XANES Studies of Amorphous Titania Thin Films and Geopolymers

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We have used X-ray absorption near-edge structure (XANES) to probe the local bonding environment in two types of amorphous materials. The first was titania thin films deposited using both atomic layer deposition (ALD) and sol-gel methods. The other samples studied were Fe-, Ca-, and Mg-doped geopolymers. All measurements were carried out at beamline 24A1.

For all the titania films, we have investigated the effect of key processing parameters on the evolution of local environments in TiO_2, using Ti L-edge and O K-edge XANES spectroscopy. Both the Ti L-edge and O K-edge XANES spectra are very sensitive to the crystallinity of the films, showing significant changes even for partially crystalline films. Therefore, this is a superior method compared to conventional X-ray diffraction to monitor the early stage of crystallisation.

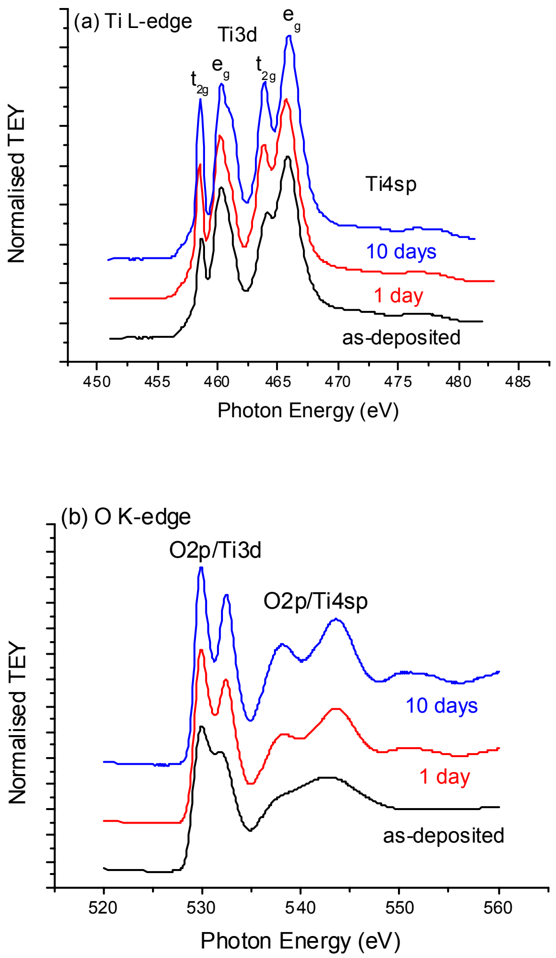

Figure 1. (a) Ti L-edge, and (b) O K-edge XANES spectra of a titania film deposited on Si and after hydrothermal treatment for 1 and 10 days, respectively.

Figures 1(a) and 1(b) show the Ti L-edge and O K-edge spectra of an as-deposited titania film on Si wafer and subsequently treated hydrothermally for 1 and 10 days, respectively. The results indicate that the as-deposited film is amorphous, the 10 day hydrothermally treated film is essentially crystalline anatase, and the film treated for 1 day is partially crystalline. These results are confirmed by TEM / electron diffraction in a separate study.

The other processing parameters we studied were the deposition temperature of the ALD films and annealing temperature of the sol-gel films. Our results show that the ALD films deposited at 250 and 300ºC are crystalline anatase, whereas the films deposited at lower temperatures (80-200ºC) are amorphous, suggesting that the structural transition from amorphous to anatase occurs suddenly (at a temperature between 200 and 250ºC). For sol-gel films deposited using $[Ti_6O_4](O^iPr)_8(OOC\text{-}CH_3)_8$ clusters $[O^iPr = O\text{-}C(CH_3)_2H]$, a post-annealing-temperature of 400ºC was required to convert the amorphous film into crystalline anatase.

We have also investigated the speciation of Ca, Fe and Mg in geopolymers. Geopolymers are amorphous alkali aluminosilicate materials which are composed of cross-linked AlO_4^- and SiO_4^- tetrahedra, with charge balancing Na or K ions. The long-term use of geopolymers as a practical material will ultimately rest on detailed understanding of the speciation of its component elements. Ca, Fe and Mg are some of the impurity components found in commonly used aluminosilicate feedstocks for making geopolymers. Therefore it is important to determine how these impurity ions are incorporated in the geopolymers. We have added up to 5 wt% of CaO, Fe_2O_3 or MgO using various precursors [$CaCl_2$, $Ca(NO_3)_2$•$4H_2O$, $Ca(OH)_2$, $Fe(NO_3)_3$•$9H_2O$ and $Mg(OH)_2$]. Initial XANES data of the Ca L-edge, Fe L-edge and Mg K-edge indicate that Ca, Fe and Mg have similar coordination to those in $Ca(OH)_2$, FeOOH and $Mg(OH)_2$, respectively. Therefore, these species have *not* been incorporated directly into the Al-Si-O geopolymer network, as it would have been in tetrahedral coordination.