Thermal Conductivity of Polyatomic Gas, Ammonia (NH3) in a simulated Plasma Enhanced Chemical Vapor Deposition (PECVD).

Research done by: **James Huang**

For

Dr. Jun Jiao

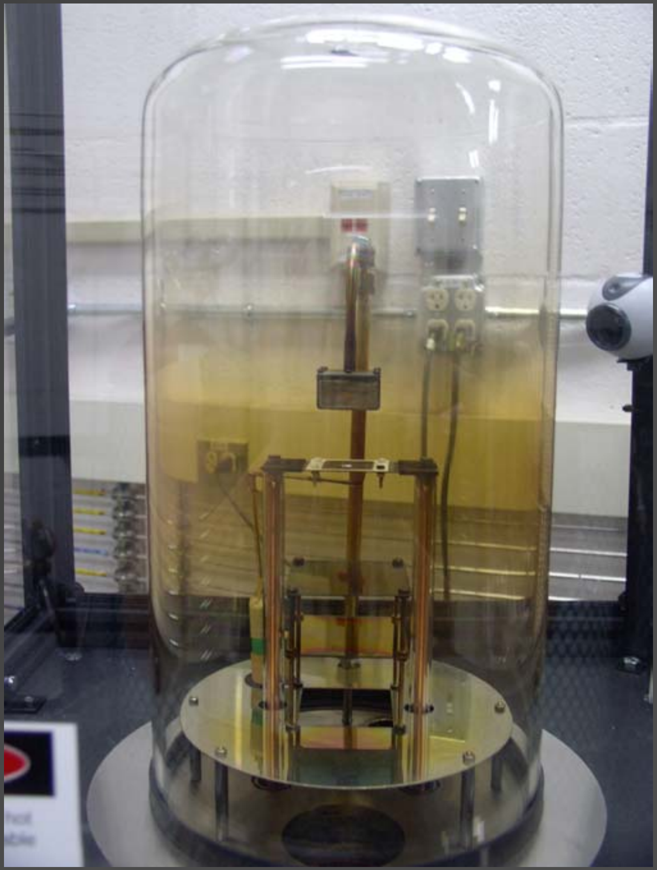
Summer 2006 at PSU funded by NSF-sponsored REU program

Chemical Vapor Deposition

- (CVD) involves the adsorption, desorption, evolution and incorporation of vapor species at the surface of a growing film.
- Can be used for growing carbon nanotubes (CNT's)
- Thermal Energy is used to activate the gas to cause growth.

Plasma-enhanced CVD

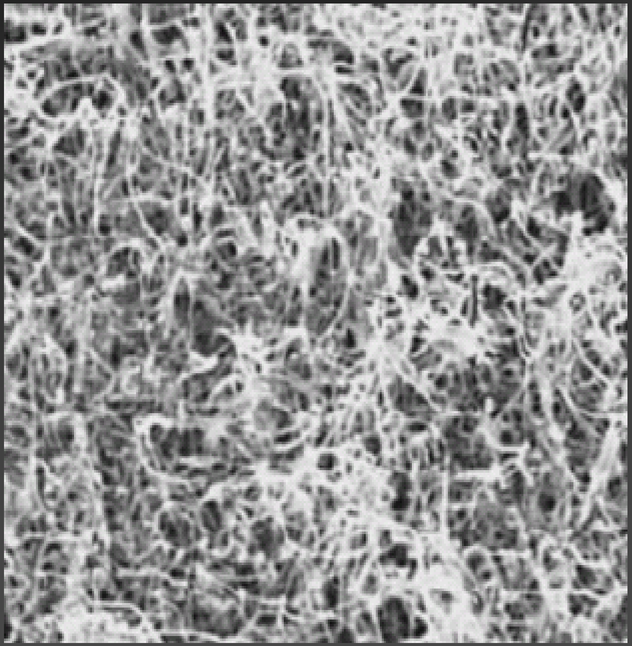
- Very similar to a CVD
- Gas molecules used to grow the CNT’s are activated by electron impact which takes place in a plasma, also referred to as a glow discharge.



