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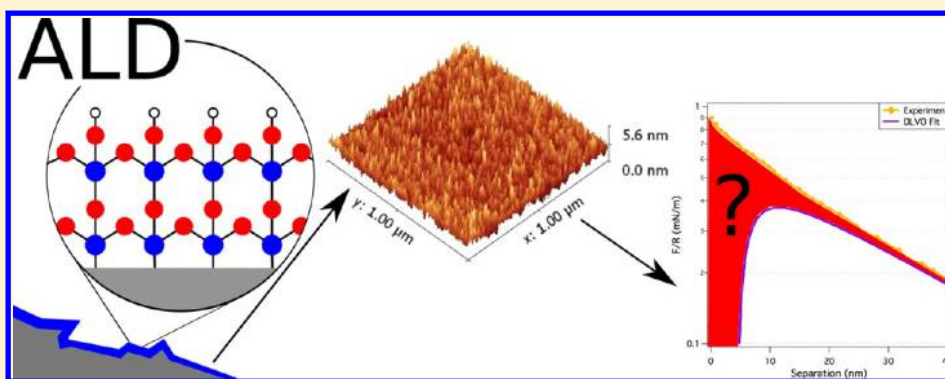
# Surface Force Measurements between Titanium Dioxide Surfaces Prepared by Atomic Layer Deposition in Electrolyte Solutions Reveal Non-DLVO Interactions: Influence of Water and Argon Plasma Cleaning

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## S Supporting Information



**ABSTRACT:** Surface force measurements between titania surfaces in electrolyte solutions have previously revealed an unexplained long-range repulsive force at high pH, not described by Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory. Here, the surface forces between titania surfaces produced by atomic layer deposition (ALD) and cleaned using a variety of methods have been measured to determine the influence of the cleaning protocol on the measured forces and test the hypothesis that water plasma cleaning of the surface results in non-DLVO forces at high pH. For argon plasma and water plasma cleaned surfaces, a diffuse double layer repulsion and van der Waals attraction is observed near the isoelectric point. At high pH, the force remained repulsive up until contact, and no van der Waals attraction or adhesion was observed. Differences in the measured forces are explained by modification of the surface chemistry during cleaning, which alters the density of charged groups on the surface, but this cannot explain the observed disagreement with DLVO theory at high pH.

## INTRODUCTION

An understanding of surfaces forces is essential for exerting control over a wide range of hard and soft colloidal systems including lubrication, rheology, colloid stability, materials science, and cellular interactions. Commonly silica,<sup>1</sup> mica,<sup>2</sup> and gold<sup>3</sup> have been studied, although other materials have also been examined.<sup>4,5</sup> Very few surface force investigations between mineral oxides have been reported,<sup>6–10</sup> despite the strong interest in these materials, as preparing them in a suitable form is difficult. Precise quantitative force measurements require suitable geometries, typically crossed cylinders or a flat and sphere with minimal surface roughness and no porosity. Use of atomic layer deposition (ALD), a technique widely used in the production of electronic devices, has provided a means to manufacture a range of previously unavailable surfaces for force and surface science investigations.<sup>7,11</sup> ALD involves the coating of a substrate with a material, one atomic layer at a time. The resulting conformal film adds little roughness, when grown

under appropriate conditions.<sup>7,12</sup> In this study, we describe force measurements between ALD produced titanium dioxide (titania) surfaces.

Titania is an industrial and technologically important mineral oxide. Primarily it has found use as a light-scattering pigment, due to its high refractive index. It also finds use in photocatalysis, optical coatings, solar cells, and as the native coating of medical implants, which promotes biocompatibility. It is a material that is chemically stable, nontoxic, nonsoluble, and has a readily accessible isoelectric point (IEP),<sup>13</sup> making it highly useful for fundamental surface science studies.

Our interest lies in gaining a better understanding of the change in the forces between titania surfaces in aqueous solution when the pH is varied. It was noted previously<sup>7</sup> that

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the surface forces between titania show behavior described by the Derjaguin, Landau, Verwey, and Overbeek (DLVO)<sup>14,15</sup> theory near the IEP. That is, the interaction is fitted by a combination of an electrostatic (repulsive) force and a van der Waals (attractive force). However, at high pH an anomaly occurs; the van der Waals component of the DLVO theory is not observed. Instead, a monotonic repulsive force is seen all of the way into contact. This repulsion is similar to the repulsion seen previously between silica surfaces,<sup>16</sup> which has been explained as originating from either surface roughness or hydration forces or a combination of these. The van der Waals attraction between titania surfaces in aqueous solution is an order of magnitude greater than that between silica surfaces in aqueous solution, as illustrated by the difference in the Hamaker constants for silica and titania across water (4.8 zJ<sup>17</sup> and 60.5 zJ, respectively). Given the low roughness of the surfaces employed in the previous study<sup>7</sup> and the short-range of the hydration force<sup>18</sup> (exponential decay length <0.3 nm), it is unlikely that the combination of these effects explains the observed interaction. That is, the dispersion forces between titania surfaces across water are of a range that is sufficiently great that hydration forces in combination with surface roughness should not counteract their influence.

