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

Josh Turner,[1,2] Danielle Mehta,[1,2] Helen C. Aspinall,[1] Simon Rushworth,[2] Kate Black,[3]
[1] Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, Crown Street, Liverpool, L69 7ZD, U.K
[2] EpiValence, The Wilton Centre, Redcar, Cleveland, TS10 4RF, England
[3] Department of Engineering, George Holt Building, University of Liverpool, Liverpool, L69 3GH, U.K
E-mail: sgjturne@liverpool.ac.uk, hca@liverpool.ac.uk, and kateblk@liverpool.ac.uk
Website: http://epivalence.com./reactive-inkjet-printing-project/

Abstract

Inkjet printing offers an attractive route for the manufacture of metal oxide films and allows a low-cost, environmentally friendly route to manufacture. Here we describe a stabilised process for the printing of TiO_2 films. This has been achieved through the use of a range of titanium (IV) ink solutions, employing stabilised $Ti(O^iPr)_4$ or titanium oxo-alkoxide clusters as the source materials. Printed tracks with feature sizes of 156μm have been achieved, along with more complex architectures of TiO_2. XRD analyses shows that the as deposited TiO_2 is amorphous.

Introduction;

Metal oxide thin films and coatings have many applications [1] [2]. Conventionally, these oxide coatings are manufactured using high temperature vacuum techniques, which cover the substrate completely. However, patterning of the metal oxide films is often required for applications. The patterning process removes large amounts of the coating resulting in an inefficient use of materials. In addition, controlling the surface architecture of the deposited films 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, less materials intensive manufacturing process [3]. Employing inkjet printing enables film thickness to be easily manipulated through multiple print passes and processing temperatures required for post-treatment of the films can be reduced by using molecular engineering and altering the surface chemistry [4].

TiO_2 films are prevalent within the literature [5], and are used in applications such as photocatalysis [6], thin film memristors [7], and hybrid photoconductor materials [8]. Although the rutile phase is generally observed at low temperatures, the anatase phase is the most catalytically active, and therefore usually the desired phase. The use of titanium tetraisopropoxide, $Ti(O^iPr)_4$, or other titanium(IV) alkoxides as starting materials for the deposition of TiO_2 is widespread.

However, due to the high moisture sensitivity of these metal alkoxides [9], the use of stabilising ligands and rigorously dry conditions are required. Furthermore, 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 [10]-[12].

The aim of this work is to develop ink formulations for the inkjet printing of alkoxide precursors, which undergo a condensation reaction with ambient moisture to form TiO_2. Firstly, ligand stabilised inks containing the simple alkoxide $Ti(O^iPr)_4$ were investigated, which react once deposited according to equation 1. TiO_2, the desired product, is formed along with volatile ^{i}PrOH which evaporates.

$$Ti(OR)_4 + 2H_2O \rightarrow TiO_2 + 4{}^iPrOH \quad (1)$$

More complex Ti alkoxides were also investigated. Ink formulations containing small preformed oxo-alkoxide clusters, with direct metal oxide frameworks, act as templates to the desired final target layer structure. Simple alkoxides react according to equation 2 under limited exposure to H_2O. Rozes *et al* describe oxo-alkoxide clusters displaying varying degrees of condensation, with O/Ti ranging from 0.33-1.55 [12].

$$nTi(OR)_4 + mH_2O \rightarrow Ti_nO_m(OR)_{4n-2m} + 2mROH \quad (2)$$

Following printing, the annealing temperature at which the films form the anatase phase of TiO_2 is of particular importance. The ultimate aim is to produce printed anatase TiO_2 at lower processing temperatures, reducing costs and allowing thermally sensitive substrates to be employed eg. PET or PEN.

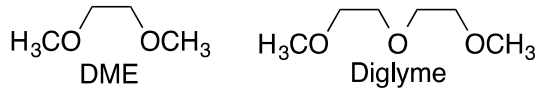
Ink formulations

Table 1: Table to show ink formulations 1-3.

