The chemical characteristics and the proposed formation mechanisms of the modified surface layer (called the Beilby layer) on polished fused silica glasses are described. Fused silica glass samples were polished using different slurries, polyurethane pads, and at different rotation rates. The concentration profiles of several key contaminants, such as Ce, K, and H, were measured in the near surface layer of the polished samples using Secondary Ion Mass Spectroscopy (SIMS). The penetration of K, originating from KOH used for pH control during polishing, increased with increase in polishing material removal rate. In contrast, penetration of the Ce and H increased with increase in polishing removal rate. In addition, Ce penetration was largely independent of the other polishing parameters (e.g., particle size distribution and the properties of the polishing pad). The resulting K concentration depth profiles are described using a two-step diffusion process: (1) steady-state moving boundary diffusion (due to material removal during polishing) followed by (2) simple diffusion during ambient postpolishing storage. Using known alkali metal diffusion coefficients in fused silica glass, this diffusion model predicts concentration profiles that are consistent with the measured data at various polishing material removal rates. On the other hand, the observed Ce profiles are inconsistent with diffusion based transport. Rather we propose that Ce penetration is governed by the ratio of Ce–O–Si and Si–O–Si hydrolysis rates; where this ratio increases with interface temperature (which increases with polishing material removal rate) resulting in greater Ce penetration into the Beilby layer. Calculated Ce surface concentration using this mechanism are in good agreement to the observed change in measured Ce surface concentrations with polishing material removal rate. These new insights into the chemistry of the Beilby layer, combined together with details of the single particle removal function during polishing, are used to develop a more detailed and quantitative picture of the polishing process and the formation of the Beilby layer.

I. Introduction

During the polishing of metals, crystals, and glasses, a modified amorphous surface layer is formed which ranges in thickness from a few nanometers to a µm. This layer is often referred to as the Beilby layer; although this name originally referred only to metal polished layers. For polished glass surfaces, this layer has also been referred to as the polishing layer, the modified layer, and/or the hydrated layer.

The Beilby layer on glasses contains elevated levels of impurities whose concentration, as measured by Secondary Ion Mass Spectroscopy (SIMS), typically decays exponentially to the bulk concentration within a few tens of nanometers of the surface.2–4 Sensitive optical reflectivity, ellipsometry,5 and x-ray reflectivity6 measurements indicate that the refractive index of this layer is typically 0.003–0.005 higher than the bulk material. The Beilby layer associated with silicate glasses can be removed by chemical etching (e.g., using HF acid) or modified by chemically leaching the cations (e.g., using mineral acids such as nitric acid).7–9 Nevot and Croce10 and later Trogolo and Rajan11 were able to successfully image the Beilby layer of silica glass in cross section using transmission electron microscopy. They showed the presence of two distinct surface layers, one that was 3–4 nm thick followed by a 15–20 nm deeper layer. More recently, Liao et al.12 performed similar measurements using FE-SEM. To date, no direct measurement of water penetration in the polishing layer has been reported, even though it is largely accepted that hydration is occurring. Wakahayashi and Tomozawa13 presented indirect evidence that H2O penetration is likely occurring.

The most accepted mechanisms associated with the polishing of glass surfaces, which in turn control the formation of the Beilby layer, involve the interplay of both chemical and mechanical interactions. These include the condensation and hydrolysis reactions between polishing slurry particles and glass surface,14 hydration of glass oxides,14,15 and nm scale plastic deformation.16 Many questions remain regarding the characteristics and formation of the Beilby layer during glass polishing. Some of these include: (1) what is the mechanism (e.g., by impurity diffusion and reaction, by direct reaction layer formation, or by redeposition) by which impurities are incorporated into the surface layer?; (2) how do polishing parameters influence the depth of the Beilby layer?; (3) what are the structural changes in the surface layer relative to the bulk silica glass?; (4) how are its mechanical & chemical properties different from the bulk?; and (5) how does this layer influence the single slurry particle removal function and the resulting polished surface roughness of the polished glass? In the following study, we attempt to answer the first three questions by measuring changes in the elemental composition of the near surface layer as a function polishing parameters. Using this information, a more detailed chemical and structural model of how material removal occurs during polishing is formulated.