Surface swelling at high pH, as the surfaces acquire a negative charge, provides a possible explanation for the observed forces. Such swelling will lead to the formation of a gel layer that will alter the surface forces by effectively adding an additional repulsion, associated with collapsing and dehydrating the gel layer, and additionally reduce the van der Waals attraction by lowering the density of the titania surface. Here, we test the hypothesis that the radio frequency discharge water plasma treatment employed to clean the surfaces used in our force investigations promotes the formation of a gel layer at the surface and is therefore responsible for the non-DLVO repulsion seen at small separations. We have measured the surface forces between titania surfaces to investigate the influence of the cleaning protocol on the measured interaction.

## ■ EXPERIMENTAL METHODS

**Atomic Layer Deposition Surfaces.** Boron doped silicon (100) wafers, MEMC, U.S., and borosilicate spheres of monomodal size distribution and radius  $10 \pm 0.1 \mu\text{m}$ , supplied by Duke (borosilicate glass 9020), were used as substrates for atomic layer deposition (ALD). Prior to the deposition of titania using ALD, RF water plasma (30 W for 90 s, followed by 50 W for 30 s) was used to clean the substrates using an in-house RF plasma reactor. ALD of titania was performed using a Savannah 100 (Cambridge Nanotech system) with titanium isopropoxide and water as precursors. The Ti precursor was heated to 80 °C. The water used in the reactor was at room temperature. Deposition was carried out with the reaction chamber at 80 °C. Nitrogen was used as the carrier gas at a flow rate of 20 sccm (standard cubic centimeter per minute). A deposition cycle consists of a 0.015 s pulse of Ti precursor, followed by a 10 s nitrogen purge, then a 0.015 s pulse of water, followed by a 10 s nitrogen purge. A total of 1600 cycles were performed to produce a 102 nm thick layer of titania.

**Surface Cleaning Methods.** The cleaning methods of interest are:

(1) Argon plasma treatment was performed using an in-house RF plasma reactor. Surfaces were cleaned with a 10 W plasma, generated using a frequency of 130 MHz for 30 s. To ensure the exclusion of water during this treatment, the system was purged multiple times with argon prior to plasma generation.

(2) Ultraviolet radiation cleaning of the surfaces was achieved by irradiating with UV light for a period of 48 h in a UV light box, containing 16 NEC FL8BL 8W lamps in a cylindrical formation.

During treatment, surfaces were enclosed in a metal container with a quartz lid. UV irradiation was performed in a humid atmosphere, achieved by placing a drop of Milli-Q water (conductivity  $\sim 18.2 \text{ M}\Omega$ ) inside the metal container during treatment.

(3) Water plasma treatment was previously<sup>7</sup> employed to clean titania surfaces, using an in-house RF plasma reactor, whereby the surfaces were exposed to plasma generated at 10 W using a frequency of 130 MHz for a period of 30 s.

**Surface Force Measurements.** The surface forces between a spherical titania-coated particle and a titania-coated surface were measured using a Digital Instruments Multimode Nanoscope III AFM, using a fluid cell, under aqueous conditions. Force measurements were performed using the colloid probe technique developed by Ducker et al.<sup>16</sup> and Butt et al.<sup>19</sup> An ALD-coated sphere was attached to the end of a rectangular silicon nitride cantilever (CSG11 supplied by ND-MDT), using purified Epikote 1004 resin (Shell). The interaction forces between an ALD titania colloid probe and an ALD titania surface were investigated. The colloid probes were imaged to determine the radius of the particle as well as the position of the particle on the cantilever using a Zeiss UltraPlus analytical FESEM. Prior to particle attachment, the cantilevers were calibrated using the thermal tune method using an Asylum Picoforce AFM. The spring constant was corrected for off-end loading due to the attachment of the colloid particle to the tip using the correction detailed in Sader et al.<sup>20</sup>

Analytical grade chemicals were used. NaCl was roasted at 400 °C for at least 12 h before use to remove organic contaminants. The pH was adjusted by the addition of either HCl or NaOH to the solution. All solutions were prepared using Milli-Q water. Prior to use, all glassware was soaked in a 10 w/w% NaOH solution for 10 min, and then rinsed with copious amounts of Milli-Q water. Before injection into the AFM fluid cell, solutions were bubbled with high-purity nitrogen gas, sourced from liquid nitrogen, to remove surface active contaminants following the method of Parkinson.<sup>21</sup> As the freshly cleaned surfaces are hydrophilic, the increase in the dissolved gas content of the solution should have no significant effect on our measurements.

**Contact Angle.** The contact angle of water droplets on the ALD surface was measured using a KSV CAM-200 optical contact angle meter. Advancing and receding contact angles of the cleaned titania surfaces were measured.

