My longtime client and friend Minoru Tomozawa has graciously allowed us to use an early paper of his for an NNS backup project. I am supposed to specify to you, however, that he is a much better writer now than he was then.

It was published in the *Journal of The Electrochemical Society.*

— Dr. Angela Eaton
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Water diffusion in silica glass and wet oxidation of Si

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Abstract

The r~~R~~elation between water diffusion in silica glass and the oxidation kinetics of silicon was considered. This report~~It is~~ suggests~~ed~~ that the diffusion of molecular water, which can diffuse faster than~~-~~ oxygen and is not observed in the normal water diffusion study in silica glass, is responsible for the faster oxidation of silicon in wet oxidation than in dry oxygen oxidation.

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~~I.~~ Introduction

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The oxidation of silicon has been one of the important steps in microelectronics processes and has been extensively investigated. The rate-controlling process of the oxidation of Si is, except in the initial transient stage, the diffusion of an oxidant through the oxidized, amorphous silica, ~~with~~ where the oxide thickness increases~~ing~~ with the square root of the treatment time. The parabolic rate constant is related to the product of the diffusion coefficient and concentration of an oxidant~~[1~~].[1] It is also well known that the oxidation of silicon in water vapor atmosphere, or wet oxidation, is faster than the oxidation in dry oxygen atmosphere.[1] ~~[1].~~ However, the reported ~~water~~ diffusion coefficient of water in silica glass[2] ~~[2]~~ appears smaller than the diffusion coefficient of oxygen in silica glass ~~[3]~~.[3] Deal and Grove ~~[1]~~ consider that this higher oxidation rate in the wet oxidation is due~~-~~ to the higher concentration of water, ~~than the concentration of~~versus oxygen, in silica glass.[1] They referred to the diffusion coefficient and concentration of water evaluated using the hydroxyl concentration profile~~,~~ when the water diffusion mechanism was not clearly understood. In view of the subsequent development of water diffusion processes in silica glass and related phenomena, especially water diffusion mechanisms and silica glass structural changes promoted by water diffusion[4,5] ~~[4,5]~~, the role of water in silicon oxidation was re-evaluated.

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~~II.~~ Water D~~d~~iffusion in S~~s~~ilica G~~g~~lasses

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Doremus ~~[4]~~ proposed a water diffusion mechanism in silica glasses, in which only molecular water diffuses and reacts readily with silica network, forming immobile hydroxyl, or SiOH, by the following reaction~~.~~

$$\equiv SiOSi\equiv + H_2O \leftarrow \rightarrow 2\equiv SiOH \qquad (1)$$

~~(1)~~

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where ≡ indicates three chemical bonds of Si and O.[4] Doremus further observed that this equilibrium reaction is heavily shifted to the right, and ~~the~~ most of the water in silica glass exists as hydroxyl, ≡SiOH. He ~~further~~ postulated that this reaction is fast and that a local equilibrium of the reaction is maintained while water diffusion ~~is taking~~ takes place at high temperature, e.g., 1000°C. In this reaction, ~~,~~ ~~with~~ the equilibrium constant is~~,~~ K = $[OH]^2/[H_2O]$, where [OH] and $[H_2O]$ are activities of hydroxyl and molecular water, respectively. During water diffusion in silica glass, the water molar concentration in silica glass is usually much smaller, compared with silica molar concentration, and the activity of silica is considered nearly ~~unity~~ united, while ~~and~~ those of hydroxyl and molecular water species can be approximated by their respective concentrations. Water diffusion in a silica glass is often studied ~~often~~ by measuring the hydroxyl concentration depth profile in a silica glass sample at room temperature, after ~~heat~~ treating~~tment~~ the sample with heat at a high temperature. The effective water diffusion coefficient obtained from hydroxyl profile, $D_{eff,OH}$~~,~~, can be represented by the following equation[4,6], ~~[4,6],~~

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$$D_{eff,OH} = 4D_{H2O}[OH]/K \qquad (2)$$

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where D_{H2O} is the diffusion coefficient of molecular water, as expected when in silica glass the molecular water diffuses, ~~in silica glass~~ unimpeded by the reaction with the glass structure. This equation also predicts that the effective diffusion coefficient, $D_{eff,OH}$, is proportional to the concentration of the hydroxyl water [OH], which is the predominant water species in the glass. The experimental water diffusion profiles show ~~good~~ strong agreement with their predicted profiles ~~[4,6]~~.[4,6] The water diffusion coefficient used by Deal and Grove[1] ~~[1]~~ in their discussion was this same effective diffusion coefficient, $D_{eff, OH}$, and the concentration of "water" used was that of hydroxyl, [OH], at the glass surface.

