ECE611 / CHE611: Electronic Materials Processing
Fall 2017
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Solutions to Homework 2
Due at the beginning of class Thursday October 19th

Question 1 [3 marks]:
   a) Piranha solution consists of a mixture of sulfuric acid and hydrogen peroxide. State the two main reactions that take place when these compounds are mixed. [1 marks]

These are found in Lecture 4:

\[ H_2SO_4 + H_2O_2 \rightarrow H_2SO_5 + H_2O \]
\[ H_2SO_4 + H_2O_2 \rightarrow H_3O^+ + HSO_4^- + O \]

b) Describe why elemental oxygen is important in cleaning wafers? [2 marks]

Organic (C-containing molecules) such as dust from humans are one of the biggest contaminants for wafers. Elemental oxygen is highly reactive with many organic compounds, in particular the following reactions are important for turning solid carbon-based molecules to gas or liquid:

\[ O + O + C \rightarrow CO_2 \]
\[ H + H + O \rightarrow H_2O \]

Question 2 [6 marks]:
We are using a galvanic cell to deposit copper onto a 300mm (diameter) silicon wafer, at an elevated temperature of 60°C. The anode is solid zinc, in an aqueous solution of \( SO_4^{2-} \) and \( Zn^{2+} \). The cathode is our wafer, in an aqueous solution of \( SO_4^{2-} \) and \( Cu^{2+} \).

a) We wish to establish a voltage of 1V in our cell. The concentration of zinc ions in the \( H_2O:SO_4^{2-}:Zn^{2+} \) solution is [10 M], what concentration of \( Cu^{2+} \) is required in the \( H_2O:SO_4^{2-}:Cu^{2+} \) solution required to establish this voltage? [3 marks]

This is from Lecture 5. Here we need to use the Nernst Equation to get the reaction quotient in terms of the modified cell potential:

\[ E = E^0 - \frac{RT}{nF} \ln Q \]
\[ E^0 - E = \frac{RT}{nF} \ln Q \]
\[ \frac{nF}{RT}(E^0 - E) = \ln Q \]
\[ Q = \exp \left[ \frac{nF}{RT}(E^0 - E) \right] \]

The reaction quotient, \( Q \), is the ratio of the product to the reactant:

\[ Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} \]
So we can say:

\[
\frac{[Zn^{2+}]}{[Cu^{2+}]} = \exp \left( \frac{nF}{RT} (E^0 - E) \right)
\]

Inverting:

\[
\frac{[Cu^{2+}]}{[Zn^{2+}]} = \exp \left( \frac{nF}{RT} (E - E^0) \right)
\]

So:

\[
[Cu^{2+}] = [Zn^{2+}] \exp \left( \frac{nF}{RT} (E - E^0) \right)
\]

The standard cell potential is given in the notes:

\[
E^0 = E^0_{\text{reduction}} - E^0_{\text{oxidation}}
\]

\[
E^0 = 0.342 - (-0.762) = 1.104 \text{V}
\]

We are told the target potential: \(E = 1\text{V}\), and the concentration of \(Zn^{2+}\) ions is \([Zn^{2+}] = 10\text{M}\).

The number of electrons involved in each half reaction is \(n = 2\).

We are told the temperature in C, \(T = 60\text{C}\), therefore \(T = 333 \text{ K}\).

The other values are constants.

Putting the numbers in:

\[
[Cu^{2+}] = 10 \exp \left[ \frac{2 \times 9.65 \times 10^4}{8.314 \times 333} (1 - 1.104) \right]
\]

\[
[Cu^{2+}] = 0.0071 \text{ M}
\]

b) With a voltage of 1V established in our cell, we want to control the deposition rate with a variable resistor between the electrodes in our galvanic cell. What resistance (in ohms) do we require to deposit a 100 nm thick layer of copper on our wafer over a period of 1 hour? [3 marks]

Here we need to use Ohm’s law:

\[
R = \frac{V}{I}
\]

We are told the potential is 1V, so we need to determine the current required for this deposition.

