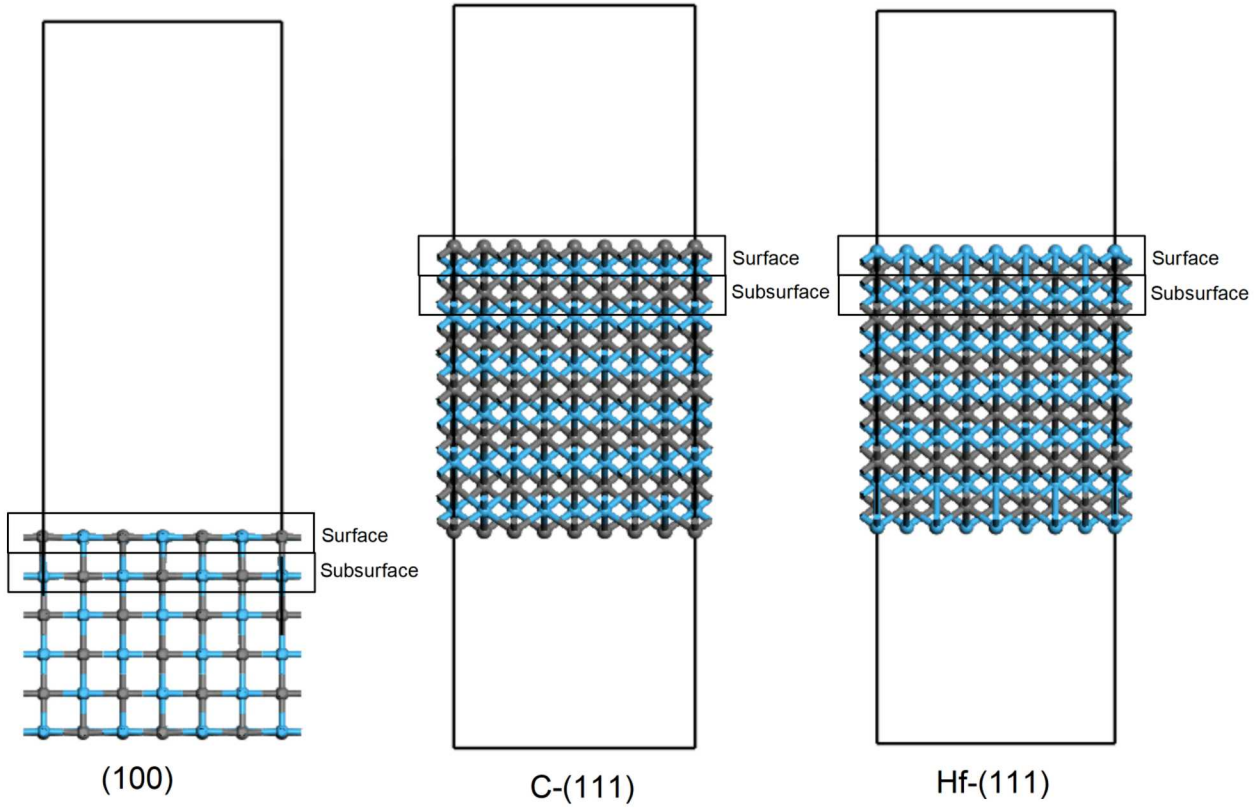
Defect formation energy:

$$E_f = E_{tot}[X^q] - E_{tot}[bulk] - \sum_i n_i \mu_i$$

Defective surface energy:

$$\gamma = \frac{E_{tot}[surf] - E_{tot}[bulk] - \sum_i n_i \mu_i}{2A}$$

Work function: $\Phi = eU_E - E_F$



Snapshots of (100) and (111) HfC surface with surface and subsurface regions outlined. Colors: hafnium (blue), carbon (grey)

