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Influence of K^+ Ions on the Interaction of Water with Silicon Dioxide at Low Temperature Relevant to CMP

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Internal reflection infrared spectroscopy was used to examine the effect of potassium ions on the interaction of water with silicon dioxide at low temperature, relevant to chemical mechanical planarization (CMP) of silicon dioxide. Silanol (SiOH) formation was enhanced in silicon dioxide samples exposed to aqueous solutions of potassium chloride and potassium nitrate as compared to those exposed to water, due to a reduction in the thermodynamic activity of the water in potassium salt solutions. However, molecular water was the predominant hydrous species observed in the silicon dioxide. The presence of potassium ions had no significant effect on the effective diffusion coefficient of water in silicon dioxide. Results presented here indicate that the potassium ion concentration, and more specifically the water activity, is a critical factor in the chemical component of the silicon dioxide CMP mechanism.

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The presence of water in silicon dioxide has a significant effect on the chemical and mechanical behavior of the material. Consequently, understanding the interaction between water and silica is important in a multitude of systems where silicon dioxide and silicate glasses are used.[1-4] In many applications, silicon dioxide is in contact with water containing dissolved ions, either naturally or artificially introduced, that affect the properties of the water and consequently its interaction with the oxide. In chemical mechanical planarization (CMP), silicon dioxide interacts with an abrasive slurry which most commonly contains aqueous potassium hydroxide. The potassium ion concentration in such slurries is expected to affect the interaction of water with silica and consequently the CMP process itself by reducing the activity of the water.

Cook has suggested that the reaction between water and silicon dioxide to form silanol (SiOH) species (see Eq. 1) is the primary factor controlling the polish behavior of silica glass[5]

$$H_2O + \equiv Si - O - Si \equiv \; \rightarrow \; \equiv Si - OH + HO - Si \equiv \qquad [1]$$

It is speculated that the hydroxylated surface is softer and more readily abraded than the nonhydroxylated surface enhancing the mechanical removal mechanisms.[5] Cook further suggests that the silanol formation rate is diffusion controlled below the surface.[5] Recent results, however, contradict this suggestion and indicate that at least at low temperatures (below 80°C) the silanol formation rate is kinetically controlled below the surface.[6]

The speciation of water in silicon dioxide is dependent on the equilibrium of the hydroxylation reaction shown in Eq. 1. At high temperatures (above ~300°C), the predominant water related species observed has been the silanol group, SiOH, characterized by an infrared absorption at ~3670 cm^{-1}.[7-12] Davis and Tomozawa have reported that at high temperatures, water exists almost exclusively as silanol groups at water content of less than about 0.2 wt % and remains the dominant water species up to a total water content of about 4 wt %.[12] At 20°C, however, no significant silanol formation was observed in silicon dioxide samples exposed to water for up to 24 h.[6]

The rate of diffusion of water in silicon dioxide is also expected to depend on the water-silica reaction equilibrium. Doremus has proposed a diffusion-reaction model where molecular water is the diffusing species and silanol groups the immobile reaction product[13]

$$\frac{\partial[H_2O]}{\partial t} = D_{H2O}\frac{\partial^2[H_2O]}{\partial x^2} - \frac{\partial[SiOH]}{\partial t} \qquad [2]$$

where the brackets represent concentrations, t is time, x is depth into a semi-infinite plane geometry, and D is the diffusion coefficient. A linear proportionality between equilibrium silanol and molecular water contents below ~600°C, as shown in Eq. 3, has also been proposed[2]

$$K_1 = \frac{[SiOH]}{[H_2O]} \qquad [3]$$

where the concentration is an approximation for activity. Using this equilibrium expression in Eq. 3 yields an effective diffusion coefficient of

$$D_e = \frac{D_{H2O}}{(1 + K_1)} \approx \frac{D_{H2O}}{K_1} \qquad [4]$$

which gives an error function concentration profile consistent with a constant diffusion coefficient in Eq. 2.

