Neutron reflectivity of titania and zirconia-based films self-assembled at the solid/liquid interface

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Introduction

The aim of the study was to examine the structure of titania (TiO_2) and zirconia (ZrO_2) based films during their self-assembly at the solid/liquid interface using neutron reflectometry. Recently the growth of TiO_2 [1] [2] and ZrO_2 [3] multi-layered lamellar films using the surfactant template method was monitored using x-ray reflectometry at the air/liquid interface. Our work here offers three novel features of value in studying such systems. First, we demonstrate that the TiO_2 and ZrO_2 -based films can self-assemble at the solid/liquid interface. Second, we show how the lamellar order within a film can be manipulated by varying the solution pH. Third, we show that the reflectivity of the TiO_2-based film, generally weakly responsive to neutrons compared with the ZrO_2 analogue, can be highlighted by the use of appropriate isotopic contrast between the bulk D_2O-based solution, hydrogenous surfactant and the silicon substrate.

Experimental Details

Film synthesis
Heavy water was used for all film syntheses. Titanium (IV) *n*-butoxide (Aldrich, 97 %) zirconium (IV) *n*-butoxide (Merck, 80 % solution in butanol), hydrochloric acid (36-39 % w/w) were used as received. Sodium dodecyl sulfate (Lancaster 99 %) was recrystallised from hot water:ethanol (1:9). A film was prepared at the solid/liquid interface from an acidic solution containing a metal alkoxide precursor, D_2O and hydrogenous sodium dodecyl sulfate (h-SDS) as the template. Films were also prepared using deuterated sodium dodecyl sulfate (d-SDS) to provide an additional contrast.

A typical preparation is as follows. Zirconium (IV) butoxide (0.2226 g, 0.46 mmol) was added to hydrochloric acid (0.3795 g, 3.85 mmol) and the mixture stirred for 10 min. The thick white precipitate was treated with D_2O (0.4922 g, 24.6 mmol) and the mixture stirred for a further 5 min to yield a clear colorless solution. This solution was then injected into the sample cell by syringe and allowed to cover the smooth inner face of the hydrophilic silicon substrate. Subsequently, a solution of sodium dodecyl sulfate (0.0727 g, 0.25 mmol) in D_2O (6.1135 g, 306 mmol) was injected into the cell. The inlet and outlet ports were then sealed.

Characterisation

Neutron reflectivity measurements at the solid/liquid interface were collected on the newly commissioned angular dispersive X172 reflectometer [4] at the HIFAR facility (Australian Nuclear Science and Technology Organisation). The data were recorded as reflectivity (*R*) as a function of scalar momentum transfer Q_z:

$$Q_z = \frac{4\pi}{\lambda} sin\theta \tag{1}$$

where λ is the neutron wavelength (2.43 Å) and θ the specular reflectance angle. Reflectivity data were collected over the Q_z range 0.01 Å^{-1} – 0.4 Å^{-1}. Neutrons entered through the side of the silicon block, and were reflected from the block/film and film/liquid boundaries, before exiting through the other side of the block. The reflectivity data were recorded over a period of 14 h. Silicon (Silrec Corporation, 100 mm diameter x 10 mm thick; (111) face single crystal; p type boron-doped; < 0.18 μm roughness) were used as the substrate. Prior to use a block was cleaned in aqua regia (HCl : HNO$_3$ 3:1) and then rinsed thoroughly with Milli-Q$^{®}$ quality water. Finally the block was dried in a stream of nitrogen.