Ink formulation	1	2	3
Ti source	$Ti(O^iPr)_4$	$Ti(O^iPr)_4$	$Ti_nO_m(OR)_{4n-2m}$
Carrier solvent	^{i}PrOH	^{i}PrOH	Toluene
Stabiliser	DME	Diglyme	None

Initial printing tests were performed using $Ti(O^iPr)_4$ in dry ^{i}PrOH, the parent alcohol. However, the ink solution was too unstable to hydrolysis which lead to precipitation and print head blockages. The printing of a range of ink formulations with a variety of stabilising ligands was then employed. Two such ligands utilised in the $Ti(O^iPr)_4$ inks were: DME (1,2-dimethoxyethane) and diglyme (bis(2-methoxyethyl) ether). These simple glymes have been chosen for a number of reasons, including their capacity to act as both solvent and ligand, miscibility with ^{i}PrOH, and noncorrosiveness. Importantly, they are volatile and so will evaporate cleanly. Furthermore, the glymes are capable of kinetically stabilising the Ti(IV) metal centre with respect to hydrolysis. Co-

ordination of H_2O to the Ti centre is blocked due to the chelating effect of the O-donating glymes.



A concentration of 0.1M with respect to $Ti(O^iPr)_4$ was chosen for inks 1 and 2, with 5 molar equivalents of stabiliser and a carrier solvent of ^{i}PrOH. Both 0.05M and 0.15M inks were investigated. 0.05M ink suffered from a low titanium loading, whereas 0.15M ink had a high tendency to block the print head and displayed low print quality. Furthermore, 3.3 molar equivalents of stabiliser was also investigated, although this resulted in reduced solution stability to atmospheric moisture.

More complex oxo-alkoxide species have also been investigated. Partially hydrolysed Ti clusters display a core titanium-oxide bridge structure, comparable to TiO_2, and a shell or periphery of reactive alkoxide functionality. This may lead to lower processing temperature requirements and higher print resolutions for TiO_2 film deposition in relation to the simple alkoxides. Synthesis of the oxo-alkoxide cluster was performed, following the experimental procedures described by V. W. Day *et al* [11]. The microcrystalline powder showed poor solubility in ^{i}PrOH, with acceptable solubility in toluene.

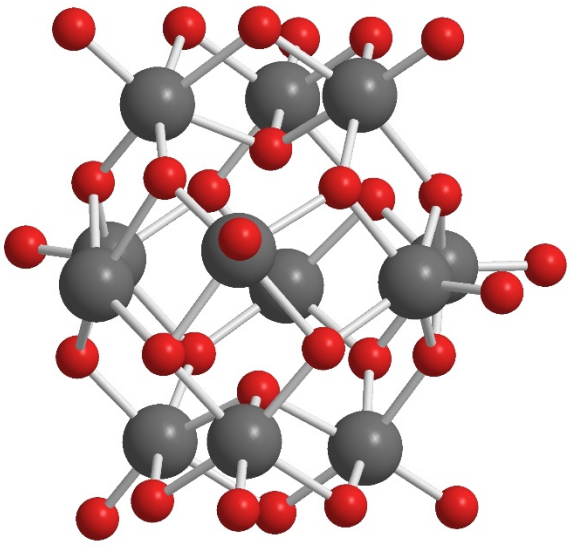


Figure 1. *$Ti_{12}O_{16}(O^iPr)_{16}$ cluster, with Ti atoms in grey and O atoms in red. C and H atoms are omitted for clarity.*

Due to the low concentration of titanium source and stabiliser the waveforms obtained for use with the pure carrier solvents are still sufficient to generate a steady stream of uniform droplets. Thus, the waveforms were not changed when printing the titanium loaded inks.

Printing with stabilised inks

Initial printing trials for both inks 1 & 2 involved screening for ideal printing parameters, namely print speed and inter-droplet distance, or step size. A range of both parameters was explored through the printing of single tracks, with print speeds ranging from 6 to 12 millimetres per second (mmps) and ranging from 0.05 to 0.2 mm step size. Ink 1 displayed optimal track printing conditions of 6mmps and 0.1mmss, whereas ink 2 displayed optimal track printing conditions of 8mmps and 0.1mmss. Figures 2 (a) and (b) show the respective print tracks. A 100x100 pixel square array was also printed with inks 1 and 2, with 0.1mmss leading to a $10mm^2$ final print. Optical micrographs are shown for the $10mm^2$ prints using inks 1 and 2 in figures 2 (c) and (d), respectively.

Table 2: Table to show the jetting parameters used for inks 1-3.

