Supporting Information

Direct Measurement of Van Der Waals and Diffuse Double Layer Forces between Titanium Dioxide Surfaces Produced by Atomic Layer Deposition

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Here we present additional information on Type A and Type C surfaces used in our investigation. This includes both characterization of the surfaces and the results of force measurements on the Type A surfaces. These surfaces differ in the conditions that were employed to produce them, resulting in films of different thickness and crystallinity as described in the main article. Aarik *et al.* [1] studied the effect of temperature on the crystal structure of ALD TiO_2 films and showed that above 350 ˚C the rutile structure dominates the film, between 165 ˚C and 350 ˚C the film will be dominated by the anatase form of TiO_2 and below 165 ˚C the film will be amorphous. We have found that for surface force studies amorphous films are preferred as they minimize the roughness of the surface. This allows the production of thicker and smoother films than would be possible with a crystalline film. In the past, others have produced amorphous films then induced a crystallisation of the film using various treatments, but the surfaces often became rough or developed pinhole defects during the transformation[2]. Therefore we did not follow these methods.

Type A Surface (Anatase)

In Figure S1 we show the X-Ray diffraction spectra obtained for Surface A. The peaks at 2θ values of ~25° and ~28° are indexed to the anatase crystal structure of titanium dioxide, clearly showing the formation of a crystalline phase. AFM images of these surfaces show that the surface roughness is much greater than for amorphous films. In Figure S2 we show the XRR data obtained for surface A. It is apparent that the fringes are indistinct. This is due to the surface roughness that accompanies crystalline titanium dioxide films. The thickness of the film was estimated to be ~ 82 nm from a Fourier transform of this data.

Surface forces between type A surfaces were measured in the presence of 10^{-3} M NaCl, close to the isoelectric point (pH 4.6). An attraction was evident below a surface separation of 30 nm. At first glance it would appear that this force is a van der Waals attraction and it even has approximately the right magnitude. However, when the data is plotted on a semi-log plot as shown in Figure S3 a straight line is obtained. This indicates that the force is increasing exponentially as the surface separation is decreased. An unretarded van der Waals attraction between two bulk phases across a medium is expected to have the form of an inverse power law and clearly does not fit the data. Similarly, we have included a calculation of the van der Waals interaction for the layered system that includes retardation (and is therefore no longer a power law) but the it is still unsatisfactory. Typically a diffuse double layer force is expected to give rise to an exponentially decaying force because of the Boltzmann distribution of ions adjacent to a charged interface. This suggests that the attraction we see is due to an electrostatic force. However, such a force is typically repulsive and here we clearly have an attractive force.

It has been proposed that surfaces that are overall neutral can have patches of positive and negative charge and that these patches can interact to give an electrostatic attractive force that decays exponentially with separation. Here it is possible that the crystallites in the film present different crystal faces to the solution. One would expect that different crystal faces would charge to differing degrees and this could result in the formation of patches of charge on the Type A surface. We used the heterogeneous charge theory of Miklavcic *et al.*[3] to model the forces that would arise from such patchy charges. The theory describes the attractive force that is the result of areas of charge on each surface, with opposite charge, attracting each other. The attractive force can be described by

$$\frac{F}{R} = Ae^{-2q_{\min}d}$$

Where A is a constant, d is the separation between the surfaces and

$$q_{\min} = \left[\left(\frac{\pi}{a} \right)^2 + \kappa^2 \right]^{\frac{1}{2}}$$

where a is the size of the areas of charge and κ^{-1} is the Debye length.

This model predicts that the *maximum* decay length of the force would be half the Debye length of the solution. The experimental data can be fitted with A=0.32 N/m and a decay length of 8.3 nm but the Debye length of the solution is nominally 9.4 nm therefore the maximum decay length allowed by the theory is only 4.7 nm, suggesting that this is not the origin of the attraction we have measured here.