Subsequently, ~~The~~ equation ~~(~~2~~)~~ can be re-written as follows in equation 3.

$$D_{eff,OH} = 4D_{H2O}[OH]/K = 4D_{H2O}[H_2O]/[OH] \tag{3}$$

S~~S~~ince $[H_2O] << [OH]$, it is expected that $D_{H2O} >> D_{eff, OH}$. Doremus estimated ~~[7]~~ the value of D_{H2O} using the experimental data on diffusion coefficient, $D_{eff, OH}$, and [OH], and he also ~~as well as~~ estimated the value of $[H_2O]$.[7] The concentration of molecular water, $[H_2O]$, was estimated from the solubility of various gas species, such as helium, neon, argon, and oxygen in silica glasses, as well as ~~and~~ the atomic, or molecular, size of these gas species. The solubility of a gas species is defined as the ratio of the concentration of the gas in glass, C_d, to that in the adjacent atmosphere, C_g, as represented together by~~i.e.~~ C_d/C_g. ~~This~~ The ratio of the molecular water was estimated to be a temperature-independent constant, ~ 0.015 ~~[7]~~.[7] For the concentration of water in the atmosphere, the ideal gas law was used. As expected, t~~T~~he evaluated diffusion coefficient, D_{H2O}, was~~, as expected,~~ ~~much higher, by~~ approximately 200~~-~~-~~~~~400 times higher~~,~~ than the effective diffusion coefficient, $D_{eff,OH}$, at 1000°C, while both~~both~~ ~~having~~ had nearly same activation energy.~~.~~

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~~III.~~ The M~~M~~olecular W~~w~~ater D~~d~~iffusion C~~c~~oefficient ~~-~~and the W~~w~~et O~~o~~xidation K~~k~~inetics of S~~s~~ilicon

According to Doremus's model ~~[4]~~, in a given diffusion profile, molecular water concentration [H_2O] and hydroxyl concentration [OH] are closely related through the equilibrium constant, K.[4] Therefore, the diffusion distance of both species should be nearly identical. In ~~the course of~~a water diffusion study on~~in~~ silica glass, it was found that a silica glass surface, when exposed to water vapor, exhibits a fast structural relaxation, even at a temperature lower than the glass transition temperature[5,8-11] ~~[5,8-11]~~, and this structural relaxation was promoted by the diffusing water. The thickness of the relaxed glass surface layer ~~relaxed~~ increased with the square time of the heat-treatment in a wet atmosphere, indicating a diffusion-controlled process. The evaluated apparent diffusion coefficient of the surface structural relaxation, $D_{eff,\ Si\text{-}O\text{-}Si}$, was greater than the effective diffusion coefficient of water, $D_{eff,OH}$, when the heat-treatment temperature ~~is~~ was 850°C or higher, as shown in Figure~~.~~ 1 ~~[5]~~.[5] This is possible only when a small quantity of molecular water species, undetected by IR spectroscopy, is diffusing faster than the measured hydroxyl diffusion profile.

~~-~~It appears that the local equilibrium of the reaction in equation 1~~(1)~~ is not strictly maintained and that some of molecular water is diffusing ~~fast~~ quickly, unrestricted by the reaction equilibrium even at high temperature, e.g., 1000°C. Possible diffusion profiles of molecular water and hydroxyl water in silica glass, therefore, should look like those shown ~~schematically~~ in the schematics under ~~in Fig.~~Figure 2 ~~[11]~~.[11] In this figure, ~~-where~~ the diffusion profiles, both concentration and distance, are plotted in logarithmic scales for a silica glass sample, which is

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heat-treated for one hour~~1 h~~ in a water vapor atmosphere of 335 torr at 1000°C. Two lines, with a shorter diffusion distance, indicate hydroxyl and molecular water diffusion profiles, under the condition that a strict equilibrium of equation ~~(~~1~~)~~ is maintained. Under normal experimental condition, the hydroxyl concentration profile can be measured but the molecular water concentration profile cannot be detected, because its concentration is extremely low. The profile with a longer diffusion distance in the figure represents the molecular water concentration profile when the molecular water can diffuse unrestricted by the equilibrium reaction in equation ~~(~~1~~)~~. While the hydroxyl diffusion profile appears to follow ~~the~~ equation ~~(~~2~~)~~, some molecular water appears to diffuse deeper, causing the surface structural relaxation of silica glasses.