**Atomic Force Microscope Imaging.** Atomic force microscope height mode images of ALD surfaces in air were obtained using a Nanoscope Multimode IIIa AFM with phase extender box in tapping mode. Tap300Al cantilevers of nominal resonance frequency 300 kHz and spring constant  $40 \text{ N m}^{-1}$ , supplied by Budget Sensors, were employed and the feedback parameters adjusted to minimize the features in the amplitude image. Atomic force microscope height mode images of ALD surfaces immersed in water were obtained using a Bruker Multimode 8 AFM in ScanAsyst mode.

**X-ray Photoelectron Spectroscopy.** Analysis of the surface chemistry for the treated surfaces was conducted using X-ray photoelectron spectroscopy (Specs, XPS) using a nonmonochromated Mg X-ray source.

## ■ RESULTS AND DISCUSSION

**Plasma Treatment.** During water plasma treatment, the radio frequency field cleaves the bonds of the water molecule, forming hydrogen and hydroxyl radicals.<sup>22</sup> Upon exposure to these radicals, organic contamination on the surface is decomposed and removed. Additionally, reaction of the radicals with the surface results in modification of the chemical groups that terminate the surface. This may change the surface wettability and charging properties. The extent of the modification of the surface is dependent on the duration and intensity of the plasma exposure. Treatment with water plasma exposes the surface to hydroxyl radicals and is therefore expected to increase the number density of titanol groups on

the surface. As these groups are acidic in aqueous solution, this will lead to an increase in the magnitude of the negative charge when the surface is immersed in aqueous solution.

**Contact Angle Measurements.** Titania surfaces exposed to air will quickly acquire a layer of contamination. Typically, this will lower the surface energy and lead to an increase in the contact angle of water. Therefore, we employed contact angle measurements to follow the efficacy of the cleaning treatments we employed. The measured advancing and receding contact angles of water on titania surfaces are summarized in Table 1.

**Table 1. Measured Contact Angles of Water on Titania Surfaces**

treatment	power (W)	duration	advancing contact angle (deg)	receding contact angle (deg)
untreated			$74 \pm 4$	<10
argon plasma	10	30 s	<10	<10
H <sub>2</sub> O plasma	10	30 s	<10	<10
UV light		48 h	<10	<10

The advancing contact angle of the untreated titania surface was measured to be  $74 \pm 4^\circ$ . In all cases, the cleaning treatments caused a reduction in the advancing contact angle to a value of less than  $10^\circ$ , indicating that contamination had been removed from the surface.

**Determination of Roughness.** Tapping mode images of argon plasma and water plasma treated surfaces are presented in Figure 1. The argon plasma treated surfaces have a roughness of 0.62 nm RMS over a  $1000 \text{ nm} \times 1000 \text{ nm}$  area, and the roughness of water plasma treated surfaces over the same area was 0.64 nm RMS. As the difference between these measures is not significant, we conclude that the surface roughness is not dependent on the type of plasma treatment. No attempts to image surfaces that had not been submitted to a cleaning treatment were made, as the presence of contaminants on the surface will influence the image obtained.

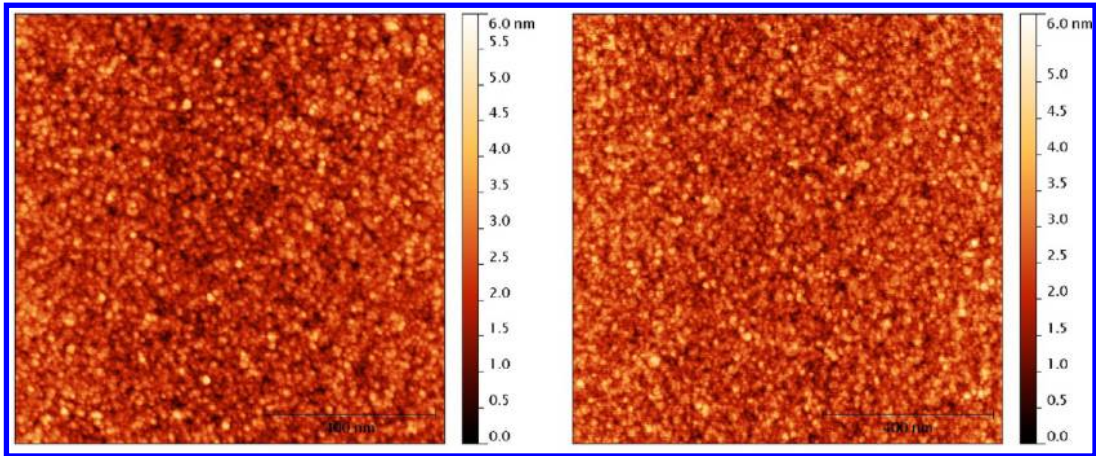
To evaluate any influence that the solvent may have on the surface such as causing it to swell, a water plasma treated ALD titania surface was also imaged under water as shown in Figure 2. We found that the image exhibited the same features as in air

and that the surface roughness was unchanged, suggesting that the solvent did not significantly alter the surface morphology. Upon increasing the pH to 9, there was no significant change to the surface, indicating that increasing the pH does not change the surface morphology.