We have also attempted to fit the experimental data with the interaction calculated using the DLVO theory where the surface potentials used are of equal magnitude but opposite sign. Experimentally this would require that the TiO_2 films produced on the sphere and flat surfaces employed in the experiments have different isoelectric points. Whilst this seems unlikely, it is not impossible as the flat surface has a silicon substrate and the spherical surface has a borosilicate substrate. It is possible that the substrate could influence the growth behaviour of the film and thereby ultimately the surface properties. The surface potentials used in the fit were + 8 mV and - 8 mV with a non-retarded Hamaker constant of 60.5 zJ. Due to the low surface potentials and the strong van der Waals interaction the DLVO fit does not have an exponential form and therefore does not match the experimental data.

The final model used to fit this data was an electrostatic double layer (EDL) fit with surfaces that have an equal magnitude of surface potential but opposite sign. No van der Waals force was included in this fit. Surface potentials of + 15mV and -15mV and Debye length of 8.1 nm were used. This model fits the experimental data better than those describe above, in that the form of the model is exponential and values of the variables in the model are reasonable for the conditions of the experiment.

However this requires an explanation for the absence of a van der Waals attraction. We attribute this to the significant surface roughness, which will diminish the van der Waals force as the interface effectively becomes diffuse and the surfaces come into "contact" when asperities touch. This will also reduce the electrostatic attraction but the form of the interaction will remain exponential.

Type C Surface (amorphous)

We include here a plot of the XRD data obtained on Surface C. The only peaks evident are due to the underlying silicon wafer. We take this as evidence that the titania films on Type C surfaces are amorphous.

References

(1) Aarik, J.; Aidla, A.; Uustare, T.; Sammelselg, V. J. Cryst. Growth 1995, 148, 268.
(2) Mitchell, D. R. G.; Triani, G.; Zhang, Z. Thin Solid Films 2008, 516, 8414.
(3) Miklavcic, S.; Chan, D. Y.; White, L. R.; Healy, T. J Phys Chem-Us 1994, 98, 9022.

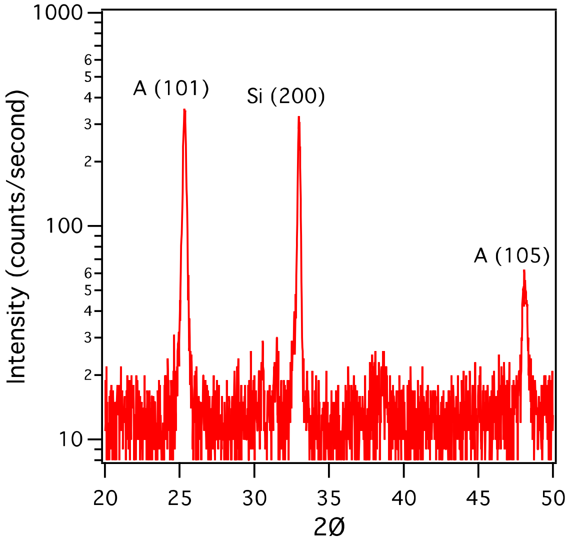

Figure S1: X-Ray Diffraction spectra of a type A TiO_2 surface showing intensity versus 2□. The diffraction peaks corresponding to (1 0 1) and (1 0 5) crystal planes indicate that the films grown under these conditions have the anatase crystal structure. The crystallinity of the underlying silicon surface is also evident.