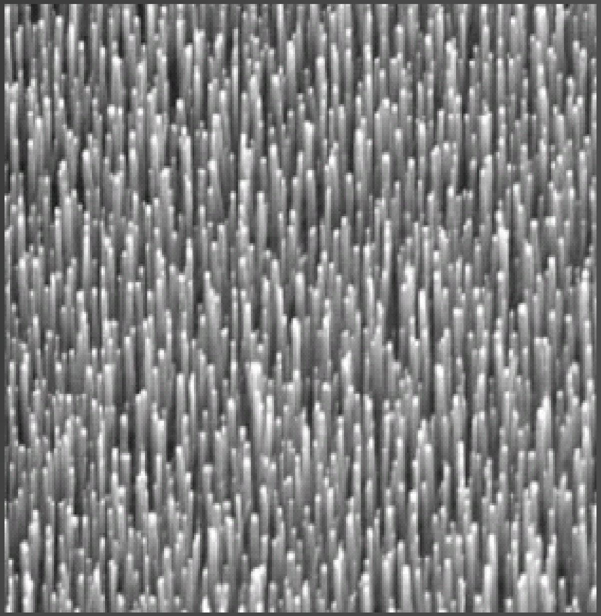
Why PECVD?

- The main purpose of using a PECVD growth process is that it reduces the activation energy for a deposition process.
- Another important benefit is using a PECVD causes the CNT’s to grow alligned rather than curled and tangled due to its interaction with the electrical field of the plasma.