II. Experimental Procedure

(1) Sample Preparation

Fused silica workpieces (50 mm diameter × 10 mm thick; Corning 7980, Corning, NY) were polished using the Convergent Polishing method7 (baseline conditions: 0.6 psi applied pressure, 0.6 mL/min slurry feed rate (single pass), Stabilized Hastilite PO polishing slurry (Baume 5; pH adjusted to 9.5 using KOH),18 20 rpm optic and lap rotation rate, 300 mm lap diameter, 50 mm linear stroke distance). The lap rotation rate (5–40 rpm), polishing pad [MHN 50
Table I. Polishing Parameters and Resulting Material Removal Rate for Each of the Samples

<table>
<thead>
<tr>
<th>Series</th>
<th>Sample</th>
<th>Treatment</th>
<th>Pad</th>
<th>Slurry</th>
<th>pH</th>
<th>Rotation rate (rpm)</th>
<th>Removal rate (μm/h)</th>
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</thead>
<tbody>
<tr>
<td>Velocity</td>
<td>V1</td>
<td>Polish</td>
<td>MHN</td>
<td>Ceria: Stab. Hastilite PO</td>
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<td>40</td>
<td>1.00</td>
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<tr>
<td></td>
<td>V2</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V3</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>V4</td>
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<td>5</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Pad</td>
<td>P1</td>
<td>Polish</td>
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<td>0.69</td>
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<tr>
<td></td>
<td>P2</td>
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<td>Chem-Poly</td>
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<td></td>
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<tr>
<td></td>
<td>P3</td>
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<td>Optivision</td>
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<td></td>
<td>P4</td>
<td></td>
<td>Polytex</td>
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<tr>
<td></td>
<td>P5</td>
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<td>Polytex</td>
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<tr>
<td>Slurry</td>
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<td>Polish</td>
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<td></td>
<td>Ceria: NanoArc 6752</td>
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<tr>
<td>pH</td>
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<td>Polish</td>
<td>MHN</td>
<td>Ceria: Stab. Hastilite PO</td>
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<td>0.54</td>
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<tr>
<td></td>
<td>H2</td>
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<td></td>
<td>8.3</td>
<td>0.88</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H3</td>
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<td>10.5</td>
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</tr>
<tr>
<td></td>
<td>H4</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H5†</td>
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<td></td>
<td></td>
<td>8.3</td>
<td>1.86</td>
<td></td>
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<tr>
<td>No polishing-soak</td>
<td>NP1</td>
<td>Soak</td>
<td>NA</td>
<td>Ceria: Stab. Hastilite PO (2 week)</td>
<td>8.3</td>
<td>NA</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>NP2</td>
<td></td>
<td></td>
<td>KOH (2 week)</td>
<td>13.7</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NP3</td>
<td></td>
<td></td>
<td>KOH (18 h)</td>
<td>13.7</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

†Pad treated for higher removal rate.

III. Results

The depth profiles of K and Ce for a series of fused silica samples polished at different velocities (and hence different polishing removal rates) are shown as a pair of semi-log plots in Figs. 1(a) and (b). Note the bulk glass Si concentration was measured at uniform value of $2 \times 10^{12}$ atoms/cm$^3$ (not shown in plot), while the noise floor of each analyte is $<10^{10}$ atoms/cm$^3$. K penetration into the glass surface was significantly greater ($\sim$500–900 nm) than the Ce penetration ($\sim$20–100 nm). Also, the surface concentration for both impurities varied significantly from $6 \times 10^{16}$ to $2 \times 10^{19}$ atoms/cm$^3$ with changes in polishing conditions. Finally, and most significantly, the K penetration was...
observed to decrease with increase in polishing material removal rate, while the Ce penetration was found to increase as a function of material removal rate.

