REACTOR SCALE MODELING OF NANOPARTICLE GROWTH IN LOW TEMPERATURE PLASMAS*

Jordyn Polito, Steven Lanham, and Mark J. Kushner
University of Michigan, Ann Arbor, MI
jopolito@umich.edu, mjkush@umich.edu

Himashi Andaraarachchi, Zhaohan Li, Zichang Xiong, and Uwe R. Kortshagen
University of Minnesota, Minneapolis, MN

Michigan Institute for Plasma Science and Engineering Symposium
November 13th, 2019

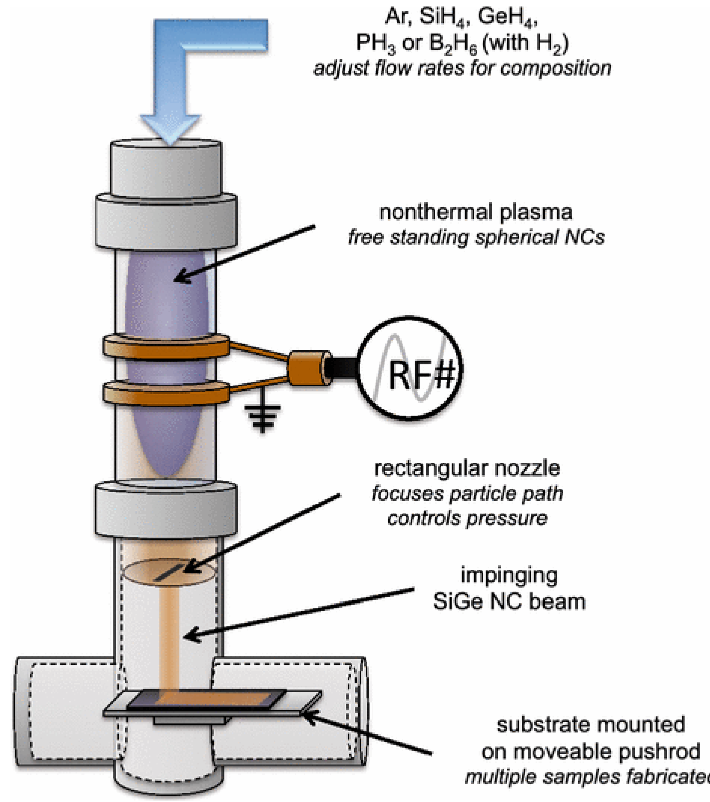
- **This work was supported by Army Research Office MURI Grant W911NF-18-1-0240 and the Department of Energy Office of Fusion Energy Science.**

AGENDA

- Plasma synthesis of nanoparticles
- Model description
- Base case particle growth results
  - SiH_4 / Ar plasma
  - SiH_4/ Ar / He plasma
- Concluding remarks

PLASMA SYNTHESIS OF NANOPARTICLES

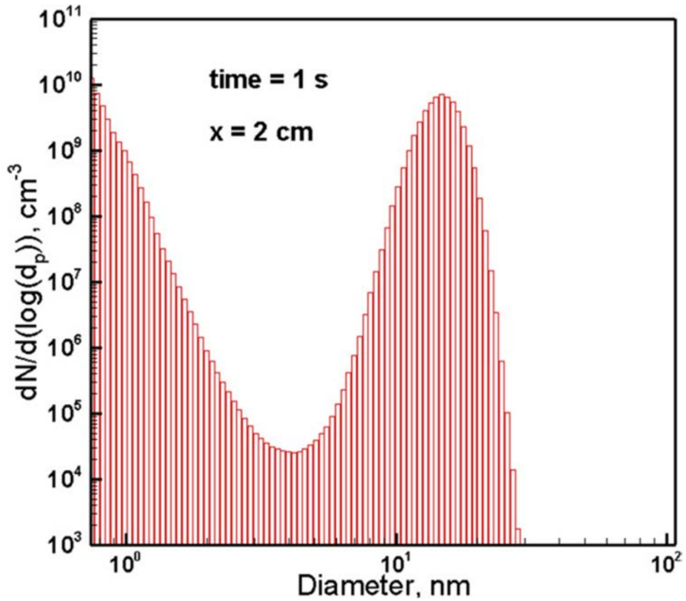
- **Plasma nanoparticle synthesis has become a viable alternative to traditional synthesis methods.**
- **Nanoparticles grown in plasma have a wide array of properties tunable by changing plasma conditions (i.e. power, flow rate, etc.)**
- **CCP or ICP can be used.**
- **Synergistic effects of growing particles in plasma are not well understood.**



