

**CHEMICAL ENGINEERING 179**

**Exam 1**

**Wednesday, February 27, 2013**

**Closed Book with 3x5 Card**

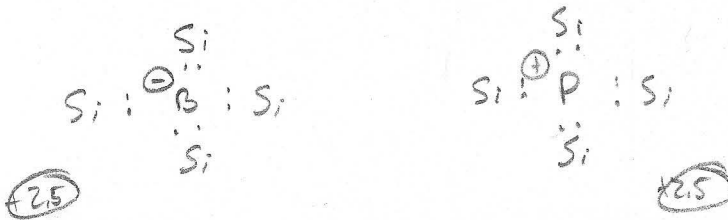
$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$ ;  $R = 8.314 \text{ J (mole K)}^{-1} = 1.987 \text{ cal (mole K)}^{-1}$ ;  $N_A = 6.022 \times 10^{23} \text{ (mole)}^{-1}$ ;  
 $e = 1.602 \times 10^{-19} \text{ C}$ ;  $m_p = 1.673 \times 10^{-27} \text{ kg}$ ; 1 liter = 1000  $\text{cm}^3$ ; STP = 273 K, 760 torr (1 atm);  
 1 atm =  $1.013 \times 10^5 \text{ Pa}$ ; 1 Pa = 1  $\text{J/m}^3$ , mass density  $\text{SiO}_2 = 2.65 \text{ g/cm}^3$ . MW  $\text{SiO}_2 = 60.08 \text{ g/mole}$

**Short Answer. 5 pts. each.**

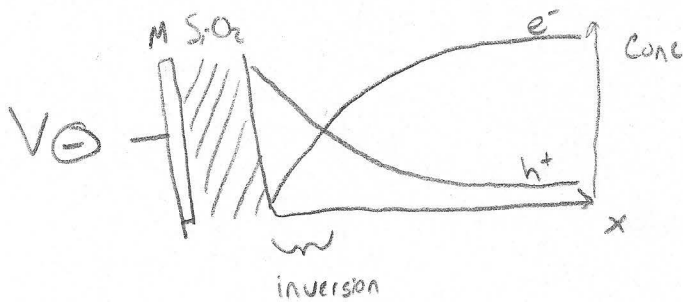
1. List 3 advantages of solid state transistors over the older vacuum tube technology.

Vacuum tubes were difficult to scale, not reliable over their lifetime, & dissipated a lot of heat

2. Show two sketches: one of boron and one of phosphorous dopants bonded to four adjacent silicon atoms, assuming the dopant is fully ionized (the extra hole of electron has left behind an ion).



3. Sketch the profile of electron and hole density for n-type silicon next to an insulator with a negatively biased electrode on the other side. Identify the region of inversion.



4. What is the problem with silicon dioxide as a gate dielectric in current device technology?

As devices shrink, need to make  $\text{SiO}_2$  thinner (+1)  
 - Necessary to continue to have gate control over channel (+1)  
 However as thickness approaches 10nm, tunneling leakage current (+1.5)  
 to the gate becomes considerable  
 Need material w/ higher  $k$  to overcome these issues (+1.5)

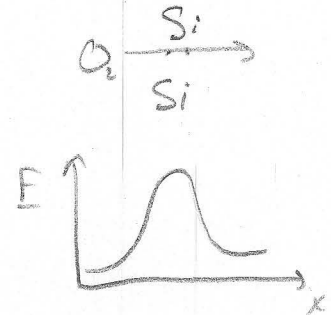
5. Describe in a few sentences how optical proximity works and why it is needed in lithography.

(+5) Changes are made to the mask around corners & edges in order to make the final exposed shape in the photoresist more akin to the shape you actually want

6. What is the typical (mathematical) dependence of solid-state diffusion coefficient in temperature and why?

(+2.5)  $D_{\text{solid}} \propto D_0 \exp\left(-\frac{E_A}{RT}\right)$

(+2.5) This is due to the activated step required to break bonds and move the diffusing atom into the solid



7. List 2 current problems with EUV lithography. (+2.5 each)

- Brightness of source is low
- Photoresist outgassing or breakdown issues
- Reflective masks & defects

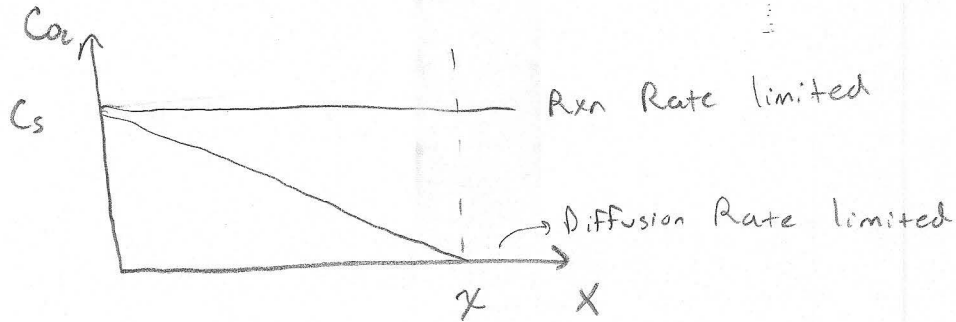
8. A reaction at an interface is first order and irreversible. In what units do we express the rate and what are the units of the rate coefficient?