Figure 2(a) shows a series of Ce depth profiles for several additional fused silica samples which were polished using different slurries and different polishing pads. As observed in Fig. 1(b), the depth of Ce penetration is found to vary significantly depending upon the polishing process used. As shown with sample NP1 in Fig. 2(a), simply soaking a fused silica sample in Ceria slurry does not allow Ce to penetrate into the surface of the polished sample. This suggests that some combination of mechanical loading and lateral motion of the particle during polishing is required to transport the Ce into the near surface layer of the glass. Again, the dominant polishing variable affecting the Ce penetration is the polishing material removal rate. This is illustrated in Fig. 2(b), which plots the Ce surface concentration as a function of polishing material removal rate for all the samples summarized in Table I. Note the Ce surface concentration here is defined as the measured SIMS Ce concentration over the first 1 nm increment into the surface.

Some additional K depth profiles are shown in Figs. 3(a) and (b). Figure 3(a) shows that soaking etched fused silica samples in KOH results in significant penetration of KOH even without polishing. This is unlike the behavior observed when glass is soaked in an aqueous solution of Ce polishing slurry as shown in Fig. 2(a). Figure 3(b) illustrates that after polishing, K continues to penetrate into the glass during storage under ambient conditions.

The H depth profiles for two polished fused silica samples are shown in Fig. 4. Here the instrumental noise floor is much higher $\sim 10^{19}$ atoms/cm$^3$. Hence, the actual penetration depth of H into the surface cannot be determined. However, the results confirm high surface concentration of H of $\sim 10^{20}$ atoms/cm$^3$ (i.e., 10 000–30 000 ppm) which is likely due to H$_2$O penetration. To the authors’ best knowledge, this is the first experimental confirmation of H$_2$O penetration into...
IV. Discussion

(1) Diffusion Versus Chemical Reactivity

One potential mechanism of incorporating cation impurities into the glass surface during polishing is diffusion. If the Beilby layer formation is diffusion induced, then there should be a steady-state relationship between material removal rate and the diffusion mass transfer of the impurity species. At steady-state, the diffusion flux of the impurities into the glass is equal to the flux of impurities removed due to removal of the surface during polishing. This balance is given by:

\[ J_{\text{diffusion}} = J_{\text{material removal}} \] (1a)

\[ C \frac{dC}{dt} = D \frac{dC}{dx} \] (1b)

where \( C \) is the impurity concentration, \( \frac{dC}{dt} \) is the material removal rate, \( D \) is the impurity cation diffusivity, and \( \frac{dC}{dx} \) is the depth into the moving glass surface. Note the right-hand side of Eq. (1b) is simply Fick’s first law. Using the Preston’s material removal equation \(^7\) and solving Eq. (1b) gives:

\[ \frac{dC}{dt} = k_p \sigma_a V_r \equiv \frac{D}{t_{\text{Beilby}}} \] (2)

where \( k_p \) is the Preston constant, \( \sigma_a \) is the applied pressure, \( V_r \) is the relative velocity during polishing, and \( t_{\text{Beilby}} \) is the effective thickness of the Beilby layer. This relationship suggests that increasing the material removal rate should result in a decrease in the Beilby layer thickness (i.e., decrease the relative penetration of a given impurity). From the results shown in Fig. 1(a), K penetration is consistent with the behavior expected for diffusion, where K penetration decreases with increase in material removal rate. In contrast, the penetration of Ce into the near surface layer is inconsistent with a diffusion mechanism, because Ce penetration increases with increase in material removal rate [Fig. 1(b)]. This suggests that another mechanism, such as by chemical reactivity, rather than diffusion, dominates the penetration of Ce into the glass surface. In the next two sections, a more detailed set of mechanisms for K penetration by diffusion and Ce penetration due to chemical reactivity are proposed and discussed.

(2) K Penetration by Two-Step Diffusion

As discussed above, K diffusion into the surface of the fused silica glass occurs both during the polishing process as well as during subsequent postpolishing, room temperature storage. Hence K penetration into the surface is modeled as a two-step diffusion process. During the first (polishing) step, diffusion occurs at a moving surface boundary and steady-state is reached.\(^1^9\) Consider a fused silica surface in the presence of K ions from the slurry with a constant surface moving boundary of \( \frac{dC}{dt} \) (i.e., the polishing thickness removal rate). Using a concentration-independent diffusion coefficient \((D)\) for K in a semi-infinite solid in one dimension \((x)\), the steady-state diffusion process with moving boundary is proposed to simply follow an advection diffusion model:

