Friction Forces in Electrolyte Solutions

Bogdan C. Donose, Ivan U. Vakarelski and Ko Higashitani

Department of Chemical Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
Email: bdonose@cheme.kyoto-u.ac.jp, vakarelski@cheme.kyoto-u.ac.jp, k_higa@cheme.kyoto-u.ac.jp

ABSTRACT

The friction between a single silica sphere attached to a rectangular cantilever and a flat silicon wafer in different concentration electrolyte solutions has been investigated using lateral force microscopy. In order to obtain clean and hydrophilic substrates the wafers have been washed in organic solvents and then, they have been plasma treated in Argon gas-moisture atmosphere. The lateral friction force as a function of applied normal loads has been collected and the range of electrolyte concentrations varied between 10^{-3} and 1.0 M. Analysis of the friction versus load data indicates that increasing the electrolyte concentration, the intensity of the lateral signal decreases. Lateral force versus scan rate graphs show a typical behavior for all investigated systems: at low values of scan rate, a transition region (from 0.4 to 20 \mu m/s) and a saturation region (between 20 \mu m/s and 55 \mu m/s). The friction trends behavior is discussed and a model is proposed.

KEYWORDS

lateral force microscopy, friction, silicon wafer, electrolyte solutions

INTRODUCTION

Understanding of the tribological phenomena in a nanoscale level is of critical importance for the fast development of existing and emerging technologies such as the Chemical Mechanical Planarization (CMP) and microelectromecanical systems (MEMS). The colloidal and frictional behavior of the silica, which is an important component in these technologies have been long known to be far more complex than expected for smooth, chemically inert surfaces (Vigil, et al.,1994). The Atomic Force Microscope (AFM), used in Friction Force Microscopy (FFM) mode proves to be an ideal instrument to study the frictional phenomenon down to atomic scale.

In our present study, we are aiming to show the influence of salt concentration on the recorded lateral force signal. It has been previously reported (using as investigation tool a Surface Force Balance) that in the case of mica-mica interaction, in aqueous salt solution, the surface attached hydration layers keep the surfaces apart because of strongly repulsive hydration forces (Raviv and Klein,2002).

MATERIALS AND METHODS

The 6.84-\mu (diameter) commercially available monodispersed nonporous silica particles were purchased from Bangs Laboratories. The silicon wafers (P-type, <100> crystal orientation, producer provided root mean square roughness about 0.2nm) have been kindly provided by Shin-Etsu Chemical Co., Ltd.
The LiCl, NaCl, CsCl (Wako, Co.) employed were of analytical grade and the water used for all the experiments was produced by a Milipore filtration system, with an internal specific resistance of $17.0 \pm 0.1 \, \text{M}\Omega/\text{cm}$. In table 1 are shown the cations properties (Israelachvili, 1992).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Diameter [nm]</th>
<th>Hydrated ionic diameter [nm]</th>
<th>Hydration number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+$</td>
<td>0.338</td>
<td>0.66</td>
<td>1-2</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.266</td>
<td>0.72</td>
<td>4-5</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>0.136</td>
<td>0.76</td>
<td>5-6</td>
</tr>
</tbody>
</table>

All the experiments were made using a Digital Instruments Nanoscope III multimode atomic force microscope, equipped with a fused silica liquid cell. In all friction sessions of measurements we have been using tipless rectangular cantilevers (nominal spring constant $K_N=1.75\, \text{N/m}$), purchased from MikroMasch Co. Prior to use, the wafers were thoroughly washed in acetone (99.5 vol.%, Sigma Aldrich, Japan), ethanol (99.5vol.%, Chameleon Reagent, Osaka, Japan) and pure water and after that they were plasma treated for 3-5 minutes in Ar-moisture atmosphere. Silica particles were attached to the cantilever end using thermoplastic epoxy adhesive (Shell Epikote).

In a typical friction force microscopy (FFM) experiment the colloidal probe is pressed against the substrate at a constant applied force while the substrate slides horizontally. The recorded data represents the semi difference of the lateral detector signal in one complete scan loop.

The lateral force magnitude, $F_L$ is determined according to eq.1:

$$F_L = \frac{1}{2}V_L S_L \frac{K_L}{H}$$

where $S_L$ is the lateral detector sensitivity, $K_L$ is the lateral spring constant, $V_L$ is the lateral force detector signal in one scanning loop, and $H$ is the distance from the bottom of the sphere to the midpoint of the cantilever (Vakarelski, et al., 2003).

The detector sensitivity in lateral direction was determined using the method of Meurk et all (1998) and the lateral spring constant, $K_L$ was determined from the rectangular lever dimensions using the following equation:

$$K_L = \frac{K_n L^2}{3(1+v)}$$

![Figure 1. Lateral Force Microscopy Setup](image)
where \( \upsilon \) is Poisson ratio, \( K_N \) is normal spring constant and \( L \) is the lever length. The normal spring constant has been determined by resonance frequency method (Cleveland, et al., 1993).

The lateral force vs. loading force trends were recorded for a scan span of 1\( \mu \)m, at 2\( \mu \)m/s scanning velocity. The lateral force vs. scanning speed curves were done at 175nN loading force.

For all the experiments the room temperature was kept constant, at values about 23°C.