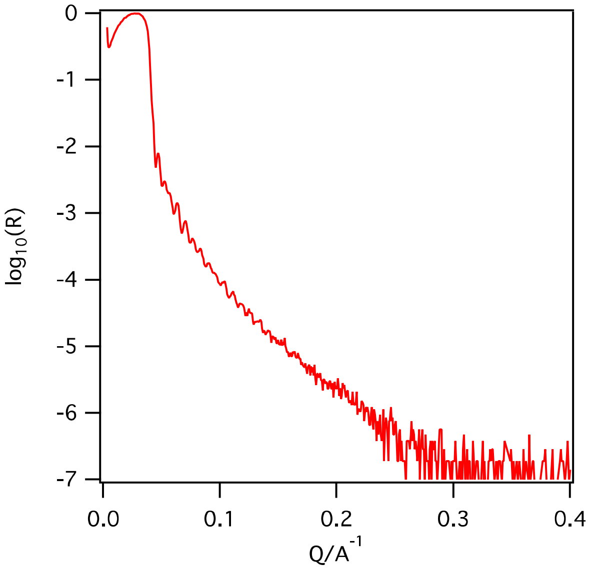

Figure S2: X-Ray reflectivity plot for a type A TiO_2 surface showing the log of Intensity versus Q. Surface roughness makes determination of film thickness difficult but the thickness was estimated to be ~82 nm using a Fourier transform of the spectra.

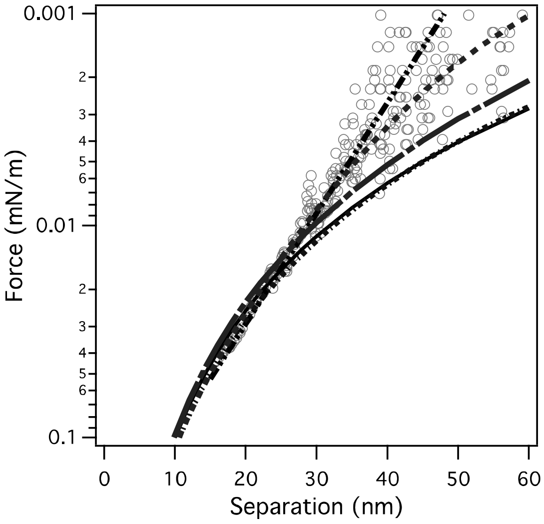

Figure S3: Surface forces measured between type A TiO_2 surfaces in the presence of 10^{-3}M NaCl at pH 4.6. The experimental data (○) has been fitted with the following; a van der Waals fit (▬) using a non-retarded Hamaker constant of 60.5 zJ; a retarded van der Waals force (▬▬ ▬); heterogeneous charged surfaces model (▬▪▪) with fitting parameters of A equals 0.32 N/m and a decay length of 8.3 nm; a DLVO fit (▪▪▪▪) using the above Hamaker constant and surface potentials of equal magnitude but opposite sign, the magnitude of the potentials used were +8 mV and -8 mV; and a fit using only and electrostatic double layer (■ ■) where the surfaces have surface potential of equal magnitude but opposite sign, the magnitude of the potentials used were +15 mV and -15 mV and the Debye length was 8.1 nm.

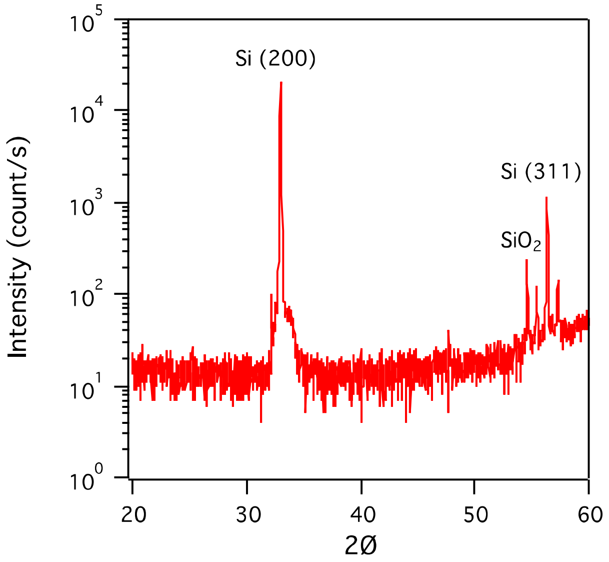

Figure S4: X-Ray Diffraction spectra of a type C TiO_2 surface showing intensity versus 2Ø. Peaks corresponding to the underlying silicon and silica materials are evident as labeled. No diffraction peaks corresponding to TiO_2 crystal structures are seen indicating that the film is amorphous.