**Surface Force Measurements.** Force measurements made between surfaces cleaned with argon plasma are presented in Figure 3. The measurements were obtained in  $10^{-4} \text{ M NaCl}$ , and the pH was adjusted by adding HCl or NaOH. At pH 6.0 a repulsion is observed from a separation of  $\sim 70 \text{ nm}$ , which increases exponentially up to  $\sim 10 \text{ nm}$  where the force begins to become attractive. As the surfaces are separated, the surfaces adhere. Increasing the pH to 7 leads to an increase in the magnitude of the diffuse double layer repulsion. The repulsion is apparent at separations of 80 nm and increases exponentially as separation is reduced. When the pH is increased to 9, the magnitude of the diffuse double layer repulsion increases further, while the decay length of the force decreases. This decrease is caused by the increased ionic strength of the pH 9 solution as compared to pH 7, associated with the increased quantity of NaOH required to adjust the pH to 9. No adhesion occurs at pH 9.

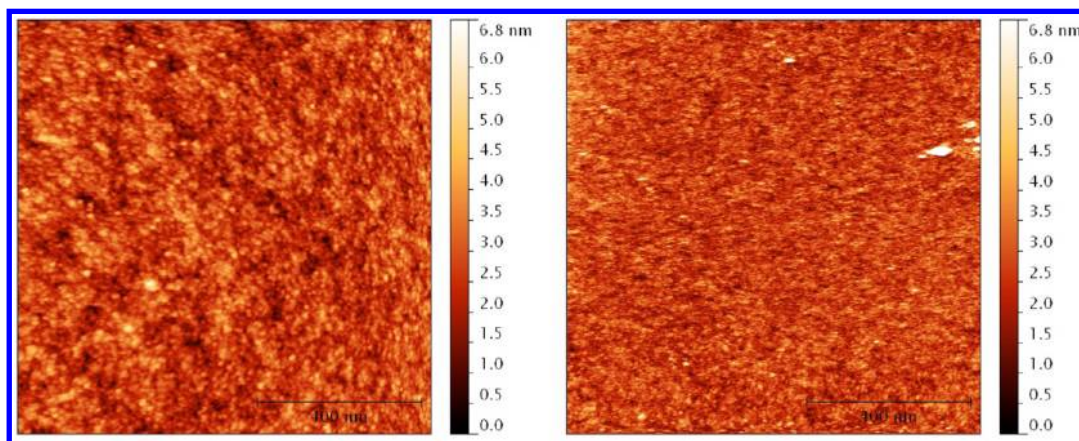
Each of the force measurements for argon plasma cleaned surfaces was fitted by DLVO theory using in-house software.<sup>23</sup> This software employs the Chan, Pashley, and White<sup>24</sup> algorithm to solve the nonlinear Poisson–Boltzmann equation. Examples of the fits obtained at pH 5.5 and pH 9 are shown in Figure 4.

Under the DLVO theory paradigm, the van der Waals attraction should be observed at small separation at all values of the pH studied here. Indeed, this is the case near the IEP, and the measured force is well described by DLVO theory at all separations, where the limits are defined by the constant charge and constant potential boundary conditions. At a pH of 7 or higher, the force can be described by the diffuse double layer force alone, as the attractive component of the DLVO theory is not observed, and instead the force remains repulsive up until contact. For comparison, an example of the surface force measurements made by Walsh et al.<sup>7</sup> between water plasma cleaned titania surfaces in aqueous  $10^{-4} \text{ M NaCl}$  adjusted for pH is presented in Figure 5. The same general features are observed, although the magnitude of the electrostatic double

