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Fall 2005

Homework # 2 : Solutions

① [Campbell 4.1] - 1000Å gate oxide required. Decided that oxidation will be @ 1000°C in dry oxygen. If there is no initial oxide, how long will it take? What regime?

From Table 4.1, we have @ 1000°C :

$A = 0.165\ \mu m$, $B = 0.0117\ \mu m^2/hr$, $\tau = 0.37$ (dry oxidation)

$1000\ \text{Å} = 0.1\ \mu m$, using Equation 4.11 :

$$t_{ox}^2 + A t_{ox} = B(t+\tau) \Rightarrow (0.1)^2 + 0.165(0.1) = 0.0117(t+0.37)$$

$$\boxed{\therefore\ t = 1.895 \text{ hours}}$$

⇒ since tox is close to the value of A, we would expect that we are neither in the linear nor the parabolic regime. tox >> A indicates parabolic and tox << A indicates the linear regime.

- As a check, we can calculate the oxide thickness using the approximations for the linear and parabolic regimes and compare it to our target thickness.

Linear : $t_{ox} \sim \frac{B}{A}(t+\tau) = .161\ \mu m$

Parabolic : $t_{ox}^2 \sim B(t+\tau) = .163\ \mu m$

⇒ Both estimates are relatively close to the desired thickness so neither regime dominates.

② [Campbell 4.2] - Repeat Problem 4.1 for wet O_2 ambient

From Table 4.1, we have @ 1000°C :

$A = 0.226\ \mu m$, $B = 0.287\ \mu m^2/hr$, $\tau = 0$ (wet oxidation)

$(.1)^2 + 0.226(.1) = 0.287(t + 0)$ $\boxed{\therefore\ t = .1136 \text{ hours}}$

Since $t_{ox} < A$, the oxidation is <u>more linear</u> than parabolic. As a check, the linear approximation gives $t_{ox} \sim .144\ \mu m$ while the parabolic approx. yields $t_{ox} \sim .180\ \mu m$.

③ [Campbell 4.3] - Decide to grow oxide in 4.1 in two steps. 500 Å oxide grown, then reoxidized to 1000 Å. carried out in 1000°C, dry O_2. Calculate time for each of the oxidations

Using what we know from Problem 4.1, we have:

$(0.05)^2 + 0.165(0.05) = 0.0117(t + 0.37) \Rightarrow t = .549$

We know it takes 1.895 hours to grow 1000 Å oxide under the same conditions.

∴ first oxidation = .549 hours
second oxidation = 1.346 hours

⇒ Note that we CAN'T do the simple subtraction if the growth conditions were different for each step. If the conditions were different, we would need the following equations:

$$t_{ox,f}^2 + A t_{ox,f} = B(t + \tau_0) \ ; \ \tau_0 = \frac{t_{ox,i}^2 + A t_{ox,i}}{B}$$

$t_{ox,f}$ = final oxide thickness ; $t_{ox,i}$ = initial oxide thickness
A and B are parameters of the growth process and τ_0 is from Equations 4.12 of Campbell.

④ [Campbell 4.4] - Necessary to grow 1 um field oxide. Due to concerns with dopant diffusion and stacking fault formation, oxidation at 1050°C. Process to be in wet ambient at atmospheric pressure. Calculate oxidation time. Assume parabolic constant proportional to oxidation pressure. Calculate oxidation time at 5 atm and 20 atm

Assuming that there is no initial oxide, and that we have a (100) wafer; from Figure 4.5, we have:

$B/A \sim 1.3$ um/hr and $B \sim 0.4$ um²/hr $\Rightarrow A \sim .3077$ um

for Pyrogenic Steam (wet oxidation) @ 1050°C and 1atm.