\[ \frac{d}{dx} \left( D \frac{dC_K}{dx} + \frac{dC}{dt} C_K \right) = 0 \] (3)

where \( C_K \) is the K concentration. The solution to Eq. (3) has the form:

\[ C_K(x) = \frac{A}{(\frac{dC}{dt})} \exp \left( -\frac{D}{(\frac{dC}{dt})} x \right) \] (4)

where \( A \) is constant. The pre-exponential term is the surface concentration which is removal rate dependent in conformity to the experimental observation. Additionally, the form of Eq. (3) implies the magnitude of the diffusive flux \( D^* \frac{dC_K}{dx} \) is independent of removal rate. Also, note in Eq. (4) that the value of the exponential term will change with \( \frac{dC}{dt} \). In other words, the slope of K depth profiles on a semi-log plot should change with removal rate. Clearly the measured data does not show a significant change in slope [see Fig. 1(a)] even though the removal rate changed by ~10×. Again, this suggests that a single-step diffusion process is not sufficient to describe the observed data.

In the second step of diffusion, during storage, the source of K is now removed and the silica glass surface boundary is fixed. In this case, the time-dependent K diffusion is determined by Fick’s second law in the form:

\[ \frac{d}{dx} \left( D \frac{dC_K}{dx} \right) = \frac{dC_K}{dt} \] (5)

with the boundary conditions of zero concentration in the bulk glass and no removal of K from the surface of the glass. The authors were unable to find literature values for the room temperature K diffusion in fused silica. However, Na \((r = 0.95\) Å\) diffusion (expected to be similar to K \((r = 1.33\) Å\) near room temperature was measured by Frischak.\(^2^0\) Extrapolating their data to room temperature gives an approximate diffusivity of \(-10^{-16}\) cm²/s. Using this diffusivity value for both diffusion steps and a best fit value of \( A = 10^{26}\) cm⁻²/(µm/µs), the calculated diffusion curves are compared with the measured data two weeks after polishing at different removal rates (see Fig. 6). The dashed lines are
the calculated concentration depth profiles immediately after polishing while the solid lines are the calculated concentration profiles after two weeks of storage. The general shape, penetration depth, and material removal rate dependence of the two-step diffusion model are in good agreement with the experimental data, using only one fitting parameter. There is, however, a deviation in the detailed shape of final measured diffusion profiles with the two-step model using a constant diffusion coefficient (see Fig. 6). The authors hypothesize this deviation is due to changes in the diffusivity \( D \) of K with depth \( x \) due to changes in the structure of the glass in the Beilby layer with depth possibly resulting from OH penetration.

### (3) Ce Penetration by Chemical Reactivity

In contrast to the behavior of the K penetration, Ce penetration into the fused silica increases with polishing material removal rate. In fact, a quantitative correlation exists between the measured Ce depth profile and the measured material removal rate [Fig. 2(b)]. It is known that ceria plays a key role in the removal of silica from the glass surface during the polishing process. The most widely accepted chemical mechanism is by condensation and subsequent hydrolysis reactions given by \( 14 \):

\[
\begin{align*}
\text{Si} - \text{OH} + \text{HO}^{-} - \text{Ce} & \rightarrow \quad \text{Si} - \text{O} + \text{O}^{-} - \text{Ce} \equiv + \text{H}_2\text{O} \\
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Ce} - \text{O} - \text{Ce} & \equiv + \text{H}_2\text{O} \rightarrow \\
\text{Si} - \text{OH} + \text{HO}^{-} - \text{Si} - \text{O} - \text{Ce} - \text{O} - \text{Ce} & \equiv \quad (6a)
\end{align*}
\]

where reaction (6a) is the condensation reaction between the Si-OH silica surface and Ce-OH ceria particle surface, and reaction (6b) is the subsequent hydrolysis of the Si-O-Si bond leading to the removal of silica from the glass surface. Here, we propose another possible reaction where the hydrolysis can occur at the Ce-O-Ce bond leaving Ce behind on the silica surface, given by:

\[
\begin{align*}
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Ce} - \text{O} - \text{Ce} & \equiv + \text{H}_2\text{O} \rightarrow \\
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Ce} - \text{O} - \text{Ce} & \equiv + \text{H}_2\text{O} \rightarrow \\
\text{Si} - \text{O} - \text{Si} - \text{O} - \text{Ce} - \text{OH} + \text{HO}^{-} - \text{Ce} & \equiv \quad (6c)
\end{align*}
\]

Clearly for material removal to occur during polishing, the rate of reaction (6b) must be much greater than reaction (6c).