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The present author ~~considers~~ proposes that this ~~fast moving~~fast-moving molecular water works as an oxidant of silicon in the wet oxidation. This proposed mechanism appears reasonable since molecular water is the true diffusing species in silica glass~~, which~~ and can act as an oxidant, even though the molecular water is not readily detected in the experiment. On the other hand, hydroxyl water, which is abundant and is readily detected in silica glass, is immobile. The parabolic rate constant, B, which represents the~~of~~ oxidation of silicon, is given by equation 4,~~[1]~~

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$$B = 2 D_{eff} C/N_1 \qquad (4)$$

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The values of the diffusion coefficient and concentration of water considered by Deal and Grove ~~corresponds, in the present notation,~~ correspond to $D_{eff,OH}$ and [OH], respectively. Since [OH] represents the number of hydroxyl molecules per unit volume, and two hydroxyls correspond to one water molecule, the number of the corresponding water molecule would be ½[OH] and the corresponding oxidation parabolic rate constant would be as follows:

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$$B = 2\text{x}½[OH]D_{eff,OH}/N_1.= [OH]D_{eff,OH}/N_1 \qquad (5)$$

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On the other hand, when the ~~fast moving~~fast-moving molecular water is considered the oxidant, the oxidation parabolic rate constant would be

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$$B = 2[H_2O]D_{H2O}/N_1 \qquad (1)$$

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Since both values of [OH] and $D_{eff,OH}$ are proportional to the square root of water vapor pressure, while $[H_2O]$ is proportional to water vapor pressure and D_{H2O} is independent of water vapor pressure, the parabolic rate constants by the two expressions are proportional to water vapor pressure, consistent with ~~the~~ experimental observation ~~[5]~~.[5]

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According to equation (3),

$$[OH]D_{eff,\ OH} = 4D_{H2O}[H_2O] \qquad (3')$$

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and nearly the same ~~quantity of~~ parabolic rate constant can be obtained by using the two expressions listed under~~,~~ equations (5) and (6). Thus, it is difficult to distinguish these two expressions ~~for the~~ by their parabolic rate constant, in ~~the~~ terms of wet oxidation kinetics, by comparing diffusion data for silica glasses and parabolic rate constant of the silicon oxidation. Also, certain errors are involved: ~~in~~ the measured diffusion coefficient, the ~~and~~ concentration of water, and the thermal histories and impurity contents in silica glasses employed can all influence the water diffusion data. In order to distinguish these two expressions ~~for~~ and determine the parabolic rate constants for oxidation of silicon, it is necessary to first determine the diffusion coefficients of the oxidant involved in the oxidation.

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This possibility was ~~examined~~ investigated by measuring the re-oxidation rate in the wet atmosphere of a silicon sample with a thick, ~~(~6 μm)~~ dried oxide film (approximately six micrometers) ~~[12]~~.[12] The pre-existing dry film would cause a delay time in the initiation of the re-oxidation, which is determined only by the diffusion coefficient responsible for oxidation, independent of the oxidant concentration. The results showed ~~the~~ data which appears to support the diffusion of ~~the~~ fast-~~-~~moving molecular water, but there ~~was~~ were some errors in ~~the~~ determining~~ation of~~ the delay time. It is the objective of this paper to show more clearly that the ~~fast moving~~fast-moving molecular water is responsible for the wet oxidation of silicon.