Results and Discussion

Figure 1 (a) and (b) shows representative *R* vs Q_z profiles obtained from the ZrO$_2$ and TiO$_2$ based films respectively. The lowest traces on both Figures (a) and (b) show no Bragg diffraction. Here the film was contrast-matched to the bulk solution using d-SDS. The (001) Bragg reflection observed was characteristic of a known lamellar arrangement of an oxide and this surfactant with a *d* spacing of about 33 Å.[2],[5] Peak position, width, area and the lamellar thicknesses (*d*-spacing) were evaluated using SASFIT 4 peak analysis software. The values are presented in Table 1.
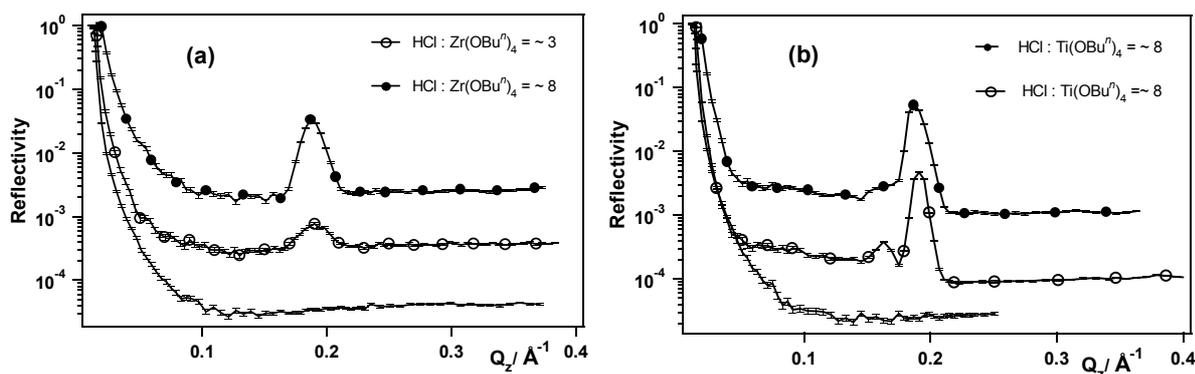

Figure 1: Neutron reflectivity profiles of (a) ZrO$_2$ -based film highlighting the effect of the HCl: Zr(OBu^n)$_4$ ratio on the intensity of the (001) Bragg reflection; (b) a TiO$_2$ -based film showing the effect of a change in the instrument resolution from 8% (closed circle) to 5 % (open circle). The films were self-assembled at the silicon/liquid interface and obtained from aqueous acidic solutions of a metal alkoxide precursor M(OBu^n)$_4$ (M= Ti or Zr), D$_2$O and hydrogenous sodium dodecyl sulfate (symbol and line) or deuterated sodium dodecyl sulfate (line). Films based on h-SDS have been offset for clarity.

An estimate of the extent of the regular layer lattice was obtained from the broadening of the diffraction peak reflection using the treatment of Warren.[6] If θ is the Bragg angle and β the full width of the peak at half maximum intensity in radians, the coherence length L_c is

$$L_c = \frac{0.89\,\lambda}{\beta\,cos\theta} \qquad\qquad (2)$$

where λ is the incident wavelength, 2.43 Å. The Bragg angle, θ, and the β the full width of the peak at half maximum intensity (fwhm) were evaluated from the data of Figure 1 and Equation (1). The coherence lengths obtained from the analysis are presented in Table 1. Instrumental broadening was subtracted from all line widths. In the case of the TiO_2 -based film measured at 8 % resolution it was not possible to extract a coherence length. We note that the surfactant template, sodium dodecyl sulfate, does not adsorb at the silicon/bulk solution interface.[7] Film formation in the present study is attributed to an electrostatic interaction between the negatively charged sulfate head group of the template and the counter-charged metal oxide oligomers, an interaction that is pH-dependent.[8] This dependency is demonstrated in Figure 1(a) where peak intensity and peak area responses to a change in the HCl : $Zr(OBu^n)_4$ ratio from 3 (open circle) to 8 (closed circle) are quite distinct. The reflectivity response of a TiO_2-based film to neutrons at the solid/liquid interface is shown in Figure 1(b). Using h-SDS as the template, a Bragg reflection of similar magnitude to that observed for the analogous ZrO_2 system was obtained. Definition of the small shoulder at $Q = 0.16$ Å^{-1} (39 Å) was obtained when the instrument resolution was changed from 8 % (closed circle) to 5 % (open circle). The origin of this small reflection is not known, however, the presence of material from a second template, possibly from the hydrolysis products of sodium dodecyl sulfate in the acidic aqueous solution is inferred by analogy with studies at the air-water interface. [2]