The equilibrium of the silicon dioxide-water reaction thus is critical in determining both the speciation of water in the oxide and the diffusion of water into the oxide. Solute species, such as ions, reduce the activity of water.[14] As illustrated in Fig. 1, aqueous solutions of potassium chloride, potassium nitrate, and potassium hydroxide of concentrations of 3 M exhibit water activities 5-10% lower than the activity of pure water.[14] Based on the equilibrium relationship in Eq. 3, we hypothesize that SiOH formation is enhanced when silica is exposed to aqueous potassium salt solutions compared to pure water due to the reduced water activity in the salt solutions.

The effective diffusion coefficient of water into silicon dioxide should also be affected by the presence of ions in the solution. From Eq. 4, it may be expected that increasing the equilibrium constant reduces the effective diffusion coefficient. However, as more silanol groups are formed, more bridging Si-O bonds are broken which are expected to make the oxide structure more open, resulting in an increased flux of water into the silica. The decreased water activity may also increase the driving force for diffusion. The diffusive flux of water into the silicon dioxide can be expressed

$$J_{H_2O} = \frac{-c_{H_2O}\overline{V}_{SiO_2}}{b}\frac{d\mu_{H_2O}}{dy} \qquad [5]$$

where J_{H2O} is water flux, c_{H2O} is water concentration, $\overline{V}_{SiO2}$ is the partial molar volume of SiO_2 (cm^3/mol), b is a constant, μ_{H2O} is the

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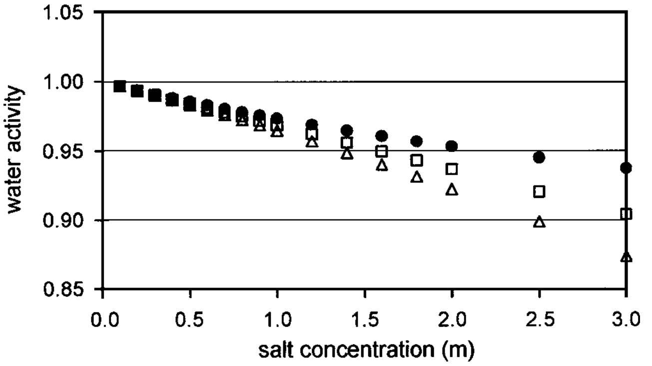

Figure 1. Activity of water in aqueous solutions of (□) KCl, (●) KNO_3, and (△) KOH.[14]

chemical potential of water, and *y* is the direction normal to the surface of the silicon dioxide film.[15] The chemical potential of water can be described by

$$\mu_{H_2O} = \mu^o_{H_2O}(T, P) + RT\ln(a_{H_2O}) \quad [6]$$

Decreasing the activity of water, as occurs in the potassium salt solutions used in this work, decreases the chemical potential of the water. If we assume that water at or near the surface of the oxide has the chemical potential of water in the salt solution while water in the oxide some distance into the silica has the chemical potential of pure water, a larger value of the derivative term is expected than for the same concentration profile with pure water. This effectively increases the flux of water into the silica.

Because the slurries most commonly used for silicon dioxide CMP contain potassium ions in an aqueous solution, potassium ion effects are of particular interest in understanding silicon dioxide CMP. The goal of this work is to examine the effects of potassium ions on the interactions between water and silica during CMP.

Experimental

Infrared transmission spectroscopy has been widely used in the study of water/silica interactions.[7-12] A drawback of this technique is its low absolute sensitivity, which limits its applicability at the low temperatures relevant to CMP (20-100°C)[16,17] when the reaction and diffusion rates of water with and in silicon dioxide are very low. Multiple internal reflection infrared spectroscopy significantly improves sensitivity as compared to transmission, and can allow information to be obtained in relatively short times and at low temperatures about the interactions between water and silicon dioxide. For this work, 45° fixed plate parallelepiped internal reflection elements were fabricated from silicon to give between 30 and 70 internal reflections (Fig. 2). Intrinsic silicon (>20 Ω cm) internal reflection elements (IREs) are transparent to IR light in the wavenumber range 1500-8300 cm^{-1}. A thermal oxide ~200 Å thick was grown on each IRE in an 850°C furnace in a dry oxygen environment. This oxide had negligible initial hydroxyl content as determined by multiple internal reflection infrared spectroscopy. Spectra of as-grown dry thermal oxides were used as background spectra. Oxidized IREs were immersed in a 20°C bath of deionized (DI) water or aqueous 1 M solutions of KCl or KNO_3 for a set time. Upon removal from the liquid, the IREs were dried externally at room temperature with nitrogen and infrared spectra were collected. Spectra were collected on a Nicolet Nexus 670 FTIR spectrometer in combination with an external optical bench with an Infrared Associates MCT detector sensitive to IR light in the wavenumber range 400-4000 cm^{-1}. This allowed detection of both the hydroxyl absorptions at 3000-3700 cm^{-1} and the molecular water absorption at ~1650 cm^{-1}.