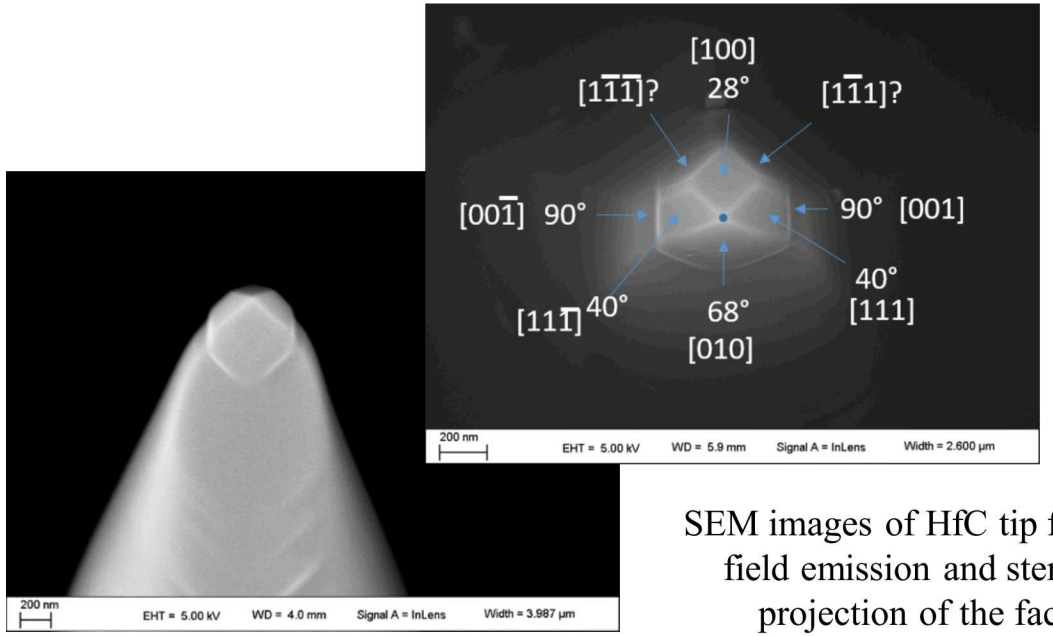
Surface Energies

- SEM images identify (100) and (111) surfaces on the faceted HfC tip

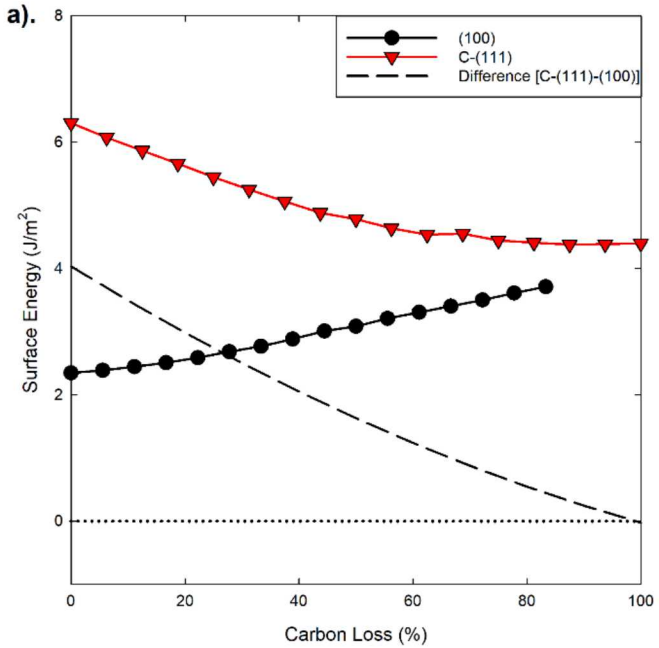
Surface	(100)	C-(111)	Hf-(111)
Surface Energy (J/m^2)	2.33	6.26	6.28

- Under equilibrium conditions the (100) surface is significantly more stable than either of the (111) surfaces
- The surface energy of the (100) surface increases with carbon defects to 4.08 J/m^2
- The surface energy of the C-(111) surface decreases to 4.06 J/m^2
- (100) v. (111) surface energy difference decreases from ~4.0 J/m^2 to < 0.00 J/m^2

Coexisting (100) and (111) surfaces form because carbon deficiencies decrease the energetic differences



SEM images of HfC tip faceting after field emission and stereographic projection of the faceted tip



Surface energy (J/m^2) with percentage of carbon loss for the (100) and carbon-terminated (111) surface of HfC.