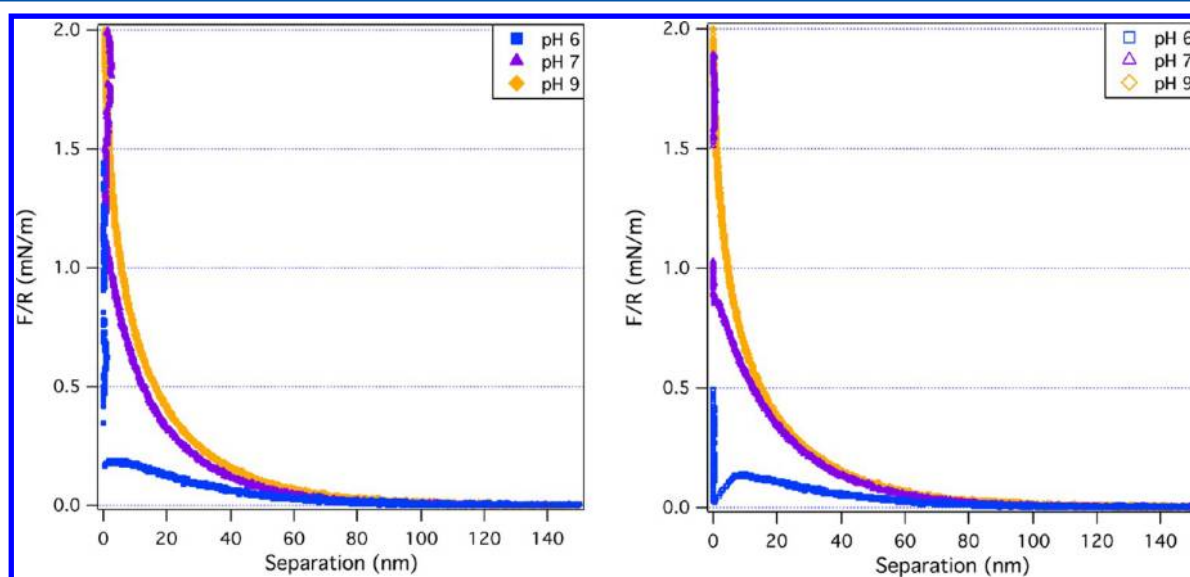


**Figure 1.** Tapping mode AFM images of argon plasma cleaned (left) and water plasma cleaned (right) ALD titania surfaces. The surface roughness over an area of  $1000 \text{ nm} \times 1000 \text{ nm}$  was determined to be 0.62 nm RMS for the argon plasma treated surface and 0.64 nm RMS for the water plasma treated surface. The scale bar in each image is 400 nm long.





**Figure 2.** ScanAsyst mode AFM image of a water plasma cleaned ALD titania surface immersed in water (left) and water adjusted to pH 9 (right). The RMS surface roughness over an area of  $1000\text{ nm} \times 1000\text{ nm}$  was determined to be  $0.67\text{ nm}$  in water and  $0.7\text{ nm}$  at pH 9. The same surface imaged in air gave an RMS roughness of  $0.68\text{ nm}$  over an area of  $1000\text{ nm} \times 1000\text{ nm}$ . The scale bar in the image is  $400\text{ nm}$  long.

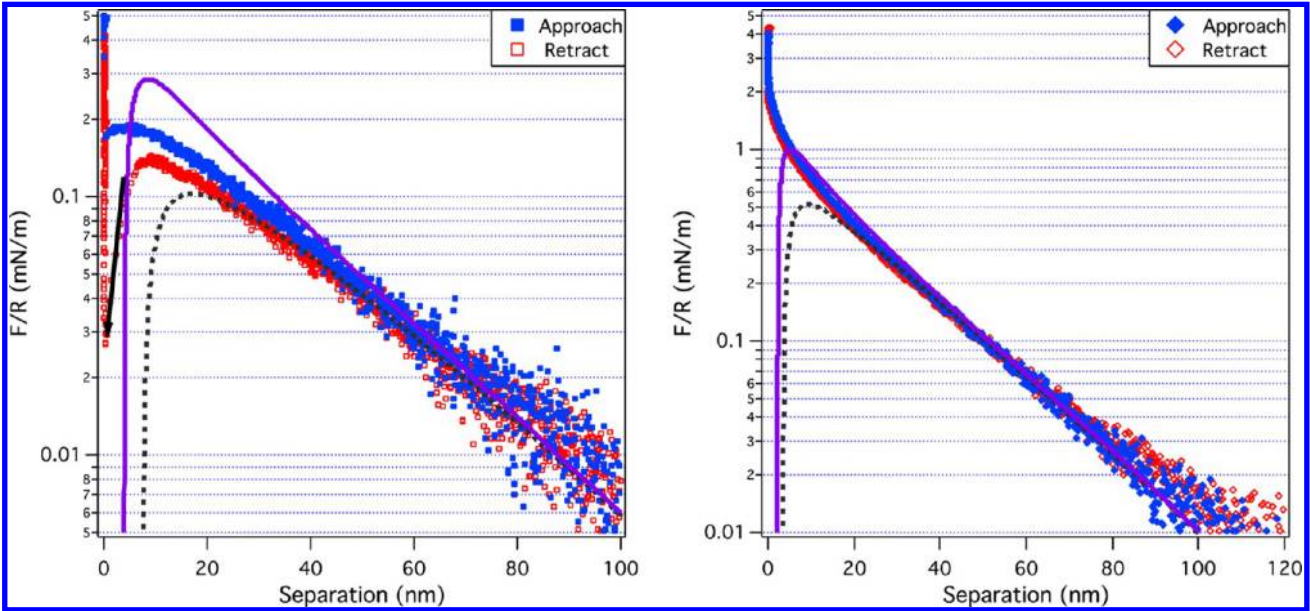


**Figure 3.** Surface force measurements between titania surfaces cleaned with argon plasma. Measurements were made in an aqueous solution of  $10^{-4}\text{ M}$  NaCl with pH adjustment. Force measurements obtained on approach are presented on the left and upon separation are on the right.