(+2.5)  $\Gamma = k C_A$   
 Units:  $\left[\frac{\text{mol}}{\text{cm}^2 \text{s}}\right]$      $\left[\frac{\text{cm}}{\text{s}}\right]$      $\left[\frac{\text{mol}}{\text{cm}^3}\right]$

9. What is the key dimensionless group in silicon oxidation? Define the terms.

(+2) rxn rate coefficient  $\rightarrow \frac{k x}{D}$   $\rightarrow$  thickness of  $\text{SiO}_2$  layer (+1)  
 Diffusion Coefficient of  $\text{O}_2$  in  $\text{Si}$  (+2)

10. In silicon oxidation, sketch the oxidant spatial profiles through the film in the reaction rate limited regime and in the diffusion limited regime.



**Problems.**

1. In planar SiO<sub>2</sub> growth from O<sub>2</sub> on a Si substrate, the film thickness (x) is observed to increase with the square root of growth time. In this regime, the film growth rate is about 1 micron/hr and oxygen concentration at the near surface of the film is estimated to be 5 x 10<sup>16</sup> cm<sup>-3</sup>.

- (15) (a) Estimate the diffusivity of O<sub>2</sub> in this film.
- (15) (b) If the activation energy for growth in this regime is 1.5 eV, how much faster should the growth be if the growth temperature increases from 1200K to 1800K?
- (5) (c) If the O<sub>2</sub> concentration in the gas phase is doubled at the beginning of the experiment how should this affect the film thickness at a given time?
- (5) (d) Would the conclusion in part (c) be different if the film growth were in the reaction rate control regime? How so?
- (5) (e) If the O<sub>2</sub> gas flow rate above the growing film were doubled, thereby increasing the external mass transfer coefficient, how would this affect the growth rate?
- (5) (f) The O<sub>2</sub> concentration in the gas phase is 1 atm. What is the value of the Henry's Law coefficient under the conditions of this experiment?

a.)  $x \propto \sqrt{t}$       know that for thick film Deal's-Grove growth have regime which  $\sqrt{t}$  dependant

$\frac{dx}{dt} = 1 \frac{\text{micron}}{\text{hr}}$        $x = \sqrt{B \cdot t}$

$C_{O_2} = 5 \cdot 10^{16} \frac{\text{atoms}}{\text{cm}^3}$        $\rightarrow B = 2 D V C_s$

$V_{Si} = 60.08 \frac{\text{g}}{\text{mol}} \cdot \frac{1 \text{cm}^3}{2.65 \text{g}}$   
 $= 22.67 \frac{\text{cm}^3}{\text{mol}}$

$1 \text{ micron} = \sqrt{2 D V C_s (1 \text{ hr})}$

$(10^{-4} \text{ cm})^2 = \left( \sqrt{2 D \cdot 22.67 \frac{\text{cm}^3}{\text{mol}} \cdot 5 \cdot 10^{16} \frac{\text{atoms}}{\text{cm}^3} \cdot \frac{1 \text{ mol}}{6.02 \cdot 10^{23} \text{ atoms}} \cdot 3600 \text{ s}} \right)^2$

$10^{-8} \text{ cm}^2 = 2 \cdot 22.67 \cdot 5 \cdot 10^{16} \cdot 6.02 \cdot 10^{-23} \cdot 3600 \text{ s} \cdot D$

$D = 2.04 \cdot 10^{-8} \frac{\text{cm}^2}{\text{s}}$

b.)  $D(t) \propto \exp\left(\frac{-E_A}{kT}\right)$   $1.5 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J} \cdot 1.5 = 2.403 \cdot 10^{-19} \text{ J}$

$$\frac{D(T=1800)}{D(T=1200)} = \frac{\exp\left(\frac{-2.403 \cdot 10^{-19}}{1.381 \cdot 10^{-23} \text{ J/K} \cdot 1800 \text{ K}}\right)}{\exp\left(\frac{-2.403 \cdot 10^{-19}}{1.381 \cdot 10^{-23} \text{ J/K} \cdot 1200 \text{ K}}\right)} = 125.6$$

For same  $x$   $\sqrt{2 D_{1800} \nu C_s t_{1800}} = \sqrt{2 D_{1200} \nu C_s t_{1200}}$

$$\frac{D_{1800}}{D_{1200}} = \frac{t_{1200}}{t_{1800}}$$

1800K should be  $\sim 125.6 \times$  faster than 1200K

c.)  $x = \sqrt{D t} = \sqrt{2 D \nu C_s t}$   
 $x = \sqrt{2} \cdot \sqrt{2 D \nu C_s t}$

$C_s = 2C_s$  for any given time the thickness will be  $\sqrt{2}$  greater w/ double  $C_s$

d.) +5 pts for everyone

e.) This would not affect the growth because mass transfer to the Si surface is negligible in comparison to the diffusion in the Silicon

f.)  $C_s = H \cdot P_{O_2}$

$$5 \cdot 10^{16} \frac{\text{atoms}}{\text{cm}^2} \cdot \frac{1 \text{ mol}}{6.02 \cdot 10^{23} \text{ atoms}} = H \cdot 1 \text{ atm}$$

$8.31 \cdot 10^{-8} \frac{\text{mol}}{\text{atm} \cdot \text{cm}^3} = H$