We use the equation relating current to the number of moles of atoms deposited, \(N\), as:

\[
I = \frac{nFN}{t}
\]

We can then substitute in the resistance:

\[
R = \frac{tV}{nFN}
\]
We are told $t$ and $V$, we know $n$, so we need to determine the number of moles deposited. For a mass, $m$, deposited, the number of moles deposited is:

$$N = \frac{m}{m_{Cu}}$$

Where $m_{Cu}$ is the mass of one mol of copper.

The mass we can determine from the geometry of the wafer and the thickness deposited:

We can work in g and cm, since none of our constants have length dimensions or mass. The thickness of the layer deposited is:

$L = 1 \times 10^{-5}$ cm.

The surface area of the wafer is:

$$A = \frac{\pi d^2}{4}$$

Where $d = 30$ cm.

So the volume is:

$$LA = \frac{L\pi d^2}{4}$$

With knowledge of the density of copper, $\rho = 8.96$ g/cm$^3$, we can then determine the mass deposited:

$$m = \rho LA$$

So the number of moles of copper deposited is:

$$N = \frac{\rho L\pi d^2}{4m_{Cu}}$$

We can finally substitute this back into our equation for resistance:

$$R = \frac{tV4m_{Cu}}{nFP\pi d^2}$$

Putting in the numbers:
\[ R = \frac{60 \times 60 \times 1 \times 4 \times 63.546}{2 \times 9.65 \times 10^4 \times 8.96 \times 10^{-5} \times \pi \times 30^2} \]

Giving us:

\[ R = 18.7 \, \Omega \]

**Question 3 [2 marks]:**

We are using a plasma to etch a SiO\(_2\) layer under a patterned photoresist, as shown in the figure below. The photoresist layer is 200 nm thick and the feature width is 100 nm. What is the minimum selectivity we require to achieve a feature with an aspect ratio of 10, without etching any undesired regions? Assume anisotropic etching is taking place.

This is from Lecture 6. The aspect ratio is just the ratio of the depth to width of the feature.

\[ AR = \frac{D}{W} \]

We are told the feature width is 100 nm and we are etching anisotropically, so the feature width will not change during the etch process.

So, to achieve an aspect ratio of 10 we therefore need to etch 1 \(\mu\)m of the SiO\(_2\), before the 200 nm of photoresist is completely removed.

The ratio of these thicknesses is:

\[ \frac{1 \mu m}{200 \text{ nm}} = 5 \]

This means we need to etch the SiO\(_2\) 5 times as fast as we etch the photoresist.

**I.e. the selectivity is 5.**

**Question 4 [4 marks]:**

We have a plasma chamber that has plates 10 cm apart, and we are using pure nitrogen (N\(_2\)) as our process gas. If the number of secondary electrons produced per ionization event is 0.5, use Paschen’s Law to determine the pressure at which the minimum ignition voltage occurs for this chamber, at what this voltage is.

For N\(_2\) the parameters in the Paschen Equation are as follows:

- \( B = 413 \, \text{V Pa}^{-1} \text{m}^{-1} \).
- \( A = 13 \, \text{V Pa}^{-1} \text{m}^{-1} \).

From Lecture 6, the Paschen Equation is as follows:
\[ V = \frac{Bpd}{\ln(Apd) - \ln\left[\ln\left(1 + \frac{1}{\gamma_{se}}\right)\right]} \]

We are given the secondary electron emission coefficient: \( \gamma_{se} = 0.5 \), and the distance between plates, \( d = 0.1 \text{m} \). Voltage is \( V \), pressure is \( p \), and we are given \( A \) and \( B \) in the question.

To find the minimum voltage we have to differentiate voltage with respect to pressure:

\[ \frac{dV}{dp} = 0 \]

We will use the quotient rule:

For:

\[ f(x) = \frac{g(x)}{h(x)} \]

The first derivative is:

\[ f'(x) = \frac{g'(x)h(x) - g(x)h'(x)}{[h(x)]^2} \]

Where we are using Newton’s notation for derivatives:

\[ f'(x) = \frac{df}{dx}, \quad g'(x) = \frac{dg}{dx}, \quad h'(x) = \frac{dh}{dx} \]

If \( V(p) = f(p) \), then:

\[ g(p) = Bpd \]

\[ h(p) = \ln(Apd) - \ln\left[\ln\left(1 + \frac{1}{\gamma_{se}}\right)\right] \]

We need to determine the derivatives of these functions with respect to \( p \).