Table 1:   Peak characteristics obtained from the analysis of the (001) Bragg reflection

Film type	HCl:M(OBu^n)$_4$	d spacing / Å	$\Delta Q/Q$ %	Peak fwhm / Å^{-1}	Peak area / Å^{-1}	Coherence Length / Å ^{a}
ZrO_2/h-SDS	~ 3	33.1	6	2.74 x 10^{-2}	2.5x 10^{-6}	(4.5 ± 0.2) x 10^2
ZrO_2/h-SDS	~ 8	33.4	8	1.66 x 10^{-2}	1.6 x 10^{-5}	(1.6 ± 0.1) x 10^3
TiO_2/h-SDS	~ 8	33.4	8	1.40 x 10^{-2}	4.5 x 10^{-5}	long
TiO_2/h-SDS	~ 8	32.9	5	1.12 x 10^{-2}	2.8 x 10^{-5}	(1.7 ± 0.1) x 10^3

The interface contributing to the scattering can be inferred from a consideration of the scattering length densities of the primary film components, surfactant sulfate ion, the dodecyl chain of the surfactant and the metal oxide. An estimation of the scattering length density of the inorganic component involves some uncertainty because the species present when the mesostructure is formed is not known. However, by considering the sol-gel precursor to be a fully hydrolysed, metal hydroxide, as illustrated for titanium in Equation (3), a neutron scattering length density can be estimated from the scattering lengths of Ti, O and D atoms.

$$x\mathrm{Ti}_4^+ \ + \ n\mathrm{D}_2\mathrm{O} \ \Leftrightarrow \ [\mathrm{Ti}_x(\mathrm{OD})_n]^{(4x-n)+} \ + \ n\mathrm{D}^+ \hspace{3cm} (3)$$
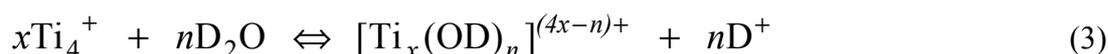
By considering the volume of the uncondensed $\mathrm{Ti(OD)_4}$ to be equal to that of $\mathrm{TiO_2}$ plus that of $\mathrm{D_2O}$ expelled during the subsequent condensation reaction [9] and calculating the mass of $\mathrm{Ti(OD)_4}$ from the amount of $\mathrm{Ti(OBu}^n)_4$ precursor, a density of ca. 2.1 g cm^{-3} for the material (cf. 3.84 g cm^{-3} for anatase) is obtained. From this density, a neutron scattering length density was estimated to be 4.9 x 10^{-6} Å^{-2}. This value is rather close to that of the de-hydrated sulfate headgroup, 2.9 x10^{-6} Å^{-2}. The hydrogenous dodecyl carbon chain, considered here to be that of dodecane, has quite a different scattering length density, -0.46 x 10^{-6} Å^{-2}. The main contribution to the scattering can then be said to originate from the hydrogenous alkyl chain of the surfactant between the silicon substrate (ca. 2 x10^{-6} Å^{-2}) and the $\mathrm{D_2O}$-based bulk solution (ca. 6 x10^{-6} Å^{-2}).

Acknowledgements

Conclusions

$\mathrm{ZrO_2}$ and $\mathrm{TiO_2}$ -based films have been prepared at the solid/liquid interface by a self-assembly method from an acidic aqueous HCl solution of the metal alkoxide precursor $\mathrm{M(OBu}^n)_4$ (M= Zr, Ti) and the anionic surfactant, sodium dodecyl sulfate (SDS). A film was characterised at the solid/liquid interface using neutron reflectometry with the newly commissioned angular dispersive X172 reflectometer [4] at the HIFAR facility (Australian Nuclear Science and Technology Organisation). Bragg diffraction from a film signalled the presence of a lamellar structure in which the film components, metal oxide and dodecyl sulfate exhibit a regular alternating 33 Å arrangement, a result of the lamellar liquid crystalline ordering of the surfactant micelles.

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