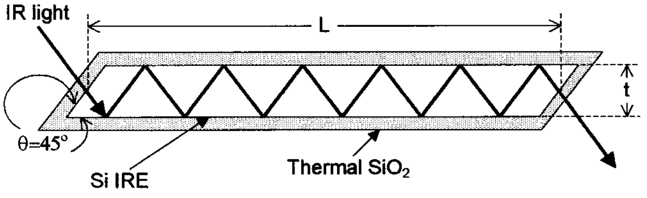

Figure 2. Experimental setup; 45° fixed plate, parallelepiped, Si IRE, thermal oxidized in dry O_2.

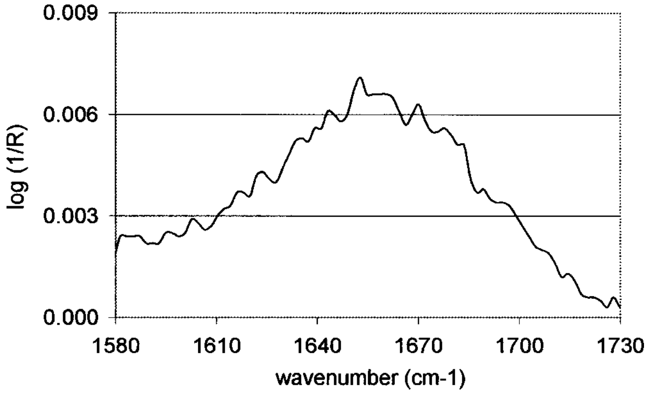

Figure 3. Infrared spectra (1580-1730 cm^{-1}) of silicon dioxide immersed in DI H_2O for 24 h at 20°C.

The experimentally measured water content was determined using a modification of Beer's law (Eq. 7), which states that absorbance (*A*) is proportional to concentration (*C*) multiplied by the path length (*d*)

$$A = \alpha C d \quad [7]$$

The proportionality constant, α, has units of L/(mol cm). The value of α varies with wavelength throughout the broad absorption from 3000 to 3800 L/mol cm. For this work values of 121 L mol^{-1} cm^{-1} for the peak fit at ~3200 cm^{-1}, 218 L mol^{-1} cm^{-1} for the peak fit at ~3400 cm^{-1}, 141 L mol^{-1} cm^{-1} for the peak fit at ~3500 cm^{-1}, 101 L mol^{-1} cm^{-1} for the peak fit at ~3600 cm^{-1}, and 81 L mol^{-1} cm^{-1} for the peak fit at ~3670 cm^{-1} were used.[12,18-20] For multiple internal reflections, a factor of *N*, the number of internal reflections, is multiplied by Eq. 5. Also, an effective path length for internal reflection, d_e, given by Eq. 8, is used[21]

$$d_e = \frac{2n_2 d\cos\theta}{n_1(1-(n_3/n_1)^2)} + \frac{n_2 d\cos\theta[1+(n_3/n_2)^4\sin^2\theta-(n_3/n_1)^2]}{2n_1(1-(n_3/n_1)^2)[(1+(n_3/n_1)^2)\sin^2\theta-(n_3/n_1)^2]} \quad [8]$$