Start with \( g(p) \):

\[ g'(p) = \frac{dg}{dp} = Bd \]

Now we need to differentiate, \( h(p) \), which is a little harder.

Since \( \gamma_{se} \) is a constant, we will just define the following variable for now:

\[ \alpha = \ln\left[\ln\left(1 + \frac{1}{\gamma_{se}}\right)\right] \]

So we can just say:

\[ h(p) = \ln(Apd) - \alpha \]

Now take the derivative:
Now substitute \( g(p) \), \( g'(p) \), \( h(p) \), and \( h'(p) \) into the quotient rule formula:

\[
\frac{dV}{dp} = \frac{Bd[\ln(Apd) - \alpha] - Bd}{[\ln(Apd) - \alpha]^2}
\]

\[
\frac{dV}{dp} = \frac{Bd[\ln(Apd) - \alpha - 1]}{[\ln(Apd) - \alpha]^2}
\]

We could multiply out the denominator, but since we are only interested in the minimum we can just set:

\[
\frac{dV}{dp} = \frac{Bd[\ln(Apd) - \alpha - 1]}{[\ln(Apd) - \alpha]^2} = 0
\]

And just multiply both sides by the denominator:

\[
Bd[\ln(Apd) - \alpha - 1] = 0
\]

Divide both sides by \( Bd \):

\[
\ln(Apd) - \alpha - 1 = 0
\]

\[
\ln(Apd) = \alpha + 1
\]

Take exponentials:

\[
Apd = e^{\alpha+1}
\]

\[
Apd = e^{\alpha}e^1
\]

Recall from earlier we defined:

\[
\alpha = \ln \left[ \ln \left( 1 + \frac{1}{\gamma_{se}} \right) \right]
\]

So now we can put this back in:

\[
e^{\alpha} = \ln \left( 1 + \frac{1}{\gamma_{se}} \right)
\]

\[
Apd = e^1 \ln \left( 1 + \frac{1}{\gamma_{se}} \right)
\]

\[
p = \frac{e^1}{Ad} \ln \left( 1 + \frac{1}{\gamma_{se}} \right)
\]

So this is the pressure at the minimum ignition voltages, as a function of \( d \), \( A \), and \( \gamma_{se} \). Note this is not a function of \( B \)

Putting numbers in:

\[
p = \frac{2.718}{13 \times 0.1} \ln \left( 1 + \frac{1}{0.5} \right)
\]

\[
p = 2.297 \text{ Pa}
\]
To get the voltage, we then just enter this pressure, along with all the other variables, into the Paschen Equation:

\[
V = \frac{Bpd}{\ln(Adp) - \ln\left[\ln\left(1 + \frac{1}{\gamma_se}\right)\right]}
\]

\[
V = \frac{413 \times 2.297 \times 0.1}{\ln(13 \times 2.297 \times 0.1) - \ln\left[\ln\left(1 + \frac{1}{0.5}\right)\right]}
\]

Giving us:

\[
V = 94.874V
\]

You can check this by plotting the function if you want:

**Question 5 [4 marks]:**
The table below shows some published values of the growth parameters of SiO₂ on silicon. For the dry growth process, the parameter \( \tau \) is already evaluated.

![Table 4.1: Oxidation coefficients for silicon](image)
a) At a temperature of 1100°C, what starting oxide thickness does this data for the dry oxide growth assume? [2 marks]

This is from Lecture 7.

Here we are given $\tau$ for dry oxide growth, as well as $A$ and $B$. So we can just use our equation for $\tau$:

$$\tau = \frac{(x_0^2 + Ax_0)}{B}$$

We need to solve this for $x_0$:

$$B\tau = x_0^2 + Ax_0$$

Writing this in standard quadratic form:

$$x_0^2 + Ax_0 - B\tau = 0$$

We can then use the quadratic equation:

$$x_0 = \frac{-A \pm \sqrt{A^2 + 4B\tau}}{2}$$

Now we just enter values from the table:

$$x_0 = \frac{-A \pm \sqrt{A^2 + 4B\tau}}{2}$$

(Alternatively, you could have just used the equation from the lectures and said $x_0 = x_{ox}$ when $t=0$).

