ESRF	**Experiment title:** Growth and structure of nanostructured titania films from non-aqueous solutions	**Experiment number**: CH-2140
Beamline: ID 10B	**Date of experiment**: from: 19 July 2007 to: 25 July 2007 (ended 22 July), 11-12 Feb 2008	**Date of report**: 26 July 2007, 27 Feb 2008
Shifts: Scheduled 21 (did 11 July +3 in Feb)	**Local contact(s)**: Dr Oleg Konovolov Dr Alexei Vorobiev	*Received at ESRF:*

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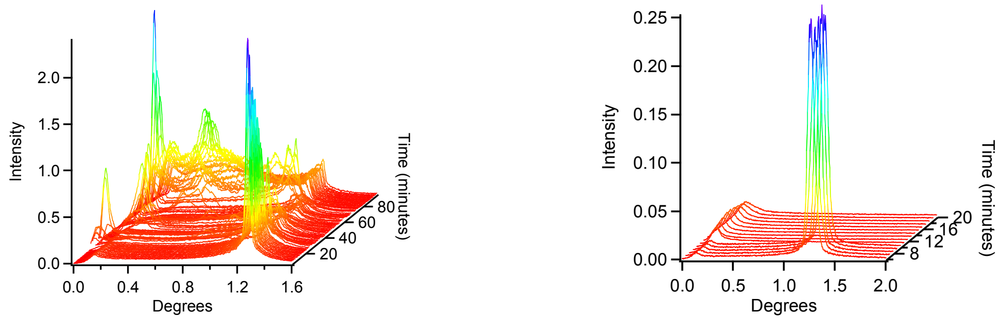
Report:

Work during this experiment represents part of our ongoing research studying the spontaneous formation of titanium dioxide-based films at the air-liquid interface from solutions containing minimal water. The ID10B, Trokia II, beamline was used to measure time resolved off-specular reflectivity, reflectivity profiles and grazing incidence X-ray diffraction (GID) patterns on surfactant-templated titania films. Series of both partially fluorinated surfactant and block copolymer templated films formed from ethanol-based solutions have been studied. Data collection is however incomplete due to loss of beam at ~4am Sunday 22 July, halfway through the allocated beamtime. One further day was scheduled in Feb 2008 which has enabled us to pursue these experiments further.

Formation times of TiO_2 films are dependent upon reagent concentrations and calcined film material shows a degree of ordering. Neutron reflectivity suggested the formation of ordered mesophases in these films at the air-solution interface. The aim of this experiment was therefore to observe the effects of acid concentration and surfactant:titania ratio on the formation and structure of the films. Work on silica systems has found these to be key factors in determining film structure and thus they may be similarly determinant in titania films.[1]

We used the partially fluorinated surfactant Zonyl FSO-100 and a polyethylene-poly-(ethylene glycol) (PEPEG) block copolymer as templates for film formation while varying surfactant, $Ti(OBu^n)_4$ and HCl concentrations. The most complete data series were collected for titania precursor variation in both cases, but loss of beam forced the experiment to end early. FSO-100 based films utilised reagent ratios of 1 FSO-100 : 135 C_2H_5OH : 4.6 HCl : 0.62 $Ti(Obu^n)_4$ with mole ratio variaitions covering 0.28 – 1.0 $Ti(Obu^n)_4$ and 0 – 5.9 HCl studied for effects on film formation and structure. The PEPEG preparations used reagent ratios of 1 PEPEG : 1250 C_2H_5OH : 13.5 HCl : 265 H_2O : 15.5 $TiCl_4$ with variation ranges of 0.5 – 2.0 PEPEG; 5.2 – 15.8 $TiCl_4$ and 0 – 6.2 HCl studied. Time resolved off-specular reflectivity experiments were conducted to observe variation of film formation with reflectometry profiles and GID measurements performed on final, developed films at the interface to observe any variation in film ordering.

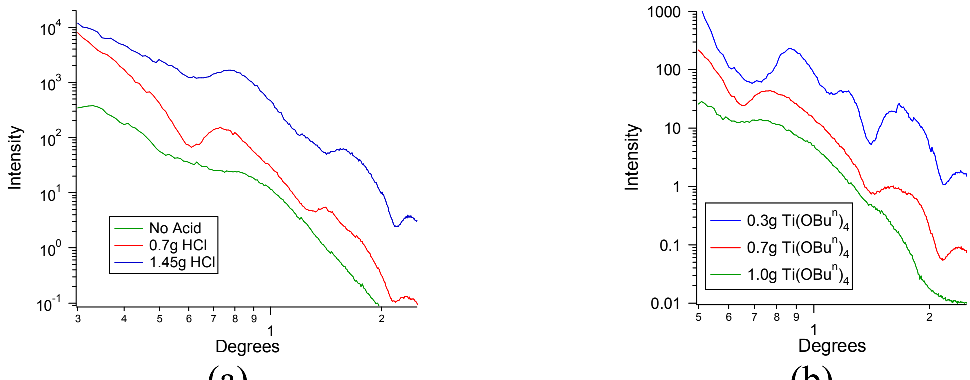
Film formation was often observed by the loss of the specular reflectivity peak in the time resolved experiments, although in some cases a new peak developed, shown in *Figure 1*. This suggests that the films, particularly the PEPEG films, form rough films quickly while FSO-100 based films both take longer to form and are smoother at the interface.



(a) (b)

Figure 1: Time resolved reflectivity of the development of an FSO-100 based film, (a), and a PEPEG based film, (b), at the air-solution interface.

Reflectivity profiles of developed films show variation with reagent concentration, however, low solution levels in the sample trough due to evaporation led to a reduction in the Q range studied, particularly in the case of the PEPEG based films. The loss of experimental time left these series of experiments incomplete. The development of peaks in the reflectivity profiles of FSO-100 based films is noted to be more pronounced with both decreasing titania content and decreasing acid content, as shown in *Figure 2*. Furthermore the confirmation of a structured film at the air-solution interface without any acid addition, although less ordered, is encouraging and worth further investigation as it is the first time to our knowledge that such a film has been formed from an entirely ethanol solution without the addition of water.



(a) (b)

Figure 2: Reflectivity profiles of FSO-100 based films at the air-solution interface showing film variation with, (a), acid and, (b), titania concentration.

The investigation and confirmation of film development and structure at the air-solution interface is ongoing and the results obtained in Feb 2008 have significantly added to our time-resolved and structural data. We are currently engaged in modelling of this most recent data and comparision of data obtained both in July and our earlier experiments on film formation in inorganic-surfactant systems.

References

(1) Edler, K.; Brennan, T.; Roser, S. J.; Mann, S.; Richardson, R. M., Formation of CTAB-templated mesophase silicate films from acidic solutions. *Microporous and Mesoporous Materials* **2003,** 62, (3), 165-175.