CVD vs PECVD



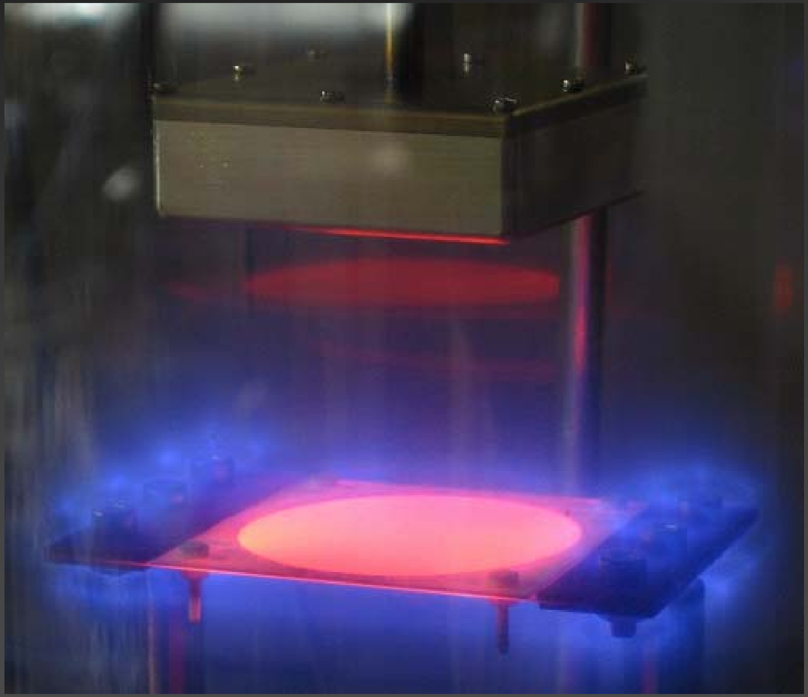
SEM image of Growth in CVD

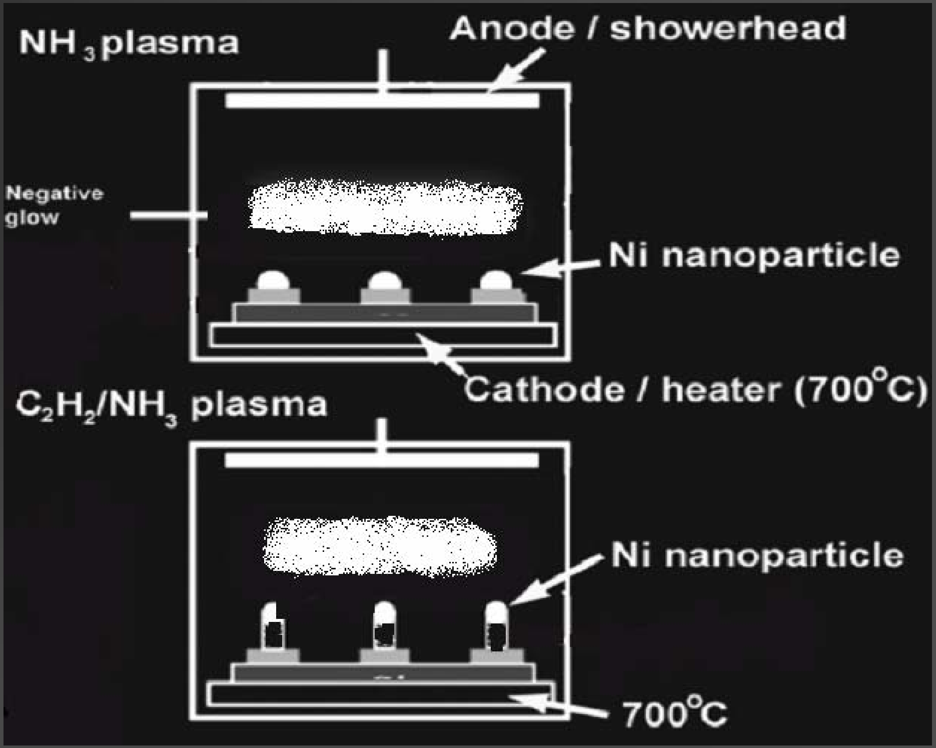


SEM Image of Growth in PECVD

Photos courtesy of Ken Teo: Growth process of vertically aligned CNT’s Pg, 5311

Diagram of PECVD





Temperature change

- The Heat source comes from the stand.
- Temperature change is present between the heat source and the shower where the activating gas comes from.
- This could effect how well the plasma works or how well the CNT’s grow.

Simulating the PECVD

- Using a program named FlexPDE we create a simluation that shows the temperature change between the heating source and the shower.
- FlexPDE uses partial differential equations to solve for the simulation

The Brick Wall

- Herein lies the difficulty because there are many variables to the simulation, one of which is thermal conductivity.
- This one constant value determines how well or not well heat is transferred through a solid, gas or liquid.
- Tables provide answers, but we are not running at normal temperatures so we need to take into account temperature and pressure differences

Thermal Conductivity

- Thermal conductivity is the intensive property of a material that indicates its ability to conduct heat.
- All materials have a thermal conductivity whether it be high or low.
- An example is Metal. We all know and can observe that metal transfers and absorbs heat quickly and effectively. This is because its thermal conductivity is high, whereas wood would have a low thermal conductivity.

Ammonia

- Ammonia(NH3) is one of the primary gases used to fill the chamber with the heating source and shower.
- The Thermal conductivity needs to be determined because it envelops the heating source and heat is transferred through the ammonia in an outwards direction.

Standard Thermal Conductivity

- First you start out with a general thermal conductivity equation which is:

$$\lambda = 2.63 \times 10^{-23} \frac{(T/M')^{1/2}}{\sigma^{2}\Omega_{v}}$$

Where

λ= thermal conductivity, W/(m·K)

T= Temperature, K

M'= molecular weight, kg/mol

σ = characteristic dimension of molecule, m

Ω_{v} = collision integral, dimensionless

Limitations

- This method only achieves thermal conductivity for monoatomic gases, which have no rotation or vibrational degrees of freedom.
- A more rigorous method is needed.
- Pressure is not taken into account as well and is assumed to be at 1 atm = 760 torr

Chung et al. method for low pressure

- Chung et al. employs a similar approach to obtain λ. Their equation is:

$$\frac{\lambda M'}{\eta C_v} = \frac{3.75\Psi}{C_v/R}$$

Where λ = thermal conductivity, W/ (m·K)

M'= molecular weight, kg/mol

η = Low pressure viscosity, N · s/m^2

C_v = heat capacity at constant volume, J/(mol·K)

R = gas constant, 8.314 J/(mol·K)

$\Psi = 1 + \alpha\{[0.215 + 0.28288\alpha - 1.061\beta + 0.26665Z]/[0.6366 + \beta Z + 1.061\alpha\beta]\}$

$\alpha = (C_v/R\} - 3/2$

$\beta = 0.7862 – 0.7109\omega + 1.3168\omega^2$

$Z = 2.0 + 10.5T_r^2$

T_r= T/$T_{c,}$ temperature/temperature critical

More math…

- The Chung et al. method is usefull because it takes into account pressure change and temperature.
- Before we can solve we need to to determine low pressure viscosity of Ammonia (η).