Parameter	Inks 1 & 2	Ink 3
Rise Time 1 (µs)	20	17
Dwell Time (µs)	20	17
Fall Time (µs)	20	17
Echo Time (µs)	40	34
Rise Time 2 (µs)	20	17
Idle Voltage (V)	0	0
Dwell Voltage (V)	45	-28
Echo Voltage (V)	-45	-28

Printing with stabilised inks

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Straight tracks with an average width of 397µm are obtained when printing with ink 1 whereas ink 2 yields an irregular, crooked track with an average width of 1020µm, a 257% width increase relative to ink 1. A comparison of the printed squares exaggerates this further with clearly defined printed lines present within the bulk of the square when ink 1 is used, yet an irregular wave-like appearance is observed for ink 2.

Print resolution was further investigated for ink 1, due to the superior print quality displayed by the tracks. This was achieved by decreasing the distance between parallel printed lines through manipulation of the image sent to the printer. Figure 3 shows the resulting prints for ink formulation 1. For image (a), which is the result of a 10 pixel line spacing, the average track width is 205µm with an average line spacing of 938µm. Image (b) shows the result of a 3 pixel line spacing, with an average track width of 156µm and average line spacing of 233µm.

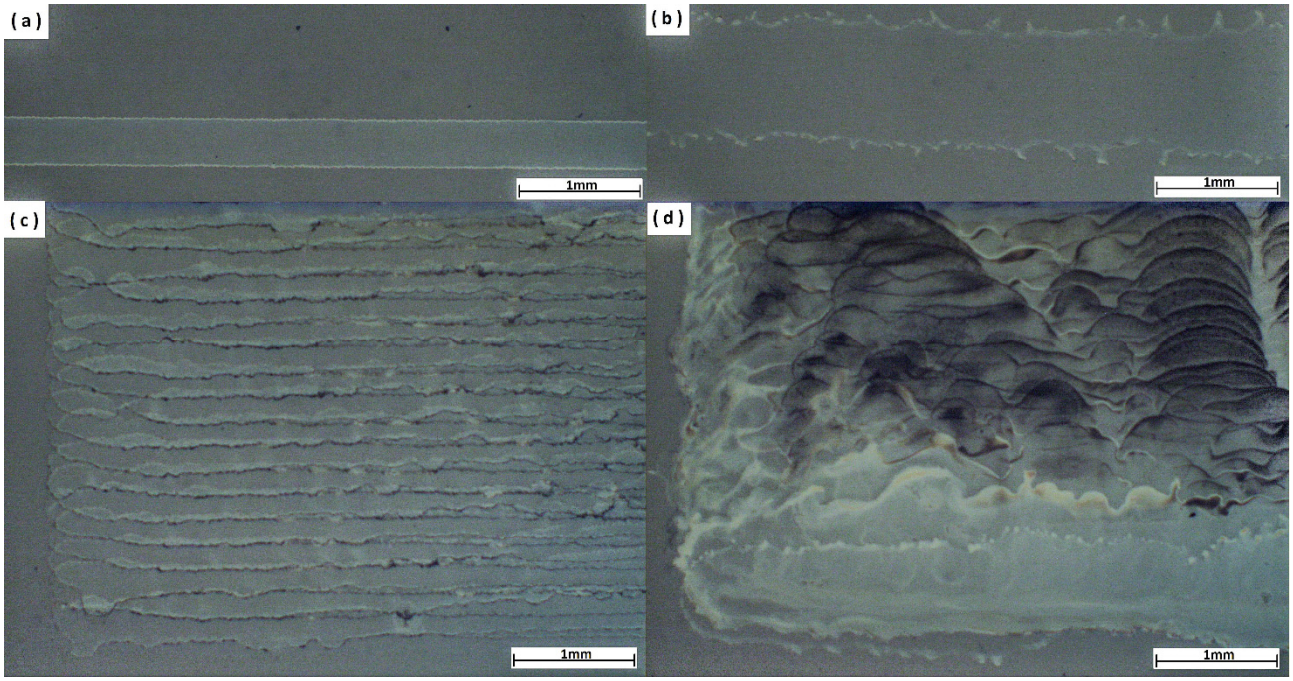

Figure 2. *25x Optical micrographs of tracks with inks 1 (a) and 2 (b). (c) and (d) show the corner of printed 1cm square with inks 1 and 2, respectively.*