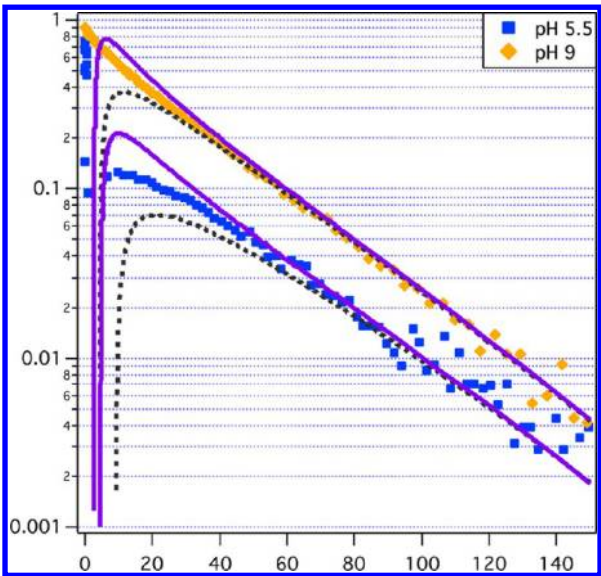
layer repulsion differs. For water plasma cleaned surfaces at pH 5.5, the force is attractive from a separation of  $15\text{ nm}$ , which leads to a spring instability at  $\sim 10\text{ nm}$ , where the gradient of the force exceeds the spring constant of the cantilever and the surfaces jump into contact. This attraction was fitted by a van der Waals interaction with a Hamaker constant of  $60.5\text{ zJ}$ . This agrees with our theoretical calculation of the dispersion forces using Lifshitz theory. We used the Hamaker constant that best fit the full calculation to simplify the fitting approach. The agreement between the full calculation and the Hamaker approach was good at all separations without the need to include retardation in the Hamaker approach. The comparison is provided in the Supporting Information. Upon separation, the surfaces adhere. At high pH the force is repulsive at all separations, no attraction is observed, and there is no adhesion. In both cases, an additional repulsion occurs once the pH is greater than 7, preventing the van der Waals attraction from being seen. Because the additional repulsion occurs for both water plasma and argon plasma cleaned surfaces, we conclude that the water plasma treatment of the surface is not the cause of the observed repulsion at short-range.

A summary of the surface charge and surface potential parameters for DLVO fits is provided in Table 2. The surface charge and surface potential are greater in magnitude for the surfaces treated with water plasma. In all cases, the fitted Debye length was between  $19$  and  $31\text{ nm}$ , and a Hamaker constant of  $60.5\text{ zJ}$  was used.

Measurements of the surface force at pH 4 were also undertaken; these are presented in Figure 6. For the argon plasma treated surface, a repulsion is observed from a separation of  $\sim 80\text{ nm}$ , which increases exponentially up to  $\sim 15\text{ nm}$  where the force begins to become attractive, which leads to a spring instability at  $\sim 8\text{ nm}$ . As the surfaces are separated, the surfaces adhere. This force measurement was fitted using the DLVO theory, with a Hamaker constant of  $60.5\text{ zJ}$ , a surface potential of  $22\text{ mV}$ , and a Debye length of  $21\text{ nm}$ . After the surface has been cleaned with water plasma, the forces are quite different. An attractive force is observed from a separation of  $150\text{ nm}$ , which leads to a spring instability at  $25\text{ nm}$ . The magnitude of this force is much larger than the predicted van der Waals attraction, and a large magnitude adhesion is measured upon separation. It was also found that



**Figure 4.** Surface force measurements between titania surfaces cleaned using argon plasma. Measurements were performed in an aqueous solution of  $10^{-4}$  M NaCl with the pH adjusted to pH 5.5 (left) and pH 9 (right). The data measured on approach were fitted with the DLVO theory, for the constant charge (solid line) and constant potential (dotted line) boundary conditions, using a Debye length of 29 nm and a Hamaker constant of 60.5 zJ. A surface potential of  $-34$  mV or a surface charge of  $-0.16$  C/m<sup>2</sup> was determined for pH 5 measurements and a surface potential of  $-61$  mV or a surface charge of  $-0.34$  C/m<sup>2</sup> for pH 9.

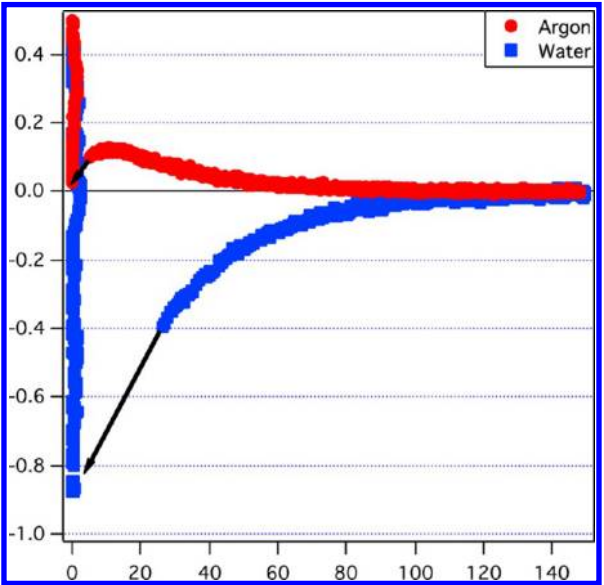


**Figure 5.** Surface force measurements made by Walsh et al.<sup>7</sup> between titania surfaces cleaned with water plasma. Measurements were made in a solution of  $10^{-4}$  M NaCl with the pH adjusted to 5.5 and 9. The data measured on approach were fitted with the DLVO theory, for the constant charge (solid) and constant potential (dotted) boundary conditions. Debye lengths of 29 and 24 nm were used in the DLVO fits for pH 5.5 and 9, respectively.