For the dry oxide growth at 1100°C, we can see these values are:

$A = 0.090 \mu m$.

$B = 0.027 \mu m^2/hr$.

$\tau = 0.076 \text{ hr.}$

$$x_0 = \frac{-0.090 \pm \sqrt{0.090^2 + 4 \times 0.027 \times 0.076}}{2}$$

$$x_0 = \frac{-0.090 \pm \sqrt{0.0163}}{2}$$

$$x_0 = \frac{-0.090 \pm 0.128}{2}$$

Since (-0.09-0.128) is negative, only the positive root is physically meaningful:

$$x_0 = \frac{-0.090 + 0.128}{2}$$

$$x_0 = \frac{0.0377}{2}$$

$$x_0 = 0.0189 \mu m$$

b) Using the parameters in the above table, determine total thickness if a dry oxidation was carried out for 5 hours at 1100°C. [2 marks]
This is a simple exercise of putting the numbers into the equation:

\[ x_{ox} = \frac{-A \pm \sqrt{A^2 + 4B(t + \tau)}}{2} \]

\[ x_{ox} = \frac{-0.09 + \sqrt{0.09^2 + 4 \times 0.027 \times (5 + 0.076)}}{2} \]

Giving:

\[ x_{ox} = 0.330 \mu m \]

**Question 6 [5 marks]:**
The rate constants associated with silicon growth are often described with an Arrhenius relationship:

\[ B = C_1e^{-E_1/k_BT} \]
\[ \frac{B}{A} = C_2e^{-E_2/k_BT} \]

Some example parameters for these relationships are given in the below table.

<table>
<thead>
<tr>
<th></th>
<th>(111) Silicon</th>
<th>(100) Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Dry O₂</strong></td>
<td>( C_1 = 7.72 \times 10^2 \mu m^2/h )</td>
<td>( C_2 = 3.71 \times 10^6 \mu m/h )</td>
</tr>
<tr>
<td></td>
<td>( C_2 = 6.23 \times 10^6 \mu m/h )</td>
<td>All other parameters same as for (111) silicon</td>
</tr>
<tr>
<td><strong>( E_1 )</strong></td>
<td>1.23 eV</td>
<td></td>
</tr>
<tr>
<td><strong>( E_2 )</strong></td>
<td>2.0 eV</td>
<td></td>
</tr>
<tr>
<td><strong>H₂O (640 torr)</strong></td>
<td>( C_1 = 3.86 \times 10^2 \mu m^2/h )</td>
<td>( C_2 = 0.97 \times 10^3 \mu m/h )</td>
</tr>
<tr>
<td></td>
<td>( C_2 = 1.63 \times 10^8 \mu m/h )</td>
<td>All other parameters same as for (111) silicon</td>
</tr>
<tr>
<td><strong>( E_1 )</strong></td>
<td>0.78 eV</td>
<td></td>
</tr>
<tr>
<td><strong>( E_2 )</strong></td>
<td>2.05 eV</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) See reference 9.

a) Using the parameters in the above table, determine the time required to grow a 100nm total thickness layer of SiO₂ on a Si (111) surface which already has a 5nm native oxide, using a dry reactor at 1200°C. [2 marks]

Again, here we are basically just re-arranging and putting numbers into the equations. For Si (111) growth in a dry reactor, the parameters are:
$C_1 = 7.72 \times 10^2 \, \mu m^2/hr$

$C_2 = 6.23 \times 10^6 \, \mu m/hr$

$E_1 = 1.23 \, eV$

$E_2 = 2.0 \, eV.$

First evaluate $B$:

$$B = C_1 e^{-\frac{E_1}{k_B T}}$$

$$B = 7.72 \times 10^2 \times \exp\left( -\frac{1.23 \times 1.602 \times 10^{-19}}{1.38 \times 10^{-23} \times (1200 + 273)} \right)$$

(Remembering to convert to Joules and Kelvin)