U. Kortshagen. *Plasma Chem. Plasma Process.* 36,73 (2016).

MODELING CHALLENGES

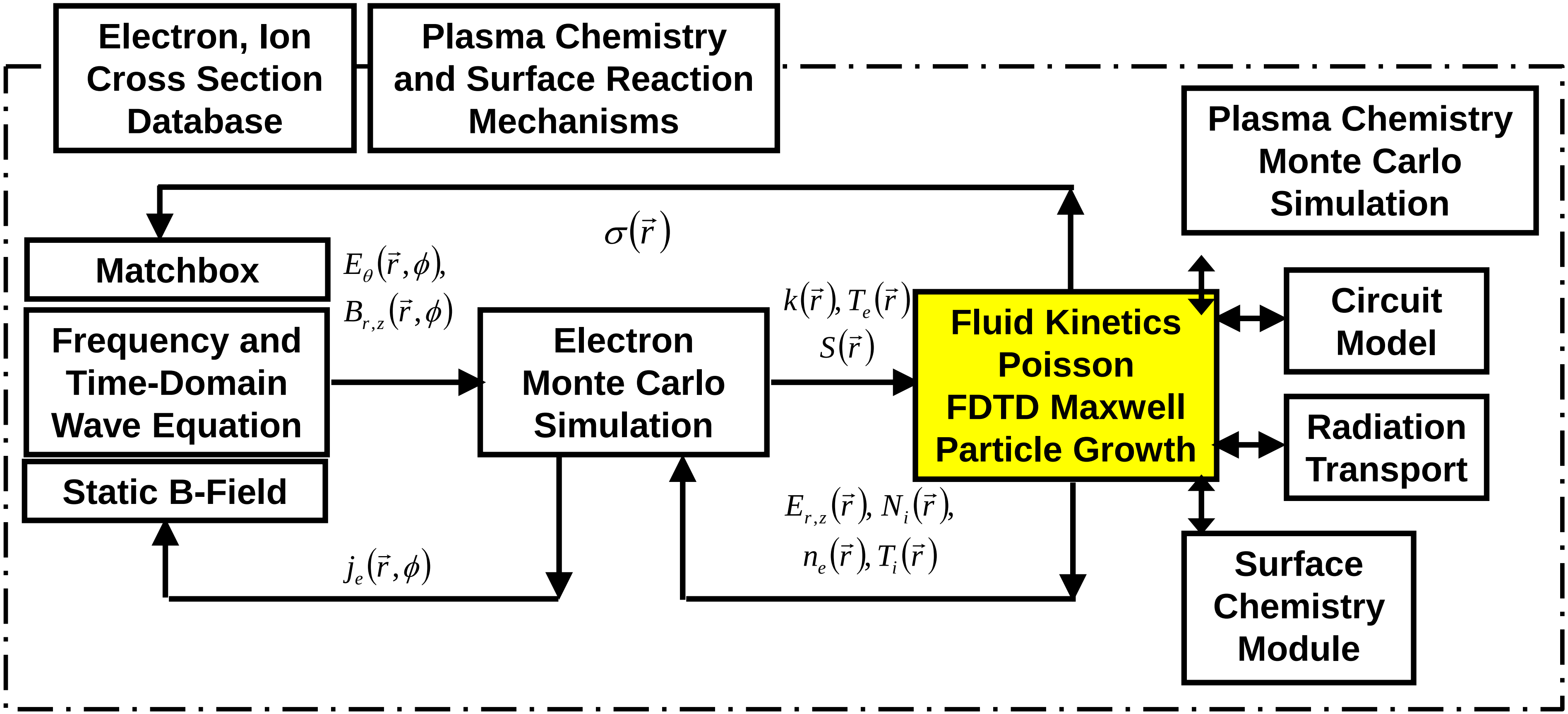
- **Previous models utilize a sectional method developed by the Aerosol Physics community.**
- **Sectional models bin particles by size and solve population balance for each size section.**
- **Sectional models are usually 0-dimensional and at best 1-dimensional models.**
- **Models provide high level of detail, but are computationally intensive when implemented in 2D.**
- **In this work we implement a 2D particle growth model directly into an existing fluid code in an attempt to overcome computational challenges.**



$$\frac{\mathrm{d}N_{j,k}}{\mathrm{d}t} + \nabla\Gamma_{j,k} = \left[\frac{\mathrm{d}N_{j,k}}{\mathrm{d}t}\right]_{\mathrm{nuc}} + \left[\frac{\mathrm{d}N_{j,k}}{\mathrm{d}t}\right]_{\mathrm{coag}} + \left[\frac{\mathrm{d}N_{j,k}}{\mathrm{d}t}\right]_{\mathrm{growth}} + \left[\frac{\mathrm{d}N_{j,k}}{\mathrm{d}t}\right]_{\mathrm{charging}}$$

P. Agarwal and S.L. Girshick. *Plasma Src. Sci. Technol.* 21,5 (2012)

HYBRID PLASMA EQUIPMENT MODEL



- The Hybrid Plasma Equipment Model (HPEM) is a modular simulator that combines fluid and kinetic approaches.
- Particle growth algorithms added to fluid modules.

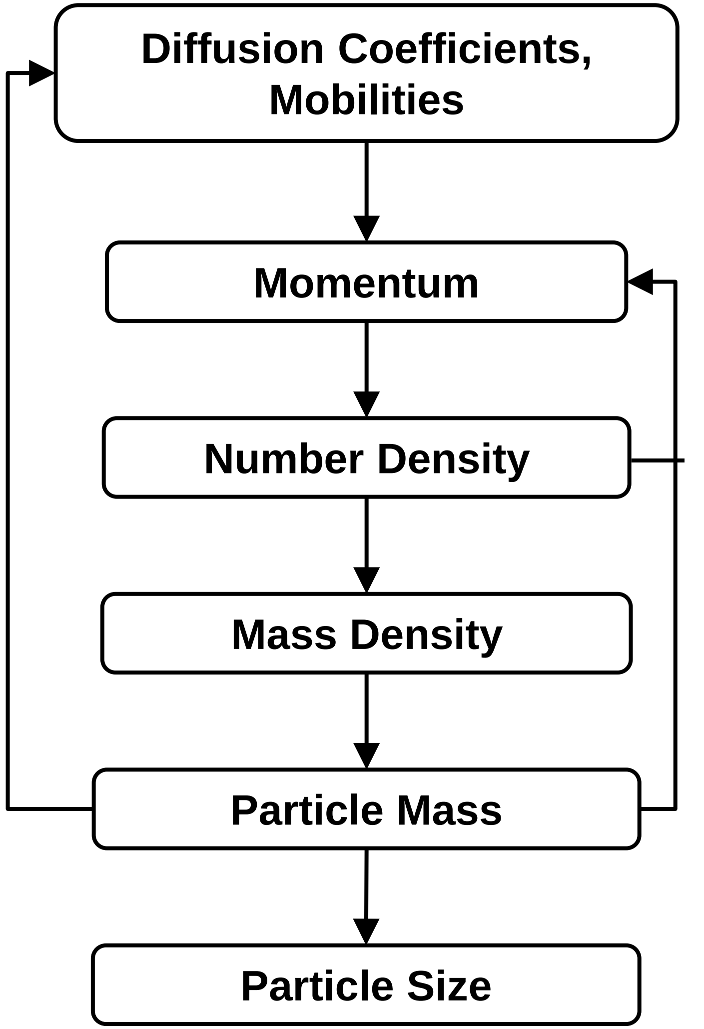
MODEL CHANGES

- **NPs included in reaction mechanism as species with variable mass.**
- **Change in mass based on net reactive fluxes,**