Chung et al. for viscosity

- Chung et al. proposes another method to estimate low pressure viscosity through this formula:

$$\eta = 40.785 \frac{F_c (MT)^{1/2}}{V_c^{1/2} \Omega_v}$$

Where M = molecular weight, g/mol

T = temperature, K

V_c= critical volume cm^3/mol

$\Omega_v = [A(T^*)^{-B}] + C[(-DT^*)] + E[(FT^*)]$

- Where $A = 1.16145$, $B = 0.14874$, $C = 0.52487$, $D = 0.77320$, $E = 2.16178$, $F = 2.43787$, and $T = 1.2593T_r$

$F_c = 1 - .2756\omega + .059035\mu_r^4 + \kappa$

Where $\mu_r = 131.3\mu / (V_c T_c)^{1/2}$

Solve for viscosity

From Appendix A in *Properties of Gases and Liquids,* T_c= 405.5K, V_c=72.5 cm^3/mole, ω = .250, M = 17.031g/mol, and dipole moment is 1.5 debyes. Assuming K is negligible because Chung et al. does not list it as a significant gas,

- $\mu_r = 131.3(1.5)/[(72.5)(405.5)]^{1/2} = 1.1487$
- $F_c = 1 - .2756(0.250) + .059035(1.1487)^4 = 0.828$
- $T^* = (1.2593)[(700+273)/(405.5)] = 3.02$
- $\Omega_v = 15.676$
- $\eta = 40.785 \dfrac{(0.828)[(17.031)(700+273)]^{1/2}}{(72.5)^{1/2}(15.676)} = \mathbf{134.4\ \mu P}$
- **134.4 μP is the Viscosity = 1.344$\times 10^{-4}$ P = 1.344$\times10^{-5}$ N$\cdot$s/m^2**

Solve for Chung et al Thermal…

From Appendix A in *Properties of Gases and Liquids,* T_c= 405.5K, P_c = 113.5 bar, V_c=72.5 cm^3/mole, C_v = 35.65, Z_c = 0.244, ω = .250, M = 17.031 × 10^{-3} kg/mol.

- $\alpha = (35.65/8.314\} - 3/2 = 2.787$
- $\beta = 0.7862 – 0.7109(.250) + 1.3168(.250)^2 = .526$
- $T_r = (973)/405.5 = 2.39$ and $Z = 2.0 + (10.5)(2.39)^2 = 61.97$
- $\Psi = 1 + 2.787\{[0.215 + 0.28288(2.787) - 1.061(.526) + 0.26665(61.97)]/[0.6366 + (.526)(61.97) + 1.061(2.787)(.526)]\}$

  $= 2.359$
- $$\lambda = \frac{3.75\Psi}{C_v/R} \times \frac{\eta C_v}{M'}$$
- $$\lambda = \frac{3.75(2.359)}{(35.65/8.314)} \times \frac{1.344\times10^{-5}(35.65)}{17.031 \times 10^{-3}}$$

λ = .05804 W/(m·K) or 58.04 mW/(m·K)