where n_1, n_2, and n_3 are the refractive indices of the silicon IRE (3.40), the oxide film (1.46), and air (1.00), respectively, θ is the angle of incidence of the IR light (45° for this work), and *d* is the oxide film thickness as determined by ellipsometry measurements. The final form of Beer's law used for this work is given by

$$A = N\alpha C d_e \quad [9]$$

Results and Discussion

Two absorption bands of interest were observed: one at ~1650 cm^{-1} and a broad asymmetric absorption at ~3000-3800 cm^{-1}. Figure 3 illustrates the absorption observed at ~1650 cm^{-1} for a sample exposed to water for ~24 h. This absorption results from the fundamental bending mode vibration of molecular water, $\nu_B(H_2O)$, and has been identified at wavenumbers ranging from 1610 to 1650

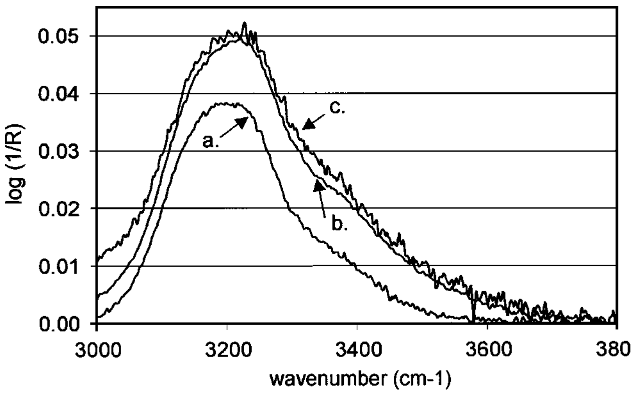

Figure 4. Infrared spectra (3000-3800 cm^{-1}) of silicon dioxide immersed for 24 h in 20°C; (A) DI H_2O, (B) 1 M $KNO_3(aq)$, and (C) 1 M KCl(aq).

cm^{-1} in the literature.[12,22] Detection of this peak indicates that unreacted molecular water is present in the silicon dioxide. This absorption was also observed in samples exposed to aqueous solutions of KCl and KNO_3.

The other significant peak observed was a broad asymmetric absorption at 3000-3800 cm^{-1}, illustrated in Fig. 4 for silicon dioxide samples exposed to DI water, 1 M $KNO_3(aq)$, and 1 M KCl(aq) at 20°C. This broad absorption was fit to peaks centered at ~3200, ~3400, ~3500, ~3600, and ~3670 cm^{-1}, respectively, using ACD Labs UVIR Processor software. The absorption at ~3200 cm^{-1} has been assigned to the first overtone of the bending mode vibration of molecular water, $\nu_B(H_2O)$[12] (Fig. 5a). The absorption at 3400 cm^{-1} is assigned to the stretching vibrations of the O-H bond in molecular water, $\nu_S(H_2O)$ (Fig. 5b).[12] Davis and Tomozawa have noted that this peak has contributions of the O-H stretching vibrations of both "free" and "bound" molecular water.[12] The nature of this "bonding" is unclear from the literature. Absorptions at ~3500, 3600, and 3670 cm^{-1} are all assigned to the OH stretching mode vibration of SiOH groups in various configurations, as shown in Fig. 4.2c-e.[12]

Negligible SiOH formation has been detected on SiO_2 samples exposed to 20°C DI H_2O for up to 24 h.[6] However, a small amount of SiOH formation was observed on SiO_2 samples exposed to the potassium salt solutions. If equilibrium is assumed, concentrations calculated as described previously can be substituted into Eq. 3 to solve for the equilibrium coefficient, K_1, of the reaction shown in Eq. 1. Doing so yields a value of 0.12 ± 0.02 for K_1 for the reaction of water in 1 M KCl(aq) or in 1 M $KNO_3(aq)$ with SiO_2 at 20°C. No significant difference was observed between samples exposed to 1 M KCl(aq) as compared to those exposed to 1 M $KNO_3(aq)$. Increasing the concentration of the potassium salt to 2 M gives a value of 0.20 ± 0.03 for K_1. Again, no significant difference is observed in samples exposed to 2 M KCl(aq) as compared to those exposed to 2 M $KNO_3(aq)$. No trend in the value of K_1 as a function of time was observed at either concentration. Molecular water remained the dominant species observed in these samples.