$$\frac{dm_i}{dt} = \sum_{j,k} k_{jk} N_j \left(\pm \Delta m_{jk} \right)$$

$$d_i = \left({6m_i}/{\rho \pi} \right)^{1/3}$$

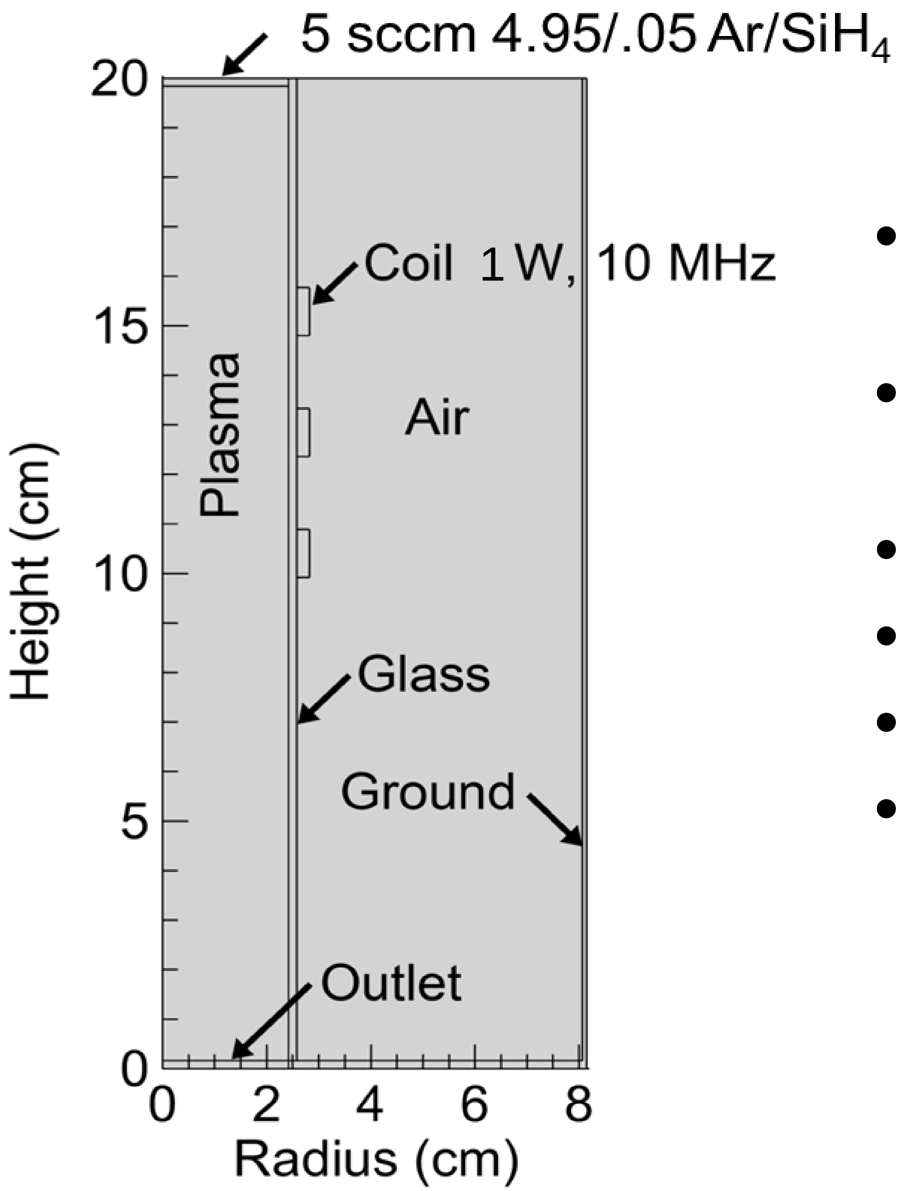
- **Prior algorithms assumed constant species mass.**
- **Significant code changes required to implement.**



BASIC Ar/SiH_4 REACTION MECHANISM FOR Si NPs

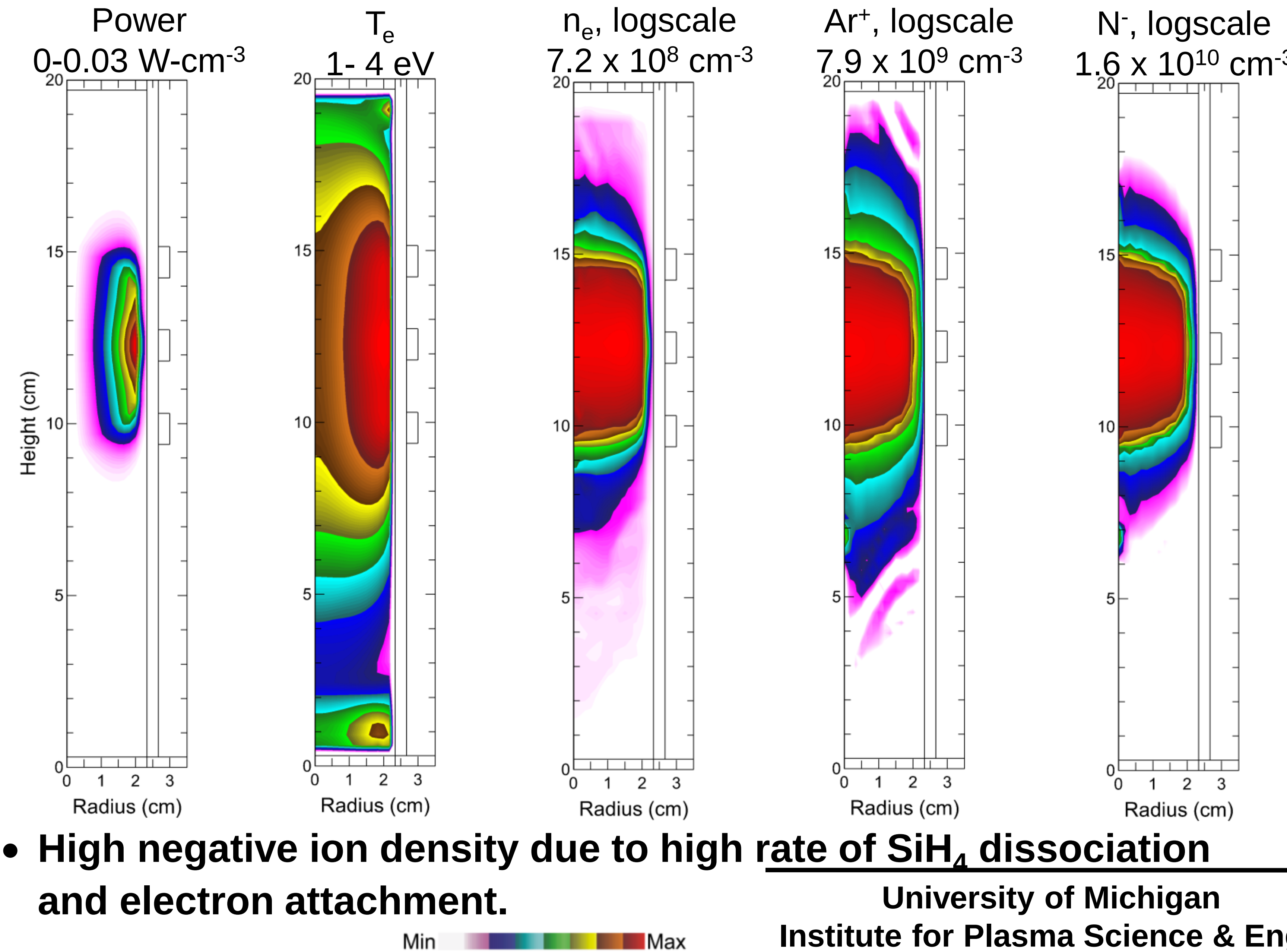
- **Species**
  - **Ar, Ar($1s_5$), Ar($1s_4$), Ar($1s_3$), Ar($1s_2$), Ar(4p), Ar(4d), Ar^+, e**
  - **Si, SiH_2, SiH_3, SiH_4, SiH_3^+, SiH_2^-, SiH_3^-**
  - **Si_2H_2, Si_2H_3, Si_2H_5, Si_2H_6, $Si_2H_5^-$**
  - **H_2, H_2^*, H, H*, H^+**
  - **NP – the nanoparticle species**
- **NP growth reactions – now only considering neutral nanoparticles.**
  - **$Si_2H_n + SiH_n \rightarrow NP$**
  - **$SiH_n + NP \rightarrow$ (bigger) $NP + H_n$**
- **Mechanism to be refined to include**
  - **H_2(v), SiH_4(v), Si, Si_2, SiH_n^+, $Si_nH_m^-$**
  - **More complete nucleation kinetics**
  - **Charged particle based growth in fluid approach.**
  - **DU temperature based on surface reactions**