Consider the rate of deposition of Ce \( (R_{\text{dep}}) \) due to reaction (6c) and the rate of removal of Ce \( (R_{\text{rem}}) \) due to reaction (6b) from the moving silica surface during polishing. At steady-state, these rates will be equal:

\[
R_{\text{dep}} = R_{\text{rem}} \quad (7a)
\]

which can be rewritten in the form:

\[
2a \, v_p \, p_p \, S_p \, r_{\text{Ce-Si}} = 2a \, v_d \, d \, p_p [\text{Ce}]_s \quad (7b)
\]

where \( 2a \) is the contact diameter of a spherical polishing particle, \( v_p \) is the velocity of the polishing particle, \( p_p \) is the particle number density per unit area, \( S_p \) is the areal number density of Si atoms, \( d \) is removal depth or the bond length, \( r_{\text{Ce-Si}} \) is the hydrolysis reaction rate ratio between Ce–O–Ce and Si–O–Si, and \( [\text{Ce}]_s \) is the resulting steady-state Ce concentration at the surface. Note that \( 2a \, v_p \) is the \( \text{areal contact per slurry particle per unit time} \) and \( 2a \, v_d \, d \) is the \( \text{volumetric removal per slurry particle per unit time} \). Simplifying Eq. (7b) gives:

\[
[\text{Ce}]_s = \frac{S_p \, r_{\text{Ce-Si}}}{d} \quad (8)
\]

which suggests that the steady state Ce surface concentration will be dominated by the ratio of the two hydrolysis reactions \( (r_{\text{Ce-Si}}) \), since \( S_p \) (areal density of Si atoms) and \( d \) (removal depth) would be largely constant.

To account for changes in the Ce surface concentration with changes in material removal rate, we propose that the hydrolysis reaction ratio \( (r_{\text{Ce-Si}}) \) changes with interface temperature which is a function of the material removal rate. The interface temperature has been previously described for a single sliding particle, generating frictional heat at the moving contact interface given by\( ^{21-23} \):

\[
T = \frac{1.464 \, a \, Q}{k_{\text{SiO}_2} \, \sqrt{\pi (0.874 + Pe)}} \quad (9a)
\]

where:

\[
Q = \frac{\mu \, P \, v_p}{\pi \, a^2} \quad (9b)
\]

\[
P_e = \frac{v_p \, a \, P_{\text{SiO}} \, C_{\text{SiO}}}{2 \, k_{\text{SiO}}^2} \quad (9c)
\]

where \( a \) is the contact radius, \( Q \) is the frictional heat flux, \( P \) is the applied load, \( v_p \) is the particle velocity, \( P_{\text{SiO}} \) is the silica mass density \( (2.2 \, \text{gm/cm}^3) \), \( k_{\text{SiO}} \) is the thermal conductivity of silica \( [1.4 \, \text{W} / (\text{mK})] \), \( C_{\text{SiO}} \) is the head capacity of silica \( [740 \, \text{J} / (\text{kgK})] \), and \( P_e \) is the Peclet Number.

In a previous study, the average contact parameters were determined from polishing experiments and using a contact mechanics model, called the Ensemble Hertzian Gap (EHG) Model,\(^ {16} \) as \( a = 55 \, \text{nm} \) and \( P = 10^{-4} \, \text{N} \) (plastic removal). In addition, the material removal rate is related to the workpiece velocity by the Preston Equation [see Eq. (2)]\(^ {7} \) where the Preston Constant \( (k_p) \) is \( 2.2 \times 10^{-13} \, \text{m}^2 / \text{N} \) and the applied pressure \( (\sigma_0) \) is 0.6 psi. Using Eqs. (9a–c) to get the velocity dependence of the temperature rise and assuming the workpiece velocity \( (v_w) \) is equal to the particle velocity \( (v_p) \), the calculated temperature rise as a function of material removal rate [from Eq. (2)] is shown in Fig. 7. The results show that the particle–workpiece interface temperature increases at a rate 55 K for each 1 \, \text{mm} / \text{h} increase in removal rate. In a previous study,\(^ {24} \) the global temperature rise was measured during polishing under very similar conditions leading to a temperature rise of 1–2 K. Because the total
particle–workpiece contact area is small relative to the whole workpiece surface area, it is expected that the local interface temperature would be much higher than the global temperature of the system.