this attraction did not follow an inverse power law such as that seen for the van der Waals force. Instead, the attraction increases exponentially, which is indicative of an electrostatic type force. Attempts to describe the interaction with a double layer force, where the surfaces have equal but opposite charges, result in a fitted surface potential of  $\sim 60$  mV, which is not credible. Another possible theory that could possibly explain the experimental measurements is the “patchy” charged surfaces model, such as those described by Miklavic et al.<sup>25</sup> and

**Table 2.** Fitted DLVO Surface Potential and Surface Charge Values for Treated Titania Surfaces

pH	argon plasma cleaned		water plasma cleaned	
	surface potential (mV)	surface charge (C/m <sup>2</sup> )	surface potential (mV)	surface charge (C/m <sup>2</sup> )
5.5	$-34$	$-0.16$	$0$	$0$
6.5	$-57$	$-0.30$	$-62$	$-0.35$
9	$-61$	$-0.34$	$-88$	$-0.61$



**Figure 6.** A comparison of surface force measurements between titania surfaces, which have been cleaned using argon plasma or water plasma. The solution was  $10^{-4}$  M NaCl with the pH adjusted to a value of 4.

Kélicheff et al.<sup>26</sup> Both of these models predict an exponential form with an upper limit for the decay length of one-half the



Debye length. The decay length observed in these measurements exceeds this and is closer to the actual Debye length of the solution and therefore cannot be explained by current models of a patchy charged surface. Normally an attractive force of this range would be explained using a hydrophobic force. However, this explanation seems unlikely in this case, as the surfaces are hydrophilic as demonstrated by the contact angle measurements. The surprising range and strength of the observed attraction between hydrophilic surfaces remains unexplained. We note that upon cycling the pH, between pH 4 and higher pH values the forces were repeatable and they did not exhibit any of the variability one might expect if bubbles are present on the surface.

In the case of surfaces treated with UV irradiation, an attraction between the surfaces was observed on approach, and upon separation a large adhesion was observed. The adhesion was large enough that the range of the piezoelectric drive (3.5  $\mu\text{m}$ ) of the E-type scanner used in the AFM was not sufficient to separate the surfaces. The magnitude of this force made the observation of any other forces impossible. The force measurements indicate that the UV treatment of the surface failed to completely clean the surface, as the forces found were characteristic of some reports of the long-range hydrophobic attraction, which occurs between hydrophobic surfaces<sup>27</sup> and can be attributed to nanobubbles on the surfaces.

**X-ray Photoelectron Spectroscopy Measurements.** Comparison of the magnitude of the surface charge obtained from the fitting of the force data indicates that the water plasma cleaned surface is more highly charged. XPS was used to investigate differences in the elemental composition of the surfaces following argon and water plasma cleaning. A summary of the XPS analysis can be found in Table 3.

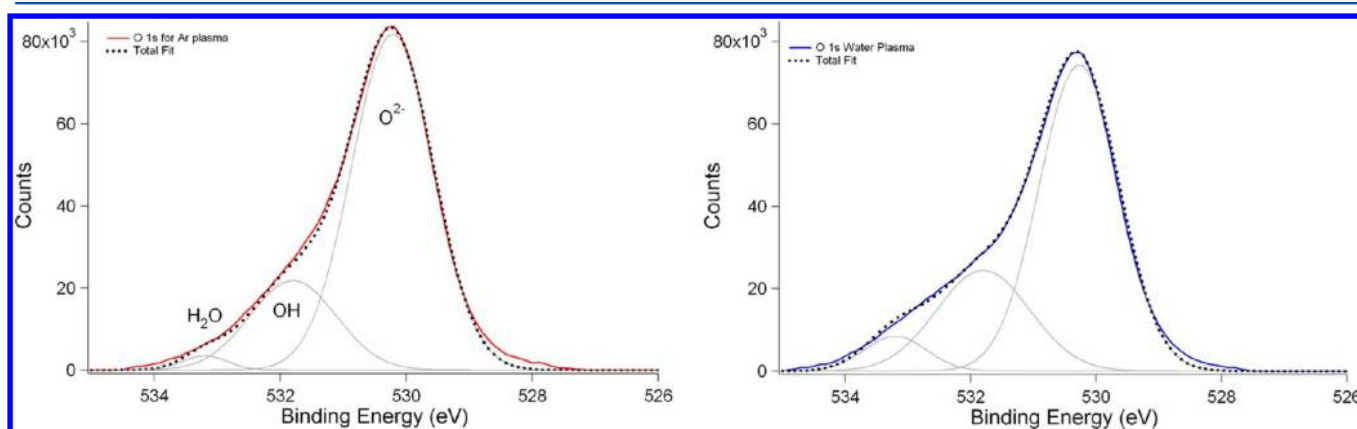
**Table 3. Percentage of Elements in Titania Film Determined Using XPS for Argon and Water Treated Titania Surfaces**

element	% present after argon plasma treatment	% present after water plasma treatment
Ti	20.1	18.4
C	20.8	24.8
O <sup>2-</sup>	56.2	38.6
OH <sup>-</sup>	1.5	14.8
H <sub>2</sub> O <sup>a</sup>	1.3	3.4