REACTOR GEOMETRY



- Based on (prior) Kortshagen reactor.
- ICP, cylindrical quartz tube, 3 coils, 10 MHz, 1 W
- Negligible NP particle density
- Ar/SiH_4 = 99/1.0, 800 mTorr
- 28 species, 186 reactions
- 4 particle growth reactions

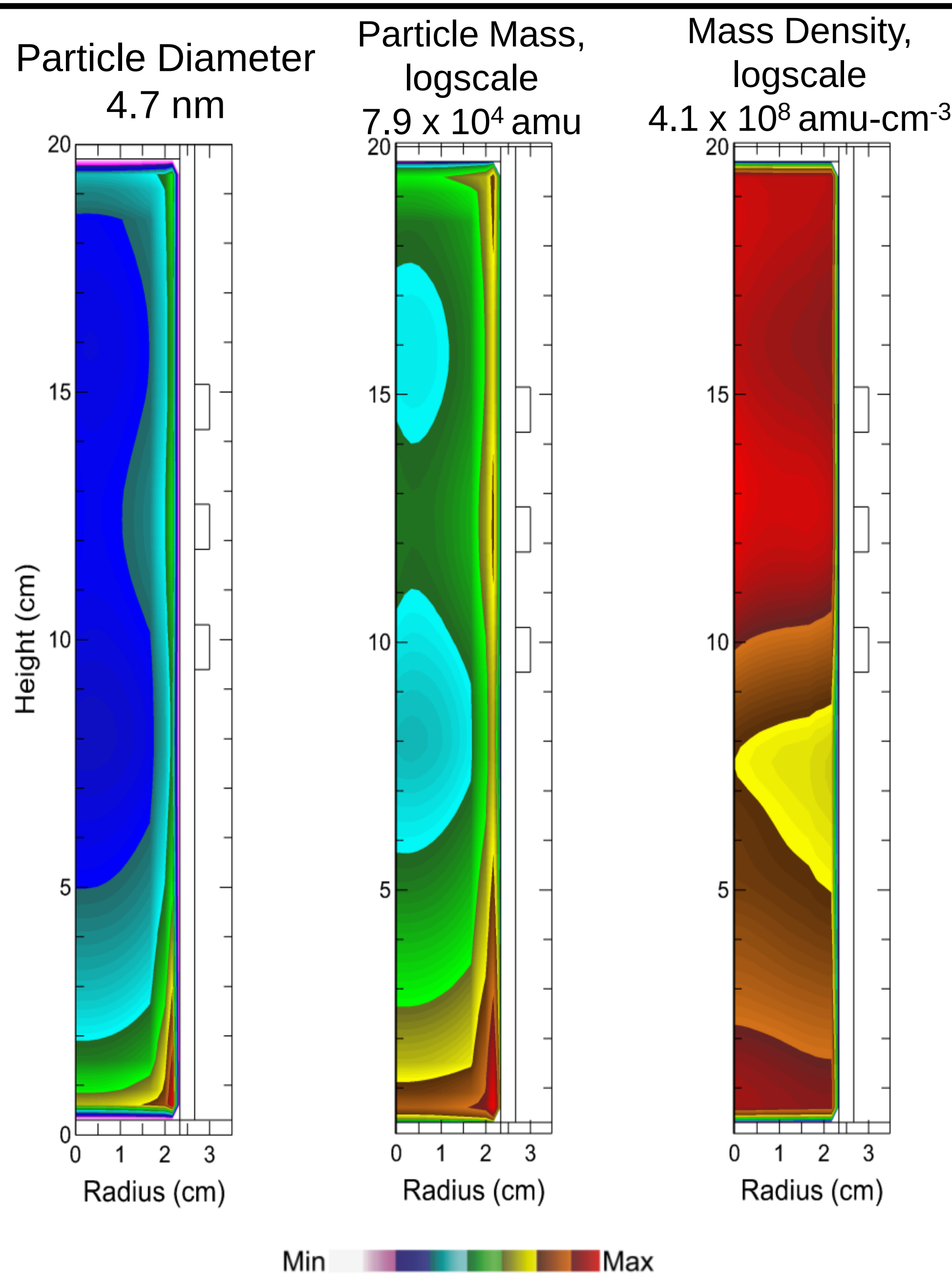
BASE CASE PLASMA PROPERTIES



- **High negative ion density due to high rate of SiH_4 dissociation and electron attachment.**

University of Michigan
Institute for Plasma Science & Engr.