The parabolic rate constant for the fast-moving molecular water ~~was~~ is given above, ~~as equation~~under equation ~~(~~6, as~~)~~ $B = 2[H_2O]D_{H2O}/N_1$. The value of N_1 is ~~clearly~~ already known, being the number of the oxidant molecules incorporated into a unit volume of the oxide layer; this is because ~~since~~ one oxygen atom is incorporated from one molecule of water into the oxide, SiO_2, ~~and~~ two oxygen atoms are involved in one molecule of SiO_2, and the density of silica is 2.2 g/cm^3, N_1 = 2x2.2 (g/cm^3)x/60(g/mol) = 0.073 mole/cm^3. The molecular water solubility in silica glass was estimated by Doremus ~~[7]~~ to be $C_d/C_g \approx 0.015$, where $C_d = [H_2O]$ and C_g is the concentration of water molecules in the atmosphere in contact with silica.[7] Deal and Grove obtained the parabolic rate constant, B, under water vapor pressure of 640 torr, i.e., the pressure P = 0.842 ~~atomoaphwerie~~atmospheric pressure, and C_g can be obtained using the ideal gas law, PV=nRT, as $C_g = n/V = P/RT = [0.0103/T(K)]$ (mol/cm^3) and $C_d = [H_2O] = [1.538\text{x}10^{-4}/T(K)]$ (mol/cm^3). Using ~~these~~ this data in equation ~~(~~6~~)~~, the diffusion coefficient of the molecular water, D_{H2O}, involved in the oxidation of silicon can be estimated. The results are tabulated first in Table I, and these ~~. The~~ same ~~results (~~data points~~)~~ are also shown in ~~Fig.~~Figure 3, together with the molecular water diffusion coefficient (line) estimated by Doremus ~~[7]~~.[7] As ~~was~~ stated earlier, these two sets of data were obtained using different methods: Doremus obtained ~~this~~ his estimation from the water diffusion data, including the water effective diffusion coefficient, $D_{eff,OH}$, hydroxyl solubility, [OH], together and the estimated molecular water solubility, $[H_2O]$, while ~~the~~ this ~~current~~ report's data set ~~were~~ was obtained using the parabolic rate constant of wet oxidation of silicon, B [1]~~[1]~~, combined with the estimated molecular water solubility, $[H_2O]$. Both data sets agree with each other reasonably well, supporting the notion that ~~the~~ fast-moving molecular water is responsible for the oxidation of silicon.

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~~IV.~~ Conclusion

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The oxidation of silicon is controlled by the diffusion of the oxidant in the oxide. The wet oxidation of silicon is known to take place at much faster rate than the dry oxygen oxidation, even though the reported diffusion coefficient of water is smaller than the diffusion coefficient of oxygen. These water diffusion data sets are based upon the diffusion profile of hydroxyl concentration. It is shown that fast moving molecular water is responsible for the wet oxidation, even though~~t~~ ~~their~~ its concentration is too low to detect.

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This research was supported by NSF grant DMR-0804043.

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Tables

Table I. Estimation of molecular water from wet oxidation of silicon.

Temperature, T(°C)	Reciprocal temperature (1/T)x10^3(1/K)	Parabolic rate constant, B (μ^2/h)	Parabolic rate constant, B (cm^2/s)	Estimated H_2O concentration [H_2O] (mol/cm^3)	Diffusion coefficient of water, D_{H2O} (cm^2/s)
1200	0.679	0.720	$2.00x10^{-12}$	$1.044x10^{-7}$	$7.14 \text{ x } 10^{-7}$
1100	0.728	0.510	$1.42x10^{-12}$	$1.120x10^{-7}$	$4.72 \text{ x } 10^{-7}$
1000	0.785	0.287	$0.80x10^{-12}$	$1.208x10^{-7}$	$2.46x \ 10^{-7}$
920	0.838	0.203	$0.56x10^{-12}$	$1.289x10^{-7}$	$1.63 \text{ x}10^{-7}$

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Figure Captions

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Figure 1. Water diffusion coefficient, $D_{eff,OH}$ and surface structural relaxation diffusion coefficient, $D_{eff,Si-O-Si}$, of a silica glass as a function of temperature [5].

Figure 2. Estimated diffusion profile of hydroxyl, OH, and molecular water, H_2O, in a silica glass heat-treated at 1000°C for 1 h under 335 torr water vapor [11].

Figure 3. Estimated diffusion coefficient of molecular water, D_{H2O}, in silica glass. Line: estimated by Doremus [7] using equation (3) and various water diffusion data; Filled squares: estimated in the present work using equation (6) and parabolic rate constant in [1].

