doi:10.1246/cl.2012.1247
Published on the web October 20, 2012

Model Surfaces Produced by Atomic Layer Deposition

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Atomic layer deposition is used with the aim of producing new model surfaces suitable for fundamental wet surface science investigations. Alumina surfaces are found to dissolve in aqueous solutions, although they can be passivated against dissolution by adsorption. Highly useful thick titania films can be produced by employing low temperatures during formation, whereas hafnia and zirconia films have a tendency to produce films that crystallize, and this increases the roughness of the films.

Fundamental investigations of surfaces relevant to colloid and surface science usually require that model surfaces are employed as natural surfaces. This is because natural surfaces are often unsuitable as a result of excess surface roughness, chemical heterogeneity, or inappropriate geometry. A number of model surfaces are commonly employed and are desirable for a range of reasons. Muscovite mica can be cleaved to produce atomically smooth regions of significant area. Highly ordered pyrolytic graphite (HOPG) can be cleaved to produce regions that are atomically smooth. Silicon wafers have a natural or enhanced amorphous oxide layer and surface roughness of <0.5 nm root mean square (RMS). Silica glass surfaces that are of similar roughness can be formed into flats, spheres, and other useful geometries such as cylinders. Both silica and silicon surfaces can be easily functionalized using silane coupling chemistry. Also, gold can be produced as low-roughness films that are readily functionalized by thiol adsorption. It would be advantageous to increase the range of model surfaces available, as this would enable a wider range of properties to be investigated and provide analogs that are closer to those that are of technical interest. We have been employing atomic layer deposition (ALD) to grow films onto substrates, in an attempt to increase the range of materials that can be used for fundamental surface forces and adsorption studies.

Atomic layer deposition[1–5] is a process whereby a material is grown in a layer-by-layer fashion onto a substrate. Typically, growth occurs in two steps, starting with a hydroxylated surface. In the first step, metal ions are introduced to the surface in the gas phase in the form of a reactive organometallic or halide compound, known as the precursor. The precursor reacts with the hydroxy groups on the surface forming a single layer of metal compound, which is bound to the surface through oxygen atoms. The remaining precursor is flushed from the system before water vapor is introduced. The water vapor displaces the remaining ligands of the bound precursor and hydroxylates the bound metal atoms. The process is then repeated, with each cycle of steps resulting in the addition of a single layer of metal oxide.

The technique is appealing because the growth of the ALD material is conformal and therefore will follow the features of the substrate material.[3] In the right circumstances, it will do so without significantly adding to the roughness. Additionally, complex shapes, including porous materials and particles,[2] can be coated with an even thickness of material. The thickness of the coating is simply controlled by the number of cycles of deposition employed. The technique is well established and has been used extensively for electronic materials engineering; hence, a wide range of precursors have been investigated, and in excess of 20 different materials have been successfully produced, including metal oxides and pure metals.[5] However, the properties relevant to colloid scientists have often not been evaluated.

Here, we briefly describe our investigations of alumina, titania, hafnia, and zirconia ALD films for wet surface science measurements. In order to use these materials with confidence, it is necessary to characterize them. We have concentrated on obtaining smooth films with bulk-like characteristics and have analyzed them for film thickness, surface properties, crystallinity, and film stability.

Atomic layer deposition was used to produce films on either oxidized silicon wafers or borosilicate or silica spheres. The borosilicate spheres are mondisperse (20 μm diameter) and very smooth and are therefore suitable for force measurements using atomic force microscopy (AFM).[6] Ballotini silica spheres were used for ζ-potential measurements. The conditions of deposition were varied in order to optimize the properties of the films; these are summarized in Table 1.

Atomic layer deposition was carried out using a Savannah 100 system (Cambridge Nanotech). Before being placed in the reaction chamber, surfaces were treated with a radio frequency (RF) discharge water plasma (30 W for 90 s, followed by 50 W for 30 s), using an in-house system. The X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements were performed using a PANalytical X'Pert Pro diffractometer located at the Australian Nuclear Science and Technology Organization. X-ray photoelectron spectroscopy (XPS) was carried out at the Ian Wark Research Institute, using a Kratos Axis-Ultra spectrometer employing a monochromatic Al Kα X-ray source (1486.6 eV)

Table 1. Details of the ALD surfaces discussed

Surface	Material	Precusor	Growth temperature /°C	No. of cycles	Thickness /nm	Roughness /nm RMS	Crystal structure
A	Al_2O_3	$Al(CH_3)_4$	200	952	108	0.22	α-Al_2O_3
B	Ti/Al_2O_3	$Al(CH_3)_4$	200	290/5	5/0.5		α-Al_2O_3
C	TiO_2	$Ti[OCH(CH_3)_2]_4$	250	280	5	0.24	None Observed
D	TiO_2	$Ti[OCH(CH_3)_2]_4$	250	2200	82	8.2	Anatase
E	TiO_2	$Ti[OCH(CH_3)_2]_4$	80	1600	102	0.47	Amorphous
F	HfO_2	$[(CH_3)_2N]_4Hf$	175	600	43	1.76	N/A
G	ZrO_2	$Zr[(C_2H_5)(CH_3)N]_4$	100	400	27	3.16	N/A

operated at 130 W. Atomic force microscope height mode images of ALD surfaces were obtained using a Nanoscope Multimode IIIa AFM with a phase extender box in tapping mode. Tap300Al cantilevers of nominal resonance frequency 300 kHz and spring constant $40\,N\,m^{-1}$, supplied by Budget Sensors, were employed, and the feedback parameters were adjusted to minimize the features in the amplitude image. Roughness was measured over 1000 nm × 1000 nm scan areas.