Work Function: Pristine Surface and Vacancies

Work function describes the energy required to move an electron from the surface into vacuum

Reported data in literature includes a wide scatter:

- (100): 3.34eV-4.63eV, lower values are reported from field emission tests and from off-stochiometric compositions

Gruzalski et al. Surf. Sci. (1990), Quesne et al. PCCP (2018), Wang & Wang Appl. Surf. Sci. (2015), Vines et al. J. Chem. Phys. (2005), Hugosson et al. Surf. Sci. (2004), Mackie et al. JVST:A (1992), Price et al. Phys. Rev. B (1993)

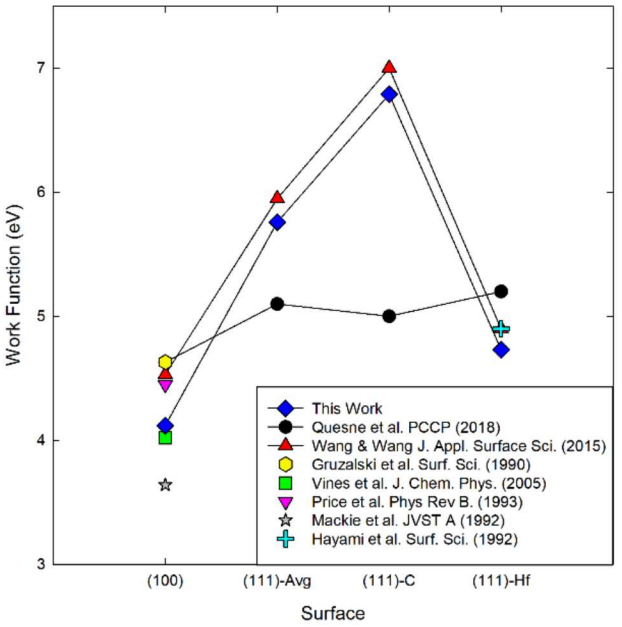
- (111): 4.9-7.0 eV, variation from computational method and geometry of sample

Quesne et al. PCCP (2018), Wang & Wang Appl. Surf. Sci. (2015), Hayami et al. Surf. Sci. (1992)

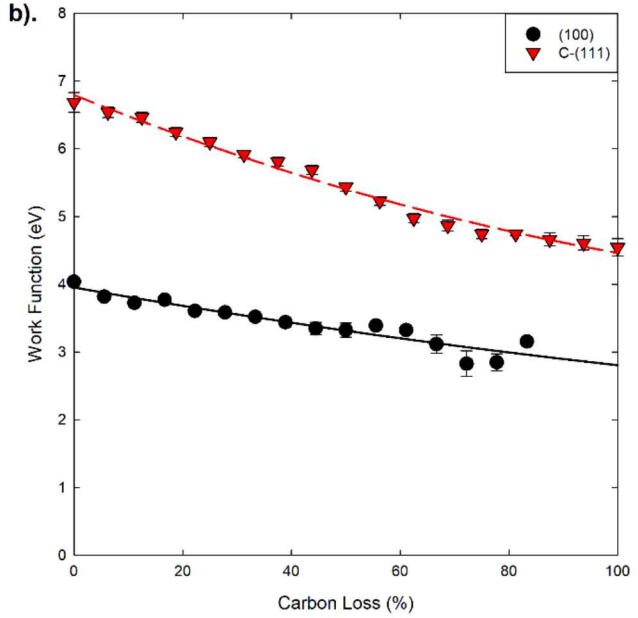
Surface	(100)	C-(111)	Hf-(111)
Work Function (eV)	4.08	6.41	4.68