**RESULTS AND DISCUSSIONS**

**Friction trends in water and data reproducibility**

In order to obtain a reference basic behavior we have measured, at first, interaction forces and lateral force trends in pure water. Figure 2 illustrates the lateral force versus loading force curves for the case of silica surfaces interacting across pure water, which exhibit a linear behavior, in agreement with Amonton’s Law:

\[
F_f = \mu \cdot F_L
\]  

(3)

where \( F_f \) is the friction force, \( \mu \) the friction coefficient and \( F_L \) is loading force.

When there is no force applied to the surfaces, the negative charge coverage of the oxide is a result of the following ionization reaction (\( \text{pH} > \text{isoelectric point} \)):

\[
\text{-SiOH} + \text{OH}^- \quad \overset{k}{\leftrightarrow} \quad \text{-SiO}^- + \text{H}_2\text{O}
\]

(4)

where \( k \) is the equilibrium constant(Franks, et al.,1997).

As the force between particle and substrate is increased, the reaction is forced to left (the equilibrium being temperature and pressure dependent). Therefore, the contact will occur between two neutralized surfaces (Figure 3) Si-OH; thus, high values for lateral force.

**Figure 2. Lateral force as a function of the applied load for a 6.84\( \mu \)m silica sphere attached to a rectangular cantilever interacting with a polished silica wafer in pure DI water.**

**Figure 3. Possible schematic view of the close contacted silica surfaces, in pure water.**
The repeatability of trends, in consecutive experiments, leads us to conclude that the sliding process does not promote a detectable change in investigated system roughness.

**Salt concentration effect**

The next step in our investigation was to study LiCl concentration effect on lateral force signal. The trends from Figure 4 show that increasing the number of adsorbed ionic species (Li⁺) on the negatively charged silica surface, we can get a drastic effect on the recorded lateral forces (from pure water to 1.0M LiCl there is a 75% drop in friction coefficient).

According to the reference hypernetted chain model (RHCM) developed by Torrie et all (1989), the layer of structured water on charged surfaces is more likely to accept small ions with high affinity for water. These ions tend to crowd near the charged surface.

The reduction of friction coefficient after the lithium injection might be explained by the fact that the strongly hydrated lithium ions create a buffer zone that prevents the contact.

At lower concentration, the direct contact is blocked by fewer adsorbed ions.

Increasing gradually the concentration, we will obtain a full coverage of surface with hydrated lithium ions, having as subsequent result lower friction. Lithium ions “steal” the water from the silica hydration layer and dominate the friction by their water shell.

![Figure 4. Lateral force as a function of the applied load for a 6.8μm silica sphere interacting with a polished silica wafer in pure DI water, 0.001 M LiCl, 0.1M LiCl and 1.0M LiCl.](image)

![Figure 5. Possible configuration of the close contacted silica surfaces, in 1.0M LiCl solution.](image)
Cation type influence

The friction trends for three types of solutions (Figure 5), at the same concentration (1.0M), show that the lubrication effect is in relation with the size and hydration properties of the involved cation.

Franks et al. suggests that large cations, as Cs⁺, prefer to reside outside of the hydration layer of silica and additional experimental reports proved that the counterions in the series Li⁺ through Cs⁺ could not be pushed away from silica surfaces, in Surface Force Apparatus experiments (Chapel, 1994) until the pressure was enough.

Knowing that in our experiments, we could not exert enough pressure to remove the cations (otherwise friction trends would be water-like) we can assume that cesium remains trapped in contact region and it is responsible for high values of friction coefficient (compared with lithium) because of its weak ability to structure water and to prevent direct contact.

Figure 6. Possible configuration of the close contacted silica surfaces, in 1.0M CsCl solution.

The intermediary behavior of friction in presence of natrium, between lithium and cesium, comes to consolidate the hypothesis about cation series influence on friction.
Scanning velocity effect

The records of scanning velocity influence on lateral force show the transition from boundary lubrication (between 0.4-20 µm/s) to hydrodynamic lubrication (~20-55 µm/s).

At low values for scan rate there is enough time to break the organized structures near silica, and close contact between hydrogen-neutralized surfaces is responsible for higher friction forces. Higher scan rates induce lower forces opposing sliding because there is not enough time to break organized structures. Beyond certain values of scan rate, the four systems reach a level of equilibrium: the organization degree reaching a saturation stage, hydrodynamic lubrication.

Going back to the first value of scan rate, at the end of each measurement session, we could attain approximately the same friction force. The width of the transition area might be a result of the ion size influence.

The trends demonstrated on Figure 6 and Figure 7 suggests that the more hydrated cations produce a stronger lubrication effect: the thicker the hydration shell – the stronger is the effect.

CONCLUSIONS

The results of this study may not be accurate enough to estimate with a high degree of certainty the molecular behavior in the case of silica-silica contact in electrolyte solutions.

The presence of metallic ions at the silica-silica interface induces gradually, the reduction of friction coefficient (µ_{Cs^{+}} > µ_{Na^{+}} > µ_{Li^{+}}).

For all electrolyte solutions, the dependence of lateral force with scanning velocity shows typical behavior: transition and saturation regions. The differences occur due to the properties of the confined layers.

The results indicate that the adsorbed layers on silica surfaces undergo structural changes during sliding.

ACKNOWLEDGEMENTS

The work was supported by a Grant-in-Aid for Scientific Research (A)(2) No. 1520685. We also thank Shin-Etsu Chemical Co., Ltd, Japan for providing us gift samples of wafers.
REFERENCES