Next, we propose that $r_{Ce:Si}$ has an Arrhenius temperature dependence, then Eq. (8) can be rewritten as:

$$C_0 = \frac{S_p}{d} \frac{r_o \exp \left( \frac{-E}{RT(dh/dt)} \right)}$$

where $r_o$ is the pre-exponential constant, $E$ is the activation energy, $T(dh/dt)$ is the interface temperature as a function of removal rate (shown in Fig. 7). Figure 2(b) shows the comparison of the calculated Ce surface concentration (using $r_o = 80$ and $E = 10$ kcal/mol) with measured values from all SIMS results for each of the polishing samples. This model does a reasonable job matching the observed Ce surface concentration versus removal rate. The best fit activation energy value of $E = 10$ kcal/mol appears to be a reasonable value since hydrolysis activation of $Si-O-Si$ has been previously been reported to have similar values.25

### (4) Chemical-Structural-Mechanical Model of the Beilby Layer and the Polishing Process

The results of the present study together with previous work on polishing parameters,16 can be used to formulate a more detailed chemical-structural-mechanical picture of the Beilby layer and polishing process that leads to its formation (see Table II. Parameters Used for Developing Chemical–Mechanical-Structural Representation of the Beilby Layer and Polishing Process

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Si:X†</th>
<th>Source</th>
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<tr>
<td>Beilby layer thickness</td>
<td>$l_{Beilby}$</td>
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<td></td>
<td>This study</td>
</tr>
<tr>
<td>H surface concentration</td>
<td>$C_{H-s}$</td>
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<td>This study</td>
</tr>
<tr>
<td>Ce surface concentration</td>
<td>$C_{Ce-s}$</td>
<td>$5 \times 10^{19}$ atoms/cm$^3$</td>
<td>400:1</td>
<td>This study</td>
</tr>
<tr>
<td>K surface concentration</td>
<td>$C_{K-s}$</td>
<td>$1 \times 10^{18}$ atoms/cm$^3$</td>
<td>20 000:1</td>
<td>This study</td>
</tr>
<tr>
<td>Bulk SiO$_2$ structure</td>
<td>$Q^4:Q^3:Q^2:Q^1$</td>
<td>87:11:2:0</td>
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<td>[26]</td>
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<tr>
<td>Surface SiO$_2$ structure</td>
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<td>86:12:2:0</td>
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<td>This study</td>
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<tr>
<td>Removal rate</td>
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<td>Particle size</td>
<td>$r$</td>
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<td>[16]</td>
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<tr>
<td>Average load/particle</td>
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<td>$10^{-4}$ N</td>
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<td>Removal depth</td>
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<td>[16]</td>
</tr>
</tbody>
</table>

† Atomic ratio of Si ($2 \times 10^{22}$ atom/cm$^3$) to that of H, Ce or K.

![Fig. 8. Schematic representation of proposed chemical and structural model of the polishing process and the Beilby layer.](image-url)
Table II and Fig. 8). Consider the specific case where a fused silica sample is polished on a MHN polyurethane pad using ceria slurry, such as stabilized Hastelit PO ceria (see for example sample P1 in Table I). As the workpiece is polished, the Beilby layer is formed as impurities such as water (observed mass spectrometrically as H) and elemental impurities, such as Ce and K, penetrate into the glass structure, ultimately leading to a concentration profile which exponentially decays into the depth of the sample. The concentrations of each of the impurities, as noted by just the surface concentrations in Table II, are quite different. H is the highest having a H:Si ratio of 1:100, followed by Ce with Ce:Si ratio of 1:400, and then K with a K:Si ratio of 1:200 000. Given this, the depth of the Beilby layer is difficult to unambiguously define since each of these species penetrates to significantly different depths. Moreover, the depth a given species penetrates may be time and/or polishing rate dependent. For convenience, we define the depth of the Beilby layer in terms of the depth of Ce penetration. More specifically, for the present work we take the depth of the Beilby layer at the point where Ce concentration is no longer detectable from the SIMS measurement noise floor of $\sim 10^{10}$ atoms/cm$^2$. In this case, the depth is $\sim$50 nm. Note, however, given the exponential decay in the concentration, the vast majority of the Ce is present within just the first few nanometers of the surface.