BASE CASE PARTICLE GROWTH



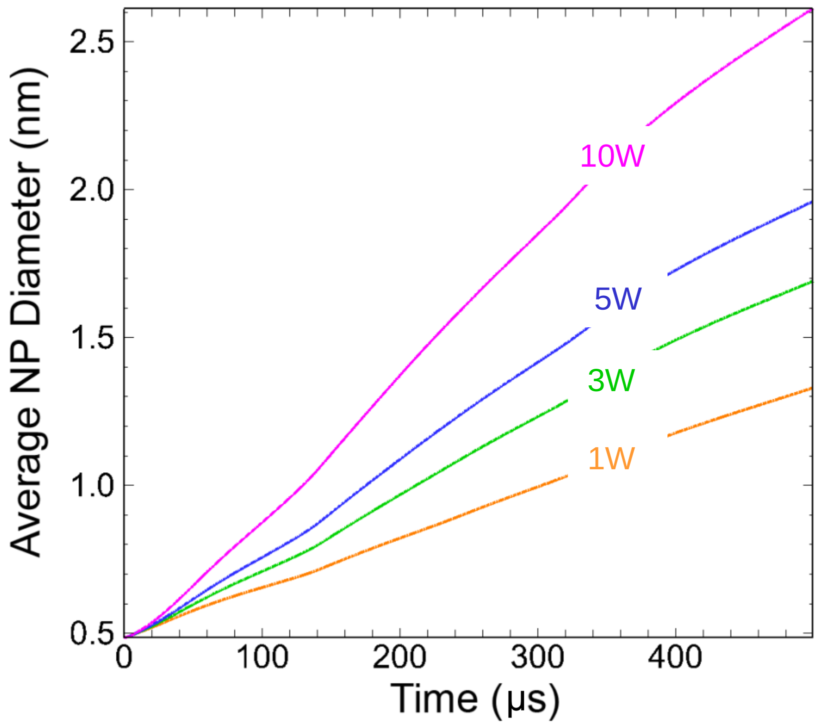
- **NP starts as Si_3**
- **Initial growth mechanism:**

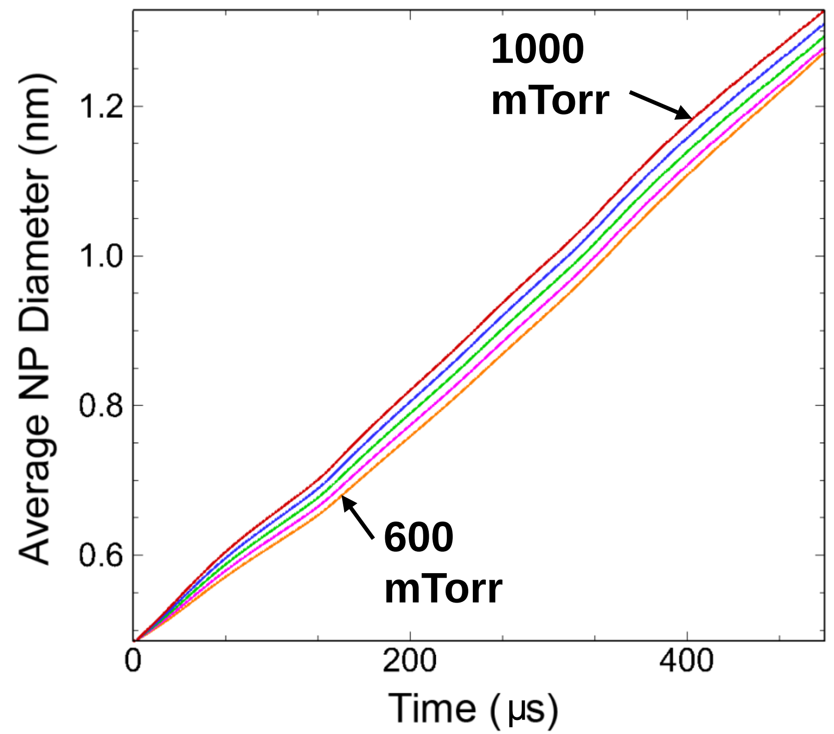
  $Si_2H_2 + SiH_n \rightarrow NP$

  $SiH_n + NP \rightarrow NP + nH$
- **Decreasing nucleation rate with increasing n**
- **Neutral NPs form near surfaces due to longer residence time and lower axial density by gas heating.**

Animation Slide

POWER AND PRESURE DEPENDENCE

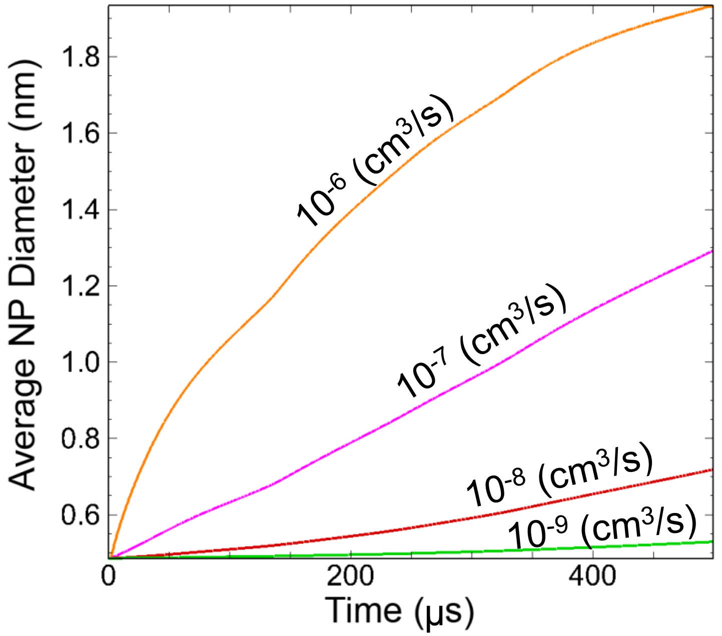


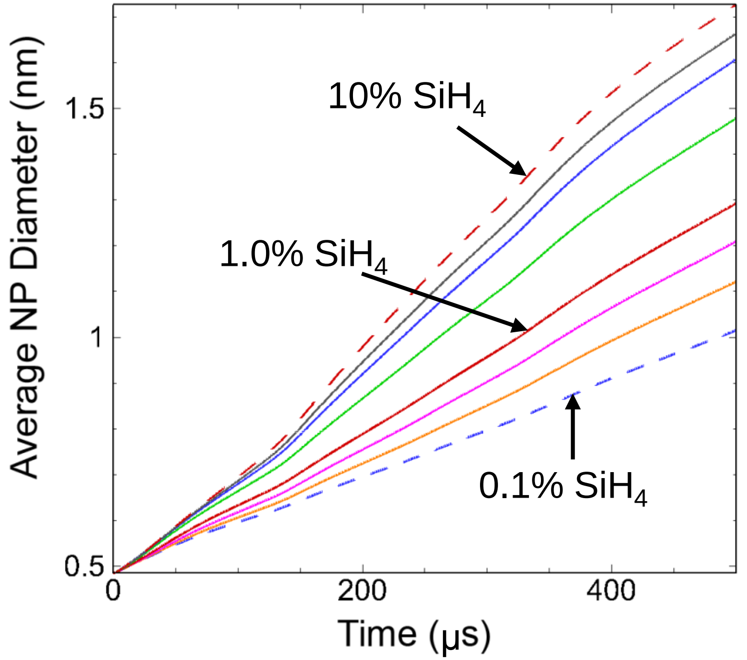


- **Vary pressure with power = 1W**
- **Vary power with pressure = 800mTorr**
- **Increase in NP size**
  - **With pressure due to longer residence time.**
  - **With power due to higher radical densities.**