Alumina is a material of interest because at neutral pH, it has a positive charge, whereas most of the model surfaces available are negatively charged at neutral pH. Additionally, alumina is a biocompatible material[7] and the handling of alumina slurries is important in the production of aluminum.[8] Smooth ALD alumina surfaces were readily produced where the surface roughness, measured by tapping mode AFM, was equivalent to that of the underlying silicon wafer (surface A). Both spheres and flat surfaces were produced. X-ray reflectivity revealed that 952 deposition cycles produced a layer that was 108.1 nm thick, indicating a deposition of ca. 0.113 nm per cycle. It is important to know the crystallinity of the ALD material that is produced, as this can influence a range of properties, including the density, refractive index, and surface-charging properties of the ALD film. X-ray diffraction revealed peaks indicative of α-alumina; the only other peaks present in the spectra corresponded to the silicon substrate (Figure 1). The presence of α-alumina was supported by valence band XPS spectra, which exhibited two nearly symmetric peaks at binding energies of 5.5 and 10 eV. The surface atomic % data showed 28.4% Al and 41.7% oxide oxygen, indicating a very slight deviation from the stoichiometric quantities for Al_2O_3.

Using optical reflectometry,[9] the adsorption of molecules, polymers, and particles onto a surface can be followed with high temporal resolution. The technique can also be applied to investigate the stability of a surface or film. Laser light is reflected from the surface of interest and the polarization of the reflected light is monitored over time. The surface is prepared in such a manner that even a small change in the surface will lead to a significant change in polarization of the reflected light, whereas a stable surface will lead to a constant signal. This polarization is typically reported as the ratio of p-polarized light to s-polarized light (p/s). In Figure 2, we show the polarization ratio measured for an ALD alumina surface on a silicon wafer with an oxide layer thickness of 107 nm. What is evident is that the signal is unstable. This instability continued for 24 h, indicating the slow dissolution of the ALD alumina surface in water. The technique is not designed to measure the rate of dissolution, but we can estimate this to be approximately 0.5 nm per hour.

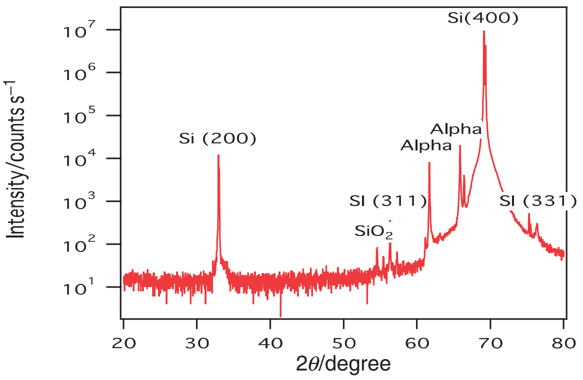

Figure 1. X-ray diffraction spectra of an ALD Al_2O_3 surface showing intensity versus 2θ. The diffraction peaks correspond to α-alumina crystal planes. The crystallinity of the underlying silicon surface is also evident.

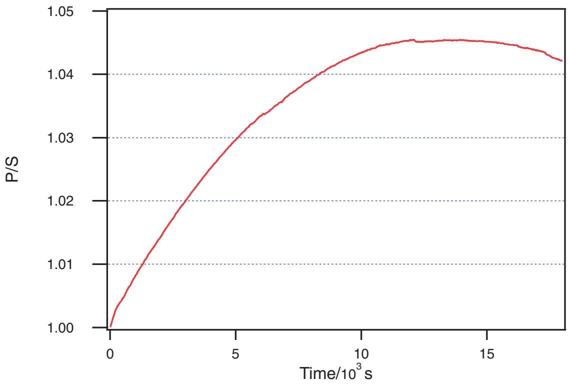

Figure 2. Optical reflectometry measurements of an Al_2O_3 surface in water showing ratio of p and s polarizations versus time. The large and ongoing change in p/s is an indication of dissolution of the Al_2O_3 film.