Thermal Conductivity at STP

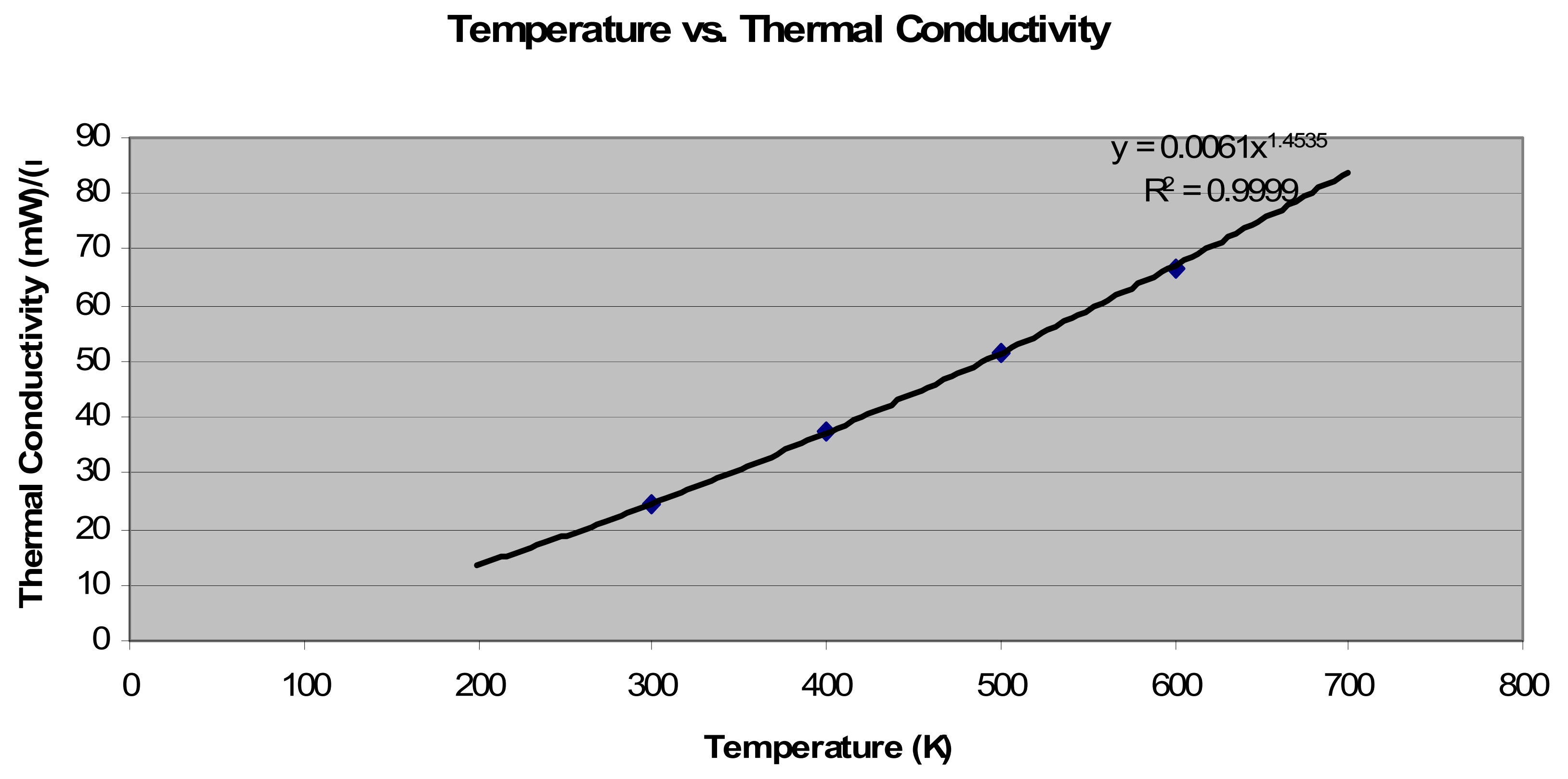
- To calculate this, several points of thermal conductivity were taken from a table and a line of best fit was fit to the graph then extrapolated to find thermal conductivity at 1 ATM and 700 degrees Celsius.

•Upon the trend line being fitted you get an equation:

•$Y=(0.006)\ x^{1.4535}$

•Solving for Y when X = 973K(700C) thermal conductivity is 118.62

Fitted and extrapolated



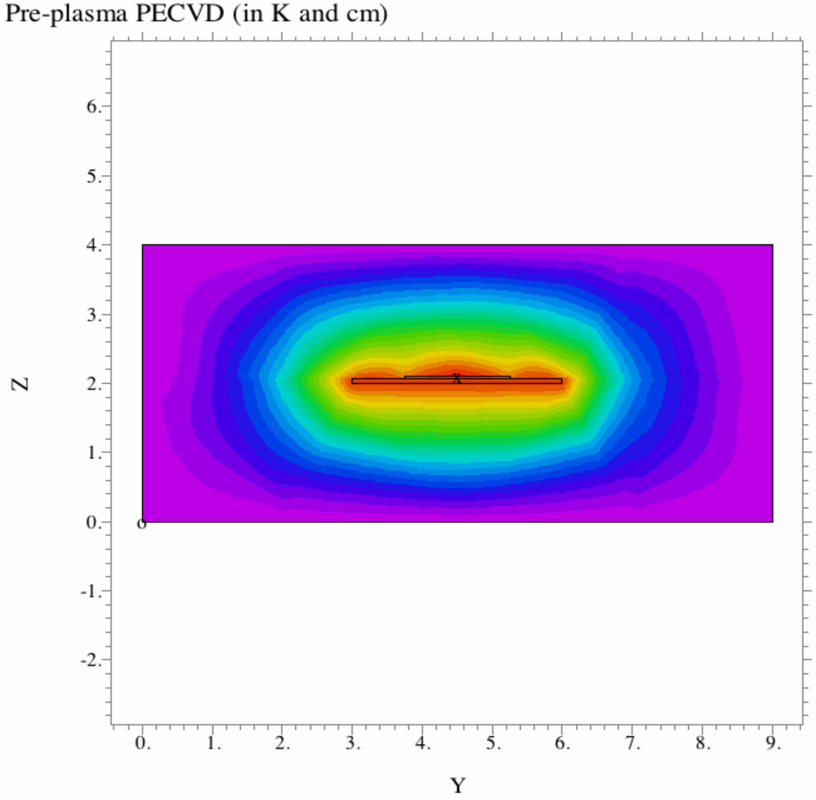
Results

- Thermal conductivity can be determined through a very rigorous process.
- There is a large difference between thermal conductivity calculated and extrapolated, which is accountable for pressure.
- Without pressure λ =118.62, with pressure being at about 4-5 mBar λ = 58.04