- **Ar/SiH_4 = 99/1.0, 800 mTorr, 1 W, 5 sccm**

INLET FRACTION AND NUCLEATION RATE

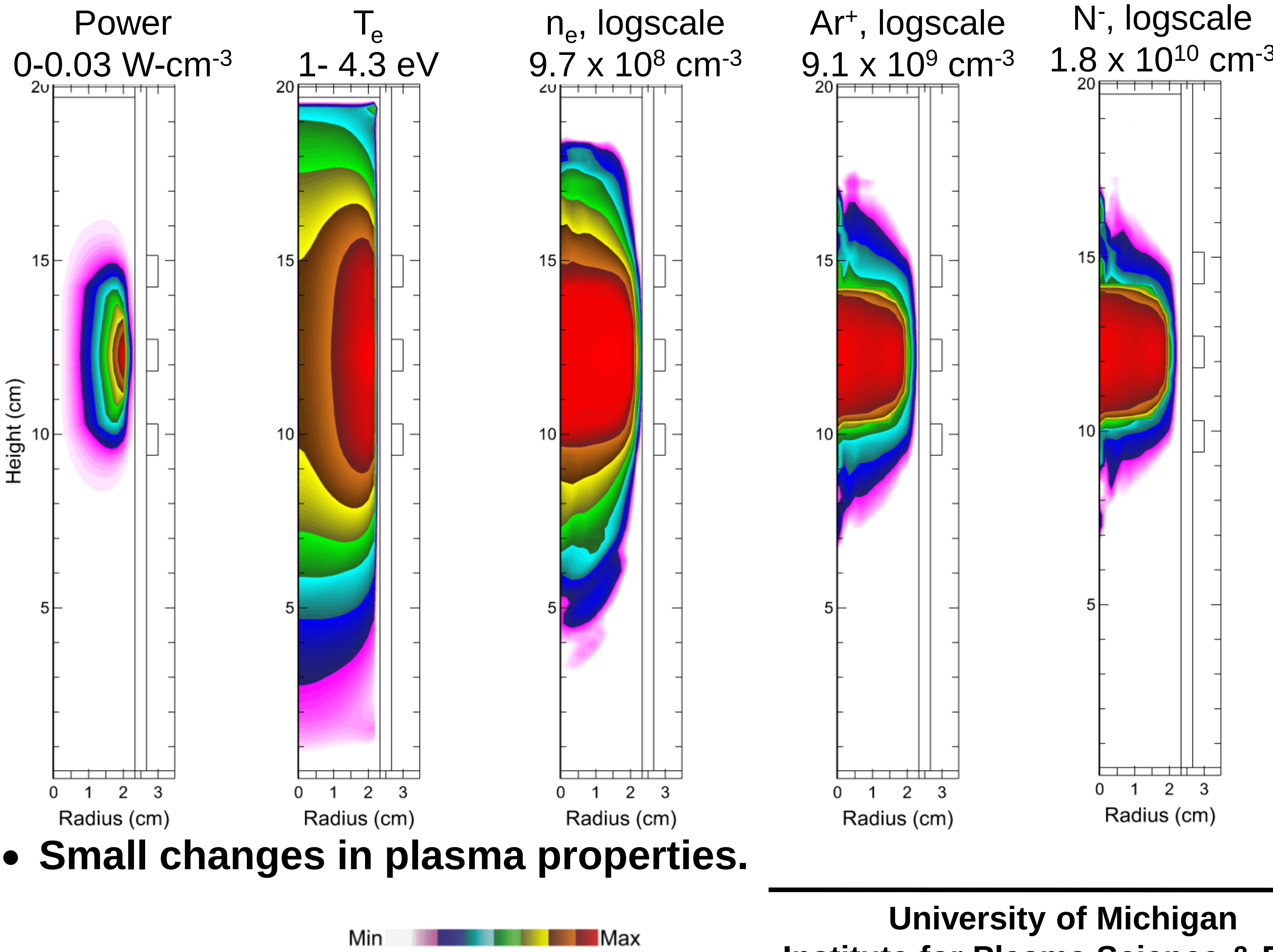




- **Higher rates of nucleation have higher initial growth rates.**
- **Average NP diameter will saturate when precursors are depleted.**
- **High inlet fraction leads to higher growth rates – simply more precursors that are not depleted.**