The instability of the ALD alumina surfaces in water prevents their use in surface investigations where they are immersed in water, except in some circumstances where an additive strongly adsorbs to the surface. In this case, we found that the additive passivates the surface and a stable signal is obtained.[10] Currently, it is unclear whether all alumina surfaces slowly dissolve in water or if this is a property peculiar to alumina surfaces prepared using the ALD technique. Annealing of the films or the use of adhesive layers such as titania was found to have no effect. This is exemplified in Figure 3, where a titania ALD film with a thin overlayer of ALD alumina

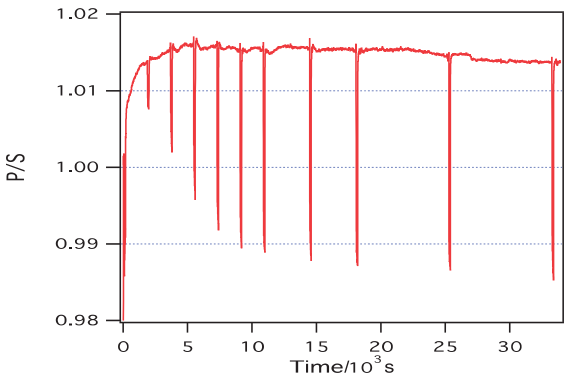

Figure 3. Optical reflectometry of CTAB adsorbing to a thin Al_2O_3 film on a TiO_2 film. The ratio of p and s polarizations versus time is shown. The surface was exposed to CTAB for 2 min periodically (see spikes). The depth of the spikes increases over time indicating that CTAB is adsorbing more strongly and TiO_2 is being exposed due to dissolution of Al_2O_3.

(surface B) is monitored using optical reflectometry. At neutral pH, titania is negatively charged and alumina is positively charged; we therefore expect that the cationic surfactant cetyltrimethylammonium bromide (CTAB) will adsorb more strongly onto a titania surface. What can be seen in this figure is that as the alumina overlayer dissolves, the titania film is exposed and the adsorption of CTAB increases. The conclusion is that the ALD alumina films we prepared are in general not suitable for surface science investigations when the surfaces are placed in water, because they slowly dissolve.

A range of ALD titania films were prepared, where the temperature of deposition or the thickness of the film was varied (surfaces C, D, and E). The roughness of these surfaces was measured with tapping-mode AFM, and the crystallinities were determined with XRD.[11] It was found that in order to obtain smooth films, it was important to produce an amorphous ALD film. This could be achieved by producing a thin film (e.g., <10 nm) or by growing the film at low deposition temperatures, which allows thicker films that remain amorphous to be produced. When a crystalline (anatase) film formed, the roughness was found to be ca. 8 nm RMS, which is still suitable for some surface investigations.

XPS investigation of ALD titania films revealed that the stoichiometry at the surface is as expected for TiO_2, with no evidence of any Ti(III) species.[11] The valence band spectra shown in Figure 4 are in agreement with published spectra for conventional titania surfaces. Importantly, unlike ALD alumina surfaces, all the titania surfaces investigated were found to be stable in water over a wide range of pH, as evidenced by the stable optical reflectometry signals. Additionally, the surface after immersion in water for 60 h showed no change in appearance or roughness, as measured by AFM. The surface-charging behavior as a function of pH was investigated by ζ-potential measurements and found to agree with published data for titania. The isoelectric point in 1 mM NaCl was found to be ca. 5.2, indicating that the surface properties of the ALD titania film are similar to those of other titania surfaces.[11]

When employing an ALD film of titania to control the surface chemistry, one has to be aware that the van der Waals interactions are dependent on the thickness of the film and that films >40 nm in thickness are required to produce surfaces with similar surface forces to that of bulk titania.[11] This is an important consideration, not only in surface force investigations but also in adsorption and adhesion studies, as the van der Waals interactions play an important role.[12,13]

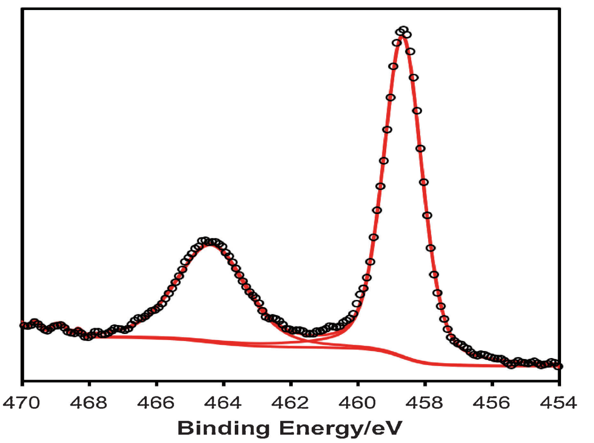

Figure 4. Titanium 2p photoelectron spectrum of an ALD titania film. Ti 2p 3/2 binding energy is at 458.7 eV, typical of Ti(IV).[11] No contribution is observed for Ti(III) at 457.3 eV.

We have also investigated hafnia and zirconia films produced by ALD (surfaces F and G). Films of thickness 20 nm were imaged by tapping-mode AFM and found to have surface roughnesses of 1.8 and 3.2 nm RMS for hafnia and zirconia, respectively, over an area of 1000 nm^2. Although this degree of roughness is suitable for some studies, it is far from ideal, and precludes, for example, force studies at small separations. The roughness is a result of the propensity of the surfaces to become crystalline.[11] Preparation of films of these materials at low temperatures failed to prevent the formation of crystallites and therefore did not result in very smooth films. Efforts to produce smooth zirconia and hafnia films are continuing in our laboratory.

Paper based on a presentation made at the International Association of Colloid and Interface Scientists, Conference (IACIS2012), Sendai, Japan, May 13–18, 2012.

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