Name/SID: ____________________

CHEMICAL ENGINEERING 179
Exam 2
Wednesday, November 5, 2014
Closed Book with 3x5 Card

$k_B = 1.381 \times 10^{-23}$ J K^{-1}; R = 8.314 J (mole K)$^{-1}$ = 1.987 cal (mole K)$^{-1}$; $N_A = 6.022 \times 10^{23}$ (mole)$^{-1}$; e = 1.602×10^{-19} C; $m_p = 1.673 \times 10^{-27}$ kg ; 1 liter = 1000 cm^3 ; STP = 273 K, 760 torr (1 atm); 1 atm = 1.013×10^5 Pa; 1 Pa = 1 J/m^3, Thiele modulus = $[k_s R_w^2/(l\ D)]^{0.5}$

Short Answer. 5 pts. each.

1. List three typically desired characteristics of a CVD process.

Uniformity, desired composition, low stress, adequate rate, few particles/defects

2. What is the primary advantage of using plasma for CVD?

Lower temperature process, better or different film properties

3. Why is low pressure sometimes used for CVD processes?

Increases diffusivity and lowers particle formation

4. Why is the polymer material used in optical lithography called 'photoresist?'

The material is photoactive and resists etching

5. How does the minimum size of a feature printed in optical lithography depend on wavelength of the exposing light?

Proportional to wavelength – shorter wavelength yields smaller feature

6. Name three techniques used to achieve smaller dimensions in optical lithography and briefly describe them.

Immersion lithography
Optical proximity correction
Double patterning
Phase shift masks
Resist trimming
Spacer etch

7. In low temperature, non-equilibrium plasma, what are typical neutral gas, positive ion and electron average energies?

Neutral gas ~ 300K
Ions ~ 300K
Electrons – 1-10 eV; 10,000-100,000K

8. How does optical emission spectroscopy work?

Light generated in the plasma due to electron-impact excitation is collected and resolved using a spectrometer; the measured spectrum gives information about the plasma properties and composition.

9. What is the difference between 'isotropic' and 'anisotropic' etching? What does this have to do with plasma?

Isotropic etch – etching is equally fast in all directions
Anisotropic etch – etching occurs in one direction only

10. True or False

T **F** In sequential rate processes, the fast step dominates the overall process rate
T F Gas phase reactions can be important in CVD
T **F** Extreme ultraviolet lithography is currently in commercial use
T F Gas plasma electrons/ions are similar to electrons/holes in semiconductors
T F Etch processes can be used to extend lithographic limitations

Problems.

(25 points)
1. An atmospheric pressure, cold wall, plug-flow CVD reactor, similar to the one considered in the homework, has a first order reaction occurring at the surface leading to the film deposition, no gas phase reactions and the reactant is dilute. The entering reactant composition is C_A^0 and gas velocity is v.

The geometry of this reactor can be considered planar: two flat plates between which the gas flows, separated by a height X, flowing a distance L down the length of the reactor. Film is deposited on both top and bottom surfaces.

The gas flow is turbulent in the bulk so the gas is well mixed between the plates and the boundary layer at each surface is very thin compared to height X.

(a) It is observed that doubling the inlet reactant concentration doubles the film deposition rate down the length of the reactor. Does this result imply that the process in controlled by diffusion through the boundary later above the surface? Why or why not?

(b) Considering both uniformity of deposition rate down the reactor length as well as reaction and diffusion through the boundary layer at any point, what ***two*** dimensionless groups govern this CVD reactor behavior? Define these dimensionless parameters, and explain how they and why they matter.

Answer.
(a) The rate of reaction at the surface in a CVD reactor like this is $r = k_s C_A/(1+(k_s \delta/D))$, where δ is boundary layer thickness, D is diffusivity, k_s is surface rate coefficient and C_A is concentration of reactant in bulk gas.

Thus, in any of the cases considered – either diffusion or reaction control or anything between, rate of deposition will be proportional to C_A, even if there is depletion along the length of the reactor and C_A is not equal to C_A^0.

(b) The two dimensionless groups are:

$k_s \delta/D$ – this determines the relative importance of 'resistance' associated with the sequential rates of diffusion through the boundary layer followed by reaction at the surface. A value much less than one means reaction rate control and a value much greater than one implies diffusion control.

$(\alpha k_s L/v)$, where $\alpha = 2/X$ (reaction area to flow volume ratio) is the argument in the exponential governing the ratio of concentration at the inlet and the exit of the reactor. It govens the depletion. A value much less than one implies little depletion, whereas a value much greater than one implies significant depletion.

(25 points)

2. Consider the model of the LPCVD reactor with multiple wafers in a tube and gas flow down the annulus. All assumptions are the ones we considered in the notes.

Consider now the case in which the last wafer at the end of the tube has an average growth rate that is about half that of the first wafer.

(a) Sketch the approximate film deposition profiles across the first and last wafer if the Thiele modulus is 2 or 20.

(b) Does the deposition rate uniformity within each wafer improve if we increase the gas flow velocity in the annulus? Why?

(c) Does the deposition rate uniformity from wafer to wafer along the length of the reactor improve if we increase the gas flow velocity in the annulus? Why?

(d) Why do LPCVD reactor designers include the possibility to change temperature down the length of the reactor?

(e) Why can't the LPCVD reactor be operated at atmospheric pressure? Consider the role of the Thiele modulus and how that is affected by gas pressure.

Answer.

(a) Thiele modulus of 2 gives flat profiles, independent of radius. So just twice the rate on first wafer compared to last wafer.

(b) No, for the first order reaction, gas velocity will not affect uniformity.

(c) Yes, higher gas velocity will improve the uniformity from wafer to wafer along the length of the reactor, since reactant depletion will be less.

(d) They do this to increase reaction rate to counteract the depletion of reactant concentration down the length of the reactor.

(e) The Thiele module would be very large since gas diffusivity is inversely proportional to pressure, so this decrease in diffusivity will result in a much larger Thiele modulus. This will cause the wafer deposition rate to occur only at the outer radial position of the wafer, giving unacceptably poor film thickness uniformity.