- **Ar/SiH_4 = 99/1.0, 800 mTorr, 1 W, 5 sccm**

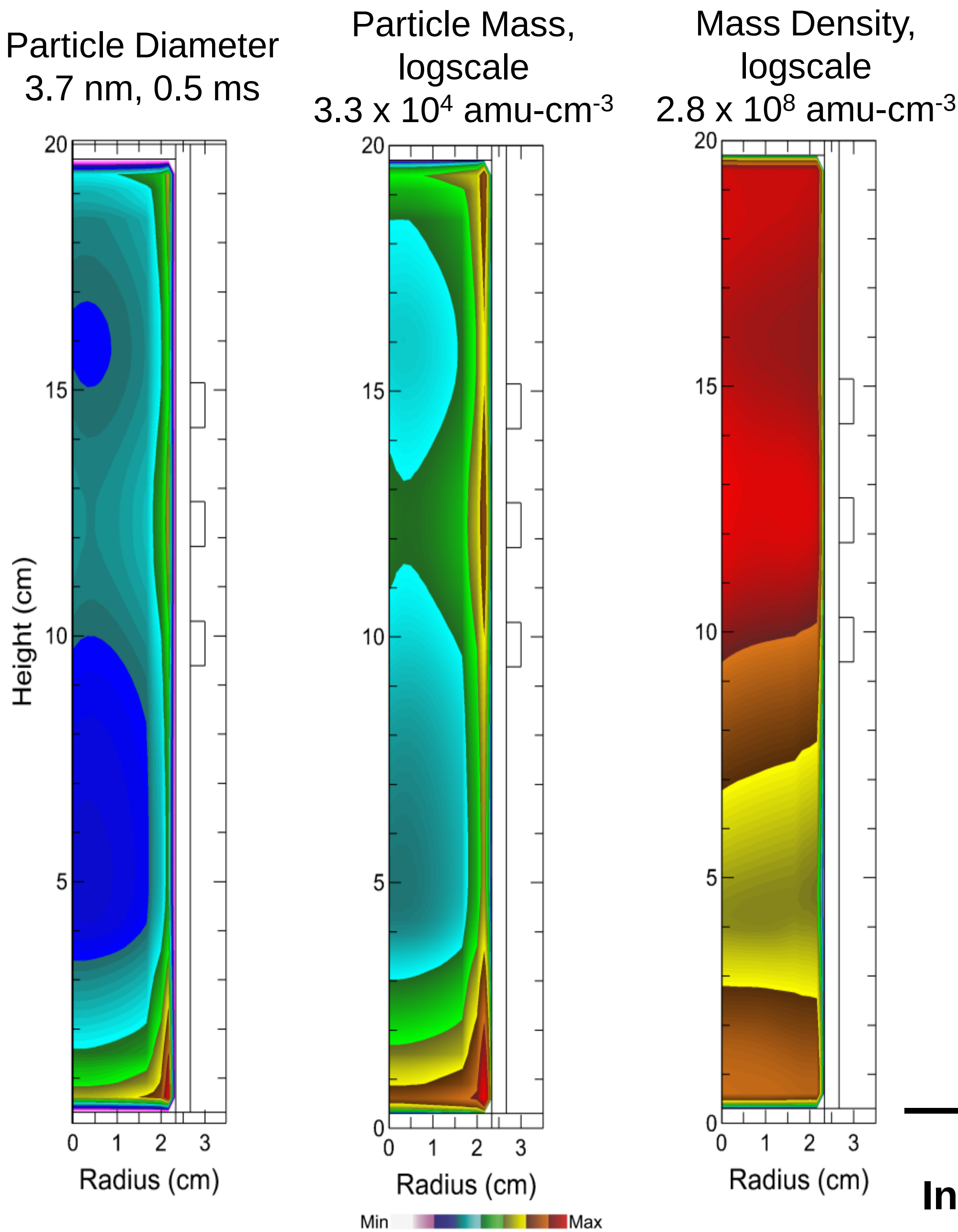
$Ar/He/SiH_4$ = 75/24/1: PLASMA PROPERTIES



- **Small changes in plasma properties.**

University of Michigan
Institute for Plasma Science & Engr.

PARTICLE GROWTH: Ar/He/SiH_4 = 75/24/1



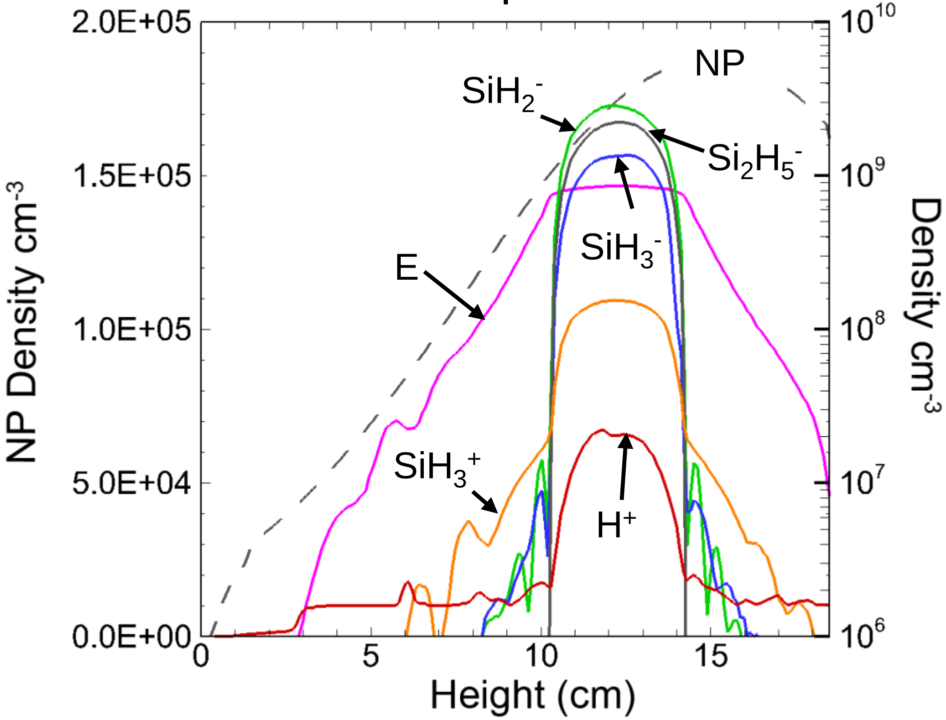
- **Growth patterns are similar to Ar/SiH_4 mixtures.**
- **Larger areas of nucleation due to higher ion concentration and rate of SiH_4 dissociation.**
- **Addition of He expected to have higher particle growth rate.**

Animation Slide

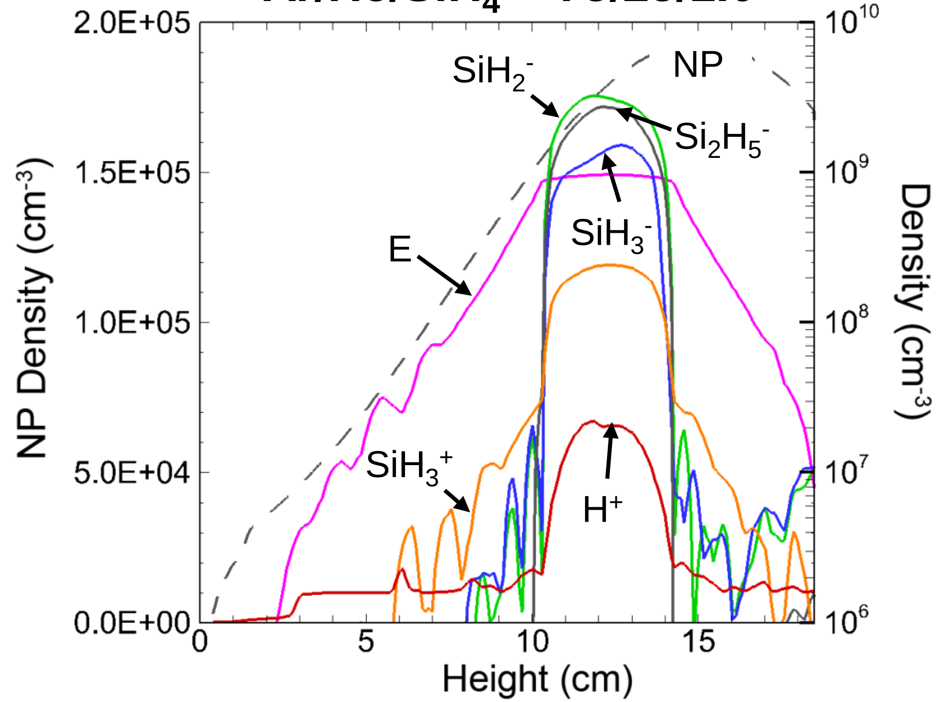
University of Michigan
Institute for Plasma Science & Engr.