$$\Rightarrow (1)^2 + (.3077)(1) = 0.4(t + \cancelto{0}{\tau})$$

$\tau = 0$ for wet oxidation (as seen from Table 4.1)

$$\boxed{\therefore\ t = 3,27 \text{ hours}}$$

Looking at Equations 4.12, we have $A = 2D\left(\frac{1}{ks} + \frac{1}{hg}\right)$ and $B = \frac{2DHP_g}{N_1}$; so $A \rightarrow$ independent of P, $B \propto P$.

$$\boxed{\begin{array}{ll} B_{5atm} \sim 2.0 \text{ um}^2/\text{hr} & \Rightarrow t = .654 \text{ hours} \\ B_{20atm} \sim 8.0 \text{ um}^2/\text{hr} & \Rightarrow t = .1635 \text{ hours} \end{array}}$$

Note that we couldn't extract the values for A and B @ 1050°C from Table 4.1 for two reasons:

first - the data is for 640 torr and 1atm = 760 torr.

second - we can't extrapolate values for A and B reliably since the A and B values do not follow a linear dependence on T, ⑤ [Campbell 4.6] - assume negatively charged O_2^- has twice the diffusion in SiO_2 as neutral O_2, but 10 times the reactivity at the surface, with same activation energy for the reaction rate coefficient. Repeat 4.1 @ 1atm of O_2^-.

From Equations 4.12, we have:

$$A = 2D\left(\frac{1}{k_s} + \frac{1}{h_g}\right) \quad ; \quad B = \frac{2DHP_g}{N_1}$$

D = Diffusivity in SiO_2
k_s = chemical rate constant
h_g = mass transport coeff.
H = Henry's gas constant
P_g = gas pressure
N_1 = $2.2 \times 10^{22}\ cm^{-3}$

$$\therefore D' = 2D \quad ; \quad k_s' = 10k_s$$

⇒ At atmospheric pressure, $k_s \ll h_g$ (independent of mass transport)

⇒ we can assume that $k_s' \ll h_g$, so we have:

$$A' = 2D'\left(\frac{1}{k_s'} + \cancel{\frac{1}{h_g}}^{\,0}\right) \sim \frac{2D'}{k_s'} = \frac{2}{10}A$$

$$B' = 2D'\frac{HP_g}{N_1} = 2B$$

@ 1000°C, dry oxidation:

$A = 0.165\,\mu m$
$B = 0.0117\,\mu m^2/hr$
$\tau = 0.37$

⇒ Assuming τ is unaffected with an O_2^- ambient:

$$(0.1)^2 + \frac{2}{10}(0.165)(0.1) = 2(0.0117)(t + 0.37)$$

$$\boxed{\therefore t = .1984 \text{ hours}}$$

* Since the initial oxidation of Si is not well known, any valid assumption that is used to estimate τ is correct. Since the growth rate has increased significantly (similar to wet oxidation), one can argue that $\tau = 0$. $\therefore t' = .5684$ hours

⑥ [Campbell 4.8] - One solution to grow thin oxide is to use a dilute mixture of oxygen and an inert species such as argon. Assume 10% O_2 and 90% Ar. If we ignore the rapid oxidation regime associated with thin oxides, assume that the parabolic coefficient is proportional to pressure of oxidant, calculate growth time of 100 Å at 1000°C. Assume no initial oxide.

Since $PV = nRT \Rightarrow PV = (n_{O_2} + n_{Ar})RT$

$$P = P_{O_2} + P_{Ar} = \frac{n_{O_2}}{V}RT + \frac{n_{Ar}}{V}RT = C_{O_2}RT + C_{Ar}RT$$

C = concentration of gas species in ambient

$\therefore$ Partial pressure of oxidant is $\frac{1}{10}$ atm

$\Rightarrow$ From what we know from earlier problems:

$$B' = \frac{1}{10}B \quad \text{and} \quad A' = A$$

$$\Rightarrow (0.01)^2 + 0.165\,(0.01) = \frac{1}{10}(0.0117)(t + \cancelto{0}{\tau})$$

from given assumptions

$$\boxed{\therefore \quad t = 1.496 \text{ hours.}}$$

Note that the parameters chosen correspond to values for dry oxidation at 1000°C. Clearly we wish to use dry oxidation to grow such a thin layer of oxide.