<sup>a</sup>This can be either water or carbon compounds associated with the surface.<sup>28</sup>

The surfaces were determined to contain titanium, oxygen, and carbon atoms. To gain a better understanding of the species present at the surface, the oxygen peak was studied in more detail. Fine scans of the O 1s peaks for argon plasma and water plasma treated surfaces (see Figure 7) were studied to determine which oxygen species are present on the surface. Deconvolution of the fine scans of the O 1s shows the presence of O<sup>2-</sup>, OH<sup>-</sup>, and H<sub>2</sub>O on both surfaces.

For water plasma treated surfaces, the ratio of Ti and O<sup>2-</sup> indicates that the film contains nearly stoichiometric TiO<sub>2</sub>, while argon plasma treated surfaces are O<sup>2-</sup> rich. Argon plasma cleaned titania surfaces have been examined before by Jun et al.<sup>28</sup> using anatase powder produced in a sol–gel process. While they determined that argon plasma treatment can change the oxidation states of both Ti and O, it does not explain the O<sup>2-</sup> rich surface we observe for our ALD titania surfaces. This suggests that the excess O<sup>2-</sup> may be due to unreacted propoxide remaining in the surface following the ALD process. A significant amount of propoxide left in the titania would diminish the dispersion forces, but in the surface force measurements we have good agreement with the theoretical calculated van der Waals attraction at the IEP. In fact, analysis of the XPS fine scans for titanium 2p and carbon 1s reveals that the titanium exists solely as Ti<sup>4+</sup> (Supporting Information Figure S1a), while approximately 12% of the observed carbon is bonded to oxygen (Supporting Information Figure S1b). Taking into account that propoxide contains 3 carbon atoms per molecule, and the total carbon atomic percentage in the ALD films is of the order of 20–25%, the unreacted propoxide makes up less than 10% of the final film composition (based on atomic percentages). Taking this into account, our conclusion is that if the excess O<sup>2-</sup> is due to propoxide it is confined near the surface, which would explain the observed van der Waals forces and the O<sup>2-</sup> rich XPS measurements. Given that the total amount of oxygen in the surface is approximately the same for either plasma treatment, it is possible that the oxygen groups on the surface are converted by the plasma treatment. The conclusion is that the water plasma converts O<sup>2-</sup> into OH<sup>-</sup> via reaction with hydrogen radicals, while argon plasma converts OH<sup>-</sup> groups to O<sup>2-</sup>. The XPS measurements show that water plasma treated surfaces have a greater concentration of OH<sup>-</sup> groups. This is consistent with the higher magnitude surface charge for water plasma treated surfaces obtained from DLVO fits of the forces.



**Figure 7.** Fine scans of XPS measurements of oxygen peaks for argon plasma (left) and water plasma (right) treated titania surfaces.

The surface forces we measure between titania surfaces are consistent with the surface forces measured between silica surfaces as in both cases the van der Waals attraction is not apparent. This implies an additional non-DLVO repulsion at small separations. Hydration forces are an obvious candidate, but they are of insufficient range to explain the results for the titania system. When combined with surface roughness this could explain the results for silica surfaces as the magnitude of the van der Waals force is relatively small. However, this is not the case for titania surfaces, which have a large van der Waals attraction, and thus the nature of the interaction at high pH remains unexplained. The possibility remains that the additional repulsion present between silica surfaces and titania surfaces has the same origin. In future work, we aim to determine if this additional non-DLVO repulsion is a unique feature of titania and silica surfaces or if the same phenomena is observed for other oxide surfaces and therefore requires reconsideration of the application of DLVO theory to the understanding of surface forces between mineral oxide surfaces at high pH.

## CONCLUSION

We have determined that the measured forces between both water plasma and argon plasma treated surfaces can be fitted by DLVO theory at pH values near the IEP. XPS analysis reveals that the use of water plasma generates a surface with greater relative levels of surface hydroxyl groups than argon plasma treatment. The relatively titanol rich surface provides a greater number of surface charge sites, leading to an increase in the magnitude of the electrostatic double-layer repulsive surface forces. For both cleaning methods, no van der Waals attraction is observed at high pH, due to the presence of an additional non-DLVO repulsive force. We conclude that the non-DLVO repulsion does not arise as an artifact of water plasma treatment. The range of the additional repulsion is too large to be attributed to surface roughness or hydration forces, and therefore its origin remains unresolved.

## ASSOCIATED CONTENT

### Supporting Information

Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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