This gives you:

$$B = 4.76 \times 10^{-2} \, \mu m^2/hr$$

Now evaluate $B/A$:

$$\frac{B}{A} = C_2 e^{-\frac{E_2}{k_B T}}$$

$$\frac{B}{A} = 6.23 \times 10^6 \times \exp\left( -\frac{2.0 \times 1.602 \times 10^{-19}}{1.38 \times 10^{-23} \times (1200 + 273)} \right)$$

Giving:

$$\frac{B}{A} = 8.90 \times 10^{-1} \, \mu m/hr$$

To get $A$, just divide $B$ by $B/A$:

$$B / \left( \frac{B}{A} \right) = A = \frac{4.76 \times 10^{-2}}{8.90 \times 10^{-1}} = 0.0535 \, \mu m$$

Now we need to evaluate $\tau$:

$$\tau = \frac{x_0^2 + Ax_0}{B}$$

We have just worked out $A$ and $B$, and $x_0$ is given in the question as: 0.005 $\mu m$.

Put in the numbers:

$$\tau = \frac{(0.005^2 + 0.0535 \times 0.005)}{4.76 \times 10^{-2}}$$

Giving:

$$\tau = 0.069 \, hr$$

We can then take our quadratic equation from the notes:

$$x_{ox}^2 + x_{ox} A = B(t + \tau)$$
Re-arrange in terms of $t$:

$$t = \frac{x_{ox}^2 + x_{ox}A}{B} - \tau$$

Finally, put in the numbers:

$$t = \frac{0.1 \times 0.1 + 0.1 \times 0.139}{1.04 \times 10^{-2}} - 0.069$$

$t = 0.316$ hr

b) If growing a wet oxide on a (100) silicon surface, again use the values in this table to determine the temperature you would need to hold your reactor at, for growth to transition from linear to parabolic when the total oxide thickness is 100nm.[3 marks]

We know the transition from linear to parabolic growth occurs at:

$$x_{ox} = A$$

We need to now get an expression for $A$ in terms of $T$. From before we have:

$$B = C_1 e^{-E_1/ k_B T}$$

$$\frac{B}{A} = C_2 e^{-E_2/ k_B T}$$

So:

$$A = B \left( \frac{B}{A} \right) = \frac{C_1 e^{-E_1/ k_B T}}{C_2 e^{-E_2/ k_B T}}$$

So:

$$A = \frac{C_1}{C_2} e^{E_2 - E_1/ k_B T} = \frac{C_1}{C_2} \exp \left[ -\left( \frac{E_1 - E_2}{k_B T} \right) \right] = \frac{C_1}{C_2} \exp \left[ \frac{E_2}{k_B T} \right]$$

We are looking for the situation when $x_{ox} = A$, so:

$$x_{ox} = \frac{C_1}{C_2} \exp \left[ -\left( \frac{E_1 - E_2}{k_B T} \right) \right]$$

$$\frac{x_{ox} C_2}{C_1} = \exp \left[ -\left( \frac{E_1 - E_2}{k_B T} \right) \right]$$

Take logs:

$$\frac{-(E_1 - E_2)}{k_B T} = \ln \left( \frac{x_{ox} C_2}{C_1} \right)$$

$$\frac{(E_2 - E_1)}{k_B T} = \ln \left( \frac{x_{ox} C_2}{C_1} \right)$$
\[ k_BT = \frac{(E_2 - E_1)}{\ln \left( \frac{x_{ox} C_2}{C_1} \right)} \]
\[ T = \frac{(E_2 - E_1)}{k_B \ln \left( \frac{x_{ox} C_2}{C_1} \right)} \]

For the wet oxidation on (100) silicon, the values are:

- \( C_1 = 3.86 \times 10^2 \text{ \mu m}^2/\text{hr} \)
- \( C_2 = 0.97 \times 10^8 \text{ \mu m/ hr} \)
- \( E_1 = 0.78 \text{ eV} \)
- \( E_2 = 2.05 \text{ eV} \)

Entering the values:

\[ T = \frac{(2.05 - 0.78) \times 1.602 \times 10^{-19}}{1.38 \times 10^{-23} \times \ln \left( \frac{0.1 \times 0.97 \times 10^8}{3.86 \times 10^2} \right)} \]

\[ T = 1455K = 1182^\circ C \]