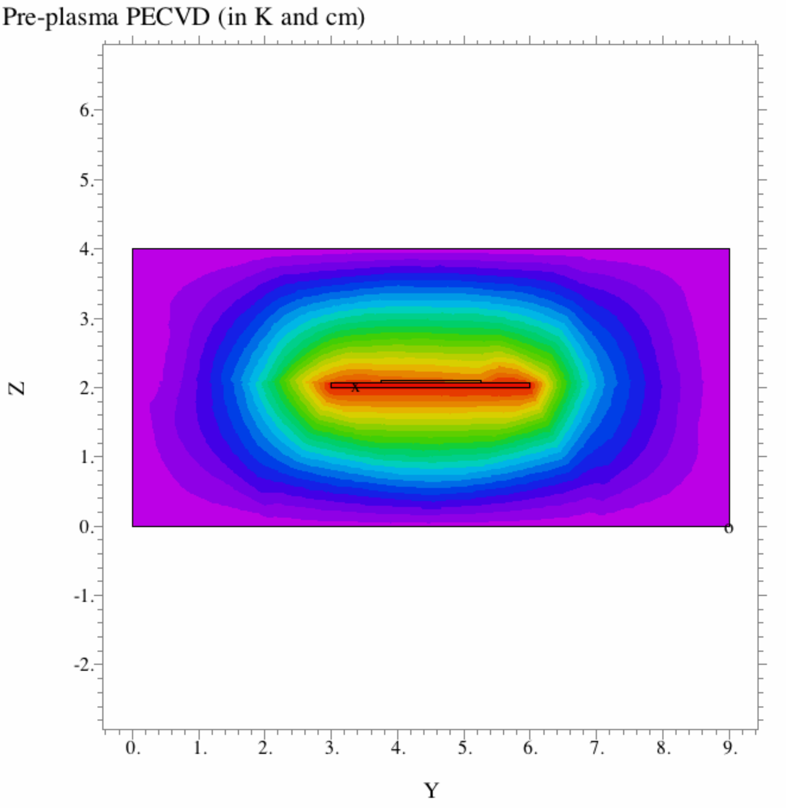
Results cont…

- Thermal conductivity falls as pressure decreases and vice versa
- As inputted in the simulation program FlexPDE, you can see that with lower thermal conductivity, as you get further from the heat source, it gets cooler.
- With a higher λ, the heat is able to transfer further while still remaining high temperatures.

FlexPDE Results



λ =118.62 (Pressure = 1ATM)



λ =58.04 (Pressure = 4-5 mBar)

Discussion

- The Results are consistent with basic theory of thermal conductivity.
- As pressure is lowered thermal conductivity is lowered due to the gas particles being more spread apart, thus being less conductive to heat.
- With the gas molecules closer heat may be transferred through each molecule but low pressure separates the ammonia in the PECVD chamber.

Significance

- The information is significant because the shower head where the gas is deposited to the heat source may have great deviations from the source temperature of 700 degrees Celsius.
- The temperature at the shower head may be as low as 400 degrees Celsius.

Further Study

- Further study to be done is for the theory and simulation to be experimentally tested to see what the temperature is at the shower head, and at the heating source.
- Also, to program in plasma so that the plasma heating can also be taken into account for the difference in temperature.

Citations

- Lide, David R. Handbook of Chemistry and Physics. 83rd ed. New York: CRC, 2002.
- Poling, Bruce E., John M. Prausnitz, and John P. O'connell. The Properties of Gases and Liquids. 4th ed. New York: McGraw-Hill, 2003.

Acknowledgements

Special thanks to Dr. Jun Jiao, Jianfeng Wu, Madeline Wyse and members of Dr. Jiao’s lab

Financial support by the National Science Foundation's Research Experience for Undergraduates Program under Award Number DMR-220926