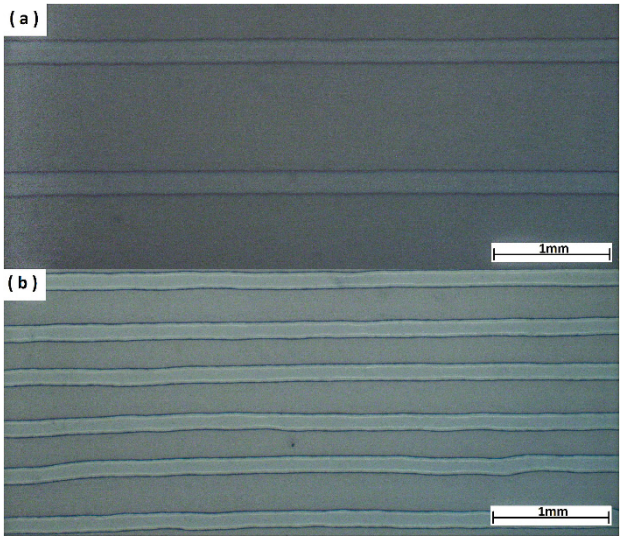

Figure 3. *25x Optical micrographs of ink 1 with (a) 10 pixel line spacing and (b) 3 pixel line spacing.*

Annealing

Phase analysis was performed on a single pass print of the 100x100 pixel array for ink 1. Before annealing, ink 1 shows an amorphous XRD trace with no clear, discernable peaks. This remains true for temperatures up to 450°C. Further investigation is required to establish the temperature at which anatase phase TiO_2 is observed for ink 1, as well as investigations into the annealing of inks 2 and 3.

Cluster ink printing

Ideal printing parameters were also investigated for ink formulation 3, yielding a print speed of 6mmps and a step size of 0.1mm. The track corresponding to these conditions is shown in figure 4, along with a micrograph of a 100x100 pixel square array which corresponds to a $10mm^2$ print. Straight tracks were obtained with ink 3, displaying an average track width of 226μm. Increased magnification yields the image in Figure 4 (b), showing the granular appearance of the printed track. Image (c) demonstrates the high print quality obtained through the use of ink 3.

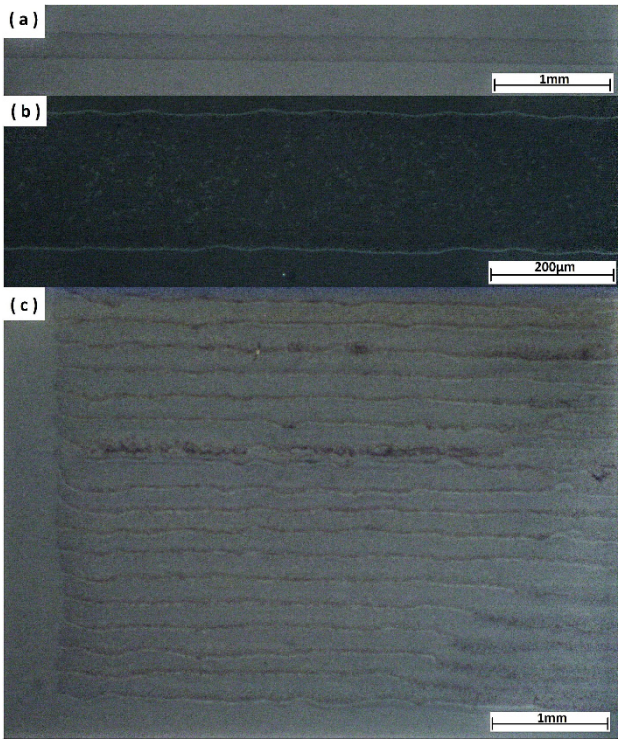

Figure 4. *(a) and (b) shows optical micrographs of ink 3 tracks under 25x and 160x magnifications, respectively. (c) 25x micrograph of printed 1cm square using ink 3.*

Comparison of inks

Printing with ink 3 yields results comparable to ink 1, obtaining prints of a similar line width (Figures 3(a) and 4(a)). Both inks 1 and 3 yield straight printed lines. However printing with ink 2 results in track widths greater than inks 1 or 3, with irregular track boundaries. Print capabilities of inks 1 and 3 were further investigated using a complex architecture, shown in Figure 5. These images capture the potential printability of both inks 1 and 3, yielding a patterned film of amorphous TiO_2.