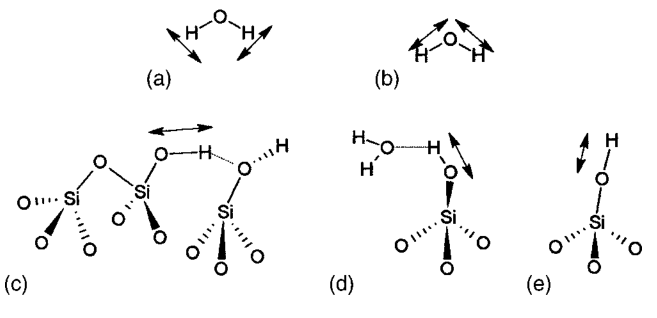

Figure 5. Structures corresponding to observed peaks in IR spectrum; (a) $\nu_B(H_2O)$, bending mode vibration of the water molecule associated with the IR peak at ~1650 cm^{-1} with an overtone at 3200 cm^{-1}; (b) $\nu_S(H_2O)$, stretching mode vibration of molecular water associated with the IR peak at ~3400 cm^{-1}; (c) $\nu_S(OH...^{H}OSi)$, stretching mode vibration of OH group hydrogen bonded to oxygen of neighboring silanol associated with IR peak at ~3500 cm^{-1}; (d) $\nu_S(OH...^{H}OH)$, stretching vibration of OH group hydrogen bonded to oxygen of neighboring water molecule associated with IR peak at ~3600 cm^{-1}; and (e) $\nu_S(OH)$, stretching vibration of isolated silanol group associated with IR peak at ~3670 cm^{-1}.

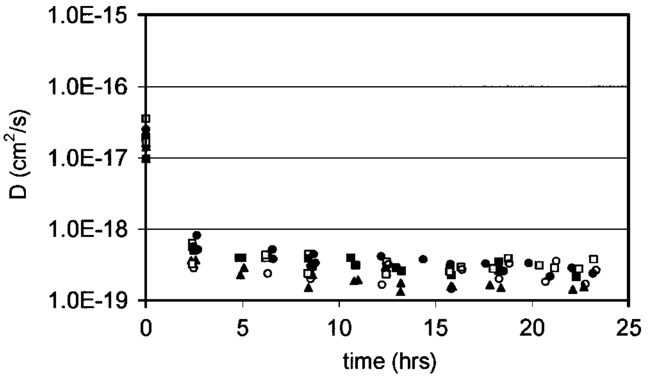

Figure 6. Apparent diffusion coefficient of water in silicon dioxide *vs.* time at 20°C for (▲) DI water, (○) 1 M KCl(aq), (●) 1 M $KNO_3(aq)$, (□) 2 M KCl(aq), and (■) 2 M $KNO_3(aq)$.

As previously discussed, the concentrations in the low temperature equilibrium equation proposed by Doremus (Eq. 3) are approximations for activity. Therefore, Eq. 3 may more accurately be expressed as

$$K_1 = \frac{a_{\mathrm{SiOH}}}{a_{\mathrm{H2O}}} \qquad [10]$$

where a_{H2O} and a_{SiOH} are the activities of water and SiOH, respectively. The presence of dissolved salts, such as KCl or KNO_3, reduces the activity of the water, as shown in Fig. 1. Consequently, the equilibrium constant is increased and enhanced silanol formation is observed in the presence of aqueous potassium salt solutions as compared to DI H_2O. The increase in K_1 with increasing K^+ concentration is consistent with the reduction in water activity with increasing salt concentration in the water. Because the magnitude of the difference in water activities for KCl and KNO_3 solutions is small, it is not surprising that no significant difference was observed in the apparent reaction equilibrium.

The water concentrations in the silicon dioxide as determined from infrared absorption intensities and from Eq. 9 were used in conjunction with the corresponding immersion times to determine an apparent diffusion coefficient for water in silicon dioxide.