Figure 1.

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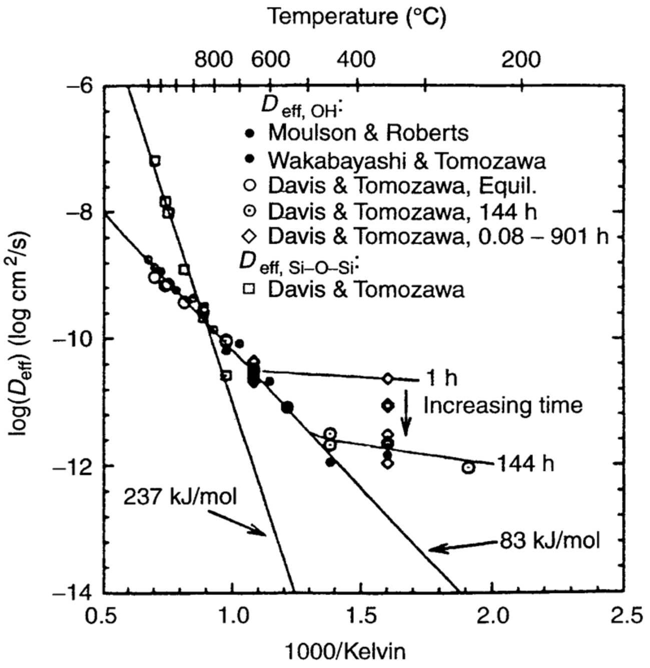

~~Figure 1.~~ Water diffusion coefficient, $D_{eff,OH}$ and surface structural relaxation diffusion coefficient, $D_{eff,Si\text{-}O\text{-}Si}$, of a silica glass as a function of temperature [5].

Figure 2.

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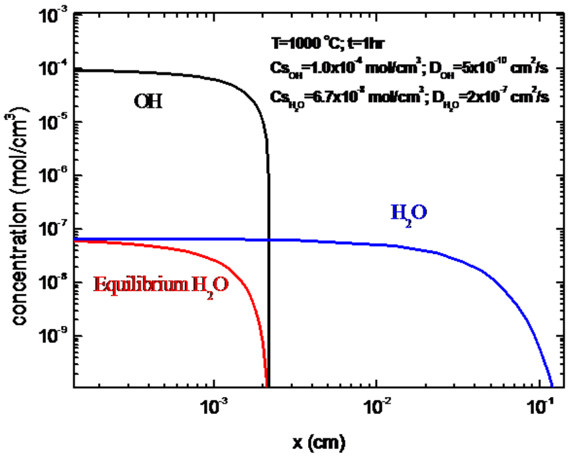

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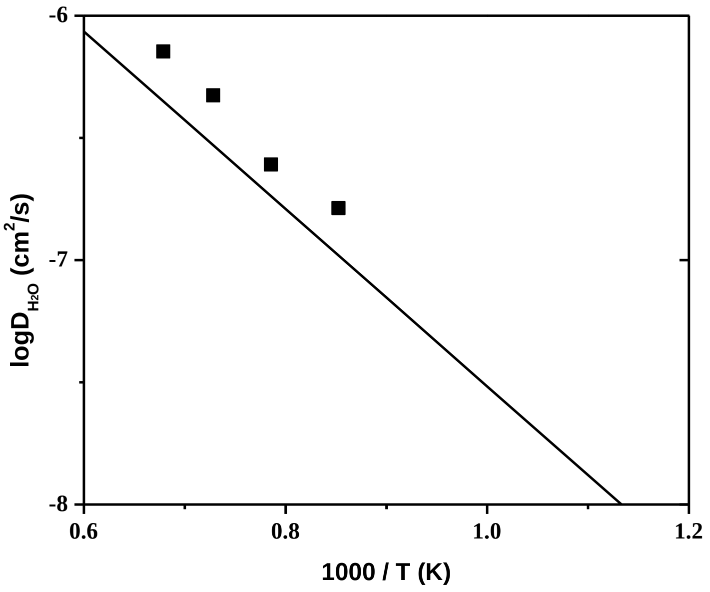
Figure 3.



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