The bonding structure of the fused silica surface is more difficult to determine. The bulk structural information for silica has been previously well characterized by solid-state NMR by many researchers. The Si Q species describes the quaternary oxygen tetrahedron in the glass structure, where $Q^4$ represent 4 Si–O neighbors, $Q^3$ represents 3 Si–O neighbors, etc. The greater the fraction of $Q^4$, the more cross-linked structure of the glass. It is reasonable that K and H behave as network modifiers, decreasing the cross-linking of the glass structure. Similarly, Ce would be expected to behave as a network former. By assuming that all the K and H species detected in the surface layer act as network modifiers, one can compare the estimated distribution of Q species in the surface layer to that of bulk fused silica (see Table II). Table II, as shown in Table II, the resulting change in the calculated Q species ratio suggests only a minor reduction in cross-linking. This small change reflects the low abundance of ions and atomic impurities such as H, Ce, and K relative to the number of Si and O atoms even in the near surface layer of the glass.

The mechanical aspects of the contact between a polishing particle and the glass surface can be determined using the results of our previous study. Here the mechanics of particles loaded on glass surface were evaluated using the measured slurry particle size distribution and the EHG model. The model is based on multiple Hertzian contacts of slurry particles at the workpiece–pad interface in which the effective interface gap is determined through an elastic load balance. Using this formulation, the load, penetration, and contact zone distributions were determined from the slurry particle size distribution. In addition, the removal function for a single sliding particle was experimentally determined in the course of this study. The resulting parameters are summarized in Table II; the average particle size (resulting in plastic type removal) was $\sim$800 nm with an average load of 10$^{-2}$ N resulting in an elastic contact zone of 110 nm, a penetration depth of 3.8 nm, and removal depth of 1 nm.

Combining these parameters with information from the present study and accounting for the material removal rate, allows the development of a schematic representation of the important chemical, structural, and mechanical aspects of the Beilby layer and the polishing process to be represented (Fig. 8). Here, a single $\sim$800 nm particle slides under load on the glass surface from left to right. The particle size, contact zone, penetration depth, and Beilby layer thickness are shown to scale. The presence of chemical impurities, such as H and Ce, in the surface layer is indicated by the colored dots; the density of which corresponds to the relative areal concentrations expected in the scale length of the model. The pictorial inserts represent a more detailed view of the glass structure both at and just below the particle–glass interface. Because of the exponential decay in the concentration of impurities, the Beilby layer resembles the bulk glass within just a few nanometers of the surface. Also, because the K concentration is so low it does not, on average, appear within the scale length of the model shown in Fig. 8.

V. Conclusions

SIMS-based measurements of the depth profile of K, Ce, and H impurities on the surfaces of fused silica glasses prepared under different polishing conditions reveal important chemical and physical characteristics of the near surface Beilby layer. For ions, such as K, penetration appears to occur as a two-step diffusion process. In contrast, ions such as Ce, which are active participants in the polishing process, the depth penetration appears to be consistent with a mechanism which depends on the relative rate of hydroxylation between Ce–O–Si and Si–O–Si, where the ratio increases with interface temperature (which increases with polishing removal rate).

Finally, using this insight, combined with mechanical loading information of individual polishing particles from a previous study, a more detailed chemical-structural-mechanical picture of the Beilby layer formation and polishing process has been formulated.

Acknowledgments

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344 within the LDRD program. Special thanks to Ed Sedillo for performing the FE-SEM measurements.

References