Results:

- The C-(111) surface has a higher work function that the Hf-(111) surface
- Work functions on the (100) and C-(111) surfaces decrease with carbon removal
- The (111) surface has a consistently higher work function, even after carbon loss



Work functions of the (100), C-(111), and Hf-(111) surfaces of HfC



Work function (eV) with percentage of carbon loss

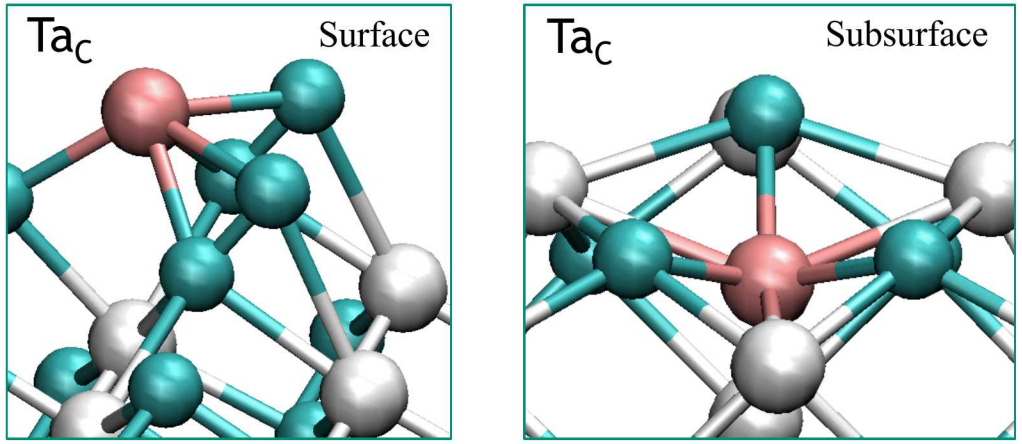
Energetics of Surface Defects

Defects

- Carbon vacancies are more stable than hafnium vacancies, due to the high carbon deficiencies that occur in HfC
- Generally C-based defects are more favorable than Hf-Based defects
- Ta prefers to sit on Hf sites, while N prefers C sites

Surfaces

- The (111) surface are generally less stable, with a lot of defects with negative formation energies
- Carbon-terminated surfaces are even less stable than Hf-terminated surfaces



Defect structure for Ta on a C site on the C-(111) surface

Defect formation energies (eV) of impurity defects on the (100) and (111) surfaces of HfC. The average of the upper and lower bound for the defect formation energies is given. Error for the defects sitting on a carbon sites is 0.25eV and the error for defects sitting on a hafnium site is 0.77eV.

Surface	Location	V_c	N_c	Ta_C	O_c	V_{Hf}	N_{Hf}	Ta_{Hf}	O_{Hf}
(100)	Surface	0.73	-2.99	1.61	-6.06	11.32	22.58	0.55	9.54
	Subsurface	1.39	-	2.15	-5.27	13.07	10.12	0.68	9.53
(111)	Surface	-4.48	-8.45	-22.59	-13.67	1.68	-3.31	-8.78	-10.87
	Subsurface	-7.74	-7.06	-30.46	-17.82	6.46	1.98	-8.95	-0.57