HELIUM DILUTION: NANOPARTICLES

- Ar/SiH_4 = 99/1.0



- $Ar/He/SiH_4$ = 75/25/1.0



- **Radius = 1.25 cm**
- **Highest NP densities occur upstream of coils (larger height) where SiH_4 density and radical densities are higher.**
- **Addition of He slightly increases ion and NP concentration, but otherwise has no significant effect on bulk plasma properties.**

CONCLUDING REMARKS

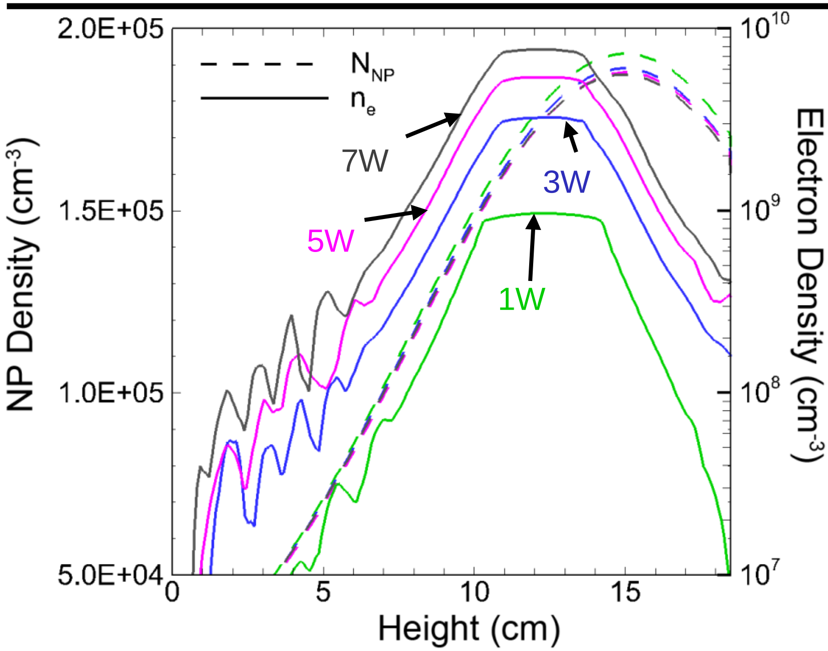
- A particle growth model was developed and implemented into existing HPEM structure.
- The neutral channel for NP growth occurs dominantly near walls where residence times are longer.
- Addition of He as an inlet gas does not significantly change bulk plasma properties while changing ion composition.
- Addition of He is expected to yield higher particle growth rates due to higher rate of SiH_4 dissociation leading to higher precursor radical concentrations.
- Mechanism to be refined to include
  - H_2(v), SiH_4(v), Si, Si_2, SiH_n^+, $Si_nH_m^-$
  - More complete nucleation kinetics
  - Charged particle based growth in fluid approach

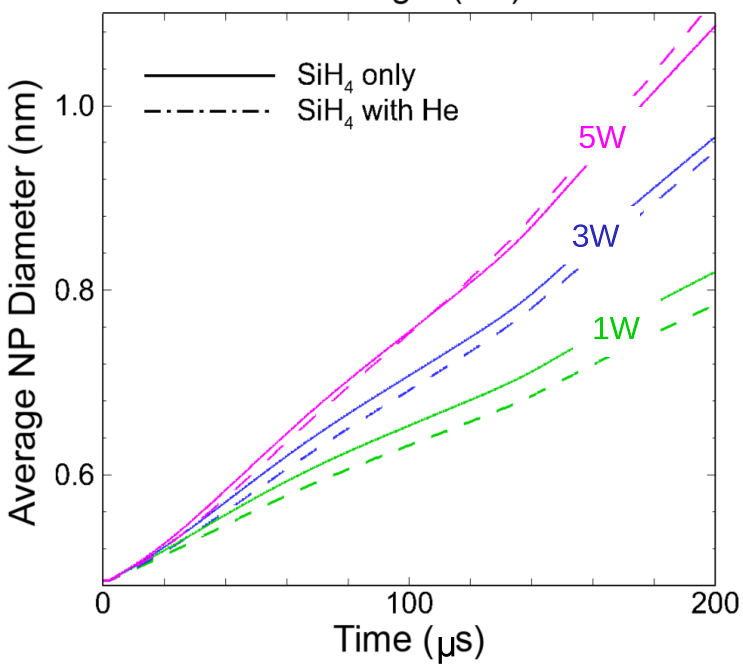
$Ar/He/SiH_4$ = 75/24/1.0 MIXTURES

- **20 cm height, 2.5 cm radius**
- **Cylindrical quartz tube**
- **5 sccm $Ar/He/SiH_4$ 0.75 / 0.24 / 0.01 inlet flow**
- **One coil set, three turns**
- **1W deposited power, 10MHz frequency**
- **800mTorr**
- **Initial particle density ~ 0 cm^{-3}**
- **39 species, 307 reactions**
- **4 particle growth reactions**

Process	Rate of Reaction (cm^3/s)
Attachment	10^{-9}
Detachment	10^{-10}
Neutralization	$10^{-7} - 10^{-8}$
Charge Exchange	10^{-11}
Hydrogen Elimination	10^{-9}
Dissociation by He	$10^{-7} - 10^{-9}$
Dissociation by Ar	$10^{-10} - 10^{-11}$
Nucleation	10^{-7}
Growth	$10^{-10} - 10^{-12}$

Ar/He/SiH_4 = 75/24/1.0 MIXTURES: POWER





- **As in the case of Ar/SiH_4 , growth rate increases with increasing power.**
- **Compared to Ar/SiH_4, addition of He lowers growth rate at lower powers.**
  - **Multiple pathways for dissociation lead to higher positive ion (N^+) concentration while negative ion concentration remains same.**
  - **Longer time needed for precursor species creation until N^- concentration balances N^+ concentration.**

- **Expect that after a longer time, addition of He will increase growth rate, as in the 5W case.**