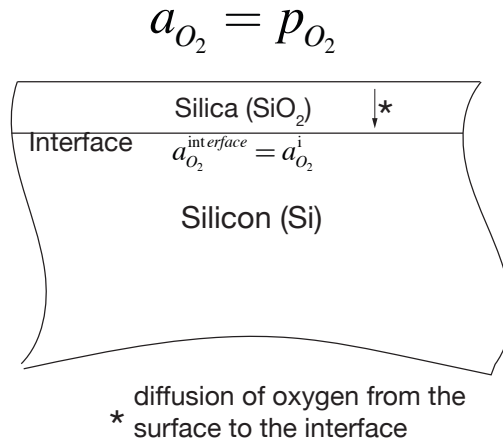


3D: Oxidation of Silicon

The Reaction Equation

We consider, qualitatively for the present, the process for the oxidation of Si at a high temperature placed within a certain oxygen pressure in the environment.



The oxidation process is the diffusion of oxygen from the surface through the thickness of the silica layer that has formed as a result of oxidation, to the interface. The driving force for diffusion is the difference in the activity of oxygen at the surface and at the interface. It is given by the following equation

$$\frac{d\mu_{O_2}}{dz} = \frac{\mu_{O_2}^{surface} - \mu_{O_2}^{interface}}{h}, \text{ where } h \text{ is the thickness of the oxide film.}$$

We may now use the diffusion equation such as the one we used in sintering to solve the “kinetics problem”

$$J_{O_2} = \frac{D_V}{\Omega_{O_2} RT} \frac{d\mu_{O_2}}{dz} \quad (1)$$

(Note that we were using k_B in the above equation before. Remember that $R = k_B N_A$; therefore to balance the units, μ_{O_2} must be expressed in J/mol, not J/atom.)

The question remains, how do we describe the activity of oxygen at the interface. We do that by asserting that at the interface the following equation exists at equilibrium



Since the activities of Si and SiO_2 are both equal to unity (they are in their pure state), we can use this equation which was derived earlier

$$\Delta G_o(T) + RT \ln \frac{a_{SiO_2}}{a_{Si} a_{O_2}^i} = 0$$

to calculate the activity of oxygen at the interface. The equilibrium partial pressure at the interface is also given by $p_{O_2}^i = a_{O_2}^i$. So the chemical potential gradient, the only unknown in the flux equation above is given by

$$\frac{d\mu_{O_2}}{dz} = \frac{RT \ln \left(\frac{P_{O_2}^{outside}}{P_{O_2}^i} \right)}{h} \quad (2)$$

With the above equations we can now calculate the growth rate of the oxidation layer at a function of temperature and as a function of the oxygen pressure in the environment. Here “h” is the thickness of the silica overgrowth.

Let us discuss the terms in Eq. (2):

- $P_{O_2}^{outside}$ is defined by the experimental conditions
- $P_{O_2}^i$ is the oxygen activity at the silica/Si interface which is isolated from the environment by the silica overgrowth. It is a good assumption to say that the oxygen activity at the interface is defined by the following reaction being in equilibrium
 $Si + O_2 = SiO_2$, which we have considered before. Therefore $P_{O_2}^i$ can be determined from the Ellingham diagram
- $h(t)$ is the thickness of the silica overgrowth which is increasing with time.

The Parabolic Rate Constant

Let us combine equations (1) and (2):

$$J_{O_2} = \frac{D_v}{\Omega_{O_2} RT} \frac{d\mu_{O_2}}{dz} \quad (1)$$

$$\frac{d\mu_{O_2}}{dz} = \frac{RT \ln \left(\frac{P_{O_2}^{outside}}{P_{O_2}^i} \right)}{h} \quad (2)$$

Combining above two equations we have that

$$J_{O_2} = \left[\frac{D_v}{\Omega_{O_2} RT} RT \ln \left(\frac{P_{O_2}^{outside}}{P_{O_2}^i} \right) \right] \frac{1}{h} \quad (3)$$

The rate of growth of the silica thickness is related to the flux of oxygen to the interface which is given by the above equation

$$\frac{dh}{dt} = (\text{flux of oxygen molecules per unit area} = \text{generation of silica molecules}) * \text{volume of Silica} \quad (4)$$

Note the balance of units on both sides of the above equation.

Combine (3) and (4)

$$\frac{dh}{dt} = \left[\frac{\Omega_{SiO_2}}{\Omega_{O_2}} D_v \ln \left(\frac{P_{O_2}^{outside}}{P_{O_2}^i} \right) \right] \frac{1}{h} \quad (4)$$

Please check the units in Eq. (4).

The terms within the brackets are only a function of temperature and oxygen activity in the atmosphere.

We write

$$k_p = \left[\frac{\Omega_{SiO_2}}{\Omega_{O_2}} D_V \ln \left(\frac{p_{O_2}^{outside}}{p_{O_2}^i} \right) \right] \quad (5)$$

We may now integrate Eq. (4)

$$\int_0^h h dh = k_p \int_0^t dt \quad (6)$$

Sometimes the factor of two on the right hand side is absorbed into k_p by writing $2k_p \rightarrow k_p$. So

$$\text{that } h^2 = 2k_p t \quad (7)$$

Note the parabolic nature of Eq. (7). Therefore k_p is called the parabolic rate constant. It is usually obtained experimentally by plotting h^2 vs t . The slope gives the rate constant.

Application

Oxidation of silicon

Refer to the attached paper. Read the first part of this paper which deals with the oxidation of silicon.