Work Functions of HfC Surfaces with Defects

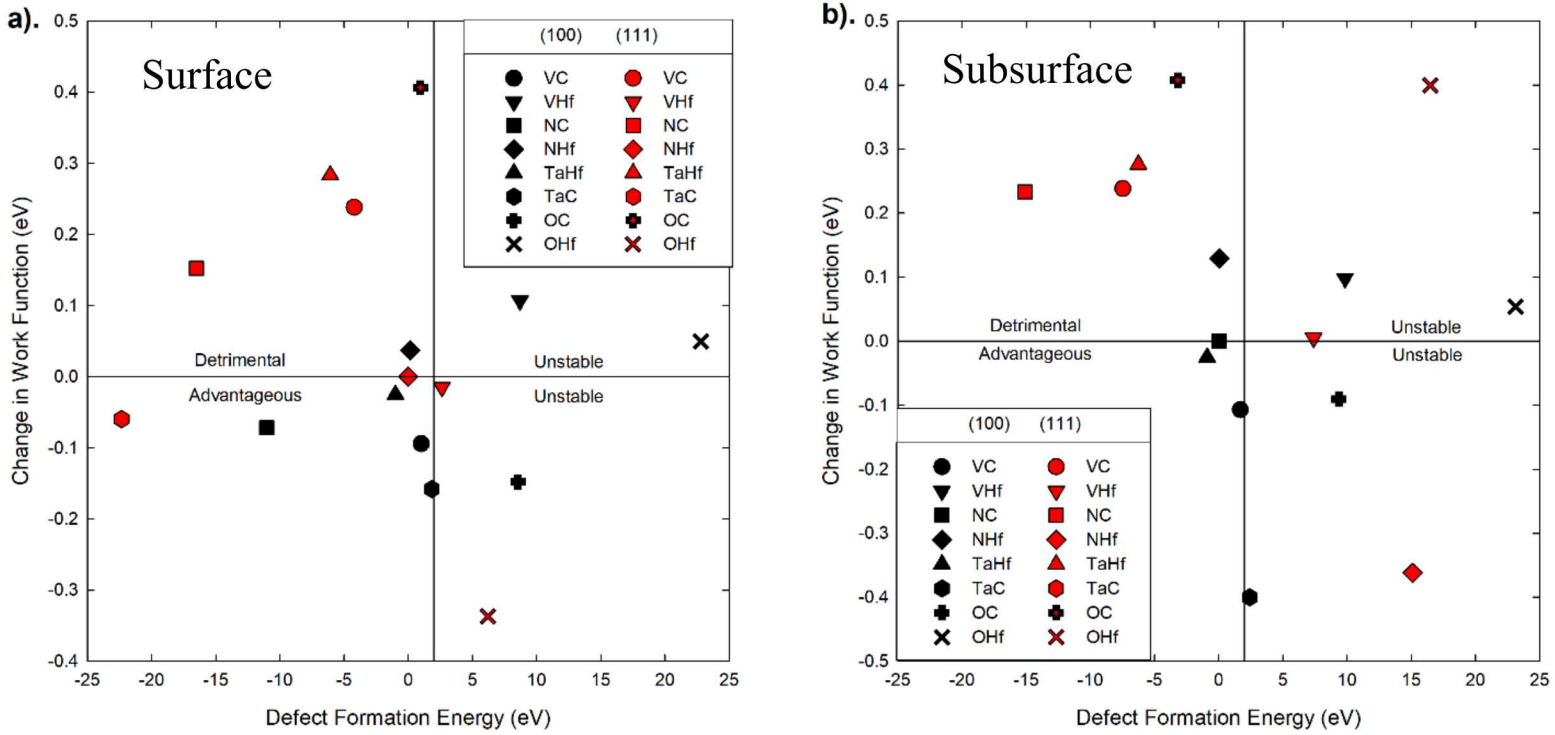
Detrimental Defects

- (100) surface: N_{Hf} (0.04eV)
- (111) surface: N_C (0.15eV), Ta_{Hf} (0.28eV), V_C (0.24eV), O_C (0.41eV)

Advantageous Defects

- (100) surface: N_C (-0.07eV), Ta_{Hf} (-0.03eV), V_C (-0.09eV)
- (111) surface: Ta_C (-0.16eV)

Ta and N impurities are energetically favorable and are either neutral or beneficial for the work function, making them candidate impurities for improving HfC performance



Defect formation energies and work function changes for defects on the (100) and (111) surfaces