However figure 5 also displays the scope for improvement of the ink formulations and print qualities. This is especially true for ink 3 in which the 3 printed passes did not overlay, resulting in the blurred final result. This may be due to a partial blockage in the printer head, and suggests that further optimisation by addition of stabilisers may be necessary.

Conclusions

Inkjet printing of both simple and complex titanium alkoxides was achieved. Identity of the glyme chosen for use as the stabilising ligand has been shown to have an effect on printed tracks for the simple alkoxides: DME stabilised ink yields a narrower, more linear printed track in comparison to diglyme stabilised ink. Titanium oxo-alkoxide cluster ink is shown to have comparable print qualities to the DME stabilised ink. However, in initial experiments, the oxo-alkoxide ink displayed lower reproducibility through displaced passes during the printing process.

Further investigation into the annealing procedure is required for all ink formulations in order to identify and compare the minimum processing temperature for anatase phase formation.

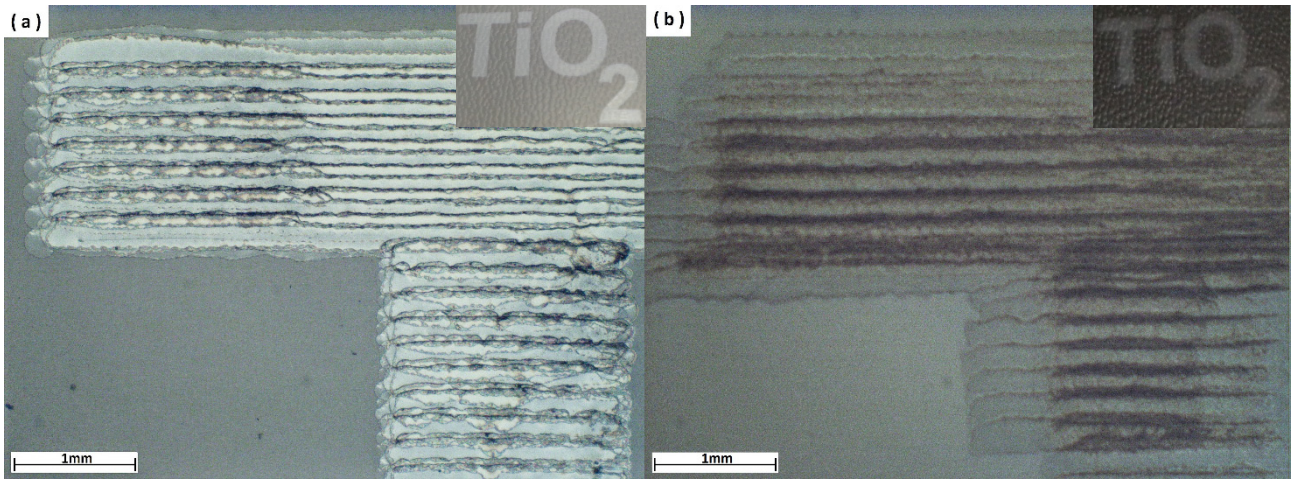

Figure 5. *25x Optical micrographs of the letter 'T' using 3 passes of ink 1 (a) and 3 passes of ink 3 (b). Inserts show the macro images of the printed 'TiO_2' patterns.*

Methods

All manipulations were carried out using standard Schlenk techniques in an inert N_2 atmosphere unless otherwise stated. Stabilised inks were prepared by the slow addition of $Ti(O^iPr)_4$ to a stirring solution of chosen stabiliser in ^{i}PrOH. Titanium oxo-alkoxo cluster inks were prepared by refluxing in hot toluene the crystals obtained by following the experimental preparation of $Ti_{12}O_{16}(O^iPr)_{16}$ described by V.W.Day *et al* [11]. Extraction of all ink solutions into an inkjet vial was performed on the day printing was to be performed in order to limit exposure to atmosphere.

All inkjet printing was performed using a Microfab Jetlab x4 printing systems (Microdrop Technologies GmbH), fitted with an 80µm nozzle, under atmospheric conditions at 22ºC onto a clean glass substrate. A drop frequency of 500Hz was used exclusively.

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 C. 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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