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HW#2 – Addendum

From grading the homework, I noticed that many of you seemed to have a problem with understanding the τ in the Deal-Grove model. It is somewhat confusing so I hope this note will provide clarity on how to use equation 4.11 of Campbell.

$$x_{ox,f}^2 + Ax_{ox,f} = B(t+\tau) \qquad \text{Eq.1}$$

The subscript *f* denotes FINAL and *x* corresponds to oxide thickness to avoid confusion with times.

In the event of $x_{ox,i} = 0$, no initial oxide, τ takes on the value of zero for wet oxidation and the values given in Table 4.1 for dry oxidation. For the special case of no initial oxide, τ is used as a correction factor to take into account the fast initial oxidation of the silicon wafer for thin oxide growths. Notice in thick oxide layers formed by dry oxidation, this correction factor will introduce a negligible effect on the growth time calculation. This correction factor is not needed for wet oxidation since wet oxidation is much faster than dry oxidation, making the correction factor insignificant. It is important to keep in mind that the fast initial oxidation regime in dry oxidation is not well understood so there is no real correct way to calculate τ. The values provided in the text are empirical values.

In the event of $x_{ox,i} \neq 0$, then τ is representative of the theoretical time it would have taken to grow the initial oxide utilizing the new process, independent of what the previous oxide growth method was. In this case, τ is given by:

$$\tau = \frac{x_{ox,i}^2 + Ax_{ox,i}}{B} \qquad \text{Eq.2}$$

If we wanted to calculate the **EXACT** time it would have taken to grow the initial oxide from a bare wafer using the new process, then the correct equation should be:

$$\tau' = \frac{x_{ox,i}^2 + Ax_{ox,i}}{B} - \tau_{book} \qquad \text{Eq.3}$$

Where τ' is used to avoid confusion and τ_{book} corresponds to the values given in Table 4.1 of Campbell (keeping in mind that $\tau_{book} = 0$ for wet oxidation). To find the time *t* needed to grow the oxide to the final thickness $x_{ox,f}$, we need to solve the following equation:

$$x_{ox,f}^2 + Ax_{ox,f} = B((t+\tau') + \tau_{book}) \qquad \text{Eq.4}$$

This simplifies to Eq.1 shown above with τ given by Eq.2 above. I hope this helps.

Additionally, I have seen many different approaches to answering question 4.4 of Campbell and I just wanted to make a few notes.

Linearly interpolating the data provide in Table 4.1 is an incorrect approach for two reasons. The first being that the values in the table correspond to a wet process conducted at 640torr when we are looking for constants at 1atm = 760torr. More importantly, the linear and parabolic coefficients have an Arrhenius dependence so a linear interpolation without considering this dependence is wrong. In the event that A and B have been interpolated factoring in the Arrhenius dependence, only B is a function of pressure so there is no correct way to find a correct value for A at 1atm.

The easiest way to answer this question was to extract values from the charts provided in the text, assume that A is unchanged, and applying the knowledge that B scales with pressure. Another simplification to notice is that 1um of oxide is quite thick and you can be quite certain that the growth is in the parabolic regime, eliminating the need to determine a value for A.

I noticed that many of you had used Figure 4.2 and Figure 4.3 to pick values for B and B/A. This isn't a problem but I just wanted to comment on the accuracy of these charts. Figure's 4.2 and 4.3 were constructed after the formulation of the Deal-Grove model and correspond to values in Table 4.1. Back in the days, wet oxidation was done by running a bubbler through water which then feeds the vapor into the tube furnace. Recent wet oxidation processes are called pyrogenic steam oxidation, where the water vapor is created from the combustion of hydrogen and oxidation within the tube furnace. Figure 4.5 has the "most accurate" information and was used in my solutions for Problem 4.4. You will notice variations in the values for B and B/A between the two wet oxidation charts -- the differences stemming from the different steam formation methods.