Assuming a constant surface concentration C_0 of pure water, Fick's second law results in a concentration profile described by Eq. 11, where D is the diffusion coefficient, t is time, and x is the position ($x = 0$ is the surface)

$$C = C_0 \,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \qquad [11]$$

Total water content in this case is given by

$$M = 2C_0\left(\frac{Dt}{\pi}\right)^{1/2} \qquad [12]$$

The diffusion coefficient was fit to experimentally measured water content using Eq. 12.

Figure 6 displays results of such calculations for water diffusion in silicon dioxide. After 1 min in DI water the effective diffusion coefficient of water in silicon dioxide at 20°C is 2×10^{-17} cm^2/s. This value drops sharply, as shown in Fig. 6, approximately two orders of magnitude at 20°C to an apparent value of 2×10^{-19} cm^2/s for water immersion times between 15 and 24 h. A similar sharp drop was observed in samples exposed to potassium salt solutions. This sharp initial decrease in the apparent diffusion coefficient has at least two possible explanations. One possible cause for this result is the presence of a physisorbed or chemisorbed layer of water present on the surface detected by the IR measurements. In this case, the diffusion coefficient calculated from spectral data collected after 1 min of exposure to DI water is not really representative of a diffusion process. Another possibility is that the surface region of the silicon dioxide is less dense and has a more open structure than the bulk material. It is expected that at the surface, bonds are more likely to be stressed, distorted, or dangling than in the bulk silicon dioxide. In this case, water more readily diffuses into the more open structure of the surface region then diffuses more slowly into the bulk material.

Values of the effective diffusion coefficient for water immersion times between 15 and 24 h are comparable to previous measurements in this temperature range in the literature.[23,24] The effective diffusion coefficient of water in SiO_2 measured from samples exposed to 1 M $KNO_3(aq)$ and 1 M KCl(aq) for 15 to 24 h is 3×10^{-19} cm^2/s, is not significantly different from that measured for samples exposed to pure water. No significant difference in the effective diffusion coefficient was observed between samples exposed to 1 M KCl(aq) as compared to those exposed to 1 M $KNO_3(aq)$. Increasing the salt concentration to 2 M likewise had no significant effect on the measured apparent diffusion coefficient of water in silicon dioxide.

Conclusions

Increased silanol formation in silica samples exposed to potassium salt solutions as compared to those exposed to DI water confirms the hypothesis that the presence of potassium ions, by lowering water activity, enhances the silanol formation reaction. The reduced water activity also increased the effective diffusion coefficient of water in silica films.

The results of this work have several implications in the understanding of the CMP mechanism. Previous results indicated that the reaction of water with the silica network is too slow to be observed in less than 24 h at 20°C in DI water.[6] The presence of potassium ions in the water, by reducing the activity of the water, causes measurable SiOH formation. If SiOH formation is as critical to the CMP mechanism as has been suggested,[5] then these results clearly indicate that ion concentration, or more specifically water activity, of the slurry is a critical variable in the silicon dioxide CMP. It is expected that as ion concentration in a slurry is increased, and hence water activity further reduced, enhanced CMP removal rates will be observed. Several factors not examined in this work are likely to further affect the silicon dioxide-water reaction during CMP, such as external stress due to contact with abrasive particles, and slurry pH. Nonetheless, results presented here provide some insight into the extent of the SiOH formation reaction that can be expected during CMP.

While the effective measured diffusion coefficient of water into silicon dioxide was not significantly affected by the presence of potassium ions in the water, the rate of diffusion remains very low compared to typical removal rates. For a Fickian concentration profile with diffusion coefficients of the order measured in this work, water (and SiOH) could be expected to penetrate less than 5 nm into the surface of the silicon dioxide during typical CMP process run times which are on the order of minutes. Typical removal rates in oxide CMP are on the order of 100 nm/min. Again, although several effects occurring during CMP not examined in this work could be expected to enhance diffusion, it appears from this work that the time scale for the penetration of water into an oxide film being polished is much less than for the time scale for oxide removal during CMP.

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