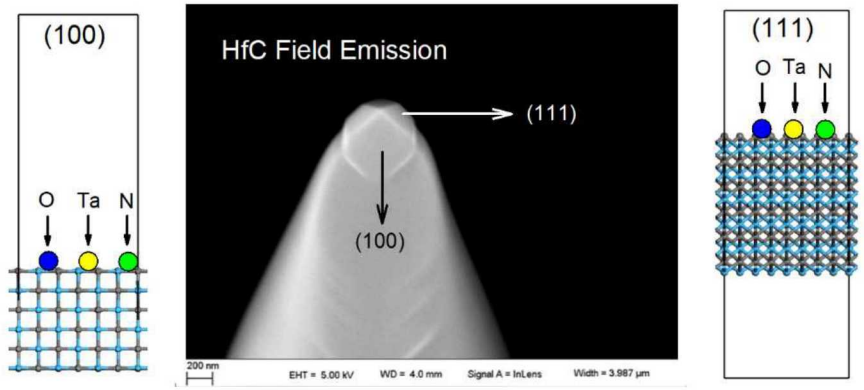
Native and impurity defects of HfC separated out by classification.

Defect Type		Detrimental Defects*	Advantageous Defects+	Unstable Defects^
(100)	Surface	N_{Hf}	Vc, N_C, Ta_{Hf}, Ta_C	V_{Hf}, O_C, O_{Hf}
	Subsurface	N_{Hf}	Vc, Ta_{Hf}, Ta_C	V_{Hf}, O_C, O_{Hf}
(111)	Surface	V_C, N_C, Ta_{Hf} O_C	Ta_C	V_{Hf}, O_{Hf}
	Subsurface	V_C, N_C, Ta_{Hf}, O_C		V_{Hf}, N_{Hf}, O_{Hf}

*Defect formation energy of less than 2eV and increase in the work function, +Defect formation energy of less than 2eV and decreases in the work function, ^Defect formation energy of greater than 2eV

Conclusions

- Faceting occurs on HfC surfaces of tips used in field emission applications
- Density functional theory (DFT) simulations were performed to investigate features of the HfC surface that maybe impacting the reliability of HfC.
- Faceting that occurs is a mixture of (100) and (111) surfaces
- Pristine (100) and (111) surface have disparate surface energies, but converge with high concentrations of carbon vacancies, indicating that surfaces present under high temperature are likely to be highly carbon deficient



- Carbon deficient (100) and (111) surface exhibit lower work functions than their pristine counterparts
- Ta and N impurities have low defect formation energies on the (100) surface and slightly decrease the work function, indicating that they may be advantageous additions to the composition.

Overall, density functional theory atomistic simulations have demonstrated the importance of understanding surface impacts on the structure and properties of HfC for use as a field emission source.

Acknowledgements

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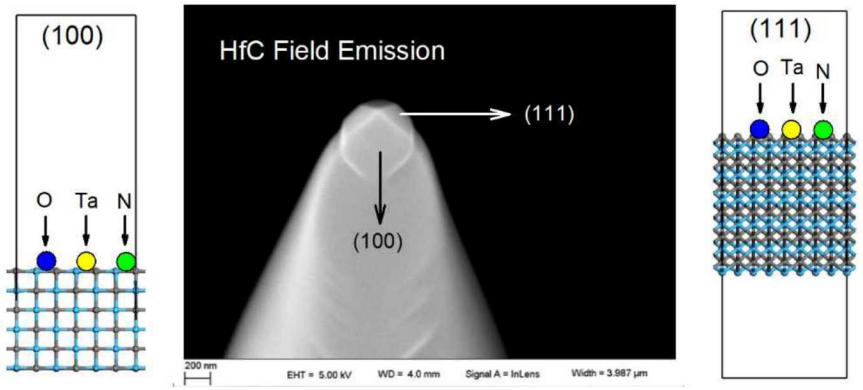

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Questions?