

Solution PROBLEM 400-3 (Oxidation , wet and dry, easy-difficult)

- a) Express short and precisely what *is* “dry oxidation” and what *is* “wet oxidation” in the context of the physics and chemistry of Si device processing.

dry: O_2 is the oxidizing agent, there is no H_2O influencing the process

wet: H_2O is the oxidizing agent

Notice Fig 4.2 gives two experimental curves for the parabolic rate constant B , and similarly Fig 4.3 gives two curves for the linear rate constant B/A . The two curves are to be taken for dry oxidation and wet oxidation respectively. Note that the data for wet oxidation is given for “640 torr”

- b) Express short and precisely what this 640 torr may refer to. If you don’t know how wet oxidation is done, try to imagine how it could have been done. At what temperature is the equilibrium pressure above water equal to 640 torr? (Hint: Units torr and $^{\circ}C$: $T=1668.21/(7.96681-\log_{10}(P))-228.0$);

640 torr is the partial pressure of H_2O . Water vapor is often made by heating pure water (and bubbling O_2 through it). The temperature is just below boiling. Calculation by the given formulae gives $95^{\circ}C$.

- c) Mention some reasons that could give a parabolic rate constant that is higher for wet oxidation than for dry.

The problem asks for what could be the reason, not what is.

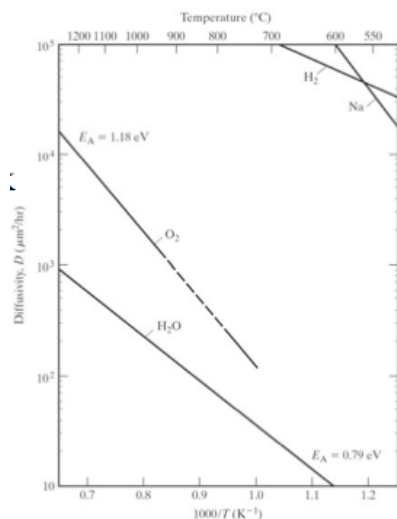
The parabolic rate constant, B , depends upon the following parameters in the Deal Grove model

$$B = \frac{2DHp_g}{N_1} = \frac{2DC^*}{N_1} \text{ where } D \text{ is diffusivity and } C^* \text{ equilibrium}$$

concentration. The only suspects are thus D and C^* .

No discussion was solicited, but we give some comments below.

- 1) Diffusivity being higher. i.e. $D_{H_2O} > D_{O_2}$: The book says this is a reason. Some independent measurements show the opposite, see fig below.



Sometimes it is argued that the diffusivity is different because the structure are somewhat different for wet and dry oxidation. It is usually stated that wet oxidation has a lower density than dry. Wet has a correspondingly lower dielectric constant. This sort of 'fit' the thought that diffusion is easier in wet oxide, but we are also comparing quite different molecules H_2O vs O_2 . Even the idea that dry oxide is much denser and of higher quality than wet oxide can be challenged and needs more precision/clarification. It seems not to apply for the thin oxide initially grown. The dry oxide then has more micro pores than the wet oxide. This also ties in with that dry oxidation has a large 'anomalous' fast initial growth rate not following Deal Grow, whereas this is not the case for wet oxide. These seem to be some of the reasons why Rapid Wet Thermal Oxidation has gained some popularity in later years.

2) Equilibrium concentration being higher: $C^*_{H_2O} > C^*_{O_2}$ This would be tied to the Henry laws constant $H_{H_2O} > H_{O_2}$. Certainly here we might have a difference for different structure/openness, but also a difference for different molecules. The Henry law constant is tied to the distribution coefficient for the interface, the equilibrium concentration C^* may sometimes be called solubility, but we should keep in mind that it is gas molecules in the solid, they really don't enter into the network, they occupy the more open structures in the network, it is not necessarily equivalent to foreign atoms entering into the lattice on substitutional positions, more like foreign atoms being segregated into grain boundaries. So I prefer to call it equilibrium concentration rather than solubility. The equilibrium concentration of H_2O is very much larger than that of O_2 in silica.. i.e. $C^*_{H_2O} \gg C^*_{O_2}$

- d) Mention some reasons that could give a linear rate constant that is higher for wet oxidation. Discuss the detail that the activation energy is nearly identical for the two oxidation processes.

Higher linear rate : Higher equilibrium concentration. Or the reaction rate could be faster. Same activation energy: can be due to similar (or the same) excitation process required for the chemical reaction e.g, associated with Si-Si bond breaking

- e) In Example 4.1 is made calculation 'steam oxidation'. Will this be faster or slower than wet oxidation?
There is no well defined difference between wet and steam, so we say they are the same