Titanium oxo-alkoxide clusters as a new source material for high quality TiO_2 structures by inkjet printing

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Introduction;

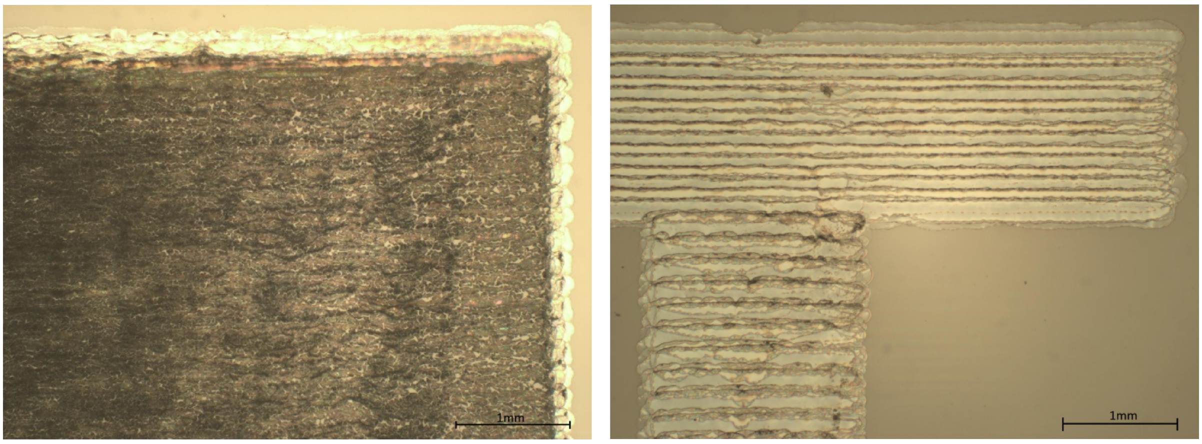
Metal oxide thin films and coatings have many applications.[1, 2] They are conventionally applied to a substrate using vacuum technologies at high temperatures, covering the substrate completely. Patterning of the thin film is often required for certain applications and this process removes large amounts of the coating resulting in an inefficient use of resources. In addition, controlling the surface architecture of the deposited film during patterning is time consuming and costly. By using inkjet printing technology to directly create the desired design, material consumption is reduced and fewer processing steps are required leading to a cheaper, more flexible manufacturing process.[3] Employing this technology enables film thickness to be easily manipulated through multiple printing passes and processing temperatures required for post-treatment of the films to be reduced by using molecular engineering and altering the surface chemistry. The research group has previous experience in the engineering of metal oxide precursors for deposition.[4]

TiO_2 thin films are prevalent within the literature,[5] and are suitable candidates for the first metal oxide to be investigated. Although the rutile phase is generally observed for low temperatures, the anatase phase is most catalytically active, thus most suitable for general applications. The use of titanium tetraisopropoxide [$Ti(O^iPr)_4$] or other titanium(IV) alkoxides as the precursor for TiO_2 deposition is standard. Due to the high moisture sensitivity of these metal alkoxides,[6] the use of stabilisers and rigorously dry conditions is commonplace. Titanium oxo-alkoxide clusters have been identified as intermediates in the hydrolysis of Ti alkoxides to TiO_2, and are an area of continued research in thin film deposition.[7-9]

Main body of the paper;

The goal of the EpiValence funded project is to deposit metal oxide thin films and patterns directly through the use of inkjet printing. The novel concept of using an ink containing small preformed clusters, with direct metal oxide frameworks, to act as templates to the desired final target layer structure is investigated. Initial work using simple metal alkoxides in solution is compared to deposition trials using cluster containing solutions. In this contribution the synthesis and characterisation of Ti oxo-alkoxide clusters, and their solutions, is reported. Inkjet printing results, for films and for thin tracks, are reported for cluster-containing solutions, as well as for stabilised solutions containing $Ti(O^iPr)_4$.

Of particular interest is the sintering temperature, jettability, and process economy of the thin films due to their impact on cost efficiency, reproducibility, and film properties. Optimisation of these parameters has been investigated through the use of molecular engineering of the small cluster inks, whilst selecting appropriate stabilising conditions for the $Ti(O^iPr)_4$ inks and a comparison of data vs control will be presented to highlight the advantages that can be achieved. Phase analysis of the TiO_2 films, before and after sintering, is also important for the applications of the thin films. XRD measurements highlighting the minimum sintering temperature at which anatase phase is dominant will be reported.



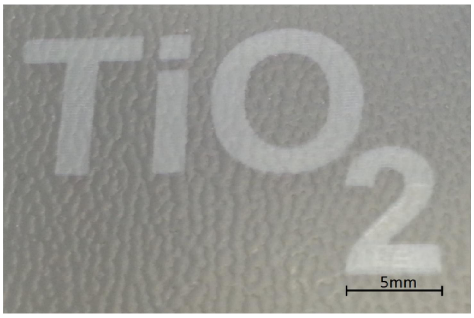


Figure 1. (Bottom left) Printed word 'TiO2'. (Left) Top right corner of a 10 pass 1cm^2 square (Right) Top right of the printed letter 'T'. All samples were inkjet printed using stabilised 0.1M $Ti(O^iPr)_4$ ink and the same printer waveformulation. (Left) and (Right) images taken using an optical microscope fitted with a 25x zoom lens using the top light.

Keywords

Inkjet, TiO_2, alkoxide

Biography

Josh Turner obtained his masters in Chemistry (MChem) at the University of Liverpool in 2015. He is a current PhD student under the tutelage of Prof. Helen Aspinall (Department of Chemistry, University of Liverpool) and Dr. Kate Black (Department of Engineering, University of Liverpool), with a sponsorship from EpiValence. His research is focused on the use of reactive inkjet printing as a technique for producing thin films of materials, such as metal oxides, with applications in electronics